in your element

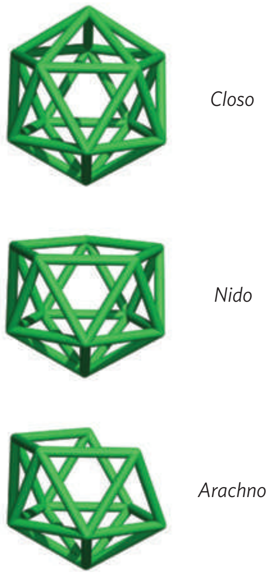
Bonding with boron

Long ago, a global search for borane superfuels led fortuitously to the discovery of carboranes. **Ken Wade** recalls his own undistinguished part in the space race, and notes how carboranes revitalized boron hydride chemistry and modified our ideas of chemical bonding.

In the 1950s, during the space race, the communist east and capitalist west built ever bigger and more powerful rockets to threaten to lob nuclear payloads at each other. Progress was marked by how far down test ranges nose cones were recovered, until bleeps emitted by the first Sputnik showed who had won the race into orbit. Down below, engineers continued designing and building better rocket motors, while chemists sought higher-energy fuels. Boron attracted attention for a while because burning its hydrides (boranes) generated more heat per kilogram than burning hydrocarbons. Although the thermally unstable boranes seemed far from ideal as fuels or fuel additives, the USA and USSR invested millions of dollars and roubles, respectively, in borane research. The UK government, not to be outdone, allocated £600 for similar work. That paid me to work on boranes with Professor Harry Emeleus at Cambridge (the alternative was to be drafted into the army).

Professor Emeleus was a delightful person to work with, kind, and with a dry sense of humour. He provided me with a face shield, asbestos gloves and a soft leather apron, suggesting, with a twinkle, that, in an explosion, the apron might not stop all the glass fragments, but those that got through should be big enough for the surgeons (plural!) to pick out. Thus encouraged, I studied assorted reactions of diborane (B_2H_6), condensing small samples with potential oxidants in glass vessels and allowing them to react as liquids or gases as they warmed up. Most did so in a controllable manner.

One day I rashly sealed together diborane and a volatile oxidant that I had felt sure would react immediately at low temperature. It didn't, so hours later my reaction vessel, clamped behind a safety screen in the fume cupboard, contained a potentially explosive mixture of the two gases at room temperature. Suddenly, with a greenish flash and a loud bang, the vessel disappeared, most of it so finely pulverized that no one was hurt. The jaws of the clamp that had held it grinned vacantly at me. Only one glass fragment remained. The sealed tube end had shot sideways, creating a bullet hole in the reinforced glass of the fume cupboard, yet falling back intact, like a rocket nose cone awaiting recovery. Was this to be Britain's fuel–oxidant mix? No. Boranes were too expensive to prepare, and proved unsuitable for satellite- or missile-launching. Other fuel–oxidant systems were developed instead.



Borane-type clusters held together by 13 electron pairs have shapes based on the icosahedron. This is complete (*closo*) with 12 skeletal atoms, as in $C_2B_{10}H_{12}$ or $[B_{12}H_{12}]^{2-}$: nest-like (*nido*, one vacancy) with 11 skeletal atoms, as in $[C_2B_9H_{11}]^{2-}$; and cobweb-like (*arachno*, two vacancies) with 10 skeletal atoms, as in $[B_{10}H_{14}]^{2-}$.

However, the money spent globally on boranes was not wasted. It led to the discovery of new borane anions $[B_nH_n]^{2-}$ and carboranes ($C_2B_{n-2}H_n$), mixed hydrides of boron and carbon with novel triangular-faced (deltahedral) structures that packed their n boron and carbon atoms closely on spherical surfaces, held together by only (n+1) electron pairs, too few to allocate a pair to each of their (3n–6) atom–atom links. Dubbed 'electron-deficient', they were really 'electron-sufficient', as adding electrons caused their structures to open up into fragments of bigger deltahedra. Plotting their shapes against formula types or electron numbers creates a pattern of complete deltahedra or fragments thereof, first reported by carborane pioneer Robert E. Williams in 1971, now routinely featured in textbooks. Many other cluster compounds conform to this pattern, as I found by teaching cluster chemistry to Durham students. Boranes, apparent rule-breakers, had become pattern-makers.

Now a mature field, carborane chemistry attracts many talented researchers, in organic, organometallic and inorganic chemistry as well as materials science. It has provided new substituents, ligands, reagents and catalysts, thermally stable polymers, ceramic materials and anticancer drugs. Carborane structures, once hotly disputed, can now be computed with a precision rivalling that of X-ray crystallography. Boranes have featured in the work of such Nobel Laureates as William N. Lipscomb (1976; structures and bonding); Herbert C. Brown (1979; hydroboration studies, so apt for his initials); Roald Hoffmann (1981; structures, bonding and reactions); and indeed George A. Olah (1994; carbocations, analogues of boranes and carboranes). They and many other chemists have been in their element in the fascinating world of boron chemistry. ❐

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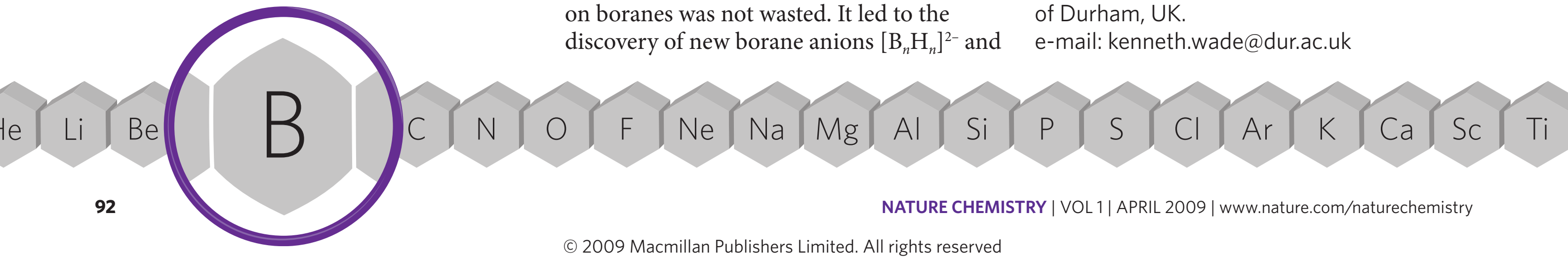


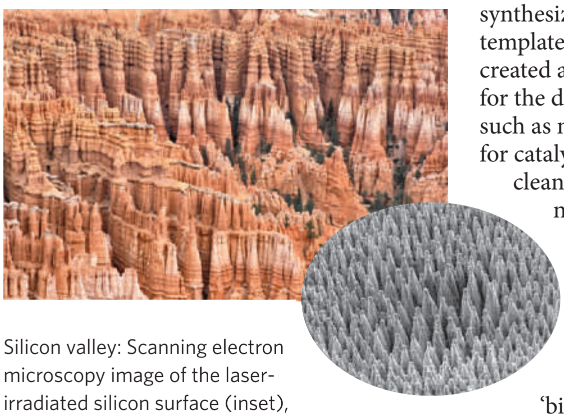
Silicon beyond the valley

Mietek Jaroniec reflects on how silicon, whether bonded with other elements in a variety of materials, in high purity for electronic devices, or in its newer ‘black silicon’ form, continues to be invaluable in many aspects of our lives.

Silicon is, after oxygen, the most abundant element of the Earth’s crust. But although about 75% of the Earth is made from silica — or silicon dioxide (SiO_2), the main constituent of silicate minerals such as sand, quartzite or granite — elemental silicon itself is only occasionally found in nature and was unknown until the nineteenth century. In 1811 Gay-Lussac and Thenard probably obtained impure amorphous silicon by heating potassium with silicon tetrafluoride; however, the discovery of this element is usually credited to Berzelius, who in 1824 added extra washings to isolate pure silicon. It is now produced on a large scale by heating silica with carbon in an electric furnace, at high temperatures (1,900–2,350 °C) far exceeding its melting point (1,414 °C).

According to the US Geological Survey, the world’s reserves of pure silicon (including that synthesized) exceeded five million tons in 2007 — the best indicator of its importance in today’s technology. Over 90% is consumed for the production of silicon-containing chemicals and alloys. Aluminium-rich alloys, for example, are commonly used in the automobile industry; silicones (which feature silicon–oxygen and silicon–carbon bonds) have found extensive applications as greases, resins, rubbers and sealants; silica, in the form of sand, is also a basic ingredient of glass and concrete, some of the most widely used materials; and aerogel, an extremely light form of silica because 90% of its volume is occupied by pores, is a very efficient insulating material.

Without diminishing the enormous importance of these applications, the greatest impact of silicon on today’s technology and lifestyle is accounted for by only a small fraction of the world’s reserves (about 5%) — the high-purity silicon used in a variety of electronic devices, ranging from computer microchips and power transistors to solar cells, liquid-crystal displays, and semiconductor-based detectors. Remarkable advances in microelectronics have been made possible by the miniaturization of silicon integrated circuits, and this field is now heading towards nanoelectronics. The use of porous silicon, for instance, for the development of a range of sensors arose from its luminescence properties and large surface areas. The high-purity silicon required for such microelectronic devices is obtained by a complex multi-step process, usually involving the transformation of a crude metallic silicon to chlorosilanes (compounds containing silicon–chlorine bonds). After separation and purification these are reduced with hydrogen to the polycrystalline silicon used to make silicon wafers (smooth thin discs).



Silicon valley: Scanning electron microscopy image of the laser-irradiated silicon surface (inset), which resembles a fragment of Bryce Canyon National Park in Utah, USA.

The richness of silicon chemistry is amazing; new discoveries arise continuously in this field. And although the surface area of 1 g of sand particles is extremely small, the internal surface area of the same amount of silica particles with accessible nanoscale pores (about 3 nm) can easily exceed 1,000 m^2 (approximately the area of an Olympic-size swimming pool). Such particles with ordered nanopores are synthesized in the presence of surfactant templates — a synthesis strategy that has created almost unlimited opportunities for the development of nanomaterials, such as nanoporous silica-based particles, for catalysis, separations, environmental cleanup, drug delivery and nanotechnology.

While discussing silica, it would be remiss to neglect the large-scale formation of silica structures with nanoscale precision by various marine organisms. Understanding this ‘biosilification’ process occurring in nature offers tremendous opportunities for the development of environmentally benign syntheses of novel silicon-based materials, and could eventually lead to advances in biosensors, biocatalysis and the engineering of biomolecules — a field now known as ‘silicon biotechnology’.

Another amazing and technologically promising discovery shows the importance of unveiling microstructure and nanostructure. In 1998, Mazur and his team at Harvard University showed that the irradiation of a silicon wafer with femtosecond laser pulses in the presence of a sulfur-containing gas transforms its shiny surface into a forest of microscopic spikes, which resembles Bryce Canyon in Utah, USA (pictured). Normally, the surface of silicon reflects a substantial amount of light — but this ‘black silicon’ strongly absorbs visible light by trapping it between its spikes, which makes it very promising for solar cells. It also absorbs infrared radiations with wavelengths as long as 2,500 nm and, surely, novel optical and electronic applications of black silicon can be expected in the future. This example shows that silicon, although known for almost 200 years, can still amaze us. ❐

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in your element

Xenon out of its shell

Like all noble gases, xenon is colourless, odourless and inflammable — but it is also more reactive, and much rarer, than its lighter relatives. **Ivan Dmochowski** ponders how xenon, though initially slow to earn a spot in the periodic table, is now at the forefront of advances in science and technology.

Xenon, initially deemed unreactive, is now finding ways to come out of its shell.

For all their nobility, elements of group 18 have lived in relative obscurity. In 1869, Mendeleev's first periodic table did not include them, as closed-shell elements remained undiscovered until Lord Rayleigh and William Ramsey isolated argon in 1894. Remarkably, Ramsey then went on to isolate helium (1895) and radon (1908) and, with Morris Travers, to discover krypton, neon and xenon (1898). It was debated whether the 'inert' monoatomic gases belonged to the periodic table owing to their lack of 'chemical properties'; elements coming late to the party, with no unpaired electrons to share, may not get a seat at the table. But Ramsey established their position between halogens and alkali metals, and was awarded the Nobel Prize in Chemistry in 1904 for these elemental contributions.

Xenon's discovery concluded an intense period of research on noble gases. Much heavier than neon and krypton, it had not been explicitly predicted, and was sufficiently rare to avoid chance detection. Its discovery was almost accidental. Travers had spent months fractionating liquid air residues, but having isolated the lighter noble gases he would typically ignore any additional volatile components. On one occasion, however, he collected the gas remaining in his apparatus. The residue (just 0.3 ml), introduced into a spectrum tube, revealed a brilliant blue colour characteristic of xenon. Its rarity in air (0.09 ml m^{-3}) combined with high density (5.8 g l^{-1}) violated common experience, and so xenon was named after ξένον, a Greek word meaning 'foreign'.

Enshrouded by five filled electron shells (electronic configuration [Kr] $5s^2\ 4d^{10}\ 5p^6$), xenon has been slow to reveal its secrets. Its scarcity in the Earth's atmosphere — 10- to 100,000-fold rarer than the lighter noble gases, despite their lower escape velocities — has been a long-standing mystery. Recent X-ray-diffraction studies now indicate that xenon can substitute for silicon in quartz at high pressure and temperature, suggesting that the Earth's 'missing xenon' may be covalently bonded to oxygen in the continental crust.

Kossel and Pauling (in 1916 and 1932, respectively) predicted that xenon's ionization potential (12.1 eV) should allow its reaction with strong oxidants. This was finally confirmed in 1962, when Neil Bartlett observed that xenon reacted with vapours of platinum hexafluoride (PtF_6) to form a yellow–orange solid compound — a discovery widely recognized as one of the most significant inorganic chemistry advances of the twentieth century. The syntheses of various fluorides, oxides and perxenates (XeO_6^{4-} salts) quickly followed. Xenon can form covalent bonds to carbon and nitrogen, and, as shown by the recent synthesis of a compound with gold ($AuXe_4^{2+}$), also coordinates metal ions.

Xenon now finds uses in fields as varied as lasers and incandescent lamps, plasma display panels, silicon etching in semiconductor manufacturing and medicine. In 2008, twelve million litres of xenon were extracted from the atmosphere, and production is growing to meet technological needs.

Xenon's polarizability (about 4 compared with 0.2 for He) contributes to its affinity for hydrophobic cavities in proteins, which is relevant not only for protein crystallography but also for anaesthetic use. Behnke deduced that xenon was an anaesthetic in 1939, after observing 'drunkenness' in deep-sea divers, and it was first used for surgical purposes in 1951. It has gained newfound popularity, based on its non-toxicity and low environmental impact (compared with halocarbons), and a xenon-based anaesthetic (LENOXe) was commercialized in 2007.

Xenon has more than 50 isotopes, including nine stable ones (second only to tin, which has ten). ^{129}Xe, with a spin-1/2 nucleus, provides large NMR signals for imaging studies in the lungs. Moreover, the ^{129}Xe NMR chemical shift is extremely sensitive to stereo-electronic perturbations of the ^{129}Xe atom, and xenon biosensors based on these phenomena are now under development.

One of the most exciting new applications is in xenon-ion propulsion engines for space travel. Onboard NASA's Dawn spacecraft, launched in 2007 to study distant asteroids Vesta and Ceres, cationic xenon atoms are accelerated towards a negatively charged grid, with exhaust speeds of approximately one million km h^{-1}. The thrust generated by xenon is only 0.1 newtons, roughly the weight of a piece of paper, but can gradually (over many months) increase the velocity of the spacecraft by 15,000 km h^{-1}. This reduces the requirement for much heavier chemical fuel, thereby lowering launch cost, while increasing travel range. Whether through oxidation, coordination or ionization, xenon has revealed properties that lead to extremely versatile applications — and this field is still in its infancy.

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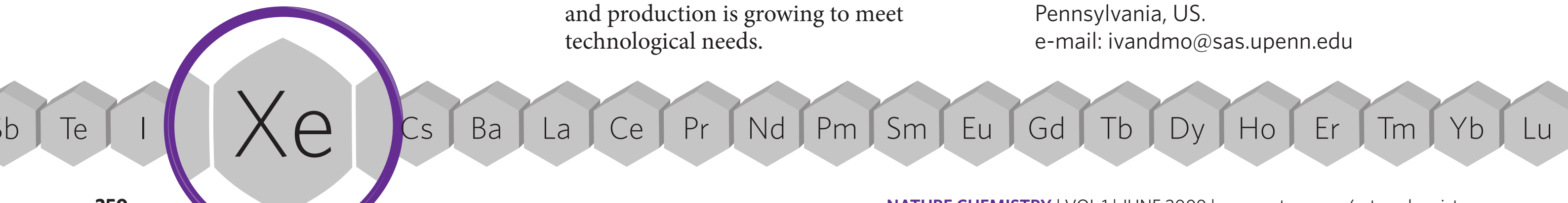

Tales of technetium

The story of the last element to be discovered out of the first 92 catalogued in the periodic table is told by **Eric Scerri**, who reminds us that technetium can be found a little closer to home than many of us might think.

Group 7 of the periodic table is something of an oddity. When the first periodic table was formulated by Mendeleev, it was the only group that contained just a single known element — manganese. In the early twentieth century, several claims were made for the discovery of the element immediately below manganese. But this alleged element, given various names such as davyum, illenium, lucium and nipponium, turned out to be spurious.

Then, in 1925, Otto Berg, Walter Noddack and Ida Tacke (later Ida Noddack), claimed to have discovered not just one but two new members of Group 7, which they named masurium and rhenium. Although their discovery of rhenium was soon accepted, their claim for the element directly below manganese has been bitterly disputed[1–5] ever since. As recently as the turn of the millennium, Belgian physicist Pieter van Assche collaborated with several US spectroscopists to re-analyse the original X-ray images. They then argued that the Noddacks had in fact isolated another element in addition to rhenium. But this claim has also been disputed by a number of other researchers.

Traces of Tc in rocks contradict the common textbook statement that it does not occur naturally on Earth.

The official discovery of element-43 is accorded to Emilio Segrè and co-workers. Technetium, as they called it, was the last of elements 1-92 to be tracked down, and in fact it had to be synthesized rather than isolated from naturally occurring sources. It is also the only element to ever be 'discovered' in Italy — in Palermo, Sicily, to be more precise. Segrè, who had been a visitor at the Berkeley cyclotron facility in California, was sent some molybdenum plates that had been irradiated for several months with a deuterium beam. Various chemical analyses by the Italian team revealed a new element, which could be extracted by boiling with sodium hydroxide that also contained a small amount of hydrogen peroxide.

It has generally been believed that any technetium that might have been present when the Earth was first formed has long since decayed radioactively. We know this because even the longest-lived isotope of the element has a half-life that is too short in comparison with the age of the Earth. But in 1956, the Japanese radiochemist Paul Kuroda predicted that a natural nuclear reactor might once have existed deep within the Earth. Five years later, he reported that a sample of African pitchblende contained about 2×10^{-10} grams of ^{99}Tc per kilogram of ore. In 1962, a team of French scientists confirmed Kuroda's earlier prediction of a natural nuclear reactor on investigating rock samples in the Republic of Gabon in Africa. Further analyses showed that there were trace amounts of technetium present in these minerals too, thus further contradicting the common textbook statement that technetium does not occur naturally on Earth.

Turning to the skies, technetium was detected in some so-called red giant stars as long ago as 1952, but not in our own Sun, a fact that has had a significant role in confirming the view that the Sun is a relatively young star. In addition, because technetium isotopes have short half-lives compared with the age of red giants, this finding suggested that the element was being produced within the stars, thus supporting theories of stellar nucleo-synthesis for elements of intermediate mass.

In spite of its exotic heritage, technetium is now widely used in medicine as a diagnostic tool. Radioactive molybdenum-99 is allowed to decay to form technetium-99m — meaning ^{99}Tc in an excited nuclear state. This metastable isotope then drops to the ground state with the loss of a gamma particle, which can be recorded in radiodiagnostic procedures for the detection of tumours, among other things. The usefulness of ^{99}Tc lies in a number of specific properties that it has. The radioactive decay of the excited form has a half-life of six hours; that is long enough to be injected into a patient before it decays, but still sufficiently short for its emission intensity to be measurable at low concentrations. Furthermore, the short half-life means that the patient need only be exposed to radiation for a brief period of time. The aqueous chemistry of technetium is also critical. The pertechnate ion, TcO_4^-, which is the form in which the isotope is administered, is both soluble and stable over the physiological range of interest, unlike, for example, the permanganate ion (MnO_4^-).

Finally, one of the best ways to protect steel from corrosion when it is in contact with water, even at high temperatures and pressures, is to use a coating of $KTcO_4$. It is unfortunate that technetium is radioactive, otherwise this method could be used in situations other than with steel in carefully sealed containers. ❐

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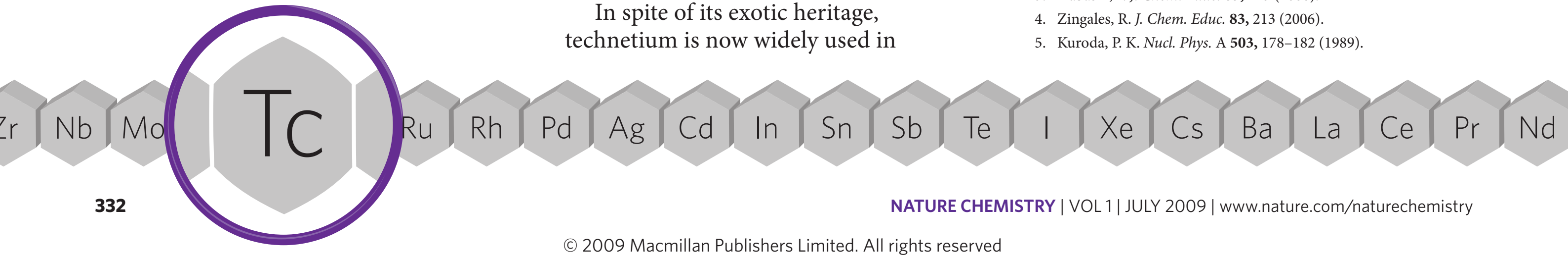

in your element

A new iron age

Iron has important roles in areas as diverse as physiological processes and industrial activities, but has traditionally been eclipsed by other transition metals in synthesis processes. **Carsten Bolm** looks at how iron is now also becoming an increasingly sought-after catalyst.

Gold is for the mistress — silver for the maid —
Copper for the craftsman cunning at his trade.
"Good!" said the Baron, sitting in his hall,
"But Iron — Cold Iron — is master of them all."

Rudyard Kipling, 1907 Nobel Prize winner in Literature, begins his poem 'Cold Iron' with these lines. Indeed, iron does appear in many different facets of our lives: from the band Iron Maiden to the Ironman championships in triathlon; in history with the Iron Curtain, or when we refer to the Iron Lady, ruling with an iron hand.

Iron is a transition metal that melts at 1,539 °C, and its appearance can be described as lustrous and metallic, with a silver–grey tinge. It is the second most abundant metal on our planet — with the first being aluminium — and is mostly present in its dense metal core as an alloy with nickel. It is also ubiquitous in the Earth's crust, and constitutes about a third of its entire mass.

More and more chemists are now working with iron catalysts and are finding it most rewarding.

For almost all living organisms iron is an essential trace element. For example, haem — an iron–porphyrin complex — is key to the activity of a few proteins, including haemoglobin where it participates in the binding and transport of molecular oxygen. Iron is not eliminated by any physiological processes, and its uptake, transport and storage is highly regulated. It is so important to living organisms that iron deficiency due to an uncontrolled loss can lead to cell damage, and eventually even death.

Only rarely can iron be found in its pure, elemental form, and iron(II) compounds are also rare. It is mostly found in hydroxides and oxides of iron(III), but these are hardly soluble in aqueous media at about neutral pH, and most organisms have developed specialist mechanisms to meet the essential iron demand. Bacteria, for example, release siderophores, which chelate iron and allow subsequent directed transport and uptake. A presentation on siderophores for the faculty at the University of Basel was, in fact, my first direct exposure to iron chemistry — it turned out to have a significant impact on my research interests, as well as being a pleasant challenge.

Iron chemistry was developed early on in the history of mankind. In prehistoric times, samples were likely to have been collected from meteors, and iron has been smelted since 2,000 BC. Pure metal can be obtained from iron oxides such as the mineral haematite (Fe_2O_3) by reduction with carbon at high temperature. Subsequent modifications with other metals (as well as a few non-metallic additives, such as silicon or carbon) lead to alloys with tunable properties — steels — which have become key components to the building, automotives and machinery industries, to mention a few.

Abundant and mostly non-toxic, iron could be expected to be found as a catalyst for many applications. The Haber–Bosch process — which uses a doped iron catalyst to synthesize ammonia from nitrogen and hydrogen — is well-known, and iron catalysis was introduced by Walter Reppe at the BASF laboratories in Ludwigshafen, Germany, for the synthesis of alcohols from olefins and carbon monoxide. However, iron is usually not the first metal of choice for catalysis, with precious metals such as palladium or rhodium often taking preference. This is probably because too many transformations have been shown to work with non-iron catalysts; why, then, should this approach be changed, and switched to the unknown?

Furthermore, iron's magnetic properties make standard mechanistic investigations difficult (for example, by NMR spectroscopy). Many iron complexes are paramagnetic, and reaction pathways often involve radical components. Theoretical studies can also be hampered by having to consider spin-state changes. Nevertheless, more and more chemists are now working with iron catalysts and are finding it most rewarding. As recent advances show, both reactivity and selectivity can often be controlled by judicious combination of iron source, ligand and additive.

This approach led to the discovery of unexpected cross-coupling activities, and even the functionalization of hydrocarbons with simple oxidants has become possible. Finally, it was also demonstrated that asymmetric synthesis with chirally modified iron complexes is feasible. More discoveries and breakthroughs will surely soon be reported, allowing the currently used precious metal catalysts to be efficiently substituted.

Is iron really cold, as noted by Kipling in his poem from the beginning of the last century? About 100 years later the scene has changed — iron is hot, and the fire has only recently been ignited. ❐

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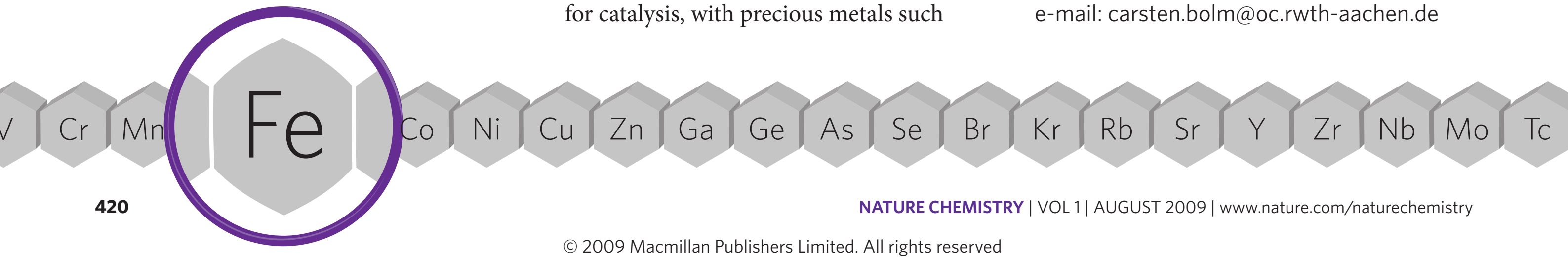


in your element

Tellurium in a twist

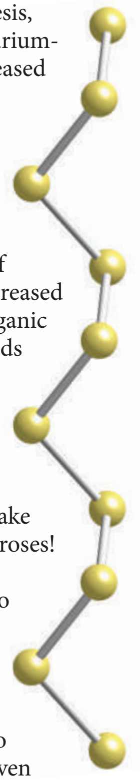
Jim Ibers takes a look at the intriguing structures and bonding found in tellurium and its compounds, and considers their uses in a diversity of fields ranging from metallurgy to electronics.

Dramatic changes in physical properties occur on descending group 16 of the periodic table. Oxygen, of course, is a gas, polonium a metal, and the in-between elements, sulfur, selenium and tellurium, are all solids that show increasing metallic properties. In fact, tellurium (Te), which I find to be the most interesting of the group, acts very much like most metals.

Tellurium is not an abundant metal. Present at about 1 ppb in the Earth's crust, it is less abundant than gold, platinum or the so-called 'rare-earth' elements. So why should one care about such an obscure element? One answer, of course, is 'because it is there', if one can borrow the phrase that George Mallory used to justify climbing Everest. However, in these days, where instant gratification of those who provide the funds is advisable, other reasons include important current industrial applications and the potential for more. For such applications to be realized, tellurium must be available for basic research in the laboratory and for use in industry. That leads us to a discussion of its sources.

Mining solely for tellurium is not profitable because it is rare and so widely distributed. However, it is most often found in nature in combination with gold, silver, copper and other commercially valuable metals. In fact, gold tellurides are the most common gold-containing minerals. As an aside, tellurium was discovered in 1782 by the Austrian mineralogist Franz Josef Müller von Reichenstein in gold taken from a mine in Hungary. Consequently, tellurium is a by-product in the refining of these other metals. The major source is in the anode sludges produced during the electrolytic refining of copper. These sludges average about 2 wt% Te. In 2007, total world production of tellurium was about 500 metric tons — a significant increase over previous years. Moreover, as demand for tellurium has increased, so has its cost.

Basic research into the synthesis, structures and properties of tellurium-containing compounds has increased markedly in recent years. As one measure, we can consider Te-containing compounds that have been structurally characterized, most often by X-ray diffraction techniques. In the past decade the number of inorganic Te compounds has increased by about 40%; the increase in organic and organometallic Te compounds is nearly 70%. This last figure is surprising given that tellurium is not an essential element for living systems and that many of the synthons and products in organotellurium chemistry make their sulfur analogues smell like roses!



From a personal perspective, when we started our research into ternary solid-state tellurides about 25 years ago it was not known whether these compounds would resemble ternary selenides or not. Some do and some do not. Dissimilarity even extends to the binaries. For example, NaTe exists whereas NaSe is not known. Ask a first-year chemistry student to describe the structure and formal oxidation states of NaTe — the answer is that the well-known propensity of sulfur, selenium and tellurium, as opposed to oxygen, to form chains and rings reaches its extreme at tellurium. NaTe is, in fact, $Na_6Te(Te_5)$, which contains the Na^+ cation together with the Te^{2-} and the Z-shaped Te_5^{4-} anions. This Z-shaped anion possesses Te–Te distances of 2.82 and 3.08 Å, and therein lies one of the exciting differences between Te and S. Structurally, the mineral pyrite (sometimes called 'fool's gold' owing to its golden lustre), of formula FeS_2, possesses S atoms separated by about 2.08 Å, the length of a S–S single-bond. The formal oxidation state of Fe is thus +II, not +IV as one might conclude from the formula. In fact, in essentially all solid-state compounds in which S–S bonding occurs, the S atoms are separated by single bonds. In contrast, in solid-state compounds where there is Te–Te bonding, in addition to normal Te–Te single bonds about 2.74 Å in length, there may well be Te–Te separations of up to 3.6 Å or more, but still less than the van der Waals separation of 4.1 Å. This often makes the assignment of formal oxidation states impossible. The only allotrope of tellurium that is stable at room temperature is an infinite helix (pictured). In that helix, the Te–Te distances are about 2.83 Å, but there are some short nearest-neighbour interactions at 3.49 Å. The bonding in Te-containing solid-state compounds, which has engendered numerous theoretical studies, is far more interesting than it is in its lighter congeners.

The major industrial use of tellurium is in metallurgy, where it is an important alloying agent. It is added to steel and to copper to make them more machinable, to cast iron to minimize heat shock, and to lead to reduce fatigue. Another significant industrial use of tellurium is as an accelerator and vulcanizer in the rubber industry. These uses do not require high-purity tellurium. However, the electronics industry increasingly makes use of high-purity tellurium in a variety of new and evolving applications. For example, tellurium is used in the newly developed phase-change memory chips as well as in rewritable CD, DVD and Blu-ray discs. Bismuth telluride is widely used in thermoelectric cooling devices. Such devices find many applications in electronics and consumer products, the latest being their increased use for portable food coolers and, believe it or not, even for car-seat cooling systems. Perhaps the greatest impact of tellurium on our lives might come from cadmium telluride solar panels — still at an early stage, they are among the most efficient for electric power generation. It is possible that tellurium may yet save mankind! ❐

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in your element

A golden future

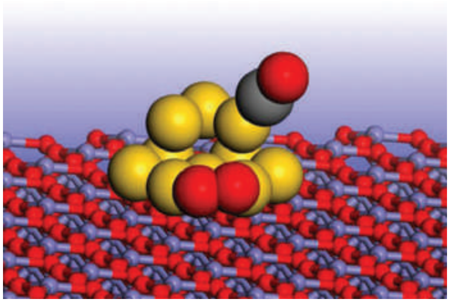
Catalysis using gold has fast become a major research field with great potential, and many new discoveries are being made. **Graham Hutchings** reflects on how this has come about.

Gold is the most noble of the elements and by virtue of this holds a central place in the world of finance, art and jewellery. It is associated with great historical objects — for example the mask of Tutankhamun's mummy — that remain as beautiful today as the day they were first made several thousand years ago. Gold is also synonymous with great wealth, and for centuries alchemists tried in vain to make gold from base elements — one sect of alchemists, known as the Mercurialists, considered gold to be made from mercury and sulfur.

Gold is considered to be a timeless element — it is immutable — so one would not expect to associate it with any chemical reactivity. Indeed, chemistry textbooks always devote the fewest pages to gold — often regarded as a rather boring element from a chemical perspective. However, since the 1980s, it has been found that this is no longer the case. Divided into very tiny nanosized pieces that comprise just a few atoms, gold becomes exceptionally effective as a catalyst, and catalysis lies at the heart of the manufacture of most goods we use today. It has taken so long for the wonders of gold catalysis to be unravelled because of our preconceptions of this element — it was thought to be chemically uninteresting and relatively unreactive, no one thought to investigate further.

Gold now lies at the heart of many discoveries in both heterogeneous and homogeneous catalysis.

It was two discoveries made at similar times in the 1980s that made chemists start to look at gold in a new light. Masatake Haruta, then working at the Government Industrial Research Institute in Osaka, Japan, tried to make mixed oxides containing gold, and discovered that these materials were remarkably active catalysts for the oxidation of carbon monoxide. He subsequently found that they comprised nanoparticles of gold supported on the oxide. This combination showed activity at temperatures as low as –76 °C — this is close to the coldest ambient temperature on this planet (–89.2 °C at Vostok in Antartica) — and gold can therefore be used widely for the oxidation of carbon monoxide at ambient temperature.


DAVID WILLOCK

Small clusters of gold atoms, such as Au_{10} schematically shown here on iron oxide, may be associated with high catalytic reactivity for the oxidation of carbon monoxide.

The discovery that gold was so active as a catalyst led to an explosion of interest in this element; the chemical world was eager to understand why gold is so effective. Initially, researchers thought that gold nanoparticles approximately 2–5 nm in diameter were the active species. However, this conclusion was based on the extent of the resolution of electron microscopy. With the advent of aberration-corrected instrumentation, single gold atoms can be resolved and we now know that catalytic activity can be associated with very small gold clusters, containing as few as 7–10 atoms.

At the time that Haruta made his discovery in Japan, I was working in industry in South Africa, trying to discover a catalyst for acetylene hydrochlorination, which is central to PVC manufacture. The industrial catalyst for this process has been the environmentally non-friendly mercuric chloride. So, on a wet Saturday afternoon in Johannesburg in September 1982, I was analysing some published data that showed great variations in catalytic activity were possible with a broad range of over 30 metal chlorides. The data could not be used predictively. Replotting the activity data against the standard electrode potential, however, immediately showed a correlation. To me this was the 'eureka' moment: I could predict that gold would be the best catalyst for this reaction, and subsequently verified this experimentally — my first wonderful involvement with using gold as a catalyst.

Gold now lies at the heart of many discoveries in both heterogeneous and homogeneous catalysis. It is providing new inroads into advances in green and sustainable chemistry. Apart from carbon monoxide oxidation and acetylene hydrochlorination — the initial two reactions for which gold was discovered to be by far the best catalyst — gold is effective for other oxidation reactions. In particular it catalyses alkene epoxidation and alcohol oxidation, including the oxidation of biorenewable feedstocks such as glycerol and sugars. Gold is also a highly selective hydrogenation catalyst. Furthermore, combined with palladium, it is an excellent catalyst for the production of hydrogen peroxide from its constituent elements, which may offer a greener route to the manufacture of this commodity chemical.

At times it is now tempting to think that gold will be the best catalyst for every reaction, and although clearly this is not the case, it is true that gold has been transformed from the Cinderella of the elements and has finally got to go the chemical reactivity ball. ❐

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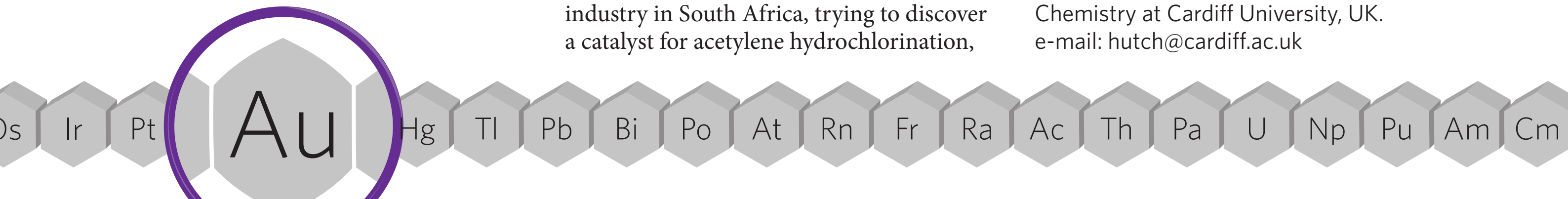


in your element

Finding francium

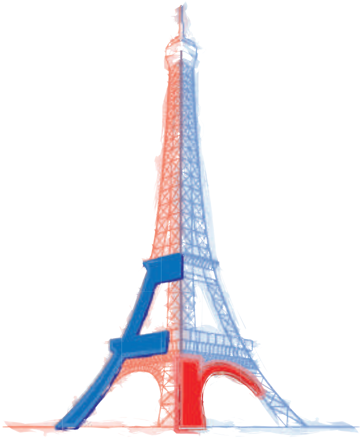
Eric Scerri recounts the story of element 87, which after a number of false starts was finally tracked down in France — and named in its honour.

One of the most remarkable things about element 87 is the number of times that people have claimed to have discovered it after it was first predicted by Mendeleev in 1871 and given the provisional name ‘eka-caesium’.

It was recognized early on that the periodic table more or less fizzles out after element 83, bismuth. All subsequent elements are radioactive and therefore unstable, with a few notable exceptions such as uranium and thorium. But this fact did not deter a number of scientists from searching for element 87 among natural sources and, in many cases, from claiming to have isolated it. For example, Druce and Loring in England thought they had identified the element by using the classic method developed by Moseley for measuring the Kα and Kβ lines of any element’s X-ray spectrum. But it was not to be.

Estimates suggest that there is only about 30 g of francium in the whole of the Earth’s crust.

In the 1930s it was the turn of Fred Allison from the Alabama Polytechnic Institute (now Auburn University). Allison developed what he called a magneto-optical method for detecting elements and compounds based on a supposed time-lag in the development of the Faraday effect, whereby the application of a magnetic field causes a beam of polarized light passing through a liquid solution to be rotated.



He mistakenly thought that every element gave a particular time lag, which incidentally was observed with the naked eye, and that this effect could be used to identify each substance. He boldly claimed in a number of journal articles and even in a special feature in *Time Magazine* that he had observed elements 87 and also 85, both of which were missing at the time. Dozens of papers were published on this effect, including a number of studies arguing that it was spurious. These days the Allison effect is often featured in accounts of pathological science, alongside the claims for N-rays and cold fusion[1].

The next principle claim came from Paris and was supported by Jean Perrin, the physicist who is perhaps best known for confirming Einstein’s theory of Brownian motion and, as a consequence, provided supporting evidence for the existence of atoms. Horia Hulubei, a Romanian physicist working with Perrin, claimed to use highly accurate X-ray measurements and that this enabled him to record several spectral lines with precisely the frequencies expected of element 87, which he promptly named moldavium. But alas, these lines also turned out to be spurious.

The eventual discovery of element 87 was made in 1939 by a remarkable Frenchwoman, Marguerite Perey, who began life as a laboratory assistant to none other than Marie Curie in Paris. Perey quickly became skilful in purifying and manipulating radioactive substances and was asked to examine the radioactivity of actinium, which is element number 89 in the periodic table. She was the first to observe the α and β radiation produced by actinium itself — rather than its radioactive daughter isotopes — and thereby discovered a weak, yet significant, branch in one of the three main radioactive decay series.

Her analysis of the data revealed a new element with a half-life of 21 minutes. When she was later asked to name the element she chose ‘francium’ to honour the country of her birth[2]. It was also an appropriate choice in marking the continuing contribution made by French scientists to the study of radioactivity. Not only was the phenomenon itself discovered by Becquerel, but other landmark achievements in the field included the isolation of the radioactive elements polonium and radium by the Curies, as well as actinium by Debierne — all of which happened within a few years, and all in France.

As it turns out, francium was one of the last natural elements to be discovered, and is the second rarest after astatine. Estimates of the abundance of francium suggest that there is only about 30 g in the whole of the Earth’s crust. It is one of a very few elements that has no practical applications, mainly because it has such a short half-life.

Nevertheless, the fact that the francium atom has the largest diameter of any element, at a huge 2.7 ångströms, and the fact that it has just one outer-shell electron, has made it the object of considerable attention among researchers wanting to probe the finer details of current theories of atomic physics. In 2002, a group in the US succeeded in trapping 300,000 atoms of francium on which they performed several key experiments of this kind[3]. ❐

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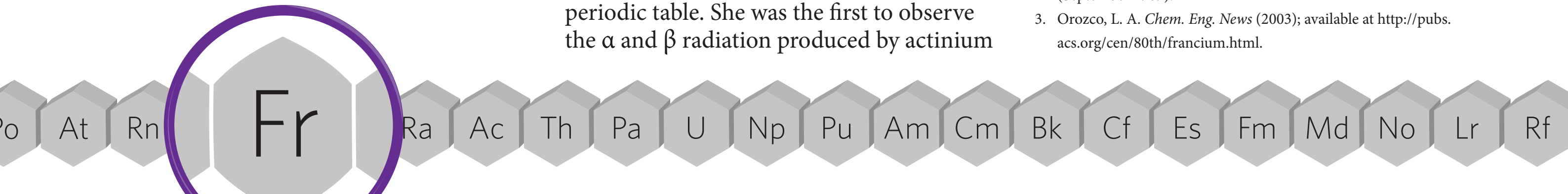

in your element

A flash of magnesium

Magnesium is commonly found in rocks and sea water as well as living organisms. **Paul Knochel** relates how this element has also sparked a great deal of interest among chemists.

One of the most abundant elements on Earth (the sixth in order of weight abundance), magnesium occurs naturally in crustal rocks, mainly in the form of insoluble carbonates, sulfates and silicates. Its name derives from the Magnesia district of Thessaly, where the soft white mineral steatite talc — a hydrated magnesium silicate — was found in ancient Greece. Magnesium was first isolated in pure form in 1808 by Sir Humphry Davy, who used an electrolytic method that had been previously developed by the Swedish chemists Jöns Jakob Berzelius and Magnus Martin Pontin to isolate sodium, barium, potassium, strontium and calcium, between 1807–1808. Elemental magnesium is a fairly strong, silvery white, light-weight metal. It tarnishes slightly in air, and is thus protected against further oxidation by a thin impermeable layer of oxide.

Magnesium reacts exothermically with most acids, and with water at room temperature to give magnesium hydroxide and hydrogen. It is a very flammable metal, able to burn in both nitrogen and carbon dioxide, and famously creates a brilliant white light on burning in air. This resulted in its use as a source of illumination in early photography. It is still employed in flash bulbs, and in fireworks to produce brighter sparks. Its very low density (1.74 g cm^{-3}) makes it an attractive component for alloys — for example, the best magnesium alloy weighs only a quarter as much as steel — and because its metallurgy is simpler than that of other metals, it is also popular in the construction and the aircraft industries, and for optical and electronic devices.

In China, the large-scale production of magnesium metal is achieved by ‘silicothermal reduction’ of dolomite (MgO·CaO), but the process used in the USA is the electrolysis of hydrated $MgCl_2$, abundant in sea water. Magnesium ions are also widely present in the basic nucleic acid chemistry of life. It is vital to the cells or enzymes of living organisms for synthesizing adenosine triphosphate, DNA and RNA, as well as to green plants — chlorophylls, which are responsible for photosynthesis, are magnesium-centred porphyrins. This also means that it is a common additive in fertilizers, and is used in medicine. For example ‘milk of magnesia’, a white aqueous solution of magnesium hydroxide, is commonly used as a laxative and an antacid.

Magnesium also has a central position in organic and organometallic chemistry. Although organomagnesium compounds have been known since the last decades of the nineteenth century, their insolubility initially precluded general applications. In 1900, the young French PhD student Victor Grignard (1871–1935) had the idea to prepare these elusive reagents in solution; this was a new concept. The reaction of various organic halides with magnesium ribbons (often called turnings) in ether led to stable solutions of organomagnesium reagents that bear Grignard’s name. In fact, his first publication in 1900 was so successful that many organic chemists around the world immediately applied his procedure — Grignard subsequently had problems finding enough examples of applications of his reagents that were still unpublished to complete his PhD thesis. This key discovery, for which he was awarded a Nobel Prize in 1912, revolutionized organic chemistry.

Organometallic compounds bearing a carbon–magnesium bond are now among the most popular nucleophilic reagents. More than 100,000 publications dealing with the reactivity of these intermediates have now appeared in the chemical literature. Why such popularity? The reactivity of a carbon–magnesium bond can be readily tuned by appropriate transmetallations with many metallic salts, increasing its use in synthesis dramatically.

Furthermore, the carbon–magnesium bond possesses an intrinsic reactivity that is compatible with the presence of many important organic functional groups in the same molecule. Now, methods for preparing polyfunctional aryl and heteroaryl magnesium compounds bearing an ester, a nitrile or an aromatic ketone are also available, which further increases the scope of Grignard reagents in organic synthesis. Moreover, the low price and low toxicity of magnesium makes these compounds suitable intermediates for large-scale applications in industry. Important drugs such as tamoxifen citrate, a non-steroidal oestrogen antagonist used in the treatment of advanced breast cancer, are prepared industrially using Grignard reagents.

Although magnesium captured the attention of chemists more than a century ago in the form of Grignard reagents, it will certainly continue to have a key role in many research fields, including materials science, biochemistry and synthetic organic chemistry. ❐

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F Ne Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu

The race for rutherfordium

Mitch André Garcia considers the disputed discovery of element 104 and takes a look at how the chemistry of this synthetic element is developing.

Rutherfordium, the 104th element on the periodic table, was first synthesized artificially in the 1960s and was the subject of international controversy for decades. The dispute centred on who should get to name the new element. Historically, the discoverer of an element is afforded the right to name it, but when two groups have competing discovery claims this becomes complicated.

The first research group to claim discovery of element 104 was a team of scientists at Dubna (in what was the USSR) in 1964 (ref. 1). They observed an isotope that underwent spontaneous fission after bombarding their ^{242}Pu target with a beam of ^{22}Ne ions. A second team of scientists — at Berkeley in California — tried for years to replicate these experiments, but were unable to do so. Finally, in 1969, the team at Berkeley made element 104 with a different nuclear reaction; they used a target of ^{249}Cf and a beam of ^{12}C and ^{13}C to produce ^{257}Rf and ^{259}Rf (ref. 2). Both of these isotopes of rutherfordium decay into nobelium by emitting α-particles. The characteristic decay energy and half-life of nobelium was also observed subsequent to the rutherfordium decays. Thus, the team at Berkeley was able to claim unambiguous detection of element 104 by following its chain of decays.

As the years went on neither group would give ground, and finally an international committee was assembled to determine which claims had more weight. The Transfermium Working Group (TWG) was put together by the International Union of Pure and Applied Physics (IUPAP) and its sister chemistry organization IUPAC. Although the TWG consisted of eminent scientists, none were heavy-element scientists or radiochemists.

In 1992 the TWG finally released its findings. The committee decided that both the Berkeley and Dubna groups should share the discovery claim for rutherfordium.

One of the greatest achievements of Ernest Rutherford — for whom element 104 is named — was the destruction of the plum-pudding model of the atomic nucleus.

This outcome was not what either research group wanted, but it was accepted with some protest. The name 'rutherfordium' was part of a broad set of compromises between both research groups that resulted in element 105 being named for Dubna and element 106 named for Glenn Seaborg. For more information about the controversial history of rutherfordium, see *The Transuranium People* by Darleane Hoffman, Albert Ghiorso and Glenn Seaborg[3].

In 1970, Ghiorso and co-workers synthesized a new isotope of rutherfordium, ^{261}Rf (ref. 4). The half-life of this particular isotope is 69 s — which is relatively long in the context of transactinide elements — and so encouraged chemists to attempt the first liquid-phase studies of rutherfordium. At the time it was not known whether rutherfordium would behave like a group 4 metal or would follow the actinide series in its chemistry. In the same year, Robert Silva and colleagues[5] in collaboration with Ghiorso's team eluted ^{261}Rf from a cation exchange resin in the presence of tetravalent zirconium and hafnium, and trivalent actinide tracers. The results of this experiment showed that ^{261}Rf eluted with the tetravalent hafnium and zirconium tracers and solidified its place as a group 4 metal.

Gas-phase chemistry studies of rutherfordium took advantage of the volatile properties of the group 4 metal chlorides. Anyone who has worked with hafnium(IV) chloride will no doubt remember the gag-inducing effect it has! Isothermal gas chromatography was performed with the chlorides of zirconium, hafnium and rutherfordium using a column of SiO_2 from set temperatures of 100 °C to 600 °C (ref. 6). The experiments measured the relative yields of products out of the column as a function of temperature, and then the adsorption enthalpies on SiO_2 from a Monte Carlo fit of their measurements were calculated. This was used as a yard stick for measuring volatility.

As expected for a heavier molecule, hafnium chloride was found to be less volatile than zirconium chloride (that is, a lower enthalpy of adsorption than zirconium chloride). However, the volatility of rutherfordium chloride was found to be nearly the same as zirconium chloride. This is a dramatic break from the trend that periodicity would predict. Presumably this is caused by some relativistic effect, but the exact mechanism that creates volatile salts of rutherfordium is still a mystery.

The future of rutherfordium chemistry will probably focus on devising chemical systems that help elucidate the role of relativistic effects in its chemistry, as well as the creation of new compound classes of rutherfordium, such as inorganic complexes and organometallics. ❐

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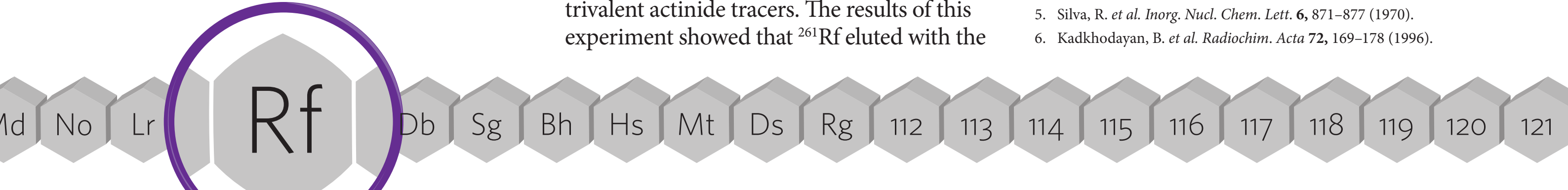

in your element

Welcome copernicium?

In the search for superheavy elements, element 112 was a stepping stone towards the 'islands of stability'. **Sigurd Hofmann** now relates the steps that led to its 'creation' and detection.

Element 112 did not invite a lot of interest when theoretical nuclear physicists predicted the famous island of stable superheavy elements — elements that have a number of nucleons that leads to arrangements in closed shells, which confers them stability despite the high repulsion forces between the protons. Rather than element 112, it was element 126, and later 114 and 120, that attracted most of the attention, because they were predicted to have half-lives up to a million years, suggesting that they could be found on Earth. Efforts to identify them in nature or in various nuclear reactions, however, remained unsuccessful, leading scientists to follow the difficult and stony path of producing these elements step-by-step. In 1976, the starting point was element 106, now called seaborgium, and for many years element 112 marked a temporary end to this progress.

Four key technical improvements were required to enable the detection of 112. The first was an accelerator delivering ion beams of as many different isotopes as possible, with beam intensities of at least 10^{12}–10^{13} ions per second, and at about 10% of the speed of light. The second was a target, also made from various isotopes, which could stand these high beam intensities. The third was a separator for fast and efficient separation of the reaction products from the beam, and finally a detector system for a reliable identification of the element obtained.

In our laboratory, these advances were made possible with the accelerator UNILAC (Universal Linear Accelerator), a rotating target wheel, the electromagnetic separator SHIP (Separator for Heavy Ion reaction Products) and the use of position-sensitive silicon detectors. This combination allowed us to detect nuclei with lifetimes ranging from one microsecond to a few hours, and detect each element from 107 to 111. In 1996 we were ready to synthesize element 112. We selected a beam and a target material so that the sum of their protons gave 112: a zinc beam consisting of 30 protons and 40 neutrons was used to bombard lead target nuclei, composed of 82 protons and 126 neutrons, resulting in a new element that had 112 protons and 166 neutrons — that is, an atomic-mass number of 278.


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Nicolaus Copernicus is best known for challenging the accepted view of the Universe by describing a system centred around the Sun, rather than the Earth.

Although forcing the two nuclei (zinc and lead) together requires a considerable amount of energy — the reacting nuclei do not easily amalgamate, and are much more likely to be repulsed by immensely strong electric forces acting between their protons — this barrier can be overcome and the attractive force between the nuclei leads to nuclear fusion. This reaction releases energy, and the hot nucleus created by this exothermic process then cools down by emitting one neutron, and the nucleus 277 remains, which is the one we were able to study.

Even with the most intensive beams, we managed to produce only one atom of element 112 in one week. In 2000, a second experiment allowed us to measure a second atom, and two more atoms were produced in 2004 by the RIKEN laboratory in Japan (K. Morita *et al. J. Phys. Soc. Jpn.* **76,** 043201; 2007), thus confirming our data. This led the International Union of Pure and Applied Chemistry to assign priority of its discovery to our team, and in April 2009 we were asked to suggest a name for element 112.

Our team of 21 researchers from four different nations discussed possible names for about a month — including those suggested by students and the public. We agreed that element 112 should be named after the astronomer Nicolaus Copernicus and suggested the name 'copernicium' with the abbreviation 'Cn'.

Copernicus, who lived 500 years ago in the transition period between the Middle Ages and modern times, had a significant influence on the political and philosophical thinking at that time and contributed to the rise of modern science, based on experiments. His representation of the planets also represents other systems governed by an attractive force between small objects revolving around a bigger centre. On a microscopic scale, this is the atom, with its electrons orbiting around the nucleus and, in the case of copernicium, 112 electrons moving around a nucleus consisting of 112 protons and 165 neutrons.

Copernicium should behave as a transition metal, as it is below zinc, cadmium and mercury in group 12, and its similarity to the latter has already been shown by initial experiments adsorbing a few atoms of it onto a gold surface. It might be a little bit more volatile than mercury, but will very likely be a liquid at room temperature. Of course, with only a few rapidly decaying atoms having been made so far, it is not likely to be of practical use for some time, but its detection paves the way to heavier elements still — the aforementioned superheavy elements. ❐

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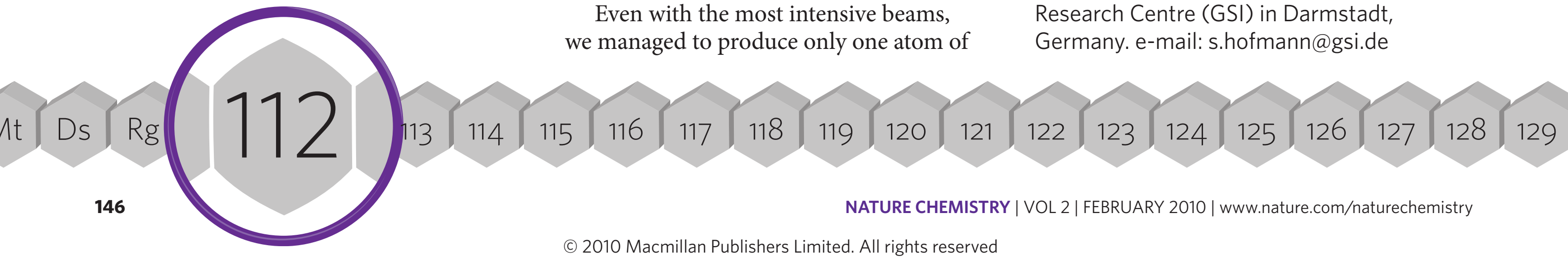

in your element

A flourish of fluorine

Herbert Roesky relates how the small, highly electronegative fluorine atom unveiled the chemical reactivity of noble gases and found many practical applications. But it can also render organic compounds highly toxic or pollutants.

Fluorine's name derives from fluorspar — or fluorite, CaF_2 (pictured) — which in earlier times was used as a flux to facilitate smelting. As early as the seventeenth century, fluorspar was found to emit light when heated, and gave its name to the fluorescence phenomenon. In 1886, the French chemist Henri Moissan electrolysed a solution of KHF_2 in anhydrous HF and obtained a gas that caused crystalline silicon to burst in flames. He immediately reported his results to the French Academy of Sciences with the following words: "One can indeed make various hypotheses on the nature of the liberated gas, the simplest would be that we are in the presence of fluorine". Moissan was to be awarded the Nobel Prize in Chemistry in 1906 for the discovery of 'le fluor'.

Fluorine chemistry developed rapidly during the Second World War, with American scientists working on the 'Manhattan project' to separate fissionable uranium-235 from uranium-238. Uranium is present in nature as three isotopes — ^{238}U, ^{235}U and ^{234}U (99.28%, 0.73% and 0.005% abundance, respectively) — but these have very similar properties and are therefore difficult to separate. It was the volatility of uranium hexafluoride that turned out to be the key discovery for their separation: the current gaseous diffusion and centrifuge processes to enrich uranium in ^{235}U, which rely on a slight mass difference between the two isotopes, both use uranium hexafluoride. Ensuring that this technology does not proliferate is one of today's key political issues.

Although other syntheses have been shown — such as from K_2MnF_6 and SbF_5 — the preparation of elemental fluorine is still largely based on the pioneering work of Moissan. On an industrial scale, the main use of elemental fluorine is in the production of UF_6 and SF_6, which is used as a dielectric medium in electric devices. A number of metal fluorides with unusually high oxidation states such as AuF_5, AgF_3, NiF_3, NiF_4 and HgF_4 have also been synthesized in recent years, and are used as very strong oxidizing agents.


ISTOCKPHOTO / WAKUKA

A milestone in chemistry was achieved through the use of fluorine: the discovery of the reactivity of noble gases — when xenon fluoride was prepared by Neil Bartlett in 1962 — which challenged the generally accepted view that noble gases were inert. This led to the preparation of an extended number of noble gas fluorides and their derivatives, as well as fluorides of krypton and radon.

Owing to its small atomic size and covalent behaviour, the substitution of hydrogen or oxygen by fluorine in organic molecules usually results in a large number of new compounds of an interesting nature, featuring very stable covalent carbon–fluorine bonds. The best-known example is the widespread use of Teflon (polytetrafluoroethylene) in non-stick cooking pans.

These stable carbon–fluorine bonds have also been used with enormous success in the design of pharmacologically active molecules. The lengths of the C–H and C–F bonds are not too dissimilar, but the stability of C–F and its powerful electron-withdrawing properties give rise to very desirable properties in drug design, and most organofluorines can be safely used without the risk of releasing toxic fluoride. For example, an aromatic ring fluorinated in its *para* position cannot be metabolized by enzymes in the body into poisonous epoxides. Currently, about 20% of pharmaceutical products, as well as 30% of agrochemical compounds, contain fluorine, and this proportion is rising.

Organofluorines can also be highly toxic, however — monofluoroacetic acid, for example, is lethal in humans at oral doses of 2–8 mg kg^{-1} through disruption of the citric acid cycle, which is important for the energy supply of the cells. Moreover, chlorofluorocarbons (CFCs) were extensively used in refrigerators and aerosols owing to their extreme kinetic stability in the atmosphere, but they proved to be catastrophic in the stratosphere, leading to depletion of the ozone layer.

Recent developments in fluorine chemistry include the use of perfluorocarbons and hydrofluoroethers in liquid–liquid extraction separation, and catalysts containing fluorinated tags. Cyclopentadienyl titaniumtrifluoride ($Cp^{*}TiF_3$ where $Cp^{*} = C_5Me_5$) and its derivatives are also very effective catalysts for the polymerization of styrene: the $Cp^{*}TiF_3$ catalyst is about 50 times more active than its chlorinated counterpart, at a lower cocatalyst-to-catalyst ratio (300 versus 900 for the chlorinated system). For industrial uses, both the high activity and low cocatalyst-to-catalyst ratio allow tremendous cost reduction.

Finally, returning to fluorspar, compounds of the type LCaF (where L is a β-diketiminate ligand) have been prepared. In contrast to fluorspar, they are soluble in organic solvents and can be used as intermediates to cover surfaces with CaF_2 — a coating that is transparent to visible light, and resistant to acids and bases.

Although fluorine compounds have a key role in electric cars, electronic devices, space technology and pharmaceuticals, they can also have disastrous effects, and scientists working in this field need to be very alert. ❒

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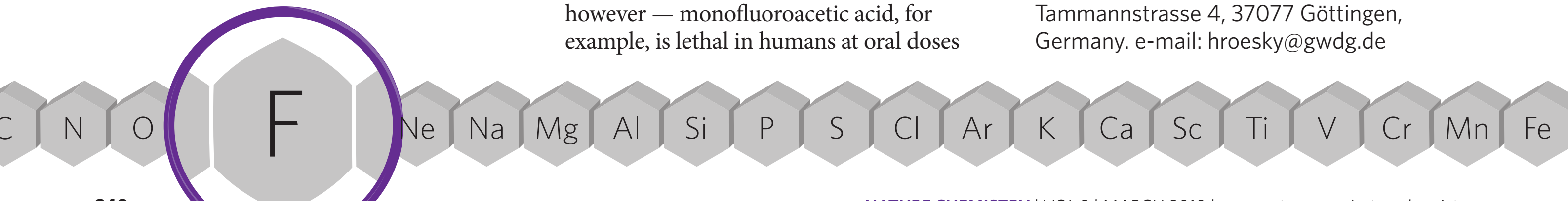


Green bismuth

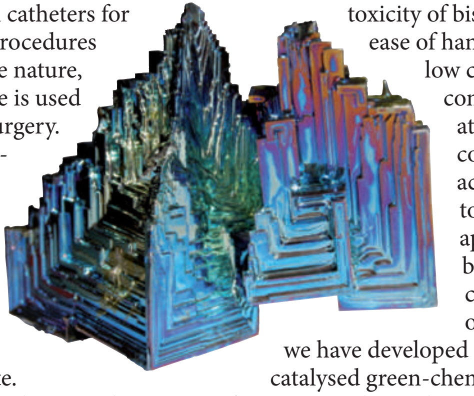
Ram Mohan looks at how bismuth — a remarkably harmless element among the toxic heavy metals in the periodic table — has sparked interest in areas varying from medicinal to industrial chemistry.

Bismuth, the 83rd element in the periodic table, has been known since ancient times, but was often confused with lead and tin. In 1753, Claude François Geoffroy from France demonstrated that bismuth is distinct from these elements. The word bismuth itself is derived from the German word 'wismuth' (white mass). Studies showed that it was used as early as the sixteenth century by the Incas, who mixed it with tin to prepare bismuth bronze for knives[1]. Bismuth was also the instrument of alchemy fraud in the London Stock Exchange — in the 1860s, a Hungarian refugee named Nicholas Papaffy convinced a large number of investors to support his alleged method to transform bismuth and aluminium into silver. This led to a surge in the price of bismuth on the metal market, and the opening of a new company in Leadenhall Street (home of the London Metal Exchange), but by then Papaffy had absconded with the rather large sum of £40,000 (ref. 2).

Bismuth is mainly found in the ores bismuthinite (bismuth sulfide) and bismite (bismuth oxide), but also occurs in its elemental state, in the form of crystals with an oxide layer of varying width that reflects iridescent colours (pictured). It is commonly obtained as a by-product in copper, lead and tin mining, and is therefore relatively inexpensive for a rare metal.

Frequently referred to as the heaviest stable isotope of any element — and for all practical purposes it is — bismuth-209 is nonetheless slightly radioactive. This was first predicted by theoretical studies, then demonstrated in 2003 by astrophysicists in France[3], who showed that bismuth-209 has an incredibly long half-life of 1.9×10^{19} years (the age of the universe is estimated to be about 1.4×10^{9} years).

Despite its location amid toxic heavy metals in the periodic table, bismuth and its compounds are remarkably harmless — many bismuth compounds are even less toxic than table salt (sodium chloride)[4]! This makes bismuth unique among the heavy metals, and has earned it the status of a 'green element'. For this reason, the world of cosmetic and medicinal chemistry has paid it particular attention. Bismuth oxychloride, for example, is used to impart a silvery sheen to cosmetics and personal care products. It is also marketed as BIRON powder, which has found applications in catheters for diagnostic and surgical procedures owing to its radio-opaque nature, and bismuth nitrate oxide is used as an antiseptic during surgery.



Perhaps the most well-known bismuth-based medicine is Peptobismol, now a widely available over-the-counter medicine in the US for stomach disorders. The active ingredient is bismuth oxide salicylate. It was first concocted by a doctor in his home in the early twentieth century to cure 'cholera infantum', an inflammatory disorder that afflicted infants suddenly, causing diarrhoea, vomiting and sometimes death[5]. Although the exact mechanisms of its action are not well understood, it is believed that it lines the abdominal walls with a protective coating that prevents further irritation.

Bismuth has many interesting properties that have led to several applications in industry, and it is commonly used in solders. It is one of the few substances (water being another) that expands on solidification, and has been used to prepare low-melting typesetting alloys that need to expand to fill printing moulds. Bismuth trioxide is also the main ingredient in fireworks called dragon's eggs — those that produce a visual display before exploding with a sharp crack. Bismuth has become popular as a replacement for the highly toxic metal lead, as it has a comparable density and many countries now prohibit the use of lead shot for hunting water birds. Bismuth is also, along with graphite, one of the most diamagnetic materials known — it is repelled by a magnetic field — and has found applications in magnetic levitation (Maglev) trains, which can achieve speeds of over 250 mph.

More recently, bismuth and its compounds in the +3 oxidation state have found significant applications as green Lewis acid catalysts in organic synthesis. The low toxicity of bismuth salts, their ease of handling and relatively low cost make bismuth compounds more attractive than other corrosive Lewis acids[6]. In addition to developing applications of bismuth(III) compounds in organic synthesis, we have developed some bismuth-salt-catalysed green-chemistry experiments for use in undergraduate laboratories[7].

Bismuth is a therefore remarkable eco-friendly metal with numerous applications in everyday life. With increasing awareness for the environment, one can expect to see a rise in the use of green metals such as bismuth in applications ranging from organic synthesis to engineering. ❐

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Hg Tl Pb **Bi** Po At Rn Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm

in your element

The riches of uranium

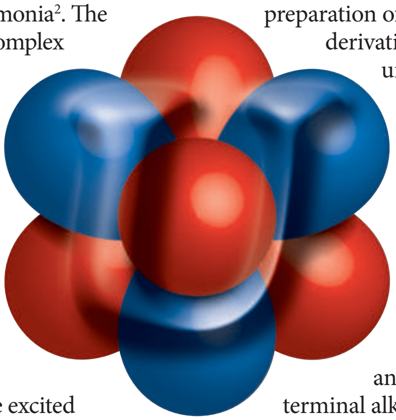
Uranium is best known, and feared, for its involvement in nuclear energy. **Marisa J. Monreal** and **Paula L. Diaconescu** take a look at how its unique combination of properties is now increasingly attracting the attention of chemists.

It is nearly impossible to find an uplifting, funny, or otherwise endearing quote on uranium — the following dark wisecrack[1] reflects people's sinister feelings about this element: "For years uranium cost only a few dollars a ton until scientists discovered you could kill people with it". But, in the spirit of rebranding, it is interesting to note that the main source of Earth's internal heat comes from the radioactive decay of uranium, thorium and potassium-40 that keeps the outer core liquid, induces mantle convection and, subsequently, drives plate tectonics.

Uranium is the naturally occurring element with the highest atomic number. Its discovery in 1789 in the mineral pitchblende (or uraninite) is credited to the German chemist Martin Heinrich Klaproth who named it after the planet Uranus, itself only discovered eight years earlier. Although at the time Klaproth thought that he had discovered uranium metal, its actual isolation was not achieved until 1841, by the French chemist Eugène-Melchior Péligot who reduced the anhydrous uranium tetrachloride present in the ore with potassium. Through the end of the nineteenth century and until the mid-twentieth century, uranium was widely used, for example, in the colouring of glass, giving it a greenish–yellow hue (from UO_2; 'Vaseline glass').

The discovery of radioactivity in 1896 by Henri Becquerel from a uranium sample, and subsequent research by Enrico Fermi and others from 1934 on, eventually showed that ^{235}U can undergo a chain reaction of nuclear fission. This made it attractive for the nuclear power industry but also for Little Boy, the first nuclear weapon used in a war. Uranium's use in nuclear weapons is, understandably, the source of the widespread phobia felt by most for uranium. However, it is only weakly radioactive — the half-life of ^{238}U is 4.468×10^9 years — and emits alpha particles. These have a low penetration depth and can be arrested by the skin, making depleted uranium (composed mainly of ^{238}U) safe to work with as long as it is not inhaled or ingested.

Studying the fundamental chemistry of uranium is an exotic endeavour, but those who embrace it will reap its benefits. Haber and Bosch found that uranium was a better catalyst than iron for making ammonia[2]. The isolation of an η^1-OCO complex of uranium[3] also showed that, even though it is not involved in natural processes, it can help shed light on their mechanism: similar complexes are proposed to be instrumental in the photosynthetic fixation of CO_2, but transition-metal models have remained elusive.



Synthetic chemists are excited about uranium's properties. Uranium brings the best of many worlds to the table: like the lanthanides, it generates electrophilic complexes that show high reactivity towards normally inert substrates. Like the transition metals, it benefits from multiple oxidation states (III to VI), a property that has been greatly exploited in redox reactions. However, unlike the lanthanides, which generate mostly ionic compounds, and unlike the transition metals, which use their *d* orbitals for coordination bonds, uranium can use its *f* orbitals (pictured) to form covalent bonds[4].

Furthermore, uranium's large radius makes unique coordination environments possible. One class of compounds in particular encompasses the many unusual properties of uranium: the inverted sandwiches of arene-bridged diuranium complexes, which showed that δ back-bonding with *f* orbitals is the equivalent of π back-bonding in transition metal organometallic chemistry[5].

Although the use of uranium catalysts for drug synthesis seems unlikely, it is worth considering that what Haber and Bosch found about uranium's superior catalytic activity may not be an isolated event. The organometallic chemistry of uranium was born during the 'Manhattan project' — code name of the development of the first nuclear weapon during the Second World War. This field truly began to attract interest in 1956 when Reynolds and Wilkinson reported the preparation of the first cyclopentadienyl derivatives[6]. The discovery of uranocene electrified the field as much as that of ferrocene had pushed forward the organometallic chemistry of transition metals. Today, examples of processes catalysed by uranium complexes include the hydrogenation of alkenes and the oligomerization, dimerization, hydrosilation and hydroamination of terminal alkynes.

Reports of researchers taking advantage of the unique properties of uranium are appearing with increasing frequency, and it is only a matter of time until these processes are transformed from stoichiometric to catalytic. Uranium may still cost more than a few dollars a ton, but scientists are using it for a lot more than just weapons. ❐

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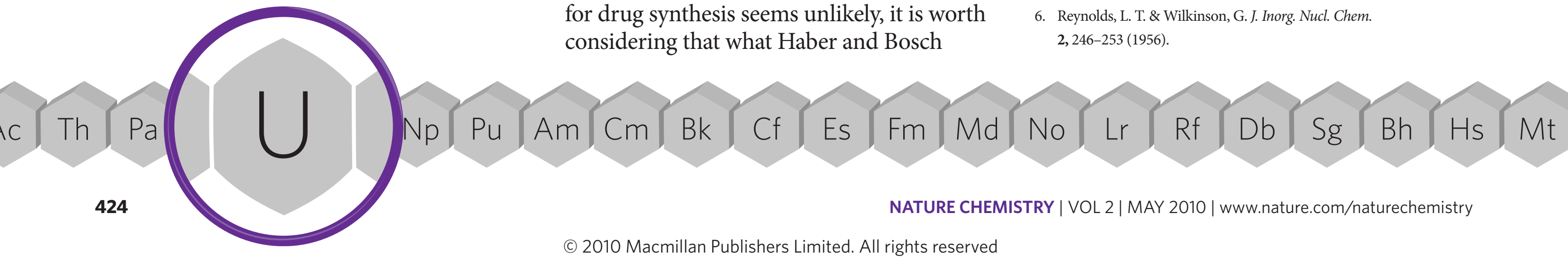


in your element

Is lithium the new gold?

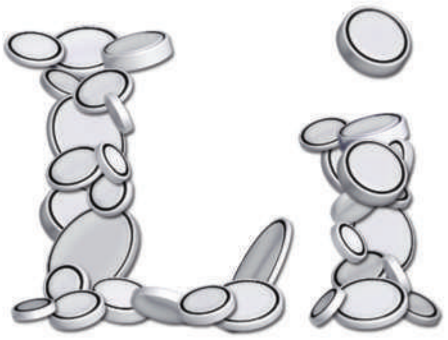
Jean-Marie Tarascon ponders on the value of lithium, an element known for about 200 years, whose importance is now fast increasing in view of the promises it holds for energy storage and electric cars.

Although it has been known for almost two centuries, lithium is suddenly making the news: it is the primary ingredient of the lithium-ion batteries set to power the next generation of electric vehicles and, as such, could become as precious as gold in this century[1]. It is also non-uniformly spread within the Earth's crust, sparking rumours that Andean South American countries could soon be the 'new Middle-East'. Together, these factors set the scene for controversial debates about the available reserves[2–4] and the anticipated demands[1]: if all cars are to become electric within 50 years, fears of a crunch in lithium resources — and thus a staggering price increase such as that faced today with fossil fuels — are permeating.

With its atomic number of 3, lithium is located in the top left corner of the periodic table. It was Johann August Arfvedson, one of Jöns Jakob Berzelius's students, who first detected its presence in 1817 while analysing the mineral petalite ($LiAlSi_4O_{10}$), itself discovered in 1800. Berzelius called this new element *lithos* (Greek word for stone).

Lithium, whose silvery-white colour tarnishes on oxidation when exposed to air, is the most electropositive metal (−3.04 V versus a standard hydrogen electode), the lightest ($M = 6.94$ g mol^{-1}) and the least dense ($\rho = 0.53$ g cm^{-3}) solid element at room temperature, and is also highly flammable. Owing to this high reactivity, lithium is present only in compounds in nature — either in brines or hard rock minerals — and must be stored under anhydrous atmospheres, in mineral oil or sealed evacuated ampoules.

Their particular physical, chemical and electrochemical properties make lithium and its compounds attractive to many fields. Apart from the recent advent of lithium-based batteries, lithium niobate ($LiNbO_3$) is an important material in nonlinear optics. Engineers use lithium in high-temperature lubricants, to strengthen alloys, and for heat-transfer applications. It is also widespread in the fine chemical industry, as organo-lithium reagents are extremely powerful bases and nucleophiles used to synthesize many chemicals. Its effect on the nervous system has also made lithium attractive as a mood-stabilizing drug, and in nuclear research tritium (^{3}H) is obtained by irradiating ^{6}Li. Annual demand has therefore grown by 7–10%, currently reaching about 160,000 tons of lithium carbonate (Li_2CO_3) per year — about 20–25% of which is for the battery sector.



Energy storage, which should help mitigate the issues of pollution, global warming and fossil-fuel shortage, is becoming more important than ever, and Li-ion batteries are now the technology of choice to develop renewable energy technology and electric vehicles. They typically consist of a Li-containing positive electrode and a Li-free negative electrode, separated by a Li-based electrolyte. From simple calculations, assuming a one-molar Li-based electrolyte and a 3.6 V $LiMPO_4$ electrode (where M is Fe or Mn), the demand is estimated to be about 0.8 kg Li_2CO_3 per kWh — and this number is not expected to decrease with recently developed batteries such as lithium–air or lithium–sulfur, which need an excess of lithium at the negative electrode to function properly. The fact that tritium might also be used with deuterium for nuclear fusion could increase demands.

Extracting lithium from hard rocks is laborious and expensive, however, and most of that produced (roughly 83%) at present comes from brine lakes and salt pans: salty water is first pumped out of the lake into a series of shallow ponds, then concentrated using solar energy into a lithium chloride brine, which is subsequently treated with soda to precipitate Li_2CO_3. Considerable amounts of lithium are present in sea water, but its recovery is trickier, and highly expensive.

It is extremely difficult to estimate the world's lithium reserves[1–3] — a debate typically fed by investors and venture capitalists. The present production of Li_2CO_3 is about half what would be needed to convert the 50 million cars[4] produced every year into 'plug-in hybrid electric vehicles' (with an electric motor powered by a 7 kWh Li-ion battery and a combustion engine). The demand becomes astronomic if we consider full electric vehicles — which require an on-board battery of 40 kWh. These numbers bring fears of a potential Li shortage in a few decades, painting a dim picture.

This alarming global situation will hopefully drive researchers to investigate new battery technologies[5] and loosen our dependence on lithium. Fortunately, the situation improves if one also considers recycling — the low melting point (180 °C) of lithium metal and the very low water solubility of its fluoride, carbonate and phosphate salts make its recovery quite easy. Combining further brine exploitation with an efficient recycling process should be enough to match the demands of a 'propulsion revolution' that would solely rely on Li-ion cells, lessening geopolitical risks. ❐

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Recognizing rhenium

Rhenium and technetium not only share the same group in the periodic table, but also have some common history relating to how they were — or indeed weren't — discovered. **Eric Scerri** explains.

Rhenium lies two places below manganese in group 7 of the periodic table and its existence was predicted by Mendeleev in 1869. In fact, when his periodic system was first published, group 7 was rather unique because it contained only one element known at the time — manganese — and had at least two gaps below it. The first gap was eventually filled by element 43, technetium[1], with the second gap being filled by element 75, rhenium.

Rhenium was the first of these two new group-7-elements to be discovered — in 1925 — and accepted by the scientific community. In the course of an arduously long extraction, Walter Noddack, Ida Tacke (later Noddack) and Otto Berg obtained just one gram of rhenium after they processed approximately 660 kg of the ore molybdenite in Germany[2]. Today, rhenium is isolated far more efficiently as the byproduct of the purification of molybdenum and copper.

The German discoverers called their element rhenium, after Rhenus, the Latin name for the river Rhine (pictured) that flows close to the place where they were working. They also claimed to have isolated the other element missing from group 7 — element 43 — that eventually became known as technetium, but this claim was hotly disputed by several other groups. As recently as the early years of the twenty-first century, however, research teams from Belgium and the USA re-analysed the X-ray evidence from the Noddacks and argued that they had in fact isolated element 43 (ref. 3). But these further claims have also been fiercely debated by many radiochemists and physicists and now have been laid to rest, at least for the time being[4].

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And while we are on the subject of Ida Noddack in particular, it was she who first proposed in 1934 that nuclear fission might be possible as the result of the break up of a nucleus into fragments. Her speculation was generally ignored and it had to wait until 1939 when Hahn, Strassmann and Meitner really discovered fission. The main reason Noddack's proposal fell on deaf ears seems to be that her reputation had been badly damaged by the controversy surrounding the announcement of the discovery of element 43 back in 1925.

By a further odd twist of fate, the Japanese chemist Masataka Ogawa believed that he had isolated element 43 even earlier in 1908, and called it nipponium. His claim too was discredited at the time, but in 2004 it emerged that he had in fact isolated rhenium, rather than element 43, and well before the Noddacks and Berg[5].

Until quite recently, no mineral containing just rhenium as the only type of cation (in combination with a non-metallic element) had ever been found. As reported in 1994, however, a team of Russian scientists discovered rhenium sulfide at the mouth of a volcano on a remote island off the east coast of Russia[6]. Based on its appearance in the field, the substance was initially thought to be molybdenite (the mineral from which Re was first extracted), but after analysis back in the laboratory it was found to contain no Mo and was shown to contain approximately 75% Re and 25% S by weight.

The chemistry of rhenium is rather diverse. Among other things, it shows the largest range of oxidation states of any known element, namely –1, 0, +1, +2 and so on all the way up to +7 — the last of which is its most common oxidation state. It is also the metal that led to the discovery of the first metal–metal quadruple bond. In 1964, Albert Cotton and co-workers in the USA discovered the existence of such a Re–Re quadruple bond in the form of the rhenium ion, $[\mathrm{Re_2Cl_8}]^{2-}$ (ref. 7).

A large quantity of rhenium is made into super-alloys to be used for parts in jet engines. Typically for a transition metal, rhenium also acts a catalyst for many reactions. For example, a combination of rhenium and platinum comprise the catalyst of choice in the very important process of making lead-free and high-octane petrol. Rhenium catalysts are especially resistant to chemical attack from nitrogen, phosphorus and sulfur, which makes them useful in hydrogenation reactions in various industrial processes.

More recently a rather simple compound of the element, rhenium diboride, has attracted some attention because it is one of the hardest of all known substances. Unlike other super-hard materials, such as diamond, it does not have to be manufactured under high pressure[8].

So, although rhenium was the last stable element to be discovered, it is certainly not the least when it comes to its properties and applications. ❐

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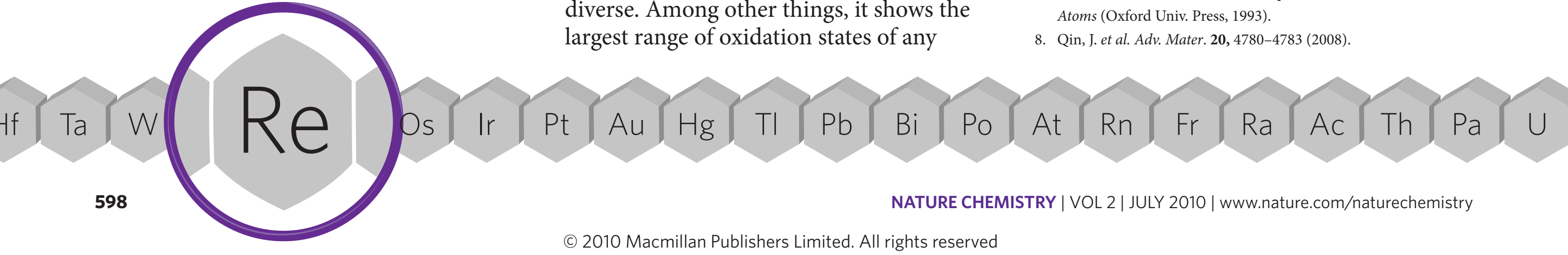


Europium in the limelight

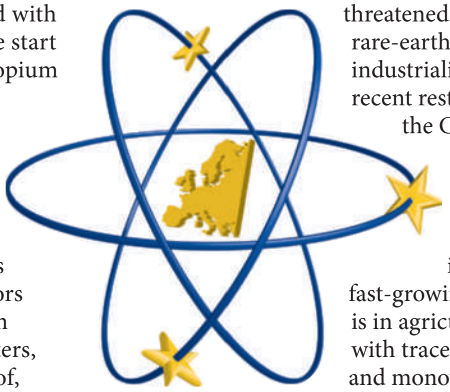
Jean-Claude Bünzli sheds light on why europium — an element that is neither abundant in the Earth's crust nor involved in biological processes — has nevertheless attracted a great deal of interest from chemists.

The story starts at the end of the nineteenth century, when gifted scientists were systematically filling in gaps in Mendeleev's table by deciphering atomic optical spectra. Today this task seems rather easy, and could be carried out by undergraduate students. At the time, however, poorly performing instruments and difficulties in purifying samples were major hindrances. As a result, the history of lanthanide discovery is full of incorrect claims and heated disputes among would-be discoverers.

The first, somewhat furtive, signal from element 63 was recorded in 1885 by Sir William Crookes, who found an anomalous red line (609 nm) in the emission spectrum of a samarium sample. In 1892–3, Paul-Émile LeCoq de Boisbaudran — the discoverer of gallium, samarium and dysprosium — confirmed the existence of this band and detected a further green band (535 nm). Enter Eugène-Anatole Demarçay who, in 1896, after patient fractionation of samarium oxide, determined the presence of a new rare-earth element between samarium and gadolinium. He isolated it in 1901, and ended the note in which he reported this discovery with "I propose for the new element the name europium, with symbol Eu, and atomic weight 151 (approx.)"[1].

The reason why Demarçay decided on this name remains a mystery. Interestingly, he was not affiliated to any university, and had been running an independent laboratory after an unsuccessful application to the Academy of Sciences. He was a rather eclectic scientist who had dealt with organic, organometallic and inorganic chemistry before becoming a talented spectroscopist. He had also toured several countries to study their geology and culture[2]. It is plausible that this opening to all aspects of chemistry and to the world led him to chose Europe over France or Paris (at that time, neither francium nor lutetium were known). Europium metal is now known to be highly reactive; the element's most stable oxidation state is +3, but the +2 state also occurs in solid-state compounds and water.

Georges Urbain, a brilliant young chemist who inherited Demarçay's spectroscopic equipment, observed in 1906 a very bright red emission for yttrium oxide doped with europium[3]. This was the start of a long career for europium as an active component in phosphorescent materials — not only as a red, but also a blue emitter, because its reduced divalent form (Eu^{II}) emits in this spectral range. Phosphors based on red Eu^{III}, green Tb^{III} and blue Eu^{II} emitters, or a combination thereof, can convert UV radiation into visible light. These materials play essential roles worldwide in applications such as X-ray-intensifying screens, cathode-ray tube or plasma-display panels, and have also been used more recently in energy-saving fluorescent lamps and light-emitting diodes.



The luminescence of trivalent europium can also be sensitized by organic aromatic molecules, making such complexes useful in a variety of highly sensitive applications such as security inks and bar codes. For example, when the European Union launched its single currency in 2002, the euro bills were printed with an anticounterfeiting ink at least one component of which is a europium phosphor, most probably a *tris*(β-diketonate), yielding an orange–red emission under UV light. The greenish-blue emission from the same banknotes could well arise from divalent europium but this is mere conjecture.

Since the beginning of the 1980s, europium has played a major role in highly sensitive biomedical analyses that use time-resolved luminescence. Such analyses are routinely carried out in most hospitals and medical laboratories. Luminescent bioprobes based on europium and other lanthanides are now ubiquitous in the life sciences, including bio-imaging. Fortunately, one kilogram of europium is sufficient for almost one billion analyses — which means that these applications are not threatened by the shortage of rare-earth elements feared by industrialized nations after the recent restrictions on exports by the Chinese government.

A recently proposed application that could have far-reaching importance to the fast-growing world population is in agriculture. Plastics doped with traces of divalent europium and monovalent copper have been shown to efficiently convert the UV portion of solar energy into visible light. This process is rather 'green' (the complementary colour of red). Using these plastics to cover greenhouses has enhanced the amount of visible light received by plants, leading to crop yields roughly 10% higher.

Such an increase could cover the growing need for food over several decades without expanding the cultivated surface — showing that europium is possibly heading towards another bright future. ☐

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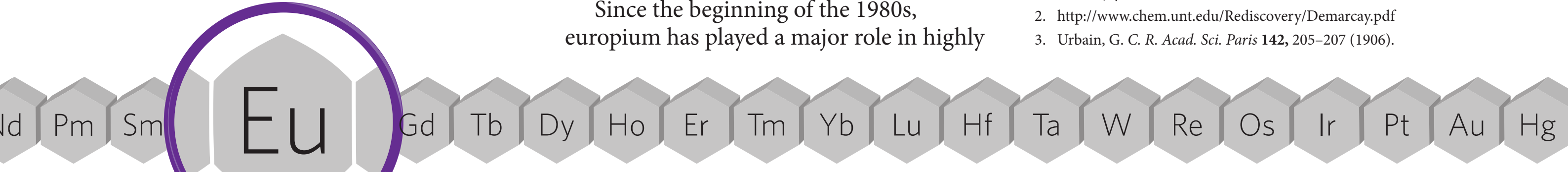


in your element

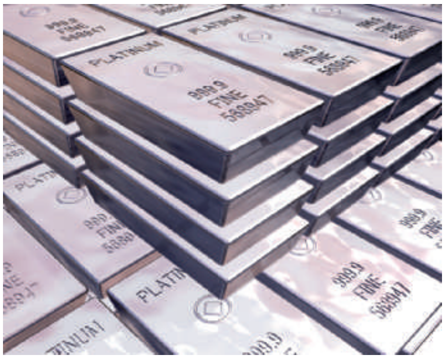
Behind platinum's sparkle

As a rare and precious metal that is also resistant to wear and tarnish, platinum is known to be particularly well-suited to jewellery. **Vivian Yam** reflects on how, beyond its prestigious image, platinum has also found its way into a variety of fields ranging from the petrochemical to the pharmaceutical industry.

Platinum was in fact named after another element — its name derives from the Spanish word 'platina' meaning 'little silver', because of its colour. It usually occurs in nature as elemental platinum, or is alloyed with small quantities of other metals, especially iridium.

The most widespread role of platinum is as a catalyst, in particular in the automobile industry, where it is used in catalytic converters to catalyse the complete combustion of low concentrations of unburned hydrocarbon from the exhaust into carbon dioxide and water vapour, and in the petrochemical industry to cleave large hydrocarbon chains. It also finds its place with the advent of renewable energy, as platinum nanoparticles are used in fuel cells for the clean production of hydrogen.

Another important area is in the development of platinum drugs, and more recently prodrugs — compounds first introduced in the body in an inactive form, which are later converted into their active form. Since the first report by Rosenberg in 1969 on the antitumour properties of the platinum complex cisplatin[1], there has been an enormous interest in understanding its action mechanism. This has led to the development of second- and third-generation platinum(II) anticancer drugs (carboplatin and oxaliplatin), and platinum(IV) prodrugs — for example satraplatin, currently under consideration for approval of the US Food and Drugs Administration. Although the mechanisms are still unclear, it is now known that square-planar platinum(II) drugs crosslink to DNA, and a number of other platinum(II) complexes with planar auxiliary ligands act as DNA metallointercalators.



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Recently, photo-sensitive moieties have also been incorporated to platinum complexes for the development of photo-activated cancer chemotherapy or (pro) drug delivery. Platinum(II) porphyrins, chlorins and derivatives can also serve as photosensitizers for singlet oxygen production for photodynamic therapy (PDT) — their heavy atom effect would facilitate intersystem crossing and improves the quantum yield of singlet oxygen ($^1O_2$), which is key to the success of PDT.

Parallel to these developments, platinum(II) porphyrins have been found to be phosphorescent compounds with long-lived triplet excited states. As such, they are highly susceptible to luminescence quenching by oxygen, and thus promising for oxygen optical sensing applications — of interest for the development of pressure-sensitive paints in pressure sensing. A number of other platinum(II) complexes, for example polypyridine compounds, also show rich phosphorescent properties combined with a rich polymorphism that gives rise to a variety of intense colours. An early example of a highly coloured platinum(II) species comes from the one-dimensional compound Magnus's green salt[2] ($[Pt(NH_3)_4][PtCl_4]$).

Square-planar platinum(II) compounds are well known for their strong propensity towards metal–metal interactions, which lead to interesting spectroscopic features — both in the UV–visible range and in emission spectroscopy. In general, a red shift in absorption and emission wavelengths would be observed in the presence of metal–metal interactions, which sometimes translates into visual colour or emission colour changes[3]. The rich phosphorescent properties of platinum(II) compounds have also led to their use for white organic light-emitting diodes, vapochromic and vapoluminescence sensors for various volatile organic compounds, chemosensors, bio-probes, labels and imaging agents.

The flat planar structure and charge-transport properties of platinum(II) compounds also leads to interesting field-effect charge mobility. The charge-transfer properties of a number of platinum(II) compounds and polymers have been exploited for photosensitizing and organic photovoltaic applications. The unique non-covalent metal–metal interactions in platinum(II) compounds — which have a comparable energy to that of hydrogen bonds — offer novel strategies for building supramolecular assemblies, organogels, polymers and nanostructures.

The characteristic colour and emission changes in these assemblies can be exploited to detect sol–gel transitions and stimuli-responsive microenvironment variation. Molecular wires and multimetallic self-assembled coordination architectures have also been constructed[4] based on platinum(II) compounds; some of which stabilize unusual guest molecules whereas others serve as site-selective nanoreactors.

Platinum has proved to be a versatile element with fascinating reactivity. It has become of great importance in very diverse areas, and there is little doubt that platinum chemistry will continue to attract increasing attention in the forthcoming decades. ❐

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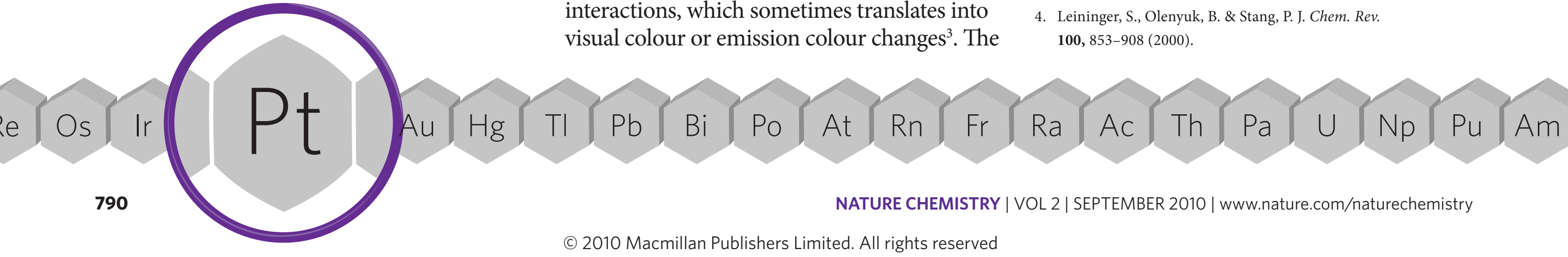

In the nickel of time

Although reports on the use of nickel can be traced back to 3,500 BC, **Catherine Drennan** points to a resurgence of interest in nickel-based chemistry in the energy and environmental areas.

Nickel is not new. Those interested in the origins of life have postulated that early life forms could have used mixtures of nickel, iron and sulfur to harvest energy from their environment rich in carbon dioxide, carbon monoxide and hydrogen[1]. Nickel's unintentional use by humans has been traced back as far as 3,500 BC in Syrian bronzes, although it was not formally recognized as an element until 1751.

Most Americans know that one use of nickel is as an ingredient in a coin — the 'nickel' to be exact. Although the face value of a nickel has always been five cents, the amount of nickel actually present in the coin has varied over the years between 25% of the content (of the original and current coins) to none at all in the 'wartime nickels'. Nickel is also found in stainless steel and rechargeable batteries, is used for catalytic hydrogenation, and can give a green tint to glass.

Nickel has several important properties that allow for these varied uses. It is one of the *d*-block transition metals, and is located between the pairs of iron and cobalt to the left, and copper and zinc to the right. Because of their *d* electrons, transition metal complexes can be visually stunning, exhibiting a vast array of brilliant colours. These complexes can undergo large changes in oxidation (nickel oxidation states range from 0 to +4), display a wide variety of geometries, and form diverse types of bonds including organometallic ones with carbon atoms.

Like its nearest neighbours in the periodic table, nickel is very important in biology. It is essential to the survival of many micro-organisms, including beneficial microbes that live in our intestines. Unfortunately, it also serves harmful microbes, for example strains of *Escherichia coli* that are responsible for bladder infections, through a protein known as nickel-iron hydrogenase, which interconverts dihydrogen with two protons and two electrons — a reaction involved in cellular energy production.

Helicobacter pylori, which is associated with stomach ulcers, is able to live in the acidic conditions of the stomach thanks to a nickel-containing protein called urease, which breaks down urea into ammonia and carbon dioxide, neutralizing the acidity. Drugs that target the nickel uptake by *H. pylori* are therefore being investigated for ulcer therapies.

Another fascinating role of nickel in biology is found in the global carbon cycle. Although we generally think of carbon monoxide, carbon dioxide and methane as pollutants and greenhouse gases, some microbes see them as a source of energy. The term global carbon cycle refers to the fact that one microbe's fuel is another microbe's waste product. For example, phototropic anaerobic bacteria 'eat' carbon monoxide and produce carbon dioxide, whereas microbes called acetogens consume carbon dioxide and produce acetate. Meanwhile, methanogens live on acetate and generate methane. Methane subsequently enters the atmosphere, where it can be converted back to carbon dioxide through anaerobic degradation, thus completing the cycle.

At the heart of this carbon cycle are three nickel-containing enzymes: carbon monoxide dehydrogenase, acetyl-CoA synthase, and methyl-CoM reductase. Each year, the combined action of these three enzymes is estimated to be responsible for removing 10^8 tons of carbon monoxide from the environment[2] and producing 10^{11} tons of acetate[3] and 10^9 tons of methane[4]. The ability of nickel to form bonds with carbon is key to this reactivity. It is also interesting to note that the proposed involvement of nickel in the primordial soup stems from microbes' ability to use it to live on carbon monoxide and carbon dioxide — gases that were abundant early in Earth's history.

Today, scientists are more interested in applying these nickel-containing enzymes to solve the world's current energy and environmental problems — hydrogenase chemistry is attractive for hydrogen fuel cell technology[5], whereas the reactivity of carbon monoxide dehydrogenase and acetyl-CoA synthase could be used in coal plants to lower carbon dioxide emissions[6,7]. With issues such as global warming, urban pollution and the recent oil spill disaster in the gulf coast, we must be aware of how our quest for energy impacts the environment as we search for alternative energy sources. 'An oldie but a goodie', nickel chemistry may be in the nick of time. ❐

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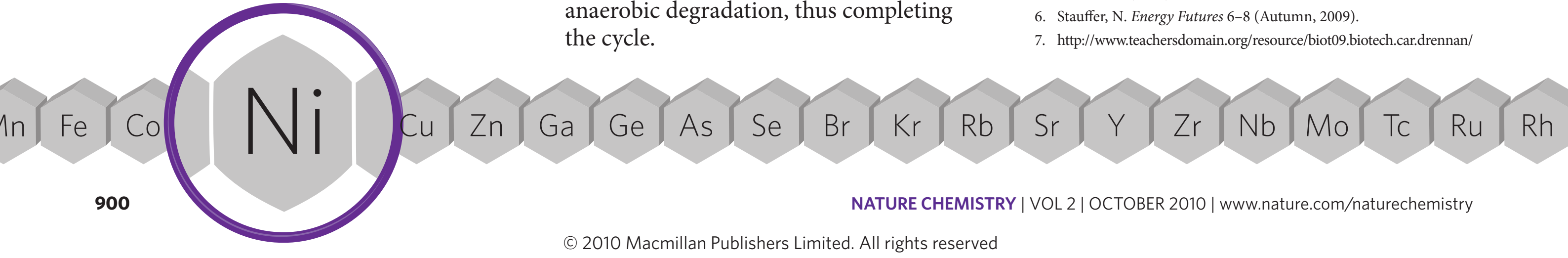


Neglected neptunium

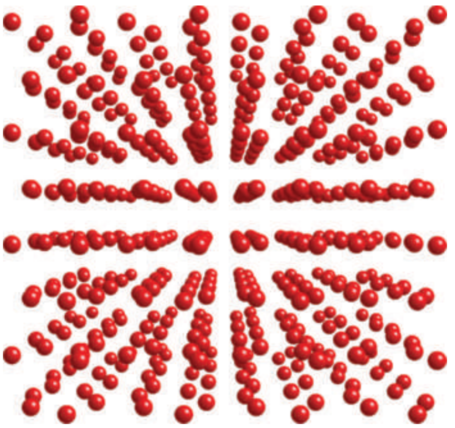
Jim Ibers talks about neptunium, an element that has remained largely unnoticed despite the flurry of activity devoted to its neighbours in the periodic table, uranium and plutonium.

The actinides, the radioactive chemical elements beginning with element 89 (actinium) and extending to element 103 (lawrencium), are a neglected part of chemical pedagogy, at least in the USA. As a result, some chemists may not know the names of most of these elements, or where they lie in the periodic table, but most would guess correctly from knowledge of the Solar System that somewhere in the periodic table uranium, neptunium and plutonium would be found in that order. Some might even guess correctly that this order reflects their year of discovery.

However, it does not reflect the relative attention these elements have received. Although neptunium is barely talked about, uranium and plutonium are famous — some would say infamous — because in the early 1940s isotopes of uranium and plutonium were found to be fissile, meaning they can sustain a nuclear chain reaction, and hence had weapons applications. Neptunium was also known to be fissile, but the quantity needed made it unattractive for such applications.

Yet neptunium ought to be famous because it was the first actinide element to be synthesized. In a classic study in 1940, McMillan and Abelson bombarded a thin layer of UO_3 with neutrons from a cyclotron[1]. Investigation of the chemistry of the product that possessed a 2.3-day half-life led them to conclude that it was element 93 with a mass of 239, now written as ${}^{239}_{93}$Np. They also speculated on the nature of the daughter product obtained from the radioactive decay of their new element, soon characterized[2] by Seaborg and co-workers as an isotope of element 94 (plutonium). Much of this work was classified for the next five years.

Now, about 22 isotopes of neptunium have been characterized. Of these, ^{237}Np is the most stable, with a half-life of 2.14×10^6 years — too short for any significant quantity of primordial ^{237}Np to remain today, 4.5×10^9 years after the Earth's formation. The mass of ^{237}Np being formed from various nuclear-decay processes in the Earth's crust is estimated to be only about 10^{-12} times that of uranium-containing minerals. Thus, neptunium could not be 'discovered'; it had to be synthesized. Today, the production of plutonium in nuclear reactors is the main source of neptunium.



Extended view of the crystal structure of neptunium.

The need to characterize new actinide elements, and to separate their compounds from each other and those of the lanthanides, has led to extensive knowledge of actinide solution chemistry. Here, oxidation states are critical: these dictate acid–base properties, coordination chemistry and solubilities in aqueous and non-aqueous solvents. In solution the elements americium to lawrencium closely resemble one another and often exhibit oxidation states of +3, as do the lanthanides. In contrast, uranium has formal oxidation states of +3 to +6, and neptunium and plutonium have those oxidation states as well as +7.

These differences are the basis for sophisticated procedures, such as the PUREX (plutonium–uranium extraction) process for removing uranium and plutonium from nuclear spent fuels, in which neptunium and small amounts of the heavier actinides are rejected into a high-level radioactive liquid waste. New advanced commercial processes are needed to remove ^{237}Np, which will otherwise become the main contributor to the total radiation from these wastes in about 10^4 years — a time being discussed at present for their containment.

As opposed to their solution chemistry, knowledge of the solid-state chemistry of the lighter actinides is far less extensive. Even here, neptunium is the 'stepchild'. Pure metals and compounds of uranium and plutonium have been produced in far greater quantities than those of neptunium. In the solid state one finds some surprising differences in structures and properties. For example, the crystal structure of neptunium under ambient conditions differs from those of uranium and plutonium, although the structural complexity of plutonium metal is another subject altogether. The intermetallic compounds $UCoGa_5$ and $NpCoGa_5$ do not superconduct, whereas $PuCoGa_5$ is a non-conventional high-temperature superconductor. Unlike isotopes of uranium or plutonium, ^{237}Np is one of the best Mössbauer nuclei in the periodic table — Mössbauer spectroscopy is a valuable tool for probing valence electrons, and hence oxidation states and chemical bonding.

Many surprises await the development of more extensive knowledge of the chemistry of neptunium compounds, particularly the solid-state chemistry. The renaissance of nuclear energy may well accelerate this development. ❐

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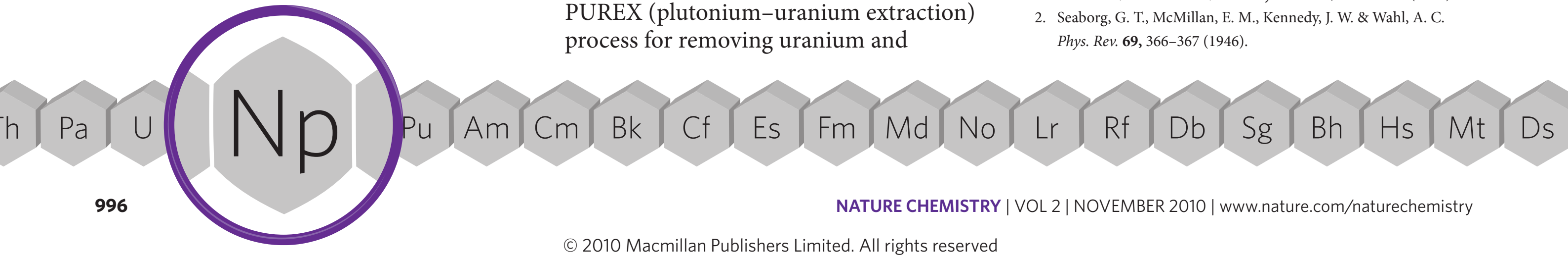

Regarding ruthenium

From humble beginnings in Siberia, ruthenium has blossomed into an incredibly interesting and useful element. **Simon Higgins** looks at its role in past — and perhaps future — Nobel Prize-winning discoveries.

Given its position in the middle of the *d*-block of the periodic table, it is not surprising that ruthenium exemplifies many of the properties of the transition metals — such as forming complexes in a wide range of formal oxidation states (from VIII to –II). First described in 1844 by Karl Klaus, who isolated it from the insoluble residue left on dissolving crude Siberian platinum in *aqua regia*, it was named after Russia (Latin *Ruthenia*) — partly in tribute to Klaus's homeland and partly in recognition of the earlier efforts of Gottfried Osann who had suggested the existence of new elements in these residues, one of which he had named ruthenium.

Ruthenium is rare (it comprises roughly 10^{-7}% of the Earth's crust). It is usually found together with its five fellow 'platinum group' metals (Os, Rh, Ir, Pd and Pt), but because of the much greater demand for rhodium and platinum, ruthenium is currently fairly inexpensive (£3.60/$5.60 per gram). Industrially, it is used as a hardener, in alloys with platinum and palladium for applications in electrical switching gear. Moreover, titanium's resistance to corrosion can be greatly increased by alloying it with small amounts (<1%) of ruthenium.

A fascinating and sometimes an enigmatic element, the chemistry of ruthenium seems to hold nearly unique charisma in the eyes of its investigators. For example, in 1984 a magisterial book, *The Chemistry of Ruthenium* by Seddon and Seddon, offered complete critical coverage of the literature up to 1978; it would be difficult to envisage a similarly comprehensive update today!

Together with osmium and xenon, ruthenium exhibits the highest known formal oxidation state in the periodic table — VIII — in RuO_4. This volatile and toxic compound, which has an odour of ozone if one is foolhardy enough to sniff it, is soluble in CCl_4 and is a strong oxidant.

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The compound usually used as a starting material in ruthenium chemistry, however, is 'hydrated ruthenium trichloride', an almost black, reflective solid that is obtained industrially by dissolving RuO_4 in aqueous HCl and evaporating to dryness. It is soluble in a wide range of solvents, is comparatively reactive, and — despite its name — mainly consists of oxo-bridged dimeric Ru(IV) chloro-complexes.

A landmark in coordination chemistry was the 1965 report by Allen and Senoff of the first synthetic complexes of N_2, $[Ru(NH_3)_5(N_2)]X_2$ (X = anion). These were originally made by treatment of 'ruthenium trichloride hydrate' with hydrazine, and showed a weak band in their infrared spectra at around 2,100 cm^{-1}, owing to the N≡N stretch. Their discovery triggered a new field — synthetic nitrogen-fixation catalysis — which has produced much new chemistry and insight, but sadly, no lower-cost rival for the Haber–Bosch process so far.

Nowadays, ruthenium is at the forefront of several important areas of science. For example, the development of air- and moisture-tolerant homogeneous ruthenium catalysts for alkene metathesis has had a major impact in total synthesis and in materials chemistry, resulting in a share of the 2005 Nobel Prize in Chemistry for their pioneer, Bob Grubbs. Ruthenium complexes are also extensively employed in enantioselective hydrogenation reactions in organic synthesis (exemplified by the work of Ryoji Noyori, who was one of the winners of the 2001 Nobel Prize in Chemistry), and are now being investigated in chemotherapy.

Perhaps the most-studied ruthenium complex of recent times has been $[Ru(2,2'\text{-bipyridine})_3]^{2+}$, sometimes called rubipy, and its derivatives. On irradiation with visible light, rubipy produces a long-lived photoexcited triplet, essentially $[Ru^{III}(2,2'\text{-bipyridine})_2(2,2'\text{-bipyridine}^{\bullet-})]^{2+}$. The Ru(III) is a strong oxidant, whereas the 2,2′-bipyridine radical anion is a powerful reductant. It was pointed out in the mid-1970s that, in principle, this photoexcited state is capable of both oxidizing and reducing water, to O_2 and H_2 respectively, giving rise to much research. In practice, the system only works in the presence of a sacrificial reducing agent and a quencher, typically methyl viologen, and gives only H_2.

More recently, related complexes have been much studied as dyes in dye-sensitized solar cells, such as the Grätzel cell. Here, the dye is covalently attached to wide-bandgap semiconductor nanoparticles (usually TiO_2) that act as an anode, to which the photogenerated state transfers an electron. The resulting Ru(III) is reduced by iodide ions in a liquid electrolyte, and the iodine produced is itself re-reduced at a cathode. Such cells are proposed as potential low-cost rivals to silicon solar cells.

Over 150 years since ruthenium's discovery, its chemistry continues to provide fascinating new findings and potential technologies. No doubt its lure will continue to attract others to its study. ❐

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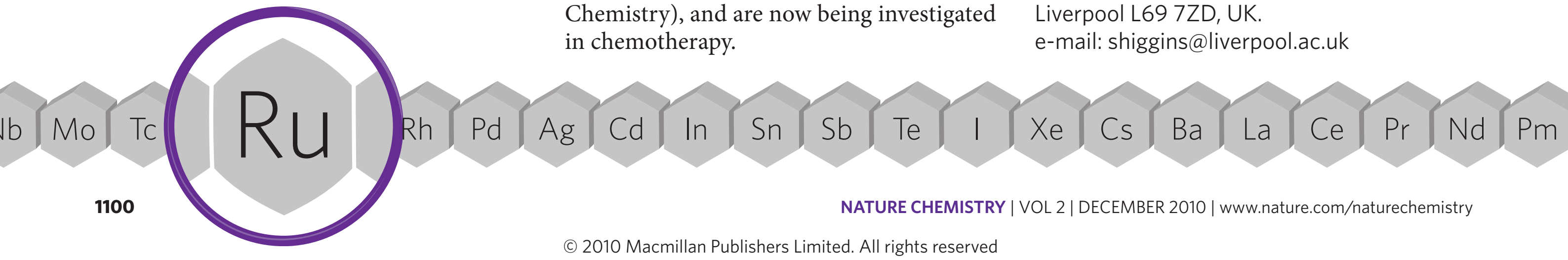

The two faces of phosphorus

Jonathan R. Nitschke considers how the story of phosphorus, an element that glows without fire, nicely illustrates the pursuit of scientific knowledge — including how such knowledge goes on to serve many purposes, for better or for worse.

Among the rainbow of other phosphorus allotropes — red, purple and black — the white allotrope, P_4, was the first discovered and has the most interesting story. Its cold glow generated awe and wonder among the seventeenth-century audience that first beheld it, and served as a beacon to the curiosity of the first modern scientists, who carried out experiments into its properties and uses. Their narrative is our own — the struggle to shine the light of reason on the dark myths of our ancestors, using the empirical method to draw deep and predictively useful knowledge out of shadows. Yet the pale fire of phosphorus also serves as a warning light to us across the centuries, for much of this knowledge was not used to benefit humanity.

The discoverer of P_4 is believed to have been Hennig Brandt of Hamburg, whose quest for the philosopher's stone led him, in around 1669, to pyrolyse in a furnace the solid residue of human urine[1]. The yellow-white sublimate he obtained displayed the remarkable property of luminescence, emitting light without the flames, heat and smoke associated with combustion. Only in 1974 were the glowing species revealed to be transient oxidation products (HPO and P_2O_2) that form on the surface of P_4 by reaction with atmospheric oxygen[2]. These species form in electronically excited states, and their decay back to the ground state occurs with spontaneous emission of visible light.

The slow, luminescent oxidation of white phosphorus can readily gain speed — in the bulk, P_4 is known to be pyrophoric, catching fire spontaneously in air. This easy flammability, moderated by combining P_4 with inert materials, served to make the first cheap and reliable matches, known as 'Lucifers', the name of the best-selling brand. Lucifers were outlawed worldwide during the first years of the twentieth century because they were dangerous to property — a fire could be started by carelessly jostling a box of matches — and also to health. White phosphorus is nearly as toxic as cyanide, and chronic exposure led to an awful form of bone necrosis among match workers known as 'phossy jaw'.


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The toxicity and spontaneous flammability of P_4 make it a terrible weapon. During the Second World War, both sides dropped many tons of P_4 on each others' cities in incendiary bombs that released an incandescent rain of burning liquid phosphorus. Phosphorus burns are grievous — P_4 continues to burn on skin and 'burrows' into flesh. In addition, the phosphoric anhydride (P_4O_{10}) produced by burning readily hydrolyses into phosphoric acid (H_3PO_4), dehydrating and causing acid burns.

Research carried out before and during the Second World War revealed an even more terrible use for phosphorus: a few organophosphate esters with P-linked substituents, such as fluoride and cyanide, were shown to act as highly potent acetylcholine esterase inhibitors. These nerve agents, as they came to be called, are among the most toxic human poisons known, killing through the disruption of essential nerve activity.

In contrast to these nefarious uses, phosphate (PO_4^{3-}) is an essential nutrient for all living organisms. It can be found, for instance, in the backbone of DNA; in adenosine triphosphate, which shuttles energy between biomolecules; and in hydroxyapatite, which is a form of basic calcium phosphate that makes up bones. Other organophosphates, although similar in structure to nerve agents, proved much more toxic to pests than human beings. Those had a role in the 'green revolution' of the 1960s, which saw agricultural yields improve in many parts of the world. Examples include glyphosate (also known as Roundup), which acts as a potent weed killer, and malathion, which inhibits arthropod versions of acetylcholine esterase more effectively than mammalian versions, thus killing insects.

Recently, phosphorus has found a variety of new uses, in particular in the context of new phosphine ligands (R_3P, where R is an alkyl or aryl group) for metal-catalysed transformations. The Nobel Committee have honoured the discoverers of both ruthenium-catalysed alkene metathesis and palladium-catalysed C–C bond-forming reactions, both of which depend on organophosphine ligands. Black phosphorus, which has a graphite-like sheet structure, is an electrical conductor of interest in rechargeable batteries. Elemental P_4 has even recently been rendered insensitive to oxygen through encapsulation in a host molecule, allowing its reactivity to be modulated[3].

New applications of phosphorus chemistry are assured by the element's utility and ubiquity. We hope that our better angels will guide us in these enquiries, rather than the demons that saw phosphorus forged into weapons of war. ❐

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in your element

Give silver a shine

Katharina M. Fromm explains how, as well as catalysis and jewellery, silver serves a myriad of medicinal applications — some of which are even behind poetic traditions such as throwing coins in wishing wells.

Silver, number 47 in the periodic table, takes its name from the Anglo-Saxon or Germanic 'seolfor, silabar', and its symbol Ag from the Roman and Greek 'argentum' and 'argyros' (meaning white, shining). It is ductile and soft, with a face-centred cubic structure and oxidation states between 0 and +3. Places are called after it, for example Argentina or the Rio de la Plata in South America, although today's main silver-producing countries are Peru, Mexico and China.

Silver has been mined, refined and used for thousands of years in ornaments and utensils, for trade, and as the basis of monetary systems (in French there is only one word 'argent' for both silver and money). Egyptians already implanted silver plates into skulls as far back as 2500 BC, and Ancient Greeks and Romans used silver containers to keep liquids fresh. Thus, the tradition of throwing silver coins into wishing wells and fountains comes from keeping water free of germs and people healthy. The first silver paste for tooth restoring was reported in China in 659 AD, and today's amalgams are still made of 20–35 weight% of silver (the rest being mainly mercury, and some additional tin, copper and zinc).

Silver production worldwide reached more than 2,700 tons in 2009 — there is now an estimated reserve of 550,000 tons in the Earth's crust. About 700 tons serve annually in heterogeneous catalysis (for example, production of ethylene oxide and formaldehyde, purification of diesel emission gases), more than for jewellery.

Although we traditionally think of silver as 'second best' after gold, as distributions of medals still reflects today, silver holds three world records: the best electrical conductivity (used for audio cables, electric power switches and circuit breakers) and the highest brilliance (which lead to mirrors and optical applications) of all elements under standard conditions, and the best thermal conductivity of all metals. Silver is stable against oxygen but tarnishes to form silver sulfide if hydrogen sulfide and water are present (such as in wool, latex, eggs or onions) — a well-known phenomenon for silverware and jewellery. Pure silver is too soft to make objects, and is generally alloyed with other metals; 'sterling silver 925' for example contains 92.5 weight% of silver, and typically copper, or alternatively germanium, zinc or platinum, to render it stronger while preserving its ductility, also to reduce casting porosity, and increase resistance to tarnish.


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An important part of silver's history is black and white photography, developed by Niépce and Daguerre in the 1830s. Initially based on a mixture of silver nitrate and chalk, it still relies today on films made of light-sensitive silver halides, stabilized in a gelatine matrix. Silver is used in art and medical radiography but also for quality control. One exotic application of silver iodide is cloud seeding; it relies on a good match in lattice constants between the ice and silver iodide crystal lattices, as discovered by Bernard Vonnegut (the crystallography of ice later played a role in his younger brother Kurt Vonnegut's novel *Cat's Cradle*)[1].

Silver nanoparticles have been known for centuries as red, yellow and orange stains for glass. They now mainly serve as antimicrobial agents in biotechnology and bioengineering, textile engineering, water treatment, and in some consumer products (such as for washing machines or refrigerators). The long-term effect of their release into the environment is currently under investigation[2].

Although silver ions are highly toxic to bacteria at low concentrations (ng l^{-1}), eukaryotic cells withstand concentrations 10 to 100 times higher[3] — overexposure leads to an irreversible grey colouring of the skin (argyria) but causes no severe harm. Silver nitrate is routinely used in eye drops for newborn babies, silver sulfadiazine is found in topical creams for burn wounds, preventing infections and catalysing skin renewal, and other species are found in a variety of products such as surgical fabric materials, cosmetics or antibiotic creams. Long-term catheters — an ideal entrance gate for bacteria and therefore prone to bacterial biofilm formation — have been made of silver alloy or nanoparticle-loaded polymer to reduce such infections[4]. Coatings of implant materials with Ag^0 or Ag^+ coordination compounds — tunable for solubility, structure and stability — have also been successfully implanted in the body, killing bacterial infections while remaining biocompatible for cell growth[5].

Thus, although the mechanism of such action of silver ions remains to be uncovered, 'use of a silver spoon a day keeps the doctor away'… ❐

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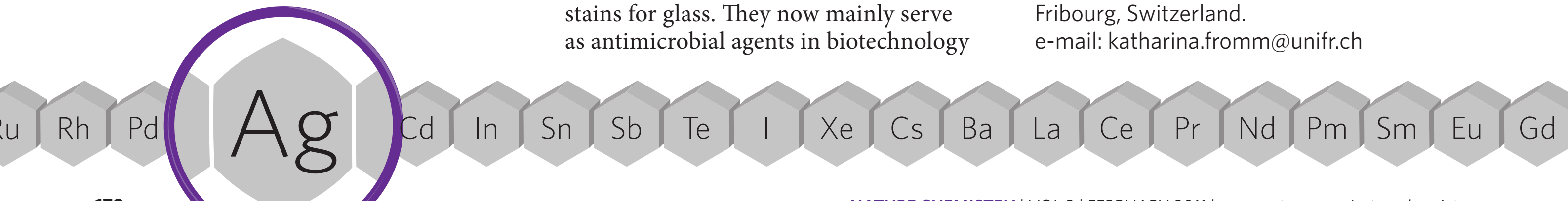

Tracing iodine

Pierangelo Metrangolo and **Giuseppe Resnati** celebrate the bicentenary of the discovery of iodine — a good time to also bring to its conclusion an international project that aims to define and categorize halogen bonding.

Two hundred years ago, the French chemist Bernard Courtois accidentally discovered iodine while investigating the corrosion of his copper vessels. Shortly after that, Humphrey Davy and Louis-Joseph Gay-Lussac independently identified it as a new element, and in 1813 Gay-Lussac named it after the Greek word *ιώδης* meaning violet. A year later, again in the Gay-Lussac laboratory, the first non-covalent adduct of iodine was prepared on reaction with ammonia — but it was only in 1863 that it was assigned the structure $I_2\cdots NH_3$ (ref. 1).

A number of adducts featuring similar attractive interactions with electron-donor species have marked the history of iodine. For example, the observation of $I_2\cdots$aromatic compound complexes made for a key contribution in the understanding of donor–acceptor adducts[2]. More recently, the development of dye-sensitized solar cells technology has relied on the I^-/I_3^- couple — the preferred redox mediator since these cells were first prepared, and still the one that yields the most stable and efficient devices[3].

Such non-covalent attractive interactions between the electropositive region of a covalently bonded halogen atom (including I_2) and the electronegative region of an atom or group of atoms (such as ammonia, aromatics, or I^- ions) are now interpreted in terms of halogen bonding. Iodine and its derivatives are the most prone to forming such bonds, and it is thus an interesting twist of fate that an IUPAC project aimed at delivering the first general definition of the halogen bond[4,5] should come to an end in the year of the bicentenary of the discovery of iodine.

The structural diversity of iodine-containing species is particularly noteworthy, and those are involved in a wide variety of fields ranging from materials science to biomedicine. Iodo aromatic compounds, for example, serve as radiocontrast agents in X-ray-imaging techniques; tincture of iodine, a common disinfectant, is a 2–7% solution of iodine along with iodide salts — the iodides form the halogen-bonded ion I_3^-, which is more soluble than elemental iodine in this ethanol–water mixture.

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Iodine is essential to living organisms as a trace element. The human body typically contains 10–20 milligrams of iodine, more than 90% of which is stored in the thyroid gland. It is used for the biosynthesis of the thyroid hormone T3 (a tri-iodo-thyrosine) and pro-hormone T4 (its tetra-iodo- analogue) — both iodo-organic biomolecules relying on halogen bonding[6]. A very complex enzymatic system protects tissues from an excess of thyroid hormones through a series of iodination/de-iodination reactions — the $O\cdots I$ halogen bonds occurring makes these reactions extremely substrate-selective. For the metabolic functions controlled by T3 and T4 to be carried out, it is particularly important that iodine is ingested — a lack of dietary iodine can cause mental diseases or goitre.

The thyroid hormones are far from being the only iodinated biomolecules. At present, approximately 120 have been isolated from living organisms — including microorganisms, algae, marine invertebrates and higher animals. Their origin, possible biological activity and significance have been discussed in more than 80,000 original articles published in the past 60 years, according to the US National Library of Medicine.

The reactivity of iodine and its derivatives has also impacted synthetic and structural chemistry. In the past 10 years, the number of studies on polyvalent iodine compounds has increased dramatically. This surge in interest is mainly due to the combination of their very useful oxidizing properties with a benign environmental character and their commercial availability. For example, chiral hypervalent iodine compounds have recently proved effective for enantioselective oxidative coupling in asymmetric catalysis[7]. Crystal structures reported in the Cambridge Structure Database that involve iodo-carbons have also more than tripled in the past decade, including widely used species such as antimicrobial agents and the antifungal drug haloprogin.

Despite its 200 years of history, iodine is still very much part of recent developments in diverse areas of chemistry, and there is little doubt that it will continue to attract attention in the forthcoming decades. On this anniversary, we wish iodine many more years of success. ❐

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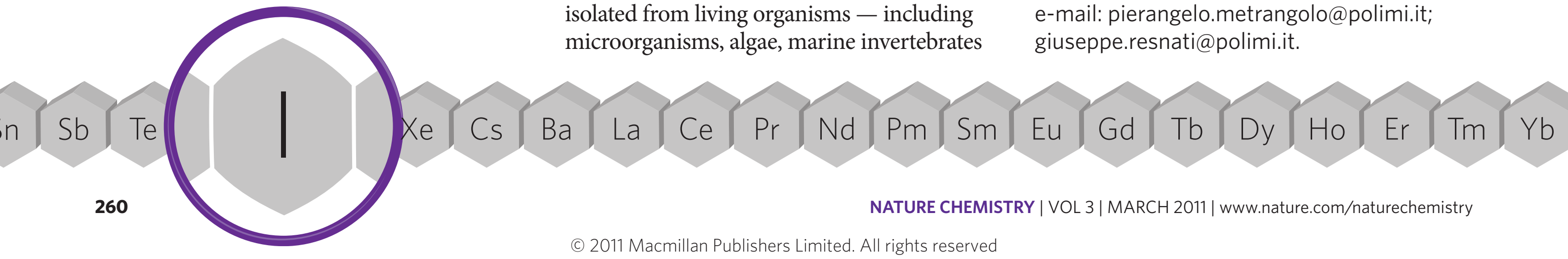

W for tungsten and wolfram

Pilar Goya, Nazario Martín and **Pascual Román** relate how element 74 can be found in lamp filaments or weapon parts and also in literature, and continues to serve many purposes — no matter which of its two names it is given.

Element 74 holds a few records in the periodic table — it has the highest melting point of all metals and has been found to be the heaviest element to be used by living organisms; its carbide also displays a hardness approaching that of diamond. The element also holds a special place in literature, having given its name to a famous uncle[1], and has become a first name in the German language, borne by the knight and epic poet Wolfram von Eschenbach around the 1200s.

An intriguing aspect of element 74's history is the origin of its name — or, rather, its names[2], as it is known as either wolfram or tungsten. In the Spain of 1783, the brothers Juan José and Fausto Delhuyar were the first to isolate it as a pure element from the mineral wolframite $(Fe, Mn)WO_4$ and decided to name it wolfram[3]. Had they chosen 'hispanium', they might have avoided any confusion around names derived from minerals — but many years would elapse before elements were given names such as francium, polonium or europium.

The confusion occurred because, two years earlier, Scheele and Bergman — with whom Juan José Delhuyar had previously worked — had isolated the trioxide, WO_3, from a different mineral, $CaWO_4$, known as either scheelite or tungsten, from the Swedish *tung* (heavy) and *sten* (stone). Although the Delhuyar brothers went a step further, treating wolframic acid with charcoal in the absence of air and thus obtaining the pure metal, the element became known around the same time as either tungsten or wolfram. Both names persist today in different languages, but it is W that was adopted internationally as the symbol.

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In any case, tungsten — as it is known in English — is a rare metal in the Earth's crust. It can be found in the form of oxide and salts in certain minerals, and is generally obtained from its ores as a dull grey powder. After compression and sintering under hydrogen at high temperatures, a grey–white lustrous metallic element, very hard and dense yet ductile, is obtained. It resembles chromium and molybdenum in many of its properties, and resists attack by oxygen, acids and alkalis[4]. It is used in a variety of commonly used objects, in the form of ballpoint pens (carbide materials), and as the metal in electrical components (lamp filaments, electrical resistances and X-ray tubes), hardening alloys (steel), tools for cutting (high-speed steel) or super alloys[5].

In industry, its compounds are most often used as catalysts. Less known is the fact that, in the eighteenth century, the German geologist Rudolf Erich Raspe proposed that the bright yellow colour of tungsten trioxide could be used by artists, as according to him "in beauty it exceeds Turner's yellow colour by far"[6]; it is currently used as a dye. Tungsten also became a strategic element during the Second World War, as its high thermal resistance and the strength of its alloys made it an attractive component for use in penetrating projectiles[5].

Tungsten oxides were the first to be identified as electrochromic materials, when Satyen Deb noticed in 1969 that WO_3 reversibly changed colour on application of an external potential[7], and are still by far the most extensively studied for electrochromic applications. WO_3 is an amorphous phase composed of clusters of a few WO_6 octahedra, arranged in a corner-sharing perovskite-like manner, in which all of the metal centres are of the same type of W(VI). It is transparent as a thin film but, on electrochemical reduction, W(V) sites are formed that produce a blue colour — giving rise to the electrochromic effect.

Although still controversial, the mechanism behind this colouration is thought to involve electrons and protons or alkali metal ions (Li^+, Na^+ or K^+) being injected into and extracted from the material. In any case, a material needs to have an amorphous structure to exhibit good electrochromic behaviour. Polycrystalline films also show considerable optical modulation — but mostly in the near-infrared region.

The commercial opportunities for the development of electrochromic materials are enormous, with applications in displays, for example, and in smart windows, which are able to limit the amount of light and heat passing through. Some smart windows are already on the market, and are soon to be present in the most technically advanced cars and buildings. From electrical components to construction sites, be it tungsten or wolfram, element 74 is continuously proving to be a versatile element.

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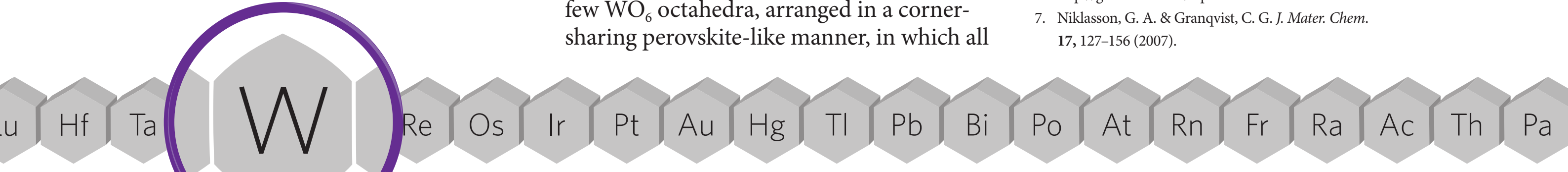

A brighter beryllium

Although it is mainly known for its toxicity, beryllium possesses an array of properties that makes it attractive for a variety of non-industrial purposes. **Ralph Puchta** discusses why it is not always best avoided.

Since ancient times, people have been fascinated by the green or red of emeralds and the light blue of aquamarines. These gems are composed of the mineral beryl — a transparent beryllium aluminium cyclosilicate ($Be_3Al_2(SiO_3)_6$) — and bear traces of transition metals that endow them with striking colours. The mineral beryl is also at the origin of the German word 'brille' for eyeglasses.

It was while analysing beryl that the Frenchman Louis-Nicolas Vauquelin separated beryllium salts from aluminium salts in 1798. At the time he proposed the name 'glucinium', in reference to its sweet taste, but beryllium was finally adopted in French in 1957, in agreement with the other languages. Beryllium was prepared in its elemental form in 1828 by Friedrich Wöhler and Antoine Bussy who, independently, reacted beryllium chloride with potassium. In 1898, Paul Lebeau obtained elemental beryllium by electrolysis of a mixture of molten BeF_2 and NaF. Today, most beryllium is produced by the redox reaction of magnesium with BeF_2, itself obtained from beryl.

Number four in the periodic table, beryllium is the smallest metal atom. It is typically protected by a thin layer of beryllium oxide (BeO), which renders it resistant against concentrated oxidizing acids — diluted hydrochloric acid, however, dissolves it, generating hydrogen in the process. The combination of its high melting point (1,287 °C), good elasticity, ability to scatter high-energy neutrons and other physical characteristics, has led to several practical applications.

Beryllium has traditionally been used to construct radiation windows for X-ray tubes, for example, as it hardly absorbs X-rays. This transparency to energetic particles also led to its use as a component in detectors of the Large Hadron Collider accelerator. Furthermore, beryllium serves in all kinds of nuclear applications, for example, as a neutron reflector in current power plants based on fission and in nuclear weapons.

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Beryllium also takes part in natural nuclear processes in space, such as the fusion reactions that generate carbon. In old stars, during the 'triple alpha process', three $^{4}_{2}He$ nuclei (also called alpha particles) are transformed into one $^{12}_{6}C$ atom. At first, two $^{4}_{2}He$ nuclei fuse into the highly unstable $^{8}_{4}Be$, which tends to simply decay into two $^{4}_{2}He$ nuclei again. However, under particular conditions, these beryllium nuclei are formed faster than they decay. Some can then fuse with an additional $^{4}_{2}He$ nucleus to form the stable $^{12}_{6}C$ atom. Our Sun will undergo this process in around six billion years, when it is around ten billion years old.

Beryllium alloys offer mechanical, thermal and electrical properties of interest to various practical usages. For example beryllium–copper alloys (which typically contain up to 2.5% of beryllium) become non-magnetic and can serve in gyroscopes or magnetic resonance imaging devices. Beryllium can also withstand lower temperatures than glass, a convenient characteristic for military and space applications.

Beryllium is used to dope semiconductors such as gallium arsenide by molecular beam epitaxy. In contrast, its oxide BeO is an electrical insulator, yet excellent heat conductor. Perhaps the most interesting new possible application for beryllium today is that beryllium ions may serve as processors for quantum computers. Such a computer has already been successfully tested for 160 programs, and operated accurately around 80% of the time. It seems likely that larger systems can be realized with a beryllium-based processing unit[1].

However, most practical applications are spoilt at an early stage by the toxicity of beryllium and its compounds, especially in the form of dust. When inhaled, small particles can cause berylliosis — a chronic lung disease that can take any time between a few months and several years to declare itself in the body, and cannot be treated[2]. This does not mean that beryllium and its compounds should not be used at all, but they must be handled with care.

Current research with this element focuses on basic investigations, such as structural and mechanistic properties, and has recently been relying more on computational rather than experimental studies. Research carried out[2] on tetra-coordinated complexes, for example, has provided further knowledge of the structural diversity of beryllium complexes. The possible coordination numbers of beryllium have also recently been clarified[3,4] and mechanistic studies are underway to elucidate solvent-exchange processes[5,6].

As further insight into the structure and reactivity of beryllium compounds is gained, this element will no doubt play an increasing role in daily life applications. In light of this, one might be tempted to conclude — to Be, or not to Be, that is not the question. ❐

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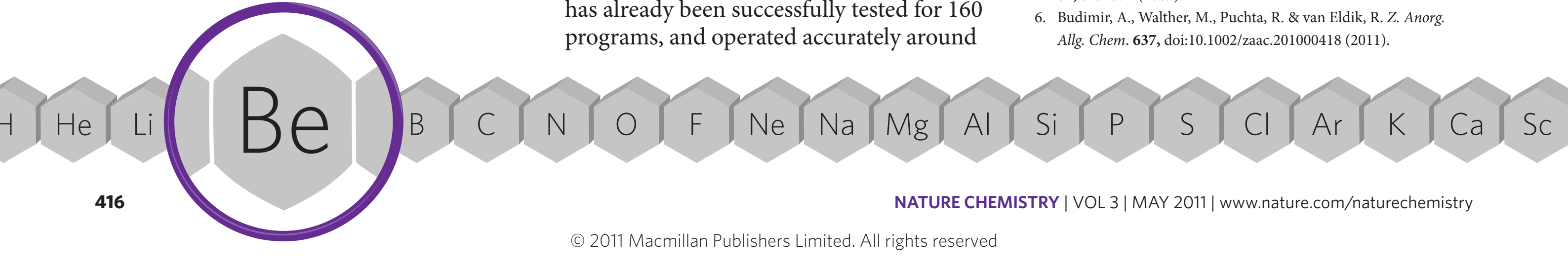


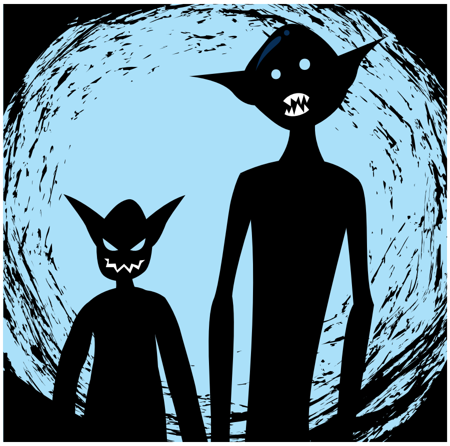
Cobalt close-up

David Lindsay and **William Kerr** remind us that where cobalt is concerned, good has triumphed over evil.

Compounds of cobalt have proved useful throughout history, and it remains an important element to this day, with applications in chemical synthesis. The name is thought to derive from the German *kobold*, meaning 'goblin' or 'evil sprite'. The difficulty in isolating cobalt from its ore — and the release of arsenic oxide that often accompanied the smelting process — were both attributed to the work of evil spirits by the miners who were tormented by this element. Undoubtedly, cobalt's relative scarcity also played a part — it makes up only 29 ppm of the earth's crust and is the thirtieth most abundant element on earth; the second rarest transition metal after scandium.

Cobalt was finally confirmed as a new element by Bergman in 1780, almost half a century after Brandt's isolation of the metal in 1735. Cobalt's history goes back much further, however, as its ore was being used as a blue dye in the Middle East over four thousand years ago. Even today, almost 30% of cobalt produced is used in the ceramic and paint industries. Cobalt is also an essential trace element for humans, and is found at the centre of vitamin B12 and a range of other co-enzymes called cobalamins. Even though the body contains only 2–5 mg of vitamin B12, its involvement in the production of red blood cells means it is vital to life. Vitamin B12 is also notable for its cobalt–carbon bond, making it the only known naturally occurring organometallic complex.

Similarly, many new developments in cobalt chemistry focus on organometallic compounds. In the field of catalysis, for example, cobalt has been found to mediate many of the cross-coupling reactions dominated for years by palladium and nickel. Furthermore, cobalt-based catalysts are also amongst the many systems being looked at for mediating the so-called oxygen evolution reaction (OER) — a fundamental step in the photochemically driven splitting of water into hydrogen and oxygen. The development of efficient technologies based on this process could ultimately lead to environmentally benign energy sources that harness the power of the Sun.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Historically, the most important application of organocobalt complexes in catalysis has been in the transformation of alkenes into aldehydes through a process known as hydroformylation. The classical catalyst for this reaction is the protonated derivative of the tetracarbonylcobaltate anion — $HCo(CO)_4$. Although more selective catalysts, often rhodium-based, have been developed over the years, the cobalt system is still used for many applications.

Being a group 9 element, cobalt does not form a neutral monometallic carbonyl complex. Instead, it forms a dimer — dicobalt octacarbonyl — with a bent cobalt–cobalt bond. This dinuclear compound is also used as a hydroformylation catalyst, but another important reaction is one in which it reacts with alkynes — with loss of two molecules of carbon monoxide — to give alkyne–hexacarbonyl–dicobalt complexes. These air-stable and deep-red compounds can catalyse the cyclotrimerization of alkynes to make substituted benzenes, but their main preparative use is in the formation of substituted cyclopentenones.

The use of alkyne–cobalt complexes in such synthetically efficient and direct ring-forming processes was serendipitously discovered at the University of Strathclyde, Scotland, in 1971. Following on from his pioneering work on the synthesis and reactivity of ferrocene, Peter L. Pauson turned his attention to the fundamental aspects of cobalt-mediated alkyne trimerization. Believing that sufficiently reactive alkenes may be able to react with alkyne–cobalt complexes in a similar fashion to alkynes, the appreciably strained alkene norbornene was investigated. The main organic products isolated from the reactions were cyclopentenones, formed from the combination of one unit each of the alkyne, alkene and carbon monoxide.

This accidental, yet extremely fortunate, discovery led to vigorous research efforts in the Strathclyde laboratories over subsequent years in an effort to establish the scope and limitations of this process for the one-pot formation of selectively substituted cyclopentenones. Indeed, such is the importance of substituted five-membered-ring ketones in organic chemistry, that many related metal-mediated processes for constructing such small ring systems have now evolved from these initial discoveries, and remain the focus of intense international research effort.

To (almost) all organic chemists the world over, this now renowned type of ring-building process is known as the Pauson–Khand reaction — that is, with the exception of one chemist: Pauson himself. The co-worker who discovered the cyclopentannulation process was Ihsan U. Khand, a postdoctoral researcher and ex-PhD student of Pauson's. Accordingly, and typical of his modesty and the generosity and support that he showed to his many students and colleagues, Pauson only ever referred to this reaction in spoken or written communications as 'the Khand reaction'. ❒

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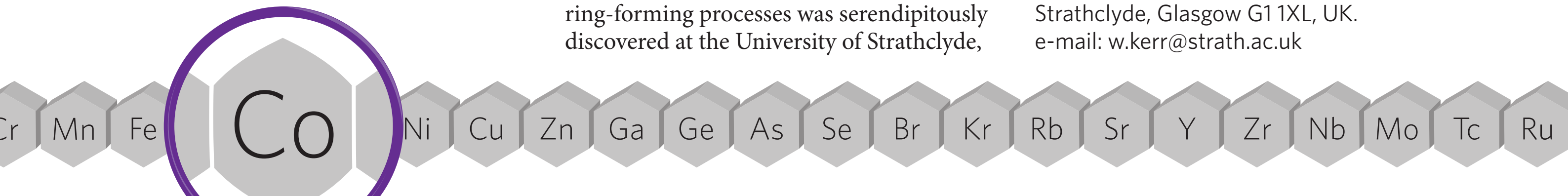

in your element

Selenium stories

Russell Boyd ponders on how selenium — despite close similarities with its neighbours of the chalcogen family, sulfur and tellurium — continues to reveal chemical and biological activities of its own.

Element 34 was discovered in 1817 by Jöns Jacob Berzelius, the 'father of Swedish chemistry'. While preparing sulfuric acid he noticed a residue, which he first thought was tellurium. Realizing it was a new element, he decided to name it after the Greek word for Moon, *selènè*, in a similar manner to tellurium, named two decades earlier by Martin Heinrich Klaproth after the Latin word for Earth, *tellus*.

In nature, selenium is rarely found in its elemental form and only occurs in a few minerals — for example in sulfide ores such as pyrite, where it partially replaces sulfur. It exists as six naturally occurring isotopes with mass numbers 74, 76, 77, 78, 80 and 82; ^{80}Se and ^{78}Se are the most common, with natural abundances close to 50 and 24%, respectively. Selenium is a semi-metallic element that belongs to the family of chalcogens (group 15). Placed just between sulfur and tellurium in that column of the periodic table, it resembles both elements in some aspects. In particular, it has similar allotropic forms and compounds to those of sulfur — for example, red selenium is a Se_8 macrocycle similar to the sulfur allotrope S_8.

The recommended daily dietary allowance of selenium can be supplied by a single dried Brazil-nut.

Although standard inorganic chemistry textbooks often seem to imply that the chemistry of selenium is not as well developed as that of sulfur, it certainly presents interesting reactivity. Selenic acid (H_2SeO_4) resembles sulfuric acid (H_2SO_4) as its first proton also fully dissociates in water, yet it is a more powerful oxidant, capable, for example, of releasing Cl_2 from concentrated HCl or of dissolving gold to form gold(III) selenate.

Most of the selenium produced worldwide is isolated from the mud that forms at the anode during the electrolytic refining of copper. Selenium was once an essential material in photocopying, but has largely been replaced by organic photoconductors. Combined with bismuth, it has replaced lead in plumbing brasses since the 1990s to meet lead-free environmental standards. Selenium is now particularly promising for various electronic devices — the grey allotrope, its most stable form, is a semiconductor that conducts electricity better in the light than in the dark, and serves in photovoltaic cells. The grey form also converts electric current from a.c. to d.c., which explains why it is a component in rectifiers. The largest worldwide use of selenium, however, resides in glass manufacturing, where it is used as a dopant to produce vivid red and pink colours.

One hundred and forty years passed between the discovery of selenium and its recognition as essential for cellular function in most mammals. It is incorporated in proteins through the amino acids selenocysteine and selenomethionine — in which it replaces the sulfur atom of cysteine and methionine, respectively. Selenoproteins, in turn incorporated in enzymes, are essential components of several metabolic pathways, including thyroid hormone metabolism, antioxidant defence systems or immune functions. There is evidence[1] that selenoproteins reduce cancer risk by preventing cellular damage from radicals produced as by-products of oxygen metabolism, and they may also prevent, or slow, tumour growth by enhancing immune-cell activity.

In many countries, meat, seafood, rice, noodles and bread are common sources of dietary selenium, but ingesting too little or too much can have serious consequences. The recommended[2] dietary allowance (55 µg per day for adults according to the Institute of Medicine of the National Academy of Sciences in the US) can be supplied by a single dried Brazil-nut. Selenium deficiency can cause heart disease or weaken the immune system, whereas excessive ingestion leads to selenosis (selenium poisoning), with symptoms such as discoloration of the skin, a garlic odour to the breath and lack of mental alertness — more than 5 mg per day can be fatal. The tolerable upper intake level set by the Institute of Medicine is 400 µg per day for adults; it thus cautions that many dietary supplements contain 50 to 200 µg per daily dose.

Elemental selenium is usually assumed to be harmless, but many of its compounds, for example hydrogen selenide (H_2Se) are extremely toxic. This is why the general perception is that selenium is toxic, even though modern science has recognized it as an essential micronutrient. Recent advances indicate that selenium has the potential to improve human lives in varied ways, including as part of more efficient solar cells[2], synthetic antioxidants[3] or nanocluster coatings for use in orthopaedic applications[4]. ❐

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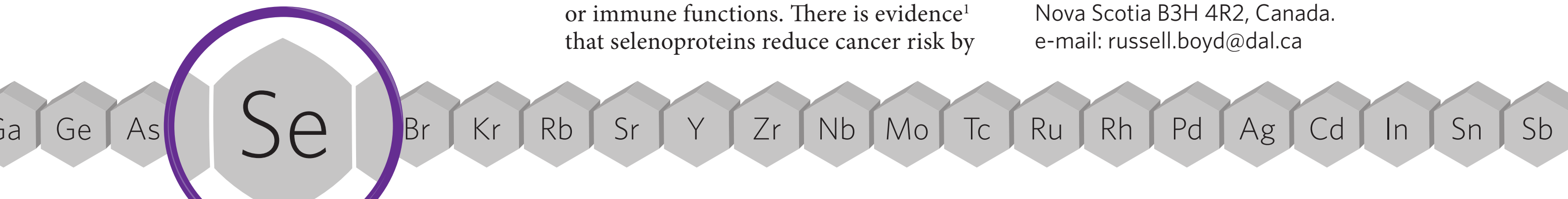


in your element

Under sulfur’s spell

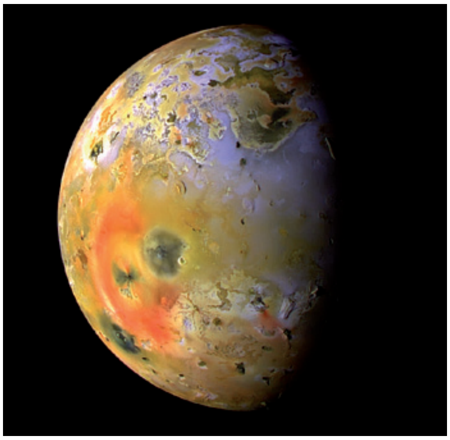
Thomas Rauchfuss marvels at the diversity of sulfur reactivity. Although it poisons most industrial catalysts, it adopts many forms in nature and takes on a variety of biological roles — including that of a biocatalyst.

What is sulfur? This is a tricky question, because many species with the formula S_x are known. The most stable at room temperature is the crown-shaped ring S_8, but elemental sulfur also contains small amounts of the bright-yellow S_7 and tiny amounts of other rings. On heating, sulfur readily converts to a metastable one-dimensional elastomer, which quickly degrades at room temperature back to the S_8 form. The tendency of sulfur to form rings and chains (to catenate) is its most distinctive property. Only at high temperatures does sulfur form S_2, the analogue of O_2.

The catenating tendencies of sulfur are also evident in its anions — the polysulfides with formula S_x^{2-}. They arise by simply adding small amounts of reducing agents to elemental sulfur. These chains of sulfur atoms, which resemble alkanes in their conformation, can be extended or further shortened by redox reactions, a process that is exploited in the sodium–sulfur battery. The anionic chains exist in dynamic equilibrium with radicals such as $S_3^{\bullet-}$— the blue chromophore in lapis lazuli. The anions that terminate these chains can be capped with alkylating agents, protons and metal cations[1]. With metals, one obtains compounds with such improbable formulae as PtS_{15}^{2-} and $Fe_2S_{12}^{2-}$.

Sulfur is readily oxidized, notably to dioxide and trioxide species. Depending on their environment, microorganisms subsist on the hydrolysed derivatives of these oxides through anaerobic respiration. Sulfur dioxide, an electrophilic, bent analogue of carbon dioxide, is produced on a massive, even weather-changing, scale by volcanic eruptions. Further oxidation gives the trioxide precursor to sulfuric acid, produced annually on the scale of about 140 megatons.

Sulfur is featured in two coded amino acids, methionine, which is fairly boring to the sulfur chemist, and cysteine, which has spectacularly diverse roles. By forming S–S bonds, the conversion of cysteine to cystine rigidifies proteins in a manner similar to the crosslinking provided by the S–S bonds in vulcanized rubber. Otherwise, the thiol group is a favoured site for post-transcriptional modifications. Sulfur is featured in many cofactors and vitamins, for example, thiamine, biotin and lipoic acid. Elucidation of their biosyntheses has been a trove of novel mechanisms.



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Io, a moon of Jupiter, has diverse colours owing to the presence of various sulfur species.

As sulfur has occurred in proteins for millennia, fossil fuels often contain a few per cent by weight of organosulfur compounds, most problematically in the form of thiophenes. A continuing focus in petroleum refining is the removal of this sulfur, especially in view of the 5 ppm allowed limit of sulfur in many diesel fuels. This technology, called hydro-desulfurization, relies on modified molybdenum sulfide catalysts to yield a low-sulfur product and hydrogen sulfide waste. Oxidation of the waste produces vast amounts of sulfur, which beckons for new applications.

Thiolates exhibit particular affinity for metal ions; in enzyme active sites metals are commonly anchored via cysteinyl residues. The resilience of the metal–thiolate bond is exploited in the role of thiols in the formation of self-assembled monolayers. These materials are formed by simply contacting thiols with gold surfaces. Self-assembled monolayers are crucial in nanotechnology because they provide a responsive interface between mobile phases (gases and liquids) and an electrically conductive device.

The role of metal–sulfur bonds in biocatalysis is a popular area of research. One of the challenges is to elucidate the mechanism of methanogenesis — the source of the majority of Earth’s natural gas and a contributor to climate change. The final stage of methanogenesis involves scission of a methyl–sulfur bond in coenzyme-M (first isolated from the sewers of Urbana, my home town). The allure of this area is heightened by the discovery that methanogenesis can run in reverse, through a nickel-catalysed reaction of methane[2].

Transformations relevant to ‘bioenergy’ are effected by Fe–S clusters, including the conversions of CO_2 to CO, of protons to H_2, and of N_2 to NH_3 (ref. 3). These processes all involve the coordinated movement of protons and electrons — a mechanistic theme of immense significance. The active sites of the relevant enzymes consist of metal clusters where sulfide ligands help ‘glue’ together the metals. Because changes in electron count barely affect their structures, metal–sulfide clusters are able to quickly accept and relay electrons, as required for efficient catalysis. Apparently the presence of the soft sulfur ligands also enables the metal centres in these catalysts to bind and thereby activate weakly basic substrates such as H_2, CO_2 and N_2 — ligands normally reserved for organometallic compounds. Our ability to master these transformations could be key to our future. ❐

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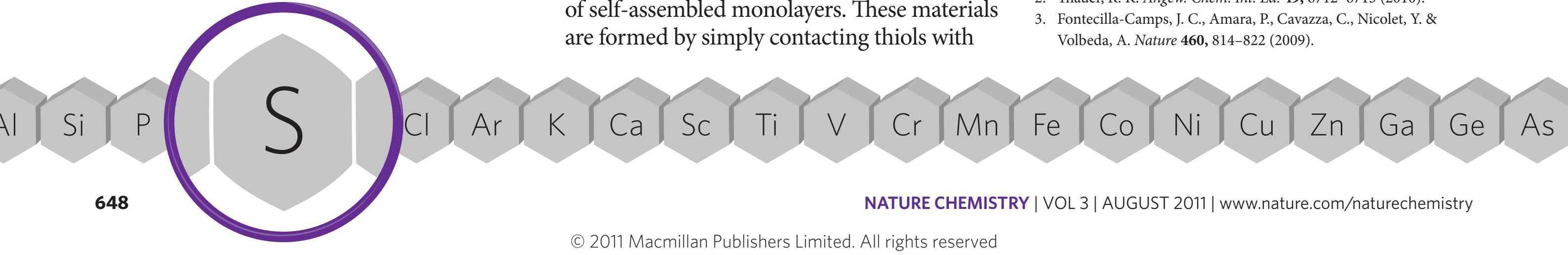

All about arsenic

If ever there was an element that epitomizes the notion that chemicals might be good or bad depending on their use, arsenic must be it. **Katherine Haxton** explains why.

Elemental arsenic was first identified in 1649, but its minerals have been known since Aristotle first described them in the fourth century BC. Arsenic compounds are perhaps some of the most notorious chemicals, particularly arsenic (III) oxide (As_2O_3), which has often — somewhat confusingly — simply been called 'arsenic'. This substance, also referred to as *poudre de succession* or 'inheritance powder' in seventeenth-century France, has been the main protagonist in many high-profile murders throughout history.

In contrast, many Victorians were fascinated by arsenic for less nefarious purposes, and frequently self-medicated with it — even using it as an aphrodisiac. Charles Darwin was said to use it to treat eczema. Arsenic compounds were also used to produce a beautiful green dye for wallpaper and other goods. Once again, however, the darker side of this element would often come to the fore, when a fungus present in damp houses converted the dye into volatile arsenic compounds and resulted in many cases of poisoning. This route of exposure to arsenic was recently implicated in the death of Napoleon Bonaparte, exiled on St Helena in the South Atlantic[1].

Organoarsenic compounds were first prepared by Louis-Claude Cadet de Gassicourt in the 1750s. Their precise chemical composition was not immediately known — a trait of arsenic chemistry that would continue throughout the twentieth century — but a fuming liquid with a strong garlic odour was produced. In the mid-nineteenth century, Robert Wilhelm Bunsen took up the challenge of identifying Cadet's fuming liquid, formed through the reaction of As_2O_3 and potassium acetate. The product, tetramethyldiarsane or 'cacodyl', a name fittingly derived from the Greek word *kakodyl* meaning 'stinking', was determined by elemental analysis with input from Berzelius[2]. This was the beginning of organoarsenic chemistry and a wide variety of cyclic and linear compounds are known today.

A key organoarsenic compound — Salvarsan (also known as arsphenamine) — developed by Paul Ehrlich was both the first treatment for syphilis and the first known chemotherapy agent. It was Ehrlich who coined the phrase 'magic bullets' to describe molecules that would rid organisms of parasites. Individuals suffering from late-stage syphilis were unresponsive to Salvarsan, and treatments were difficult because the drug had to be protected from the air. Inspired by the positive results seen in patients in the early stages of the disease, however, Ehrlich spent considerable time developing better handling procedures and ultimately a derivative that had fewer side effects and was easier to administer. Salvarsan was later identified as a mixture of cyclic structures with As–As bonds[3].

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Arsenic is the twentieth most abundant element on earth and is fairly ubiquitous in living systems — consequently arsenic poisoning poses a real threat to many people around the world. In countries such as Bangladesh, wells are frequently dug to provide clean, fresh drinking water, eliminating the need to draw water from stagnant ponds rife with disease-causing microbes. Unfortunately the nature of the underlying geology in many areas means that the ground water is often contaminated with arsenic, and poisoning symptoms are becoming commonplace — an estimated 70 million people in Bangladesh have been exposed to high levels of arsenic.

Arsenic undergoes a range of chemical reactions in the environment and this speciation makes it difficult to remediate. Moreover, arsenic contamination does not always come purely from natural sources — arsenic compounds have been used as feed additives for livestock, and as insecticides, providing other routes through which the element may enter living systems. A brief literature survey reveals that most of the hits for arsenic are concerned with the health implications of involuntary consumption, rather than the elegance of organoarsenic chemistry.

In early 2011, the discovery of bacteria that could survive in conditions high in arsenic caused quite a stir. Taken from Mono Lake in California, initial studies suggested that arsenic might replace phosphorus in the DNA of the bacteria, resulting in a high tolerance to the element[4]. This was widely debated, with many scientists arguing that arsenic esters are simply too labile to result in a stable analogue of DNA.

This twenty-first-century discovery may offer some hints regarding the nineteenth-century arsenic eaters of Styria (southeast Austria), where arsenic was consumed to freshen the complexion. Reports of people consuming large (300 mg) quantities of As_2O_3 — a substance that is typically fatal at doses above 65 mg — without deadly consequences prompted theories that organisms may become habituated to the poison, although later studies refuted this. Whatever the eventual consensus on the Mono Lake bacteria[5], arsenic continues to be one of the most fascinating elements, a would-be saviour and deadly assassin. ❐

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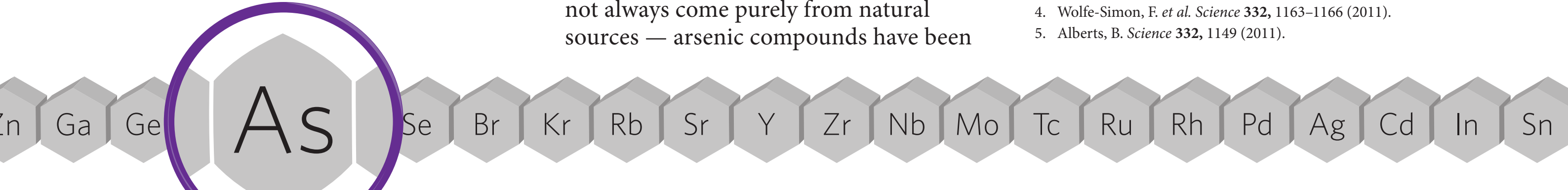


in your element

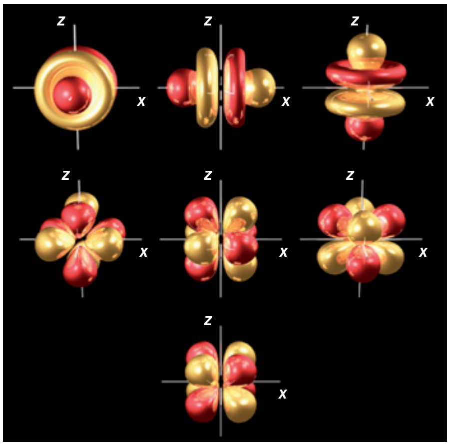
Anisotropic dysprosium

Beginning with its origins as the archetypal and eponymously elusive rare-earth element, **Dante Gatteschi** explains why dysprosium and other lanthanides have cornered the market in molecular magnetism.

Why should one be interested in dysprosium? As a member of the rare-earth elements it has been, as Giuseppe Verdi and Francesco Maria Piave described love in *La Traviata*, *croce e delizia*: a curse and a blessing. The similarity in the chemical properties of rare-earth compounds made the separation of their elements a difficult task, demanding the use of large amounts of mineral. The laboratory of Luigi Rolla at the University of Florence in the 1920s and 1930s was one of the places where the separation of the rare earths was actively pursued. There was also a claim to have isolated another element, number 61, tentatively called florentium, but the attempts to confirm its presence in pure form failed. It is to this difficulty in isolation that dysprosium, for which 2011 is the 125th anniversary, owes its name: from the Greek *dys* meaning 'hard' and *prositos* meaning 'to get at'.

The magnetic properties of rare earths, like their chemical ones, depend on the nature of the 4*f* orbitals (pictured) that interact only weakly with the environment. The magnetic properties of electrons are due to spin and orbital components. Spin is isotropic, whereas the orbital component reflects the symmetry of the system and can be anisotropic. For *f* electrons, the orbital moment is largely unquenched and the magnetic properties are therefore highly anisotropic.

Dysprosium is a good example of how anisotropic interactions induce interesting properties, which can then be used in applications. Its alloy with iron and terbium has the highest magnetostriction at room temperature — that is, it changes size when exposed to a magnetic field. The magnetic properties of dysprosium can also be exploited in magnetic resonance imaging — it can be used as a contrast agent when combined with chelating ligands.



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Recently, the interest in magnetic properties of the dysprosium(III) ion has increased in parallel with the interest towards molecular magnetism. In the 1990s, my and other groups were involved in the design of molecule-based magnets: bulk magnets based on molecules rather than on the metals and oxides that are found in nature.

Remembering the Florence tradition in rare earths 60 years before, we decided to try to exploit the magnetic properties of the lanthanides. We started with gadolinium, whose orbital contribution is completely quenched, and dysprosium as an example of an anisotropic ion. Why dysprosium and not, say, thulium? There was not much rational design: one of them simply had to be first. With some surprise we found that the dysprosium-based material ordered as a bulk magnet at a temperature very close to that of the manganese-based material (C. Benelli, A. Caneschi, D. Gatteschi and R. Sessoli *Adv. Mater.* **4,** 504–505; 1992). The manganese-based material was expected to have stronger interactions between the magnetic building blocks, so these results gave an indication of the role that dysprosium anisotropy plays in the magnetic properties of molecular magnets.

Among the possible types of magnetic anisotropy that favour the orientation of magnetization along an easy axis, the Ising anisotropy showed its relevance in 'single-molecule magnets' (SMMs) — molecular systems in which the large anisotropy blocks the relaxation of the magnetization, transforming each molecule into a tiny magnet. There was a 'gold rush', and lanthanides were in the forefront when it was discovered that dysprosium ions sandwiched between two phthalocyaninate rings behave as SMMs (N. Ishikawa *Polyhedron* **26,** 2147–2153; 2007). Other systems containing up to three dysprosium ions showed unique features associated with the anisotropy being larger than the exchange interaction. This opens new possibilities to store information in the chirality of the spin arrangement without any net magnetic moment.

The results showed the potential of dysprosium in molecular magnetism, highlighting the fact that although the interactions involving lanthanides are weak, magnetic anisotropy can yield novel properties. These properties are now actively investigated in the frame of molecular spintronics — the exploration of the opportunities for developing new electronics using molecules. However, to get to the *delizia* of using these molecules for new spintronic applications, one has to go through the *croce* of detailed quantum mechanical investigations to rationalize the electronic and magnetic structure of the rare earths.

The initial question "why should one be interested in dysprosium?" has become "why should one be interested in magnetic anisotropy?" My firm view is that chemists must tackle all aspects of the correlations between structure and properties. The rationalization of, say, room-temperature magnetic moments of metal ions seemed to be exotic at the time molecular magnetism was discovered. More complex phenomena must be tackled and chemistry is needed to transform concepts like magnetic anisotropy into real objects. ❐

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u Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi

in your element

Meteoric calcium

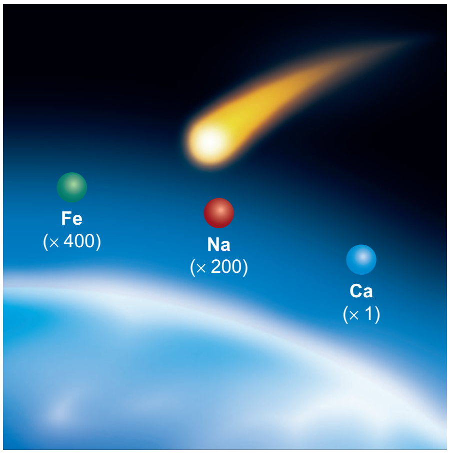
Calcium is found throughout the solar system, the Earth's crust and oceans, and is an essential constituent of cells, shells and bones — yet it is curiously scarce in the upper atmosphere. **John Plane** ponders on this 25-year-old mystery.

The discovery in 1808 of element 20 is credited — just like its neighbours in the periodic table, potassium, sodium and magnesium, among others — to the English chemist Humphry Davy, who had developed an electrolysis technique for isolating elements from rocks. Calcium is essential for living organisms and takes part in various cellular processes. Yet, any present in the upper atmosphere is extra-terrestrial.

As interplanetary dust particles enter the atmosphere at very high speeds (11–72 km s^{-1}), collisions with air molecules induce flash heating, which often causes the particles to melt at around 1,800 K, and the constituents to evaporate. This 'meteoric ablation' process typically occurs between 75 and 110 km of altitude, and directly injects metal atoms in the atmosphere.

Several of these meteoric metals can be observed from the ground using the 'lidar' technique: a pulsed laser is tuned to a spectroscopic transition of the metal of interest — blue light at 422 nm for calcium — and directed up into the atmosphere. This induces a resonance fluorescence from the metal, subsequently detected with a telescope. Lidar is an extraordinarily sensitive technique, able to detect calcium atom concentrations of less than 10 atoms cm^{-3} at a distance of 90 km.

The first lidar measurements of calcium, made at the French Observatory of Haute Provence in 1985[1], showed a peak concentration of around 20 atom cm^{-3} — about 200 times lower than the typical sodium atom concentration and 400 times lower than that of iron (see picture). This is in stark contrast with the Sun's photosphere, meteorites, or the Earth's crust, where calcium is nearly as abundant as sodium, and only 16 times more scarce than iron. Where does the enormous relative depletion of calcium in the upper atmosphere come from?



A layer of metallic atoms, produced between 80 and 100 km in the Earth's atmosphere by the ablation of cometary dust particles. The concentration ratio of Ca:Na:Fe is about 1:200:400.

There are only three possibilities: calcium is already depleted in the interplanetary dust particles entering the atmosphere; it does not ablate efficiently from meteors; or its atmospheric chemistry is quite different from that of sodium and iron. Until recently, our knowledge of the composition of interplanetary dust particles was restricted to meteorites recovered on the surface of the Earth. No significant calcium depletion was observed — but these samples survived atmospheric entry (the definition of meteorites), and so the bulk of the incoming dust might already have been calcium-poor. The current consensus is that most interplanetary dust particles that reach the Earth originate from comets. In 2006, the NASA Stardust spacecraft collected particles from Comet 81P/Wild 2 — unfortunately, their analysis revealed no depletion of calcium[2].

The second possibility is that the ablation process favours relatively volatile elements (sodium and iron) compared with refractory ones (calcium). This is consistent with thermodynamics, because calcium forms very stable oxides in silica melts, and in fact there is evidence that such a 'differential ablation' does occur. However, models predict a relative depletion of calcium with respect to sodium of only about a factor of 3, rather than the observed factor of 200 (ref. 3).

Is the atmospheric chemistry of calcium different from sodium and iron? As a result of laboratory studies, we now have a fairly clear idea of why such reactive metallic elements occur in their reduced form in what is a highly oxidizing atmosphere[4]. The key factor is that around 85 km of altitude, the photolysis of O_2 and H_2O by extreme ultraviolet radiation leads to high concentrations of oxygen and hydrogen atoms. Hydrogen and oxygen atoms attack metallic compounds such as hydroxides and oxides, reducing them back to metal atoms. However, the relevant reaction rates of calcium and its compounds are quite similar to those of the other metals[5], which means that the difference in reactivity accounts for no more than a factor of 5 in the relative abundance of calcium to sodium.

Thus, there remains an unexplained depletion of calcium by at least one order of magnitude. This is probably due to our poor understanding of the extreme chemistry that occurs during meteoric ablation, combined with continuing (and controversial) uncertainties about the velocity and mass distributions of interplanetary dust particles, which depend on their cometary and asteroidal origins. The calcium mystery may therefore end up telling us a great deal more about the evolution of the solar system. ❐

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A pinch of sodium

Sodium, ubiquitous on Earth in living organisms, oceans and minerals — all the way to table salt — may seem like one of the more ordinary elements. **Margit S. Müller** highlights why we, like the fairytale king, should not take it for granted.

In an old eastern European fairy tale a king asks his three daughters to describe their love for him. Whereas two of the daughters compare their affection to diamonds, pearls and gold, the third girl declares, “Father, I love you more than salt”. Deeply offended to be likened to something so ordinary, the king banishes her. The princess disappears from the kingdom and, through a bit of witchcraft, so does all the salt. The story goes on to convince the king, and the reader, of the importance of seemingly mundane things in life, like salt. To make the same point without witchcraft, science had to go to much greater lengths.

The elements that make up what we refer to as table salt, sodium and chlorine, are both linked to Sir Humphry Davy. Davy discovered sodium in 1807 by isolating it from sodium hydroxide through electrolysis, and in 1811 he gave chlorine its name after unambiguously recognizing it as a pure element — although discovered in 1774 by the Swedish chemist Carl Wilhelm Scheele, chlorine was at the time considered to be a mixture with oxygen.

Sodium — an alkali metal, extremely reactive with oxygen and water — was thoroughly characterized in the years following its discovery. Reports dating back more than 150 years vividly describe[1,2] its chemical and physical properties, most notably its bright yellow flame and its oxidation with water that releases hydrogen gas so rapidly that sodium fragments seem to ‘dance’ on the water’s surface. As well as containing valuable chemical information, these early reports illustrate much of the excitement arising from scientific curiosity: the reader can learn, for example, how hitting a spatula on sodium pieces sizzling on water will generate a loud bang along with a fountain of water and shattering of the bowl[1]. The intense yellow colour sodium imparts to flames went on to make for a beautiful application in fireworks.

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On a less festive note, in 1957, the first nuclear reactor that became a commercial power source in the USA was cooled using sodium. A better conductor of heat than water, it is a liquid with low vapour pressure around 260 °C, the temperature at which the reactor operated. Although the ‘Sodium Reactor Experiment’ took a disastrous turn a couple of years later, involving a damaged core and some radioactivity release, it demonstrated the possibility of using sodium as a coolant[3].

Yet the most essential role of sodium might be in biology. Although its involvement in hypertension and cardiac diseases has given it a bad name, sodium is actually keeping us alive. Our cells constantly balance high potassium and low sodium concentrations within cells (~140 mM K^+, ~15 mM Na^+) with an opposite distribution (~5 mM K^+, ~150 mM Na^+) outside. This balance is a fundamental part of almost everything we do, from seeing to thinking, not to mention breathing and the beat of our hearts. Proteins in the membrane of specific ‘excitable’ cells form sodium channels, opened by a trigger (a ligand binding, or a change in the membrane voltage) to enable a rapid influx of Na^+ ions into the cell. This regulates secretion in endocrine cells, contraction in muscle cells, and neurotransmission in nerve cells — the communication pathway within the brain.

In fact, disrupting this sodium influx is a very effective way of killing someone. Tetrodotoxin (TTX), a compound found in pufferfish (or fugu) that blocks voltage-gated sodium channels in nerve cells, is one of the most toxic substances on earth and has no known antidote. Intoxication with a sufficient dose — most commonly ingested through fugu dishes not prepared with enough care — will lead to death by respiratory failure within minutes to hours. The same characteristics, however, make TTX a very valuable research tool for studying neural networks that form the basis of the workings of the brain, of which we are just now beginning to gain an understanding.

Chemists have also recently gained a surprising insight into the nature of sodium itself. Yanming Ma and co-workers demonstrated[4] that compression dramatically changes the optical properties of the metal. Exposing sodium to increasing pressure causes a successive loss of visible light reflection, turning it into a transparent material at about 200 GPa. This transition is ascribed to a hybridization between *p* and *d* electrons, repelled by core electrons to occupy the interstices within the sodium lattice.

From fireworks and nuclear reactors to the human brain and structural insights, sodium is undoubtedly part of an exciting history of scientific discovery, with no end in sight just yet.

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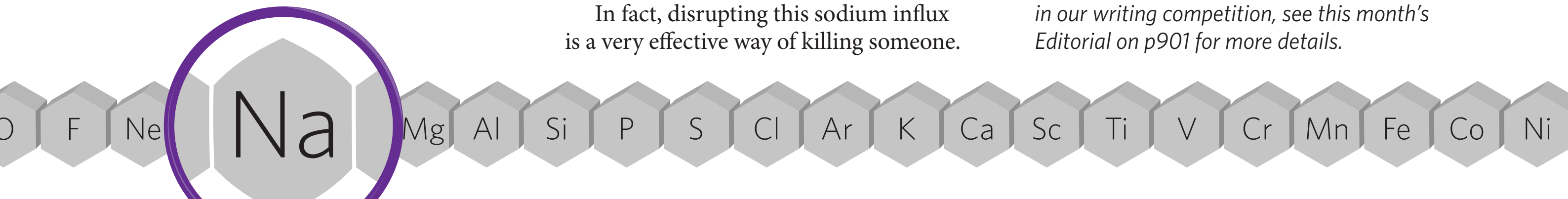
This essay was selected as a winning entry in our writing competition, see this month’s Editorial on p901 for more details.



Oxygen origins

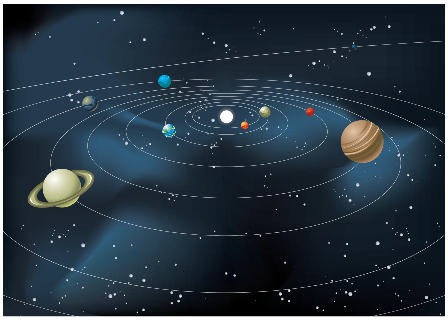
Oxygen has contributed to our understanding of the evolution of life on Earth by providing invaluable clues to geological processes — yet it still holds the key to some unsolved mysteries, as **Mark H. Thiemens** explains.

Long before oxygen bars made it cool, element number 8 was somewhat magical. In the nucleus, there exist levels that when filled provide additional nuclear stability beyond that expected from normal binding-energy considerations, much like the filled shells of the noble gases for electrons. These nuclear 'magic numbers' occur at proton or neutron numbers of 2, 8, 20, 28, 50, 82 and 126. Consequently, oxygen's most common isotope ($^{16}O_8$), with its eight protons and eight neutrons, is 'doubly magic'. This accounts for its abundance — it is the third most abundant element in the universe after hydrogen and helium.

During nucleosynthesis, in which protons and neutrons organize to form atom nuclei in stars, three ^{4}He nuclei combine to form ^{12}C — a two-step process, with two ^{4}He nuclei forming ^{8}Be that in turn fuses with the third ^{4}He. ^{12}C is subsequently converted into ^{16}O by further fusion with another helium nucleus.

Positioned at group 16 and period 2 in the periodic table, oxygen is an unusually reactive non-metallic atom that forms compounds with nearly all other elements. Its cosmic abundance combined with its chemical properties lead to its participation in a range of processes that build or protect planets (as part of silicate material or through the allotrope ozone, respectively) construct living organisms (in DNA, proteins, lipids and carbohydrates), as well as serving metabolic roles (photosynthesis and respiration). It is ubiquitous in the Earth's crust, mantle, atmosphere and surface water, and biological reservoirs that are connected through oxygen transfer. Carbon dioxide — a dominant greenhouse gas — is a major agent of the transfer between these reservoirs.

Since its original discovery by Carl Wilhelm Scheele in Uppsala in 1773, and publication by Joseph Priestley two years later, oxygen has had a long and interesting history. Lavoisier played a major role in the identification of the process by which oxidation or combustion occurs — and provided oxygen with its name, borrowing Greek roots (*oxys* and *-genes*) to refer to it as 'creator of acids' because he thought all acids contained oxygen. Oxygen's role throughout the history of civilization is extensive, from energy production (whether hydrological or as a general fuel oxidant) to agriculture and as a component of textiles and ceramics, as well as many drugs.



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Going back further in time, oxygen is intimately associated with the origin and evolution of life. In the Precambrian era, atmospheric oxygen levels were significantly lower than now, probably less than 0.1% of the current ones — although it is still difficult to quantify this with precision. Using multi-isotope measurements of sulfur[1] these low oxygen levels were estimated to have occurred between about 3.8 and 2.7 billion years ago. Only a little later — 2.2–2.5 billion years ago — the 'Great Oxygenation Event'[2] occurred and oxygen levels abruptly rose, largely owing to activities of cyanobacteria producing noticeable changes in the redox state and distribution of oxygen in minerals, such as the globally pervasive banded iron formations.

Measurements of oxygen isotopes (^{16}O, ^{17}O and ^{18}O) have been crucial in resolving natural processes. Stemming from work in the Urey laboratory in the 1950s[3,4] analyses of oceanic biological carbonates have been used to quantify the temperature change of the oceans over geological timescales. Similarly, the role of marine and terrestrial organisms in global photosynthesis, respiration and their change over time was deduced from measurements of atmospheric oxygen — which depend on the difference in the ^{18}O to ^{16}O ratio between air and water (the Dole effect).

Since 1973, we have known that the oldest objects in the solar system — the calcium- and aluminium-rich inclusions of 'carbonaceous chondritic' meteorites — possess a multiple oxygen isotope distribution that is inconsistent with conventional isotope effects[5]. Experiments a decade later suggested that this might be because of processes such as photochemical isotope self-shielding, or chemical reactions that depend on symmetry factors rather than the conventional mass effect, which can produce a similar anomalous isotopic distribution[6]. Recently, however, measurements of solar wind samples collected[7] by the spacecraft Genesis — which may reflect the dominant reservoir of oxygen in the solar system — have shown that their isotopic distribution is not similar to that of meteorites.

This means that the oxygen isotopic distribution of the Sun may potentially not reflect the original distribution of the isotopic reservoir of meteorites and stony planets. Consequently, the nebular source of that original distribution, and how these celestial bodies went on to produce the current meteorites and planets, remain unresolved. ❐

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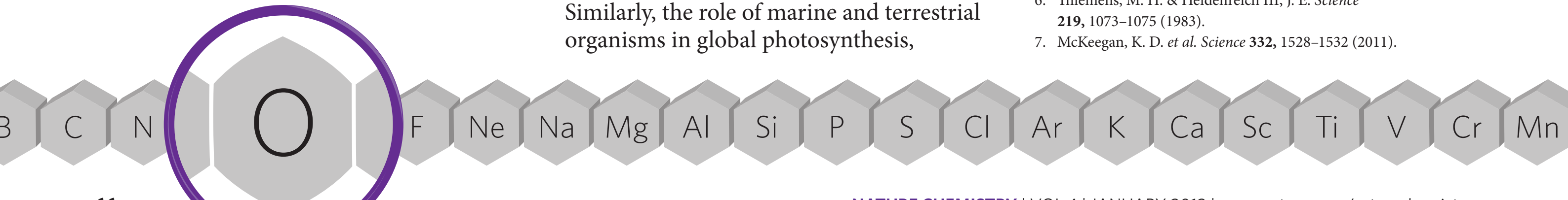

in your element

Cool as helium

Owing to peculiar properties, helium has taken both the main and supporting roles in scientific discoveries over the years. **Christine Herman** explores just what makes it such a cool element.

I was one of those starry-eyed children who loved helium because it sent colourful balloons into the sky and made me speak with a squeaky voice. As a chemist, I have learnt there are a myriad of other reasons scientists get excited about the odourless, colourless second element in the periodic table. Helium is a cool element. Literally.

It has the lowest melting and boiling points of all the elements — and below 2 K, it enters a superfluid state with no apparent viscosity and extremely high thermal conductivity. These qualities make it a fantastic cryogen for cooling superconducting magnets, rendering them free of electrical resistance. Physicists, physicians and nuclear engineers alike rely on liquid helium to run atom-smashing experiments, carry out magnetic resonance imaging, and cool nuclear reactors to suitably low temperatures.

Helium was discovered in 1868 by the astronomers Jules Janssen and Norman Lockyer, who independently observed its yellow spectral line signature from the Sun. Lockyer — the first editor of *Nature* — named it after the Greek word for the Sun, helios. It was the Scottish chemist Sir William Ramsay who first isolated helium in 1895, by treating the uranium mineral cleveite with mineral acids and removing nitrogen and oxygen — only to notice the same yellow spectral line that had been observed from the Sun three decades earlier. That same year, Swedish chemists Per Teodor Cleve and Abraham Langlet also isolated helium, independently, and determined its atomic weight.

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Although helium is the second most abundant element in the universe after hydrogen, it is not bound by the Earth's gravitational force and so the atmosphere contains only about 0.0005% by volume. In contrast, the atmosphere of Uranus boasts 15% by volume, or 26% by mass, which is also approximately what our galaxy consists of. Helium accumulates in natural gas fields in the form of alpha particles (He^{2+}), which are a by-product of the natural decay of heavy radioactive elements. On extraction, natural gas can contain up to 7% helium by volume, which commercial suppliers isolate by fractional distillation.

In addition to playing a supporting role as a cryogen for physics, medicine and nuclear-energy applications, helium serves numerous other purposes in industry, research and everyday life: arc welders use it as an inert protective shield, rocket scientists to pressurize fuel tanks, and deep-sea divers use it mixed with oxygen to keep from suffering nitrogen narcosis during long dives. Scientists study the quantum mechanical phenomenon of superfluidity in the various forms of helium and, because radioactive decay produces helium nuclei, paleontologists determine the age of rocks by measuring the ratio of helium to uranium and thorium. Helium–neon lasers are widely used in applications that require visible-wavelength coherent light. In fact, the first commercial optical disc storage medium in 1978 used a HeNe laser to read the information. More recently, scientists have demonstrated the use of helium ion beams for the fabrication and imaging of nano-electronic and nanophotonic devices[1].

An inert gas, helium does not readily combine with other elements — but that hasn't stopped chemists from trying. Investigations into the preparation of HeF_2 through the β-decay of tritium[2] began in the 1960s, but with no success yet. Synthetic chemists have made a step in that direction, however, with the preparation of fullerenes — carbon cage molecules — that are able to non-covalently encapsulate a helium atom at their core[3]. Helium can also combine with other elements to form excimers — short-lived dimeric or heterodimeric molecules. Excimers composed of helium and another element, for example, iodine, tungsten or sulfur, form under conditions of high pressure and electrical stimulation. They are most commonly used to make lasers for applications such as semiconductor processing and eye surgery.

In more recent news helium's antimatter cousin, antihelium, took the spotlight for being the largest antimatter atom ever observed[4]. Particle beams made of gold ions were smashed together at nearly the speed of light, yielding a spray of trillions of particles, among which were the as-yet-unobserved antihelium particles. This experiment came exactly a century after Ernest Rutherford performed the reverse experiment; colliding an alpha particle beam with gold foil, to discover the nucleus in 1911[5].

From providing an inert atmosphere and cooling systems at very low temperatures to advances in quantum models to applications in medicine, the diversity of the roles adopted by helium in scientific discoveries makes me inclined to pronounce it, both literally and figuratively, the coolest element. ❐

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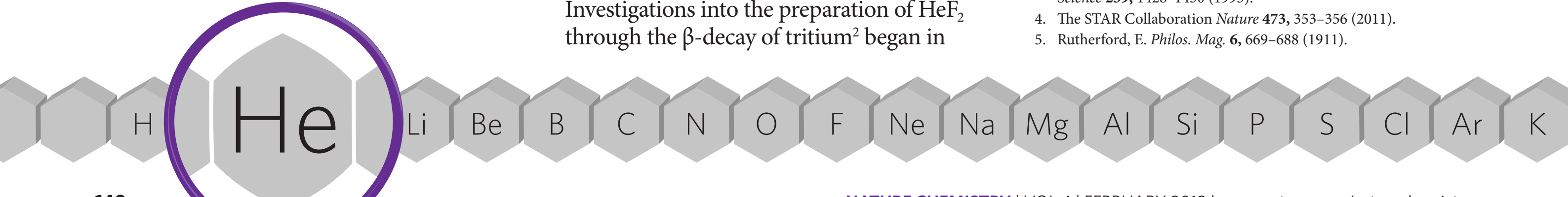


The deeds to deuterium

Dan O'Leary examines Harold Urey's decision to name the mass-2 hydrogen isotope 'deuterium'.

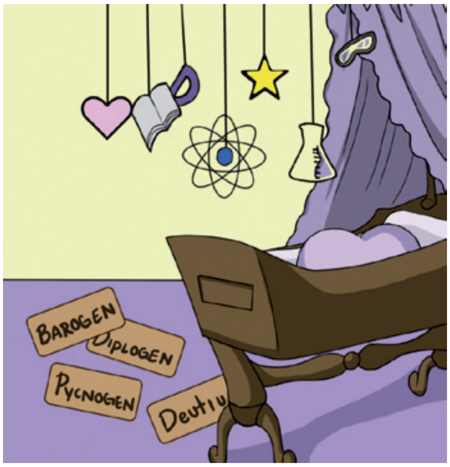
Harold Urey discovered the Nobel-worthy mass-2 hydrogen isotope in 1931, and is generally credited with naming it deuterium in June 1933 (ref. 1). Correspondence[2] between Urey and his collaborator Ferdinand 'Brick' Brickwedde reveals, however, that as late as May in that year the team was still struggling to find an acceptable name for the isotope.

On 9 May, Urey wrote to Brick to say that he was very much undecided as to what to call 'the hydrogen'. Pycnydrogen, barhydrogen ($\bar{H}$) and barogen had all been suggested, but he was not enthusiastic about any of them. Instead, Urey asked Brick what he thought about pycnogen as a suitable name for 'H^2'. Just over a week later, Brick responded to say that he preferred barhydrogen, but barogen and pycnogen were acceptable. He then muddied the water by also suggesting haplogen or haplohydrogen and diplogen or diplohydrogen.

Urey acknowledged Brick's letter on 23 May and wondered if protium and deutium might work. He revealed an ongoing correspondence with Gilbert N. Lewis, Urey's former doctoral advisor who had privately proposed the name dygen and with whom Urey had shared the names pycnogen and barogen. Urey shared the content of a telegram from Lewis:

> PLEASE DISREGARD SUGGESTION IN MY LETTER NO ONE LIKES THOSE NAMES NOR DO I STOP HAVE TEMPORARILY ABANDONED ATTEMPT TO FIND NAME FOR THE ISOTOPE AS A SUBSTANCE STOP HOWEVER FOR THE NUCLEUS OF HYDROGEN ISOTOPE WE ALL THINK THAT DEUTON IS BEST NAME AND ARE USING IT PROVISIONALLY

Urey continued, "I took my time about answering this and wrote him a letter by ordinary mail, a copy of which I enclose. I hope G. N. gets the point to this for he seems to consider it a duty to find a good name for this isotope." He then wrote, "The thing I have against this is the fact that Lewis suggested the name. I am getting to a point where I wish they would stop suggesting names so that I would not feel prejudiced against any of them."



SEO (SARAH) ROH

In his reply on 26 May, Brick said that he found protium and deutium acceptable. Haplogen and diplogen he still liked, but were losing ground because they had been suggested by a colleague. On 29 May, Urey wrote back to say "The more I think about names for the hydrogen isotopes, the more I lean towards the use of protium and deuterium (our Greek experts tell us that deutium would not be a suitable word derived from Greek). In case a H^3 isotope is discovered, it can be called tritium."

Brick wrote back on 4 June to say that proterium and triterium were more euphonious but that protium, deuterium, and tritium were agreeable. Urey responded on 6 June: "I am not entirely satisfied with the names protium and deuterium, but I cannot think of anything better. You would prefer proterium to protium, and I have a letter from G. N. Lewis expressing the feeling that deutium would be better than deuterium; in fact, he would prefer protum and deutum."

Urey's team published a letter to the editor in *Journal of Chemical Physics* on 15 June proposing the names protium, deuterium and tritium[3]. They cited Lewis' personal communication regarding the nuclear deuton, but reject the proposal because it is not a fundamental particle. If a nuclear name was necessary, Urey and co-workers suggested deuteron as more desirable. These names survived a brazen attempt (published[4] in *Nature* and endorsed by Lord Rutherford) in early 1934 by a UK-based group to name the isotope diplogen. *Time* magazine even reported[5] on the dust-up, calling it a source of 'very tense' transatlantic scientific relations. Urey and his cohorts responded, essentially saying 'thought of it, tried it, and it doesn't work.'

For his discovery of deuterium, Urey was named the sole recipient of the 1934 Nobel Prize in Chemistry. Lewis, despite furiously publishing his own work on heavy water, was passed over. He reportedly never recovered from this — and other perceived slights — and died in 1946, possibly by his own hand[1]. Urey later wrote[6] of his advisor's role in the deuterium hunt: "I have always felt badly about Professor Lewis' attitude in this matter. I have tried in the years since then, whenever my former students make an important discovery, to help them as much as possible rather than to try to take the subject matter away from them."

Would Urey's team, working alone, have conjured a name based on the Greek *deuteros*? This question is answered by Urey's own grudging admission to Brickwedde, that it was Lewis who suggested the root of the eventual name. ❐

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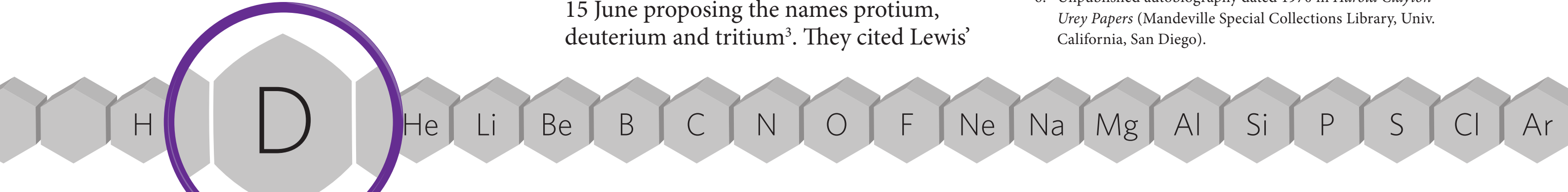
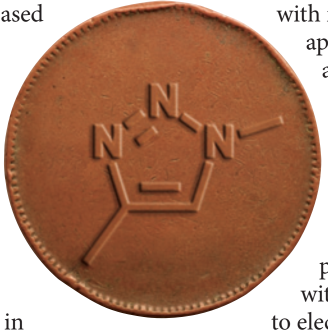


in your element

Counting on copper

Copper, routinely encountered in daily life, may at first glance seem a little unexciting. **Tiberiu G. Moga** relates how science, however, has not overlooked its promise.

At the end of the Finnish epic *Kalevala*, the hero Väinämöinen sets sail into the heavens, leaving behind the mortal realm in a copper boat. Modern engineers seem to have taken this to heart: ships' hulls are lined with materials based on copper, which inhibits the growth of bacteria, barnacles and other unwanted passengers. Väinämöinen's vessel is just one example of how the reddish-brown lustre of copper has spurred human imagination throughout history.



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To the ancient Romans, copper was known as *cuprum*, in reference to the island Cyprus, where much of their copper was mined. Nowadays the word copper typically conjures visions of pennies, electrical wiring or perhaps the Statue of Liberty, who owes her green complexion to copper(II) carbonate. But despite its seemingly unremarkable presence in everyday life, copper continuously plays an active role in science for its essential, life-saving biological functions and its diverse chemical properties. Much of copper's versatility arises from its ability to carry out three different chemical processes: Lewis acid catalysis, single-electron-transfer processes and two-electron-transfer reactions.

In Lewis acid catalysis, Cu^{+} or Cu^{2+} ions bring together different molecules and facilitate a chemical reaction between them. A famous example is the copper-catalysed azide–alkyne cycloaddition, known as click chemistry. In this reaction, one of the starting materials is tagged with an azide moiety whereas the other bears an alkyne group; the two first coordinate to copper, then covalently bind to each other to form a triazole ring[1]. No transition metal is as effective a catalyst as copper for this step. Owing to its reliability and high selectivity, this click reaction is widely used, from the total synthesis of natural products and their derivatives to the preparation and modification of polymers.

Another example of Lewis acid catalysis mediated by copper ions is the synthesis of cyclic peptides — a class of compounds with numerous biological applications. Cyclosporin A and gramicidin S, for example, are antibiotics; octreotide and calcitonin act on the endocrine system; and eptifibatide helps prevent clot formation and strokes. Owing to its positive charge, Cu^{2+} (along with other ions) is able to bind to electron pairs of the oxygen, nitrogen and sulfur atoms of the linear peptide precursors, thereby bending them into curved shapes that can more easily form closed ring structures[2].

Mechanistically more complex than Lewis acid catalysis, single-electron-transfer processes carried out by copper — alternating between its Cu^{+} and Cu^{2+} forms — are indispensable in biology. Cellular respiration in which an organism extracts energy from glucose involves the copper-containing enzymes of the mitochondrial membrane. These enzymes oxidize glucose and reduce oxygen through stepwise single-electron transfers, also forming water in the process.

Other enzymes that carry out copper-mediated single-electron transfers include the somewhat lesser known, yet also important, superoxide dismutase and tyrosinase[3]. The copper–zinc-based superoxide dismutase protects cells from reactive oxygen species by converting those into the less toxic hydrogen peroxide molecule, itself subsequently transformed into oxygen and water. Copper-containing tyrosinase converts tyrosine into L-dopa, a precursor to the hormone adrenaline, which mediates 'fight-or-flight' responses under acute stress. L-dopa is also used to treat Parkinson's disease; it is metabolized to dopamine, which mediates communication between brain nerve cells.

The last type of common copper catalysis are two-electron-transfer reactions — also called coupling reactions — which take place in three steps: oxidative addition, trans-metallation and reductive elimination. First, Cu(0) breaks a carbon–halogen bond to form a carbon–copper bond and a copper–halogen one, while being oxidized to Cu^{2+}. Next, the halide ion is displaced from the copper metal centre by a nucleophile or another entering group. Finally, the carbon–copper and copper–nucleophile bonds are both cleaved to yield a carbon–nucleophile bond and the Cu(0) catalyst is regenerated[4].

Coupling reactions were first popularized with palladium catalysts, and earned Heck, Negishi and Suzuki the 2010 Nobel Prize in Chemistry. These reactions now find widespread use in drug synthesis and will most likely only continue to attract attention. As a catalyst, copper produces efficient yields under mild reaction conditions and is relatively resistant to poisons that would disrupt other catalysts, making it a desirable alternative to palladium.

From the synthesis of pharmaceuticals to the design of new structures in nanotechnology[5], copper is continually being rediscovered as catalyst and a versatile building block. This trend shows no sign of abating, perhaps suggesting that the use of copper may only be limited by one's imagination. ❐

This essay was selected as a winning entry in our writing competition, see http://go.nature.com/oi187X

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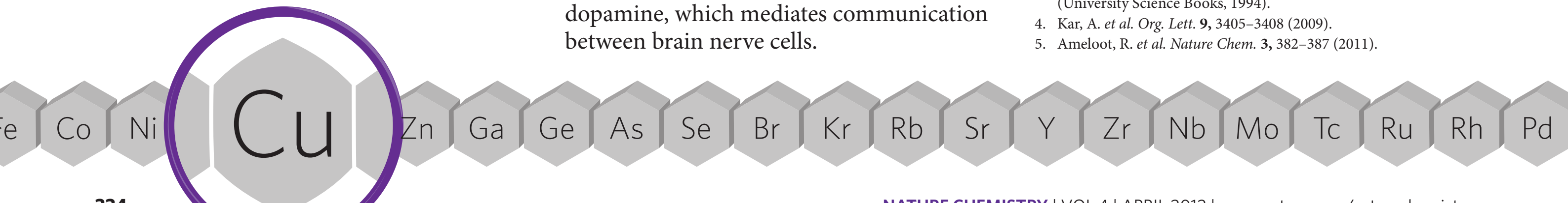
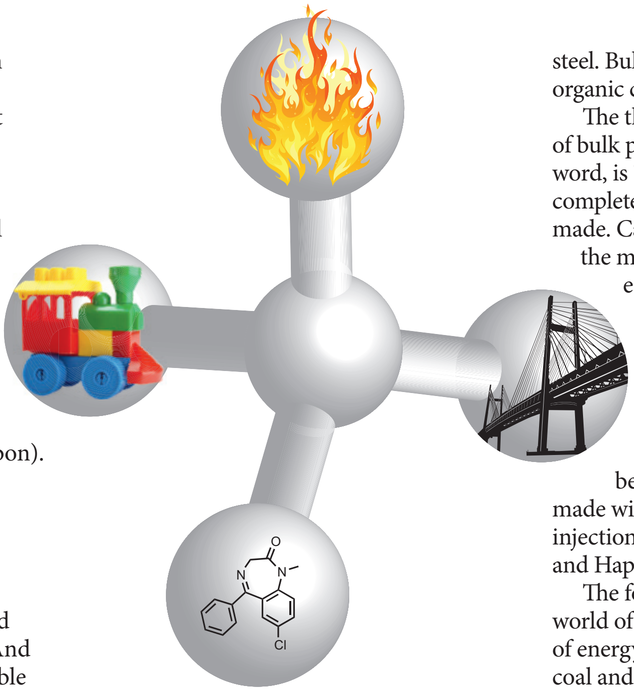


in your element

The four worlds of carbon

Simon H. Friedman explores the various ways in which carbon is inherently tied to our lives — beyond its elegant, treasured role in organic chemistry.



The organic chemist's view of carbon can be like the New Yorker's view of the world, which to them ends at the edge of Manhattan. For the organic chemist, carbon is the element that makes the beautiful, predictable, regular scaffolds of drugs, pesticides and dyes: all that wonderful stuff that saves lives, increases crop yields and allows for the convenient printing of T-shirts with timely messages. And all constructed with the enticing angles that Pauling explained but that Euclid and the ancients conceived (the 180°, 120° and 109.5° of sp-, sp^2- and sp^3-hybridized carbon).

The diversity of stable structures that are possible with carbon is unrivalled in the periodic table. With the addition of the fullerenes in the 1980s, the already impressive list of allotropic forms of carbon (including diamond, graphite and amorphous carbon) further expanded. And one estimate is that there are more possible carbon-based small molecules than there are atoms in the universe. This suggests continued employment for organic chemists for the foreseeable future.

> The diversity of stable structures that are possible with carbon is unrivalled in the periodic table.

Yet, in the same way in which there is an entire world west of the Hudson river, there are entire worlds of carbon that have had an equal if not bigger impact on our lives. At the risk of offending the delicate sensibilities of some organic chemists, and for the sake of completeness, I am forced to elaborate on these now.

If organic chemistry is the first world of carbon, then the second is steel. Without carbon you still have iron, which is just fine if all you need to do is shoe a horse, but not quite up to the task of making things that are large and durable. Add about one per cent of carbon to your iron, however, and you have made steel — you can now construct useful things, like bulldozers and buildings that are half a mile high. This effect of carbon arises from structural characteristics. By itself, iron forms a regular crystalline lattice that consists of closely packed planes that can slip over each other. The slipping of these planes allows iron to fail structurally under relatively light loads.

Carbon helps to solve this problem because carbon atoms find a niche in interstitial sites of the iron lattice. Although irregularly located, they give rise to interactions that prevent the planes of iron atoms from slipping over each other, leading to an increase in strength for the resultant steel. Here, however, there is no atomic-level aesthetic at play, no regularity and no appealing geometry. In fact, that percentage of carbon can even vary, resulting in different bulk properties — hardness, ductility, tensile strength — of the steel. Bulk properties; you can almost hear the organic chemists shuddering.

The third world of carbon is also a world of bulk properties. And that world, in a word, is 'plastics'. Plastics, or polymers, have completely reshaped the way things are made. Carbon allows for the construction of the monomers that conveniently link to each other to make a wide diversity of polymers that have all sorts of useful properties, for example mouldability or biodegradability. An item that needed dozens of operations to machine in the first half of the twentieth century could be replaced in the second half by one made with one squirt of polymer into an injection mould. Owners of intraocular lenses and Happy Meal toys the world over rejoiced.

The fourth and final world of carbon is the world of energy. Carbon is the major source of energy our civilization runs on: crude oil, coal and natural gas. These carbon sources are simply burned to drive pistons or turbines and in the process create carbon dioxide. Carbon dioxide is the final thermodynamic sink, because the two oxygen–carbon double bonds formed are strong, and there is nowhere lower on the energy landscape for carbon to conveniently go.

But for all the roles adopted by carbon in its many worlds, to the organic chemist, simply burning carbon for its energy must surely be akin to burning your books when you are cold, or eating next year's seeds when you are hungry. It suggests a level of desperation and a betrayal of the wonders the carbon atom has the potential to create. Perhaps it is in the refined aesthetic of the organic chemist that we can find an important message about the beauty of carbon that can be delivered to the rest of the world. ❐

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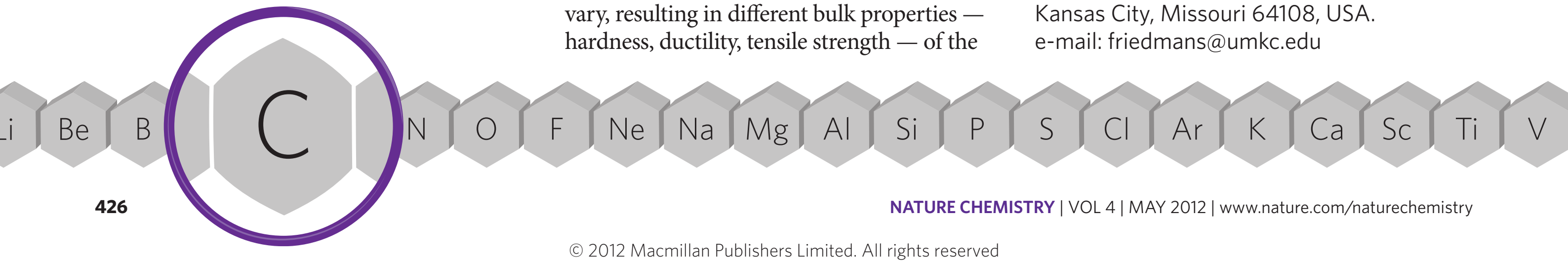


Ambiguous bromine

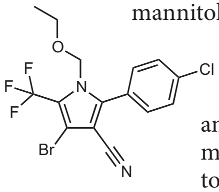
Many chemical elements behave quite differently depending on the compound they are found in, but **Matt Rattley** argues that bromine does so in a particularly striking manner.

Every element is a little bit schizophrenic in its own way. Carbon's split personality is best exemplified through two well-known allotropes, graphite and diamond; transition metals transform from bland grey blocks to wonderfully colourful salts; and even notoriously inert noble gases, for example xenon, can be coaxed into reacting with other members of the periodic table to produce exotic species including fluorides and oxides. And so it is with bromine too. Sitting quietly in the middle of the *p*-block, it is one of the most deadly elements, yet one with intriguing and useful properties.

It is one of bromine's less pleasant characteristics — a more biting, sour smell than that of chlorine gas — that gave it its name, from the Greek *βρώμος* (*brómos*) meaning 'stench' or 'foul odour'[1]. Despite being a liquid at room temperature, it is highly volatile and produces a thick vapour layer.

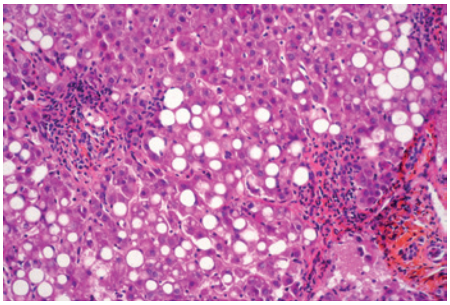
The only redeeming feature of the vapour is its distinctive orange colour, which means that you can readily avoid it. And avoid it you should. Bromine is highly toxic, especially in sunlight; radicals generated on ultraviolet irradiation will wreak havoc on anything and everything they encounter, including lung tissue. Bromine atoms are also found in some astonishingly toxic natural products synthesized in some marine sponges and corals, which can exhibit lethal doses more than 1,000 times more potent than aqueous arsenic.

It may sound surprising, therefore, that anyone should want to go near this noxious element. Yet brominated molecules have attracted much attention. The widely used insecticide chlorfenapyr[2], for example, is an unusual species containing three different halogens (fluorine, chlorine and bromine).



Chlorfenapyr

Perhaps nothing shows bromine's equivocal character quite like potassium bromide. A not-too-distant cousin of table salt, this deceptively simple compound was used for much of the nineteenth and twentieth centuries as an anticonvulsant and a sedative. It exhibits chronic toxicity — abuse leads to a condition called bromism, characterized by seizures, vomiting, psychosis, skin lesions and delirium — but when suitably administered it works remarkably well by inhibiting the central nervous system. Although for human use it has now been replaced by alternative compounds such as pregabalin[3] that act more rapidly and with fewer side effects, it still fulfils this sedative role today in veterinary medicine.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Other attempts to tame and use brominated compounds have not been so successful. This is no recent trend — and perhaps something the women of ancient Egypt might have preferred to know. They often added small amounts of bromine mannite (a derivative of polyalcohol mannitol found in plants) to a mixture used to colour their lips to obtain a rich red-brown colour. Unfortunately, even the small amount of residual bromine in the mixture was likely to be enough to accidentally kill both women wearing it and men kissing them.

The ambiguous nature of bromine also shines through in uses that were initially intended to keep us safe. A variety of compounds, such as the polybrominated aromatic compound tetrabromobisphenol A, have been incorporated in clothes and other textiles to prevent, or slow down, the spread of fire should they be placed near an open flame. These compounds may, however, have a harmful effect on human health — the extent of which remains unclear — and some polybrominated diphenyl ethers have recently stopped being used as flame retardants in various countries; whether alternative compounds now in use are harmless is still an open question[4].

Although a somewhat volatile and unpredictable element, bromine has played an important part in advancing the field of molecular biology in the form of the polybrominated dye eosin, in which this heavy atom ensures efficient absorption of light. Alternative dyes do exist, but in tandem with another small organic compound, haemotoxylin, eosin is used almost universally to stain the cytoplasm in a cell and numerous other protein-based structures (although, notably, the nucleus is preferentially stained by haematoxylin). The resulting cell images are rather striking, with rich purple colours arising from eosin (pictured for Hepatitis C cells).

The diverse reactivity that bromine brings goes far beyond simply acting as a relatively sizeable anion to balance charge, taking part in cross-coupling reactions, or forming the basis of a good partner in an S_N2 reaction. We may yet find other ways to make the most of brominated species, owing to, or in spite of, their frequent toxic side effects. ❐

This essay was selected as a winning entry in our writing competition, see http://go.nature.com/oi187X

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Peculiar protactinium

Richard Wilson relates how the rare, highly radioactive, highly toxic element protactinium puzzled chemists for a long time, and was discovered and named twice from two different isotopes before finding its place in fundamental research.

The first glimpse of element 91 came in 1900, thirty years after Dmitri Mendeleev predicted its existence, when William Crookes, the discoverer of thallium, put down his studies with cathode rays and spectroscopy to investigate Becquerel's newly reported phenomenon — radioactivity.

Crookes separated a highly radioactive material from his uranium salts that was able to expose a photographic plate, yet could not be detected by a spectroscope[1], leaving him unable to identify the material as a new element. It was in 1913, based on the work of Rutherford and Soddy on the nature of radioactive decay and isotopes, that Fajans and Göhring identified element 91. They named it brevium because the isotope they had encountered ($^{234\mathrm{m}}$Pa) had a brief half-life of only one minute[2].

Meanwhile, a hunt was on for the element whose decay would generate actinium, which Fajans's isotope was not. Soddy hypothesized that this element must be an alpha particle ($^{4}_{2}$He) emitter of the group v elements positioned under tantalum in the periodic table, and thus named eka-tantalum in those days. In March of 1918, Lise Meitner and the conscripted Otto Hahn beat Soddy in the hunt for eka-tantalum and discovered the isotope ^{231}Pa, code-named "abrakadabra" in their correspondence, which indeed converted into actinium through alpha decay. Their suggested name protoactinium — meaning 'parent of actinium' — superseded Fajans's brevium because of the longer half-life (roughly 32,000 years) of their isotope ^{231}Pa (refs 3,4). In 1949, IUPAC would simplify it to protactinium, Pa.

Little chemical research would be conducted with protactinium for the following forty years — a consequence of its rarity, difficulty of isolation, radiotoxicity and lack of commercial application. In the 1950s, the development of nuclear power, along with the recognition of uranium as a strategic resource for weapons, inspired the investigation of a thorium-based nuclear fuel cycle, which involves protactinium as a major player. This newly identified use for protactinium resulted in the separation of approximately 100 grams of it from 60 tonnes of uranium-refining sludges. The availability of this stock for research in the 1950s led H. W. Kirby, an American pioneer in protactinium research, to speculate that the 1960s would see much of the "mystery and witchcraft" fade from the chemistry of this element[5].

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The mystery and witchcraft mostly came from protactinium's confusing chemical properties, not quite truly actinide yet not quite transition metal. This confusion persisted until the actinide elements were identified as a discrete periodic series. Element 91 shares a pentavalent oxidation state with the transition metals niobium and tantalum, and possesses a tetravalent oxidation state accessible under reducing conditions, in a similar manner to the other tetravalent actinides. However, unlike the other pentavalent actinides, protactinium exists as a mono-oxo ion rather than the di-oxo ones archetypical of uranium, neptunium, plutonium and americium, which makes it a truly unique actinide. But Pa(v)'s most lamented property is perhaps its insolubility, which causes protactinium to adsorb to glass surfaces. It proved fortunate for Meitner and Hahn, however, because it was the silica fraction of their pitchblende residues that contained the protactinium they succeeded in isolating.

The 1960s and 70s saw our knowledge of protactinium's chemistry expand vastly to include its oxides, halides, coordination complexes and organometallic complexes such as protactinocene. A declining interest in a thorium fuel cycle, however, and the abandonment of research on its chemistry by all but a few by the mid-1980s, sent protactinium back into relative obscurity despite its importance in the actinide series.

Protactinium's significance stems from the fact that it is the first actinide to possess a $5f$ electron, with intermediate properties between those of thorium and uranium. Its ground-state electron configuration [Rn]$5f^{2}6d7s^{2}$ is only marginally more stable than the [Rn]$5f6d^{2}7s^{2}$ configuration, a result of its nearly degenerate $5f$ and $6d$ orbitals. Its unique electronic structure makes protactinium a critical stepping stone for understanding the electronic structure and bonding of the $5f$ elements.

This becomes increasingly evident as computational chemists continue to demonstrate the important interplay of the $5f$, $6d$ and even the core $6p$ electrons, when describing the electronic structure and bonding behaviour of the actinides, suggesting that protactinium still has more contributions to make to chemistry. Although laboratory work with protactinium has been largely abandoned, its future contributions to chemistry may well come from where Meitner and Hahn first found it, *in silico*. ❐

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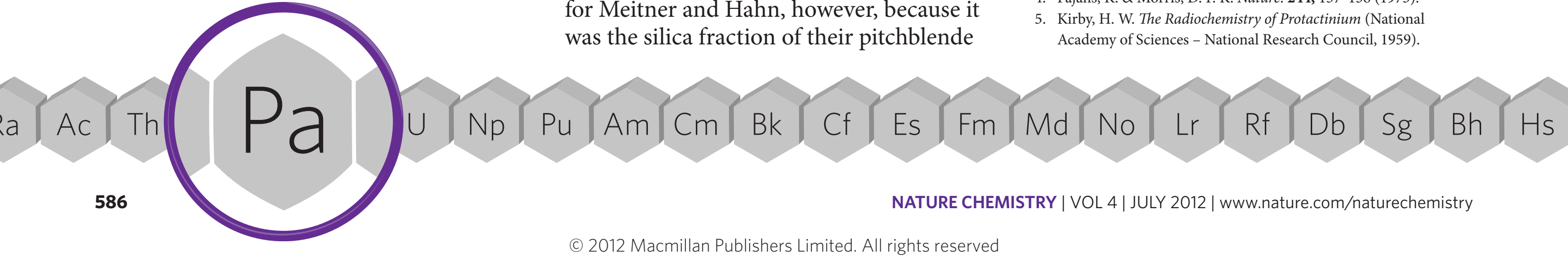


in your element

Life and death with nitrogen

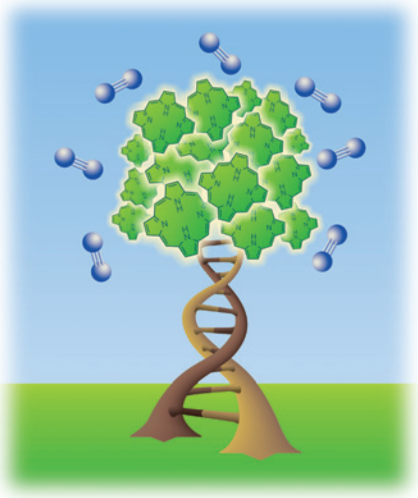
Although first known among chemists for its noxious or lifeless character, nitrogen was later revealed to be involved in many life, and death, processes. **Michael Tarselli** ponders on this unforeseen characteristic.

Noticing that nitrogen gas (N_2) supported neither combustion nor life, many scientific luminaries of the eighteenth century — Scheele, Priestley, Lavoisier... — referred to nitrogen as 'noxious air', or even 'lifeless'. Yet element 7 has boasted an unparalleled career in the ensuing 300 years, participating in organic catalysis, bombs, power generation, food contamination, and the elucidation of DNA's structure.

Nitrogen heads up Group 15, the appropriately named pnictides (from the Greek *pnigein*, 'to choke'), which includes other life-and-death players: arsenic, a poison also found in drugs, and phosphorus, toxic yet present in the backbone of DNA. These elements have three unpaired electrons in their *p* valence shell, and may also bond through their *s* electrons, so they ideally want 3 to 5 bonds. In its elemental state, nitrogen forms the diatomic gas N_2 that makes up more than 70% of the air we breathe.

Nitrogen's penchant for forming three covalent bonds while keeping a lone pair 'open for business' leads to numerous catalytic and biochemical applications. Much of the burgeoning field of organocatalysis[1] relies on small species derived from two nitrogenous precursors: proline, an amino acid, and urea, the first organic molecule prepared synthetically (Friedrich Wöhler, 1828). In nature, porphyrins — polypyrrole macrocycles present in haem enzymes and chlorophyll — host transition metals to perform basic life functions: photosynthesis, oxygen transport and destruction of toxins in the blood. Several heavy metals (molybdenum, vanadium, iron), allow soil bacteria in the roots of legumes to fix N_2 into usable plant metabolites.

Life is intricately linked to nitrogen, found in every DNA nucleobase. Isotopic labelling with heavy isotope ^{15}N allowed Meselson and Stahl to verify that a single strand of DNA could template its own replication. Chemists interested in tinkering with life's codes have designed 'extended' nucleobases[2], which can replicate and pair up much like normal DNA.



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Newborn babies owe a lot to another nitrogenated compound, folic acid (vitamin B_9), critical to proper foetal development during pregnancy. Melamine ($C_3H_6N_6$), however, recently made darker headlines. In food, nitrogen normally comes from proteins, and nitrogen analysis thus serves to measure protein content. Used to dope infant formula and pet food to artificially inflate their apparent protein content, melamine made both people and pets ill.

Nitrogen plays a pivotal role in the development of renewable energies. Nocera's 'hangman' assemblies[3], which generate oxygen and hydrogen gas from water splitting to power fuel cells, feature an octafluoro–corrole backbone, which binds cobalt through coordination to four nitrogen atoms. One possible way to safely transport hydrogen fuel is through ammonia borane ($H_2N–BH_3$) complexes. New solar cells[4] also rely on dyes containing metal–nitrogen bonds to catch ambient light, making for flexible, highly efficient, cost-effective devices.

Entire wars have turned on nitrogen compounds: the Haber–Bosch process (ammonia production by catalytic reaction of N_2 with H_2) was developed around the First World War; before then, explosives were produced from concentrated nitrates found in guano (bird droppings). Nitrogen's penchant for explosion extends to TNT, ammonium nitrate, nitroglycerin and nitrogen triiodide — which decomposes at a feather's touch, making for a thrilling demonstration tool. Despite knowing that compounds with high nitrogen-to-carbon ratios, like azides and tetrazoles, are potentially explosive, chemists cannot resist. Recently, Klapötke and co-workers synthesized a compound with a 10-nitrogen-atom chain, which was barely stable enough to allow analysis and shattered several pieces of lab glassware[5].

The life-or-death duality is observed throughout medical and pharmaceutical history. Nitrogen is often associated with stench and death: we can smell putrescine and cadaverine, two volatile amines emitted from dead tissues, in vanishingly small amounts. Cyanide, a poison known since antiquity, contains a C≡N moiety. Feeling faint? 'Smelling salts' that bring a person back to consciousness often consist of ammonium carbonate. Aniline dyes, originally thought useless waste from coal tars, exhibited potent biological activity, giving rise to the modern pharmaceutical industry[6].

Given its tendency to corrupt, catalyse, nurture, or destroy, nitrogen has proved its lifeless reputation dead wrong. ❐

This essay was selected as a winning entry in our writing competition, see http://go.nature.com/oi187X

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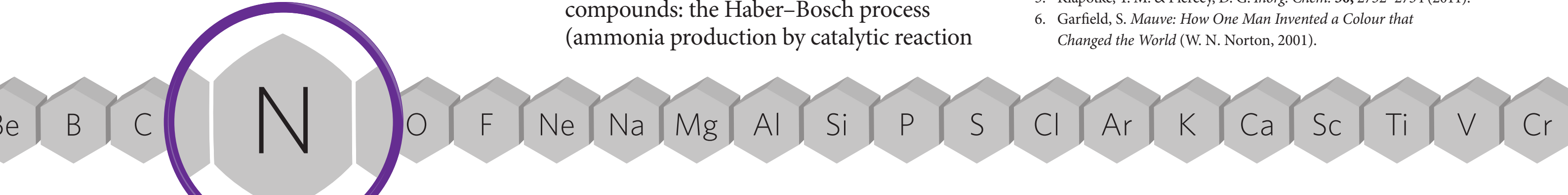


Reactions coupled to palladium

You would be forgiven if you thought the most important element in an organic transformation was carbon. **Matthew Hartings** argues that, for just over half a century in many of chemistry's most renowned organic reactions, it has actually been palladium.

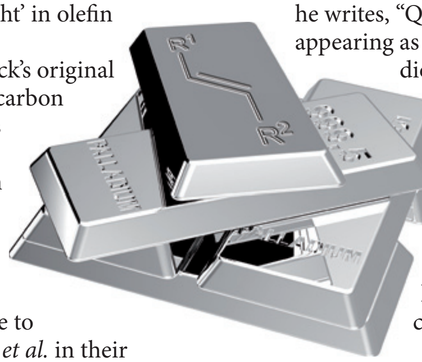
The science of palladium gained fame beyond the industrial and chemical communities in 2010, when Richard Heck, Ei-ichi Negishi and Akira Suzuki received the Nobel Prize in recognition of their development of palladium-catalysed carbon–carbon bond formation. Their reactions, and the many similar ones that they inspired, have had a profound impact on the way chemists make molecules that are used in a diverse array of products, from industrial materials to pharmaceuticals. In addition, palladium has been used as a catalyst in the Wacker process — regarded as the first industrially applied organometallic reaction — for the past fifty years.

Intriguing questions arise: Why palladium? What is it that makes the metal such a great catalyst for these processes? And when did chemists begin to realize that this was the case?

Among transition metals, good catalysts are those unsaturated ones with open coordination sites. Palladium(II) is one of several metal ions with d^8 electron configurations that tend to adopt square-planar geometries — which, conveniently, have two empty axial coordination sites.

More importantly, to run the reactions involved with the Wacker process and Heck/Sonogashira-type couplings, a metal catalyst must be able to associate with a carbon–carbon double bond[1]. It turns out that nickel, palladium and platinum all have the proper orbital energies to be able to do this. Platinum, however, is a poor catalyst, in part because the kinetics of olefin–Pt bond formation are slow[1]. Several nickel complexes do show catalytic activity towards olefin reactions[1], but it is palladium that continues to forge its way as the metal centre of many successful olefin catalysts.

Palladium certainly has some unique characteristics. Its ground-state electronic structure is $4d^{10}5s^0$, making it the only transition metal to combine a filled *d* orbital with an empty frontier *s* orbital. Also, palladium's lowest *d* to *p* transition is decidedly larger in energy than the equivalent transition for similar metals[2]. These two facts seem to indicate that its catalytic activity occurs mainly through its 4*d* electrons, with low percentages of hybridization from the 5*s* and 5*p* orbitals, and surely play some role in making palladium 'just right' in olefin reaction catalysis.



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By the time Heck's original paper on carbon–carbon coupling reactions appeared, the value of palladium as a catalyst for olefin reactions was already established[3]. This is, in part, due to the work of Smidt *et al.* in their development of the Wacker process, first using platinum, then palladium three years later[4]. But the history of palladium-based olefin oxidation goes back further than this. The initial publication of the Wacker process referenced an article from 1894[5], by Francis C. Phillips, as the first observation of the ability of palladium to catalyse the oxidation of olefins.

Phillips was an expert on the reactions of gases in the late 1800s, at Western University (currently known as the University of Pittsburgh). He had received funding to identify the components of gases mined in Western Pennsylvania, and to do this needed to understand the physical and chemical characteristics of the individual gases that might be present in the mined gas mixture.

Phillips set out to study the way different gases are oxidized by air in the presence of various metals and their chloride salts[5,6] — a two-part study that is impressive in terms of both experimental effort and sheer scope. In the first stage, he attempted to quantify the oxidation of gases over different metals dispersed in asbestos fibres[6]. In the second, he aimed to describe these reactions qualitatively, by bubbling the gases through solutions containing metal salts[5]. For this, he tested twenty different gases and nineteen different catalysts.

It is in this second study that Phillips describes the reactions of olefins over palladium chloride. For the case of ethylene, he writes, "Quickly reduced, the metal appearing as a black powder. No carbon dioxide is formed"[5]. So, he understood that the gas was being oxidized over palladium, and that the oxidation product was not CO_2. Had he been able to isolate and characterize acetaldehyde, he would have had described the substantive chemistry of the Wacker process.

I think it is important to note here that Phillips was not looking for industrially important reactions in his experiments; he was just trying to better understand chemistry. In what may be the most understated line in the paper that would set the framework for the Wacker process and Heck/Sonogashira couplings, he concludes his report by writing, "To be continued." ❐

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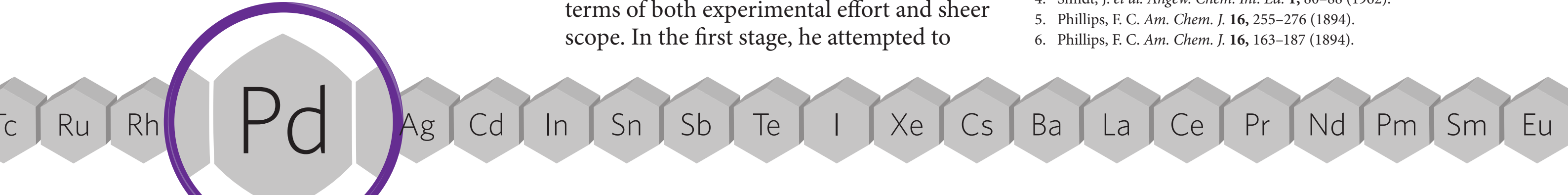


in your element

A touch of indium

Catherine Renouf describes how indium went from being a rather inconspicuous element to one whose role as a component of high-technology devices and gadgets may deplete its worldwide resources.

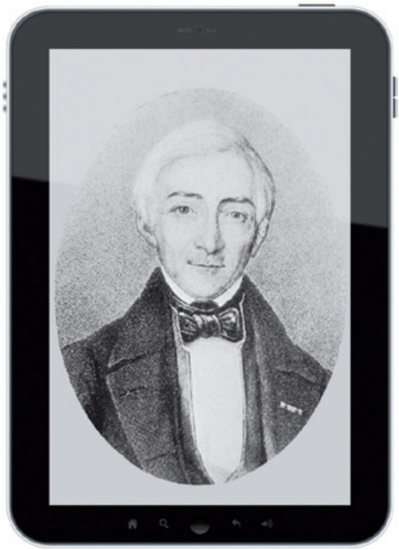
A mysterious blue line in an 1863 atomic spectrum was the first indication that a new and unknown element was present within zinc ores. The indigo colour of that line gave its name to the new element, indium, and zinc ores are still its primary source today.

Ferdinand Reich (pictured) and Hieronymus Richter, who had observed the blue line and isolated the new element, were meant to present an ingot of indium at the World Fair in 1867; but, fearing its theft, they displayed a lead ingot instead. Members of the audience were probably easily fooled as these two very soft metals have similar appearances. What they could not have known at the time is that indium shares an unusual property with only one other element: tin. These two elements — neighbours in the periodic table — emit a crying sound when they are bent.

For 50 years after the World Fair, indium was merely a curiosity to be stored in chemists' cupboards. No-one had yet come up with a use for indium that justified persevering with a process-heavy purification, and the world's indium supply could be measured in grams.

It was during the Second World War that indium found a large-scale application: the malleable metal could be processed into thin films used to provide a lubricating coating for the bearings in aircraft engines. Lubrication, along with soldering — a second application that arose around the same time — remained its only uses until the late 1950s.

Worldwide demand increased from the 1970s onwards. Indium, an efficient neutron absorber, was used to make control rods for nuclear reactors. The low melting points of its alloys (some as low as 50 °C) were useful for soldering, and also made for excellent fuses in heat regulators and sprinklers[1]. But the breakthrough discovery that sparked a widespread interest in indium was its use in the form of indium tin oxide (ITO). Today, the part played by ITO in most people's lives has led to element 49 being given a critical alarm for supplies depletion by the US Department of Energy[2].



PORTRAIT OF REICH ©SPL; IPAD ©ISTOCK PHOTO/THINKSTOCK

Indium is expensive and rare, and ITO is brittle and inflexible, yet overcoming these issues has allowed us to produce much-prized gadgets: our touchscreen devices, smartphones and liquid-crystal-display televisions. ITO is a unique material in that it is both electrically conducting and, crucially for all of these uses, optically transparent[3]. In addition, it is an important component of most solar cells, whatever their bulk composition, as transparent ITO is generally used to complete the electrical circuit at the front, light-absorbing surface[4].

This transparency in the visible part of the spectrum arises from its wide bandgap at 3.3–4.3 eV; when it is used as a thin film, its transmission of visible light and electrical conductivity are both high enough for ITO to be put to use in touchscreen applications. The first such devices consisted of two separated layers of ITO that were joined through a stylus, but modern devices have evolved to exploit the user's electrically conducting finger instead, which makes for a more user-friendly — and a more spectacular — experience. Touching the ITO layer on the screen changes its capacitance at that particular position, which in turn sends a signal to the device.

The current touchscreen market is rapidly growing, and although the worldwide stores of indium are unknown — because it is still only a by-product from mining other metals, mostly zinc and tin — it is estimated that there will only be enough indium to supply our growing needs until 2020. We can therefore expect it to become increasingly expensive as its rarity escalates.

Rollable displays are often touted as the next ground-breaking development in computing, a development for which the simple properties of ITO are not well suited. Whereas ITO's brittleness is not a problem in smartphones with an expected usage of a couple of years, and is acceptable for robust tablets and e-readers with slightly longer lifetimes, it will not transfer well to flexible or rollable devices. This new endeavour is sparking research into semiconductors that are indium-free, such as carbon nanotubes and graphene[5], which can only be a good thing if we are to preserve our stock of this scarce metal, and maintain its availability — at affordable prices — for solar cells for green electricity generation.

Chemists played a large part in the development of ITO and all its uses, and we must now also lead the way in the search for its alternatives. ❐

This essay was selected as a winning entry in our writing competition; see http://go.nature.com/oi187X

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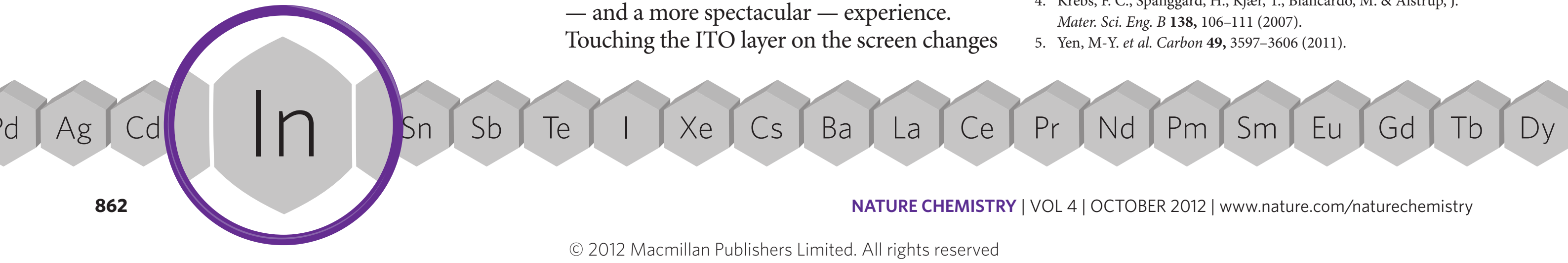

in your element

Osmium weighs in

Gregory Girolami recounts how element 76 beat a close competitor to the title of densest known metal and went on to participate in Nobel Prize-winning reactions.

The road to the title of heavyweight champion among the chemical elements began with the work of English chemist Smithson Tennant (1761–1815). Tennant obtained a medical degree, but after discovering that the sight of pain upset him too much, he abandoned the practice of medicine and decided to devote his life to chemistry[1,2]. He also developed some unconventional laboratory habits; for example, when a piece of linen was not available for a filtration, he often used his handkerchief or cut off a piece of his shirt.

In 1800, Tennant co-founded a business to sell platinum metal and began to prepare large quantities of it. He noticed, as had others before him, that extracting platinum out of its crude ores with aqua regia — a mixture of concentrated nitric and hydrochloric acids — left behind an insoluble black residue. In 1804, he announced his isolation of two new metals from the residue: iridium, named for "the striking variety of colours which it gives", and osmium, named after the Greek word for 'smell', *osme*, for the "pungent and peculiar smell of its oxide".

Osmium is the rarest of the stable elements: its average abundance in the Earth's crust is about 1 gram per 200 tonnes. Today, osmium is obtained commercially as a by-product of refining nickel and some of the more common platinum-group metals. The back seat of an automobile could easily accommodate the worldwide annual production of osmium — approximately 500 kilograms, which is about 5,000 times less than its gold counterpart.


PEN © ISTOCKPHOTO/THINKSTOCK

Neighbours in the periodic table, osmium and iridium have long been known to be the densest of all metals (both are over twice as dense as lead), but which is the heavier of the two has been fiercely contested. Measuring their densities directly (by weighing samples of known volume) is not particularly accurate, owing in part to the difficulty of ensuring that the samples are free of internal voids. A better method involves a calculation based on their crystal structures and atomic weights but, because the densities are so similar, refinements in these measurements have occasionally resulted in the champion and challenger reversing positions.

Osmium metal rivals diamond as the least compressible of all known substances.

Since its discovery, osmium has most often held the title of densest metal, but for many decades in the twentieth century it was iridium that occupied that position. More accurate studies carried out in the 1990s showed that osmium's density just slightly exceeds that of iridium[3]: the current values, 22.587 (Os) and 22.562 (Ir) $g\ cm^{-3}$ at 20 °C differ by only 0.1%.

Despite its rarity, osmium is currently far less expensive than gold, partly because it has few commercial uses. Osmium metal — bluish-grey in colour, hard and brittle — lacks somewhat in visual and tactile appeal. But element 76 does have some redeeming qualities.

Osmium metal strongly resists being compressed under pressure, so much so that it rivals diamond as the least compressible of all known substances. Osmium can be mixed with other platinum-group elements to form alloys that, owing to their hardness, find speciality uses as electrical contacts, wear-resistant machine parts, and tips for high-priced ink pens. An urban legend is that osmium alloys are used in some surgical implants such as cardiac pacemakers and replacement heart valves, when in fact such alloys have never been used in these devices.

Although its metallic form has few applications, osmium's chemical behaviour is far from dull — it can exist in eleven different oxidation states, from −2 to +8; a versatility matched only by its chemical cousin ruthenium and a few other transition metals. Furthermore, the high +8 oxidation state reached by osmium — along with iron, ruthenium and xenon — is the highest seen for any chemical element under normal circumstances.

The most useful osmium compound is the tetroxide OsO_4, a colourless solid used as a stain in microscopy and in fingerprint detection. Osmium tetroxide is also used as a catalyst in a few commercial processes, such as the manufacture of certain anti-obesity and anti-diabetic drugs. These processes are based on the Nobel Prize-winning work of chemist K. Barry Sharpless, who used osmium tetroxide as a key component in a remarkable catalyst mixture that adds two hydroxyl (alcohol) groups to carbon–carbon double bonds[4].

So 'heavy as lead' turns out to be a rather half-hearted way to describe something that weighs a lot — but somehow I doubt that 'heavy as osmium' will ever catch on. ❐

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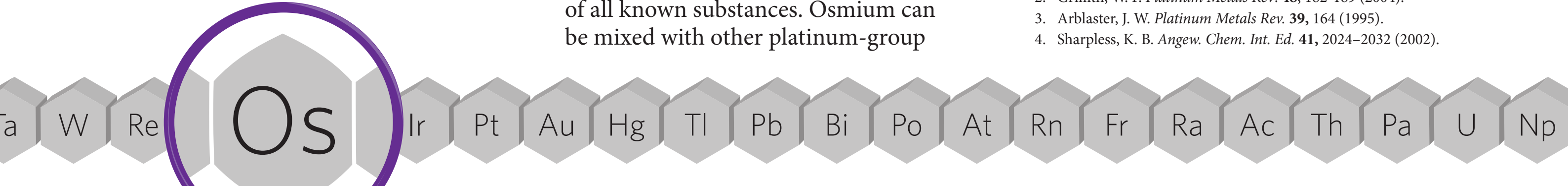

Plutonium's new horizons

For historical reasons, plutonium brings to mind nuclear weapons. **Jan Hartmann** brings another side of element 94 to attention, which features an upcoming trip to its eponymous celestial body.

Plutonium has had an undeniable influence on the twentieth century as a key contributor first to the end of World War II with the atomic bombing of Nagasaki in August 1945, then to the nuclear arms race of the Cold War.

After a false start in 1934, when Enrico Fermi mistook a mixture comprising barium, krypton and other species for element 94, plutonium was produced and isolated in 1940 by Glenn T. Seaborg and his colleagues. It was obtained through the bombardment of a uranium target with deuterium nuclei, but that success was kept secret until the end of World War II. The name 'plutonium' had already been suggested in 1816 for barium, after the Roman god Pluto, but abandoned. Seaborg gave it to element 94, this time continuing with the tradition of naming of the preceding actinides in the periodic table — neptunium and uranium — after the outermost planets of our Solar System[1].

In the strictest sense, plutonium is naturally occurring: in 1951 D. F. Peppard isolated minute quantities of ^{239}Pu from uranium ore. But it makes up just 2×10^{-19} per cent (by mass) of the lithosphere, so virtually all of the plutonium on Earth is produced artificially in nuclear reactors.

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Otto Hahn discovered nuclear fission of uranium in 1938, sparking fears that Nazi Germany might be working on the development of nuclear weapons. This resulted in the setting up of the 'Manhattan Project' to develop nuclear weapons during World War II, during which plutonium was identified as a suitable fissile material. Kilogram-scale production of the new element began less than four years after its discovery. Germany surrendered in May 1945, ending the war in Europe before nuclear weapons were combat-ready. They were used against Japan instead, greatly accelerating the end of the war in the Pacific region. Despite the end of the war, large-scale production of plutonium continued in the nuclear arms race between the United States and the Soviet Union. Most of these nuclear stockpiles now necessitate research on the ageing process of plutonium metal; self-irradiation changes its physical properties over time in a way that remains poorly understood.

Yet there is more to plutonium than sheer destructive power: it exhibits surprising physical properties and fascinating chemistry. All of its known isotopes are radioactive, the most stable one (^{244}Pu) with a half-life of about 80 million years. Some other isotopes, most notably ^{239}Pu, are capable of self-sustaining nuclear chain reactions, releasing enormous amounts of energy. It has six allotropic modifications, leading to its being called "a physicist's dream, but an engineer's nightmare"[2]. The different phases, close in energy, are prone to interconversion, leading to dramatic changes in properties with little stimulus. Its 'delta' allotrope is the only known metal with a negative thermal expansion coefficient, meaning that it contracts on heating.

Element 94 exists in the oxidation states +III to +VII, all intensely coloured, and is also the only known element for which four oxidation states (from +III to +VI) can coexist in aqueous solution in nearly equal concentrations. In fact, a neutral, aqueous solution of Pu^{4+} reaches equilibrium of all four within a few hours[3]. In its most stable oxidation state, +IV, plutonium tends to form coordination complexes, some of which are soluble in organic solvents such as diethyl ether or tributyl phosphate. The latter is used to separate plutonium from uranium in the 'PUREX' process.

Uses of plutonium include fuel for nuclear reactors, both for energy and for scientific research. In 2010, more than 13% of the worldwide electricity demand was covered by nuclear reactors[4]. As a source of high-intensity neutron radiation, research reactors are invaluable tools, for example for neutron diffraction experiments. The non-fissile isotope ^{238}Pu is used in radioisotope generators, which have a long productive life and high energy density. This makes them suitable as sources of electrical energy for unmanned spacecraft such as the Mars Curiosity Rover and New Horizons. The latter is scheduled to reach Pluto and gather data on it in 2015, with instrumentation powered by 10.9 kg of $^{238}PuO_2$ (ref. 5). Thus, of all the elements named after celestial objects, plutonium is the only one so far to be sent to its astronomical namesake.

Plutonium might instead have been named after the two-faced Roman god Janus; its history lucidly illustrates the ambivalence of scientific inquiry. No scientific discovery is inherently good or evil. It is how it is used that decides how it will come to be seen. ❐

This essay was selected as a winning entry in our writing competition; see http://go.nature.com/oi187X

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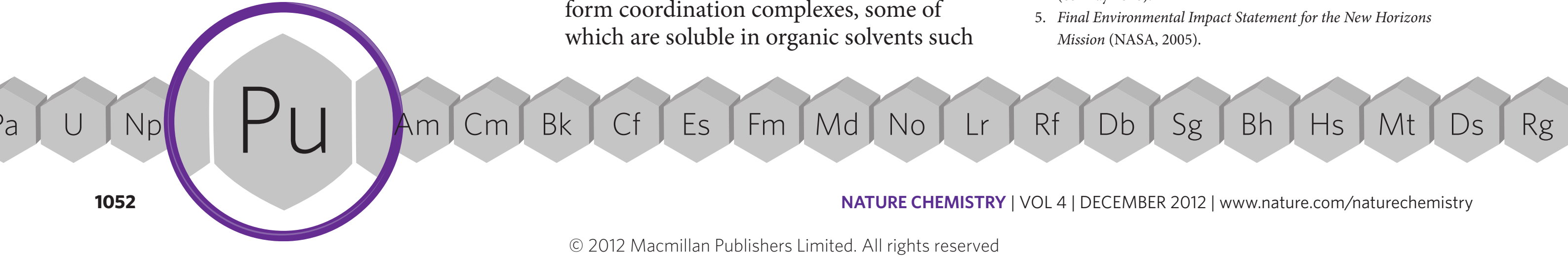

The allure of aluminium

Daniel Rabinovich outlines the history, properties and uses of aluminium — one of the most versatile, pervasive and inexpensive metals today, yet it was considered a rare and costly element only 150 years ago.

It is hard to believe that aluminium was once more expensive than gold and that, in the mid-nineteenth century, Napoleon III used silverware made of the light metal when he really wanted to impress his guests at stately dinners. Even though element 13 is the most abundant metal in the Earth's crust (~8%) and is present in more than 270 different minerals, its high affinity for oxygen and the chemical stability of its oxides and silicates precluded its isolation in pure form for a long time. The first pure sample of aluminium was obtained in 1827 by the German chemist Friedrich Wöhler, who also began studying its fascinating physical and chemical attributes.

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The French chemist Henri Sainte-Claire Deville (1818–1881) developed a method of preparing larger quantities of aluminium in 1854, and soon published the first comprehensive book describing its manufacture, properties and emerging applications[1].

The attractive properties of the newfangled metal quickly became clear, including low density, high tensile strength and malleability, good thermal and electrical conductivity, and a remarkable resistance to corrosion. Jules Verne eloquently wrote in *From the Earth to the Moon* (1865) that "This valuable metal possesses the whiteness of silver, the indestructibility of gold, the tenacity of iron, the fusibility of copper, the lightness of glass. It is easily wrought, it is very widely distributed, forming the basis of most of the rocks, is three times lighter than iron, and seems to have been created with the express purpose of furnishing us with the material for our projectile." The price of aluminium, however, was still comparable to that of silver, which hampered the development of large-scale applications and motivated the search for an alternative and more economical preparation process.

It was only in 1886 that Charles M. Hall in the US and Paul L. T. Héroult in France, almost simultaneously and completely independently, devised aluminium production processes that relied on the electrolysis of alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). An efficient process for the extraction and purification of alumina from bauxite, the most important aluminium ore, was developed within a couple of years by the Austrian chemist Karl Josef Bayer, son of the founder of the famous German chemical and pharmaceutical company, and the 'Hall–Héroult' process became economically viable. By the early 1960s element 13 became the most widely used non-ferrous metal in the world, even more so than copper.

Applications of aluminium and its alloys range from construction and the transportation industry to the manufacture of electric power lines, packaging materials, cooking utensils and a myriad of other household goods. Another important feature of this ubiquitous metal, one that has significant economic and environmental consequences, is the ease with which it can be recycled. The recovery of secondary aluminium requires only about 5% of the energy necessary to produce new metal from bauxite, while also leading to a decreased use of landfill space and a reduced emission of greenhouse gases.

In contrast to the relatively short history of the pure metal, compounds of aluminium have long been known: alum, a hydrated sulfate of potassium and aluminium, $KAl(SO_4)_2{\cdot}12H_2O$, was used as an astringent and a dyeing mordant in ancient Greece and Rome. Aluminium chloride, $AlCl_3$, a common Lewis acid, is extensively applied in Friedel–Crafts acylation and alkylation reactions, and aluminium chlorohydrate, $Al_2Cl(OH)_5$, is the active ingredient in many antiperspirants. Large quantities of methylaluminoxane, a generic name used to describe the ill-defined mixture of species obtained by partial hydrolysis of trimethylaluminium, are employed in the Ziegler–Natta polymerization of olefins.

The availability of an ever-increasing variety of aluminium coordination complexes has also prompted many recent developments in the chemistry of this metal, often with potential applications to catalysis and organic synthesis[2]. Other active areas of research range from the preparation of unusual aluminium(I) compounds, including organometallic species[3] and metalloid clusters[4], to the synthesis of Schiff base derivatives that effectively break down organophosphate nerve agents and pesticides[5].

The element once dubbed the magic metal by *National Geographic* continues to be a source of inspiration for scientists, engineers and even artists and designers[6]. Let us remember its rich chemistry, fascinating history and multifarious applications the next time we wrap a sandwich in aluminium foil or drink a carbonated beverage from a can! ❐

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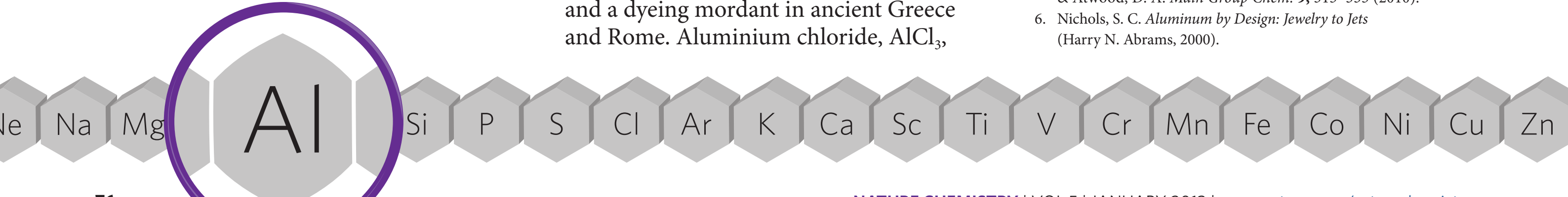


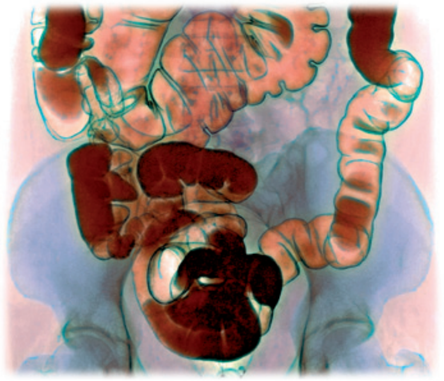
Barium bright and heavy

Katharina M. Fromm relates how barium and its ores went from a magical, glowing species that attracted witches and alchemists to components in a variety of compounds that are key parts of modern life.

In 1602, the shoemaker and alchemist Vincenzo Casciarolo became fascinated by an ore — named Bologna stones or *lapis solaris* — containing small shiny crystals that continued to glow long after having been exposed to daylight, which captivated witches and alchemists alike. Ulisse Aldrovandi published this phenomenon, but it was so extraordinary that scientist Giulio Cesare Lagalla remained unconvinced, even when Galileo Galilei presented him with one of the stones. Investigating further, Lagalla observed that persistent luminescence was mainly observed after calcinations of the stone, as he described in his book *De Phenomenis in Orbe Lunae*, 1612. The luminescence of the Bologna stones was thought to originate from baryte ($BaSO_4$), principal component of the mineral, but it was recently shown to arise from $Cu^{+/2+}$-doped BaS, which was also present[1].

In 1774, the Swedish chemist Scheele discovered barium oxide in gypsum, and in 1808 Sir Humphrey Davy isolated some metallic, but impure, barium. It was Robert Bunsen who obtained the metal in pure form by electrolysis of molten $BaCl_2$ in 1855. Element 56 went on to play important roles in other scientific discoveries — some 50 years later, Marie Curie discovered the heavier atom radium in a mixture with barium. In 1938, when Otto Hahn and Fritz Strassmann found barium among the products obtained on bombarding uranium with slow neutrons they, together with Lise Meitner, concluded correctly that the nucleus of uranium had been fissioned.

Metallic barium is very reactive with air and water, and serves in vacuum tubes and pipes to remove unwanted gases, suppressing high pressures and preventing blowouts. The once mysterious baryte — main source of barium and its compounds — is mass-produced today (more than 5 million tons in 2010) to serve in the oil industry, as a weighting agent that increases the density of drilling fluids in oil and gas explorations. In fact, this high density gave barium its name, after the Greek word βαρύς (*barys*) meaning 'heavy'.



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Baryte is found in many, and varied, materials: as a white pigment in photographic papers; as filler in paints, plastics and automobile coatings for smoothness and corrosion resistance; in high-density concrete and radiation-shielding cement; and even for medical applications. Indeed, barium sulfate can be introduced in the digestive system, from either end and with notable discomfort, as a contrast agent for X-ray scans to detect stomach or bowel disorders. Although barium ions are toxic — they can severely interact with the calcium and potassium metabolic reactions, inducing cardiac irregularities and tremors that can cause paralysis — barium sulfate's insolubility ensures that it can be ingested safely. In contrast its carbonate counterpart, which dissolves in stomach acid, is put to use in rat poison. Despite this toxicity, barium uptake and accumulation has been observed in some plants; the green algae Chlorophyta even seems to need barium to grow well, but its role remains unclear[2]. Brazil nuts can contain up to 1% of barium, as well as some selenium (also toxic in excess), and should be consumed with moderation[3].

Another noteworthy salt is barium dihydroxide. On mixing it with an ammonium salt, for example ammonium chloride, a strongly endothermic reaction occurs between the two solids that produces a liquid ($BaCl_2$ and water) and gaseous ammonia; water placed under the reaction vessel will freeze — making for a striking demonstration experiment. $Ba(OH)_2$ is also used as a strong base (pK_B of −2) in organic synthesis to hydrolyse esters and nitriles[4]; as nanoparticles it is used to restore old wall frescoes by combating gypsum (calcium sulfate) through barium sulfate formation[5]. This method, developed after a catastrophic flood in Florence in 1966, has been used successfully on fourteenth- to eighteenth-century frescoes, for example in Venice, and in the cloister of Brixen in South Tyrol, Italy.

The mineral witherite ($BaCO_3$) is also commonly used. Synthesized from barium sulfide and carbon dioxide it serves as ingredient in glazes and, combined with other oxides, produces unique colours. Other barium-containing oxides show attractive properties — $BaTiO_3$ is a photorefractive, ferroelectric and piezoelectric ceramic, and $YBa_2Cu_3O_7$ a high-temperature superconductor. Barium halides are useful for preparing low-temperature precursors for such oxide materials[6].

Amongst the diverse applications that now involve barium, one has remained particularly close the original attraction it exerted through its intriguing glow — barium nitrate and chloride salts serve to endow fireworks with striking green colours. ❐

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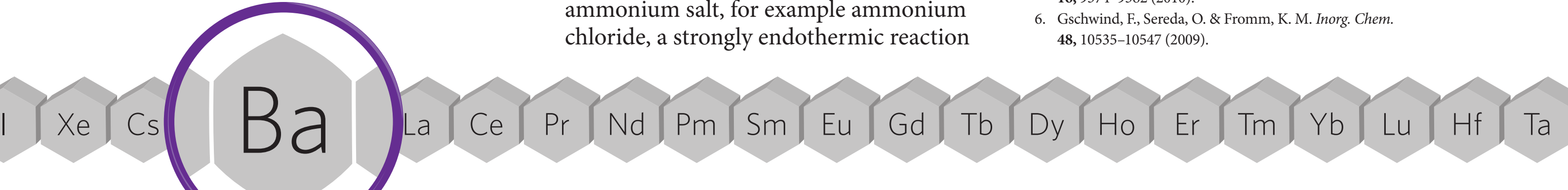

Enigmatic astatine

D. Scott Wilbur points out the difficulty in studying the transient element astatine, and the need to understand its basic chemical nature to help in the development of targeted radiotherapy agents.

Since the discovery of astatine over 70 years ago[1], many of its characteristics have remained elusive. Unlike the other halogens, abundant and ubiquitous in nature, astatine is one of the rarest of all elements. This arises from the fact that it has no stable isotopes; the longest lived of its 32 known radioisotopes, ^{210}At, has a half-life of only 8.1 hours. The rarity and radioactive nature of element 85 lends to its mystery, as it cannot be observed or weighed in a conventional sense. Even its colour is unknown; based on increasingly dark colours for halogens from fluorine to iodine, however, black seems a logical guess.

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The rarity of this radioactive element is reflected in its name, derived from the Greek word αστατος (astatos) meaning 'unstable'[2]. What little astatine is present in nature comes from the decay of heavy radioactive elements found in the Earth's crust. The total amount of natural astatine at any given time has been estimated to be between a few hundred milligrams[3] and 30 g. In any case, naturally occurring astatine isotopes are too unstable, and would be too difficult to obtain, for characterization. Fortunately, the two longest-lived isotopes — ^{210}At and ^{211}At (half-life = 7.21 h) — can both be produced by α-beam irradiation of bismuth-209 targets (pictured, on aluminium support).

Nevertheless, these longer-lived isotopes can only be produced in small quantities[4], which, combined with their short half-lives and high costs, have considerably limited astatine research. Of the artificial isotopes, ^{211}At has been the primary focus of chemical studies owing to its potential in medicine.

The other 'long'-lived isotope, ^{210}At, is not suitable because it decays into polonium-210 — the notorious radiation poison used to kill the Russian Federal Security Service officer Alexander Litvinenko in 2006, after he took political asylum in the United Kingdom.

Although some chemical data has been compiled for astatine isotopes, many physical properties have only been extrapolated. Similar to other halogens, astatine undergoes nucleophilic and electrophilic reactions. The reproducibility of some reactions however has proved highly variable. This may arise in part from the low amounts of astatine present, resulting in very high reaction dilutions. Quantities of ^{211}At used in chemical and radiolabelling reactions range from 37 kBq to 4 GBq. These only represent from $\sim 4.8 \times 10^{-13}$ to $\sim 5.2 \times 10^{-8}$ g of ^{211}At — and this upper limit is rarely encountered, because of the costs involved and the potential for radiation damage to the molecule being labelled. For most reactions, the quantity of ^{211}At present ranges from 10^{-13}–10^{-9} g, and can be smaller than that of trace organic species and metals in solvents. Impurities may thus interfere with the reactions studied, and might even catalyse reaction pathways other than that expected.

The interest in ^{211}At in medicine mentioned above arises from its potential use in systemically targeted therapy of cancers — it is one of only a few α-emitting radioisotopes considered appropriate for medical use[5], as most others can cause severe damage to internal organs. Its short path length (60–90 μm) and high-energy α-particles (6.0–7.5 MeV) are very effective in killing cells bound by a carrier-targeting agent[6]. However, a major impediment to practical applications is the low stability of astatine bonds with aromatic carbon bonds *in vivo*[7]. The development of labelling reagents containing more stable aromatic astatine–boron bonds has improved that situation, and studies evaluating bonding with other elements may further advance it.

To determine *in vivo* stability, the same cancer-targeting molecule can be labelled with ^{211}At and (stably) with radioiodine (^{125}I, ^{123}I or ^{131}I), and the two co-injected. The concentrations of ^{211}At in various tissues (higher lung, spleen, stomach and thyroid) indicate whether it is being released from the carrier molecule. However, even in studies in which low stomach and thyroid (neck) concentrations suggest that ^{211}At and ^{125}I are both stable to *in vivo* dehalogenation, very dissimilar concentrations may be observed for the two elements in other organs such as kidney and liver. This is likely to be due to variations in metabolism of the radioiodinated and astatinated molecules, or may arise from preferential clearance of the radioiodinated metabolites.

In the quest to produce targeted therapeutics for treatment of cancer and other diseases, many of the basic chemical studies with ^{211}At have unfortunately been set aside. Although some of its physical properties will continue to elude direct characterization, it is apparent that we need to gain a better understanding of its basic chemical and radiochemical properties to unravel the enigma of astatine. ❐

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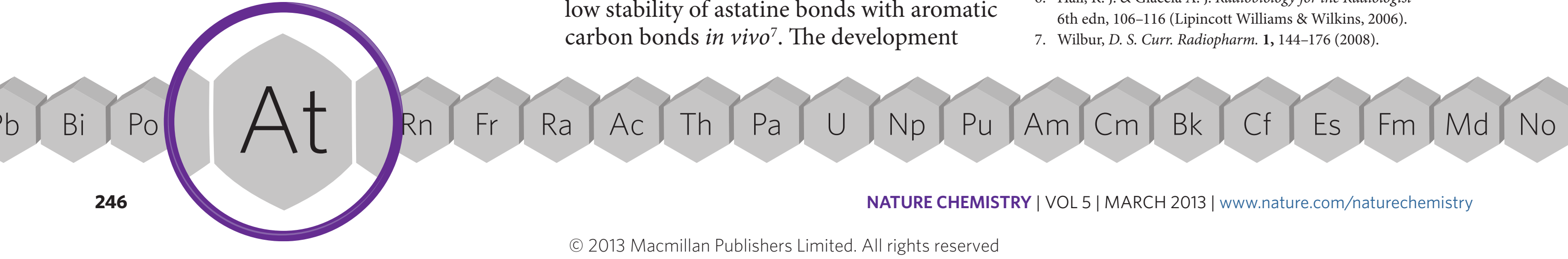


in your element

Cerium under the lens

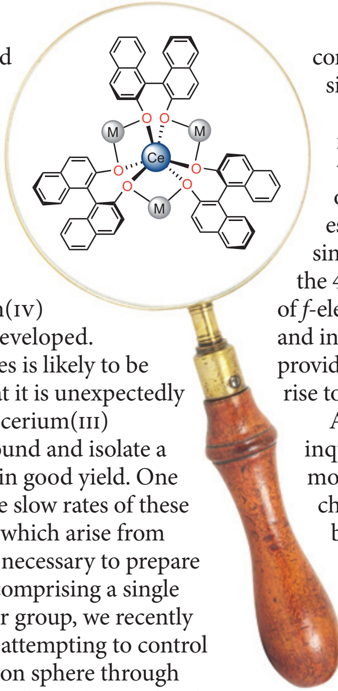
Eric J. Schelter ponders on cerium's rather puzzling redox reactivity, and the varied practical applications that have emerged from it.

Cerium is one of the seventeen rare-earth metals (scandium, yttrium and the lanthanides La–Lu) but, despite the group's name, is fairly abundant — only slightly less so than copper in the Earth's crust. Element 58 is much more present in modern life than it may seem. Aqueous slurries consisting of ceria (CeO_2) are used for the chemical–mechanical polishing of surfaces, including microelectronic device wafers, electronic displays, eye-glass lenses and other optical materials. Through chemical attack of basic sites on surfaces, ceria provides greater polishing rates than simple mechanical techniques.

The use of cerium in many applications comes from the interconversion between $4f^1$–Ce(III) and $4f^0$–Ce(IV) oxidation states — a unique behaviour among the rare-earth metals. Cerium(III/IV) redox chemistry makes oxides useful in heterogeneous catalysis through the storage and release of oxygen. The non-stoichiometric cerium oxide system CeO_{2-x} has unusually high ion mobilities owing in part to octahedral oxygen vacancies in its lattice[1].

Cerium oxides also serve in the promotion of the industrially important water-gas-shift reaction, and in solid-oxide fuel cells. Hydrocarbon fuels encounter element 58 at both the beginning and the end of their useful life: a zeolite (faujasite) impregnated with cerium and lanthanum serves as a petroleum-cracking catalyst in refining. And harmful fuel exhaust gases are converted into N_2, CO_2 and H_2O using ceria and precious metals in automotive three-way catalytic converters. Owing to their uptake of reactive oxygen species, ceria nanoparticles are also being explored in medicinal applications as antioxidant therapeutics.

For the synthetic chemist, cerium is most familiar as a potent oxidizing agent in the ubiquitous ceric ammonium nitrate (CAN) — a drastic 'nuclear option' for oxidation reactions. In contrast to the utility of cerium oxides and the widespread use of CAN as a one-electron oxidant in both organic and inorganic chemistry, the coordination and organometallic chemistry of cerium(IV) is not particularly developed.



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This lack of studies is likely to be linked to the fact that it is unexpectedly difficult to oxidize a cerium(III) coordination compound and isolate a cerium(IV) product in good yield. One possible reason is the slow rates of these oxidation reactions, which arise from the steric hindrance necessary to prepare discrete complexes comprising a single cerium cation. In our group, we recently tackled this issue by attempting to control the metal coordination sphere through heterobimetallic complexes[2] (generalized structure pictured). Surrounding the cerium atom with an interlocked, flexible structure of lithium cations and aryloxide ligands kept it accessible and enabled its quick and easy conversion to cerium(IV), lending support to the idea that cerium oxidation reactions are under kinetic control.

Another fun aspect of element 58 engendered by its redox activity is the somewhat unconventional and controversial electronic structures of its compounds, such as cerocene ($Ce(C_8H_8)_2$), an 8-fold symmetric, eclipsed sandwich complex. The most accurate picture of the valence at its cerium cation has remained somewhat ambiguous[3]. Energy decomposition analysis suggests a strong ionic interaction between the cerium centre and each cyclooctatetraene ring, and X-ray absorption spectroscopy indicates that cerocene has a ground state that is strongly multiconfigurational[4] — so much so that the compound is now described as 'intermediate valent'. It is trapped between configurations of Ce(III) and Ce(IV) character that are quantum-mechanically admixed and comprise a strongly stabilized open-shell singlet ground state[4,5].

This deceptively simple compound represents a stimulating case where the very human concept of a formal oxidation state fails to capture the essential essence of a molecule. The simultaneous local/non-local character of the 4*f*-electron in cerocene is reminiscent of *f*-element superconductors' behaviour[6], and investigations on cerium compounds can provide insight on how local behaviour gives rise to exotic materials properties.

Alongside all this fertile academic inquiry are also excellent practical motivations for studying cerium chemistry. Cerium is found naturally in bastnaesite and monazite ores, together with other light rare-earth elements such as neodymium. Neodymium presents a high value owing to its parentage of $Nd_2Fe_{14}B$ — a hard magnetic material that finds diverse uses, such as in wind-power generators. In a typical rare-earth-metal separations process, cerium, in as much as three-fold excess of neodymium by mass, is removed and discarded as a byproduct. This is an excellent opportunity to search for new applications and add value to cerium 'waste' — even more so when the tight economic margins of rare-earth-metals mining are taken into account. ❐

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s Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re

Neon behind the signs

Felice Grandinetti ponders on the peculiarity of neon among the noble gases — and whether it should occupy the top-right position in the periodic table.

The noble gases — helium, neon, argon, krypton and xenon — all occur as minor constituents of air. Although this seems to make them very accessible, they remained unknown until the end of the nineteenth century. The most abundant, argon, was actually isolated in 1785 by Henry Cavendish, but he did not recognize this unknown component of air as a new element. It was only in 1894 that Sir William Ramsay and Lord Rayleigh jointly announced its discovery. This marked the beginning of an extraordinary scientific adventure, which led Ramsay and his co-workers to isolate, in the space of few years, an entire group of new elements.

Among the group 18 elements, neon (from the greek νέον, 'new', a name suggested by Ramsay's 13-year-old son), krypton and xenon were obtained by fractionation of liquid air using an apparatus that had just been invented by the engineers William Hampson and Carl von Linde, which efficiently produced large amounts of liquid gases — a wonderful example of pure and applied science working in concert. The fraction containing neon was distilled in June 1898. Element 10, once isolated, presented peculiar spectroscopic lines, including the bright reddish–orange lights that now brighten up our city tours by night. The same red emission is also behind the helium–neon lasers employed, for example, in barcode scanners, CD players and medical applications such as laser eye surgery and the analysis of blood cells.

In 1912, J. J. Thomson observed that the canal rays (beams of positive ions) obtained from ionized neon followed two distinct trajectories when passed through a magnetic and an electric field. He deduced the presence of neon atoms with two different atomic masses, ^{20}Ne and ^{22}Ne, thus discovering isotopes of a stable element. The separation of ions by their mass was soon improved by Arthur Dempster and Francis Aston, and developed into the modern technique of mass spectrometry.

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Naturally, chemists attempted reactions with the noble gases, but early attempts were unsuccessful. No negative results, however, proved more informative: this reluctance to react became a founding principle of the modern theories of chemical bonding, which considers the elements' valence electron shells. In the case of the noble gases, their complete shells lead them to being inert.

Yet, unfazed, chemists didn't give up on reacting the noble gases. If chemical bonds form by electron sharing or donation, it was reasonable to expect that the inertness of these elements would progressively decrease from helium to xenon. Moving down the periodic table in this order, polarizability increases and ionization potential progressively decreases, to reach values comparable to those of commonly oxidizable molecules. Guided by these arguments, on a Friday afternoon of March 1962, all alone in his lab, Neil Bartlett succeeded in oxidizing xenon using platinum hexafluoride. Xenon chemistry soon greatly increased, and is now well established. Several krypton compounds also went on to be prepared, as well as one argon compound[1] (the triatomic HArF); no helium and neon compounds have yet been reported.

By the same token, neon should be more reactive than helium. Yet according to theoretical investigations, neutral and even anionic species such as HHeF, H_3CHeF, $(LiF)_2(HeO)$ and $FHeX^-$ (X = O, S, Se) are metastable structures featuring covalent helium bonds, whereas the neon analogues of these species are predicted to be unbound. These calculations are in agreement with the fact that complexes of neon with neutral metal acceptors, including the compounds NeAuF and NeBeS recently detected in cold matrices[2,3], are also in general less stable than their helium counterparts. There are also examples of helium and neon cations that feature this reversed order of stability[4].

Neon is bigger than helium, and possesses occupied *p* orbitals. This is thought to produce less effective electrostatic interactions and higher orbital repulsions, which typically make the neon compounds either unstable or only marginally stable, although the contributions of these factors are still to be further investigated. Chemists studying neon thus face two challenges: the experimental preparation, but also the accurate theoretical prediction of its compounds.

There have been suggestions to shift helium to group 2 of the periodic table, next to hydrogen and just above beryllium. Supporting arguments are the isoelectronic analogy (it has two electrons in its outside shell), and the anchoring of otherwise concealed periodic regularities. The lower stability of neon compounds compared with helium ones is in line with this proposal; moving helium would make neon occupy the top position in that column of the periodic table, which would suit well its situation of the most inert noble gas. ❐

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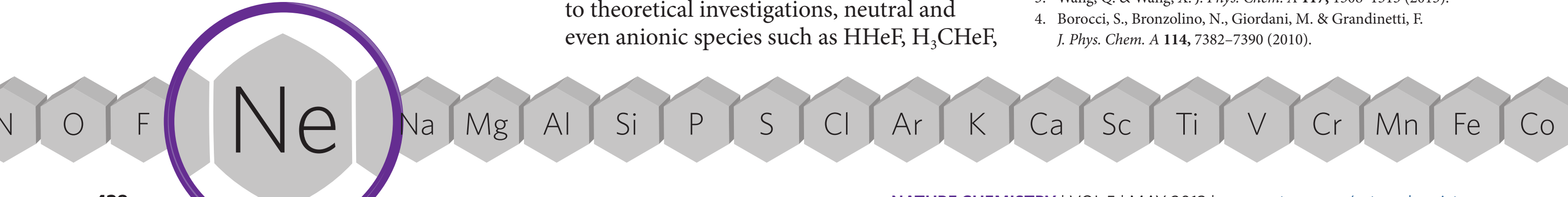


Titanium tales

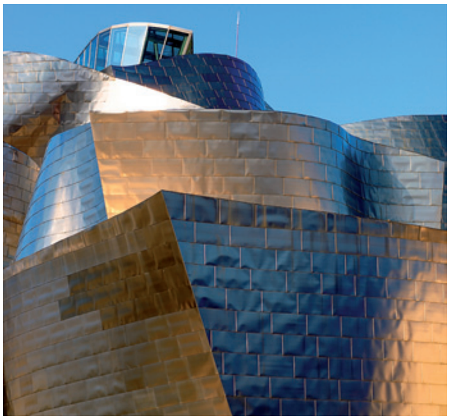
From toothpaste to Tebbe reagents, **Michael Tarselli** takes a look at the many different faces of titanium.

While writing, I stare through lenses held in place by lightweight and durable titanium frames. We adorn ourselves with titanium in many different ways, whether in earrings, marriage bands, or certain pins and fasteners used to hold together broken bones. You might brush your teeth with TiO_2-whitened paste, and that same glimmering white pigment can be found in the paint on your bedroom walls or the coatings on your pharmaceuticals. Single-crystal titania semiconductors will soon find homes in solar panels and tablet computers. Titanium has even been shot into space, built into the heat-resistant hull of NASA's Space Shuttle[1].

Element 22 is found almost everywhere — it ranks ninth in abundance among elements in the Earth's crust. A ubiquitous element demands a strong name, and titanium is fittingly named for the Titans, the ancient Greek immortals. Titanium's tough to isolate: you'll never find it in its metallic state in nature. Only in the past century has the pure metal become readily available; two common refinement processes require heating to around 300 °C with alkali-metal reductants.

Titanium (s^2d^2) lives on the outer fringes of the periodic table's '*d* block', which includes redox champions such as manganese and chromium. Certainly no slouch when it comes to redox chemistry, titanium is commonly found in +2, +3 or +4 oxidation states, carrying heteroatoms (such as N, S and O) along for the ride.

Most organic chemists know titanium from $TiCl_4$, the prototypical Lewis acid involved in everything from aldol reactions to sugar deprotection. Prefer radical chemistry? Drop down one reduction level to $TiCl_3$, and you get pinacol adducts from imines and carbonyls. Titanium's rich coordination chemistry shows up best in 'half-sandwich' complexes, which can simultaneously tie up three ligands and unite them into short oligomers. Add another arene, and we're talking titanocenes — you'll find the Tebbe and Petasis reagents, two such complexes used for olefination, in many synthetic laboratories.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The titanium-clad Guggenheim Museum, Bilbao.

Titanium works pretty well as a Lewis acid when starved of all four valence electrons. But, what if you give a few electrons back? Although attractive to heteroatoms in the +4 oxidation state, titanium(II) has a 'softer side' — it coordinates to alkynes and carbonyls, creating *umpolung* dianions. The Kulinkovich reaction, which generates cyclopropyl alcohols from aldehydes treated with a 'low-valent' titanium(II) reagent, kicked off a renaissance in titanium-coupling chemistry. Several research groups (including those of Micalizio, Cha and Panek) have utilized this unique reactivity to stitch together a wide array of alkaloids[2] and polyketides.

It's hardly surprising that such a well rounded metal has played its part in Nobel-worthy research. Ziegler and Natta's titanocene-based olefin polymerization catalysts cost little but exhibit high activity, such that polyethylene soda bottles and trash cans have traces of catalyst embedded in their walls — no sense in recovering the few nanograms of easily made complex! Sharpless's titanium-promoted epoxidation proved that single-enantiomer products could be generated from chiral catalysts. Even the early days of olefin metathesis used titanium carbenoids, long before the now familiar molybdenum and ruthenium systems. Titanium may even make a name for itself in silicon metathesis — scientists in Japan and France recently characterized stable silacyclobutenes[3].

The low cost and high abundance of titanium obviates any guilt over throwing away the relatively non-toxic salts produced as by-products in the reactions described above. However, new evidence suggests that this perspective might not be so simple: a recent *Analytical Chemistry* review[4] investigates bio-accumulation and negative impacts on soil and water biomass imparted by varying doses of nanoparticulate titanium dioxide.

To limit environmental problems further down the road, we could translate stoichiometric titanium reactions into catalytic ones, much like earlier efforts for its transition metal cousins iron and copper. One 'green' approach to water purification uses photocatalysis: on ultraviolet light irradiation, doped TiO_2 catalysts form reactive oxygen species, which tear apart bacteria and biotoxins present in drinking water. Variants that utilize visible light[5] are just starting to emerge. Several groups have also recently tackled multicomponent reactions in which titanium catalysts quickly stitch together drug-like molecules.

From pharmaceuticals to paint and from chemistry to jewellery, titanium pops up everywhere. In a numerical twist of fate, this year element 22 celebrates 222 years since its discovery. So raise a titanium silicate-coated champagne glass, and enjoy some titania-frosted cake. Delicious! ❐

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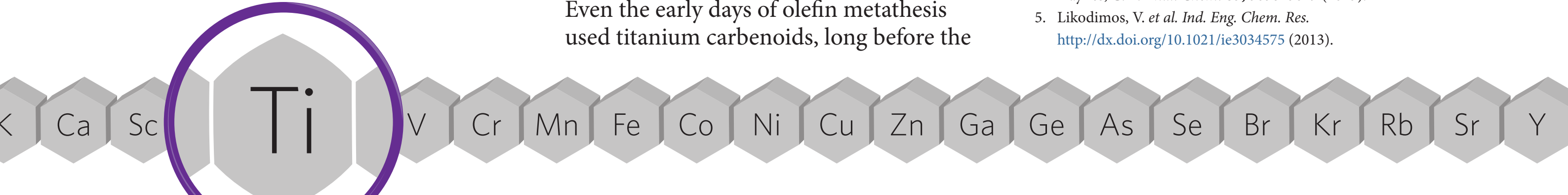


One flerovium atom at a time

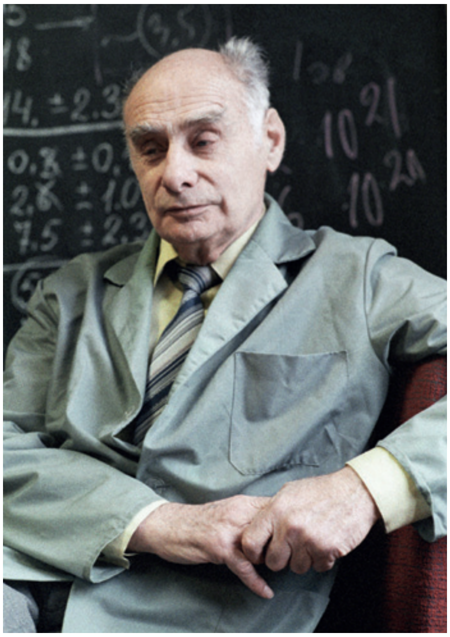
The chemistry of element 114 seems to be in reach, yet **Peter Schwerdtfeger** cautions that we should expect the unexpected from this young element, which is so different to its lighter counterparts.

The last primordial element in the periodic table — with a lifetime comparable to the age of our Earth — is plutonium, which is found only in trace amounts in a mineral named bastnasite. All elements beyond $_{94}$Pu have been produced in nuclear fusion reactions in a few laboratories around the world, most recently from an ongoing Dubna–Livermore collaboration that led in 2004 to the discovery of flerovium.

Four isotopes of element 114, with atomic numbers from 286 to 289, have been produced at a heavy-ion cyclotron from nuclear fusion reactions between ^{48}Ca ion beams and targets made of several isotopes of plutonium or curium. In 2011, the International Union of Pure and Applied Chemistry agreed to name element 114 after the Flerov Laboratory of Nuclear Reactions in Dubna, which itself took the name of its founder, Georgii Nikolajevich Flerov (pictured), a prominent Russian nuclear physicist and co-discoverer of spontaneous nuclear fission. Flerovium takes its place in the periodic table as the last member of group 14, which begins with carbon and until recently ended with lead.

This exotic superheavy element has such a high nuclear charge that it can only be produced one-atom-at-a-time by fusion over several months — a rather long period of time compared with its nuclear decay, which is in the range of seconds. Flerovium is exciting in several aspects; in particular, it may help to understand nuclear matter in the high proton limit, and in the search for the island of stability, with isotopes of high nuclear stability in a certain proton and neutron range.

The atomic nucleus consists of proton and neutron shells, very much like the electronic shells we are all familiar with in chemistry. A completely filled shell would have a 'magic number' of neutrons and protons, which would confer particular stability to the element. For more than four decades, shell closure has been predicted at $Z = 114$ for protons and at $N = 184$ for neutrons. However, although most scientists have long agreed on the number for neutron shell closure, that for proton shell closure depends very much on the model used to determine the underlying nuclear structure.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Unlike for the electronic structure, the strong interactions between the nucleons are difficult to model accurately, and shell closure has also been predicted at $Z = 120$, 122 or even 126. Accurate measurements of the radioactive decay properties of superheavy elements are therefore required to refine these nuclear models. The most neutron-rich isotope of flerovium known at present is ^{289}Fl with 114 protons and 175 neutrons, but it still falls short of neutron shell closure by 9 neutrons and it is less than clear how to get them inside the nucleus.

Nuclear decay times in the range of seconds are sufficient to perform atom-at-a-time chemistry on superheavy elements, but the design of such experiments at the cutting edge of current chemical technology requires some knowledge of their chemical behaviour. The use of modern relativistic quantum chemical methods that deal with the Dirac instead of the Schrödinger equation offers an ideal tool for probing flerovium's reactivity.

It was the late Kenneth Pitzer who pointed out as early as 1975 that strong relativistic effects could lead to an electronic shell closure in element 114. Large spin-orbit coupling effects sufficiently separate the $7p_{1/2}$ from the $7p_{3/2}$ shells (by more than 300 kJ mol^{-1}), and flerovium adopts a $7s^2(7p_{1/2})^2$ closed-shell configuration. It is therefore predicted to be rather volatile and chemically inert. Pitzer even went as far as to suggest that element 114 could be a gas at room temperature in contrast to lead or tin, its lighter counterparts in group 14.

It is, however, not always possible to predict bulk phenomena from simple atomic properties. Recent solid-state calculations in our group gave some surprising results. Atoms in bulk metallic flerovium are only weakly bound, less than in mercury, but more than in xenon (cohesive energies of 50, 75 and 16 kJ mol^{-1}, respectively). This suggests that flerovium would be a metallic liquid at room temperature, much like mercury. Moreover the $7s$ orbitals, stabilized by relativistic effects, may become chemically inert.

Heinz Gäggeler and co-workers have probed the adsorption of $_{112}$Cn and $_{114}$Fl on gold surfaces. So far, only three events have been seen that can be assigned to flerovium atoms, suggesting that element 114 behaves more like a noble, yet still metallic, gas. However, the results are not yet conclusive and confirmation experiments are ongoing. What kind of chemistry can flerovium engage in? Let us expect the unexpected! ❒

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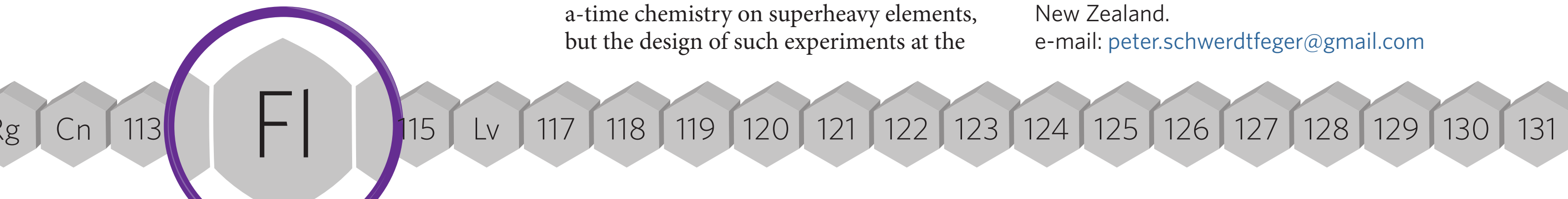

Chlorine chronicles

Barbara Finlayson-Pitts muses on how chlorine has come to play a role in many aspects of our lives — for better or for worse.

Chlorine is ubiquitous in both natural and man-made environments. Abundant in the Earth's crust and seawater, it is also present throughout the human body, for example as hydrochloric acid in gastric fluids, and is a major component in our cleaning products and pesticides.

The first documented observation of what would later be identified as molecular chlorine (Cl_2) appeared in 1774, when Scheele observed[1] a yellowish green gas from the reaction of "brunsten" (manganese dioxide) with "muriatic acid" (hydrochloric acid). The gas — at the time thought to be "oxymuriatic acid", a compound of oxygen and muriatic acid — was observed to kill insects and have bleaching abilities. It was not until 1810 that Davy proposed[2] that it was in fact a separate chemical element, which he named chlorine the following year (from the Greek word *chloros* meaning yellowish green).

Gaseous Cl_2, not practical for bleaching applications, was soon replaced by hypochlorite solutions that are still in use today for bleaching and disinfecting purposes, for example in the pulp and paper industry and in treatment of drinking and swimming pool water. Chlorine has also found its way into a wide range of products, from solvents and plastics (such as polyvinyl chloride) to pharmaceuticals.

Regrettably, deleterious effects of chlorinated compounds have also emerged: Cl_2, phosgene ($COCl_2$) and mustard gas ($(ClCH_2CH_2)_2S$) have all been used as chemical weapons in a destructive and disturbing manner. Another example is DDT (dichloro-diphenyl-trichloroethane), whose impacts are chronicled in Rachel Carson's book *Silent Spring*[3].

Element 17 is also linked to disastrous effects in the atmosphere, through the chlorofluorocarbons (CFCs) developed in the 1930s, and then widely used as refrigerants, aerosol propellants and blowing agents for foams. They are non-toxic and unreactive in the troposphere (the lower ~15 km part of the atmosphere), which initially seemed advantageous, but in 1974 Molina and Rowland discovered[4] that it actually had significant global consequences — a finding that led to them being awarded the 1995 Nobel Prize in Chemistry, jointly with Crutzen.

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Because the CFCs have no significant sinks in the lower atmosphere, they are transported to the upper atmosphere. There, irradiation at wavelengths below 240 nm induces their photodecomposition, which generates chlorine atoms that take part in a chain destruction of ozone (O_3). In the stratosphere (between ~15–50 km above the Earth's surface), ozone blocks ultraviolet light from solar radiation. Its concentration, normally well regulated, is lowered by the CFC-induced decomposition processes, causing enhanced ultraviolet light to reach the Earth's surface. The most dramatic manifestation of this chemistry is the development of the Antarctic ozone 'hole' in the polar spring, with essentially complete destruction of O_3 at some altitudes[5]. Furthermore, CFCs are also quite potent greenhouse gases[5].

Another intriguing contribution of chlorine to tropospheric chemistry has come to light over the past few decades[6]. Wave action generates submicrometre airborne salt particles that consist primarily of NaCl from the sea. Dust from alkaline dry lakes also contains chlorine. Trace atmospheric gases such as HNO_3, NO_2, N_2O_5 and the OH radical react with chloride ions in and at the surface of the particles, producing chlorinated products such as HCl, ClNO, $ClNO_2$, Cl_2 and HOCl (ref. 6).

Surprisingly, recent measurements show that this tropospheric chlorine chemistry seems to also occur quite broadly in mid-continental regions where $ClNO_2$ has been observed. The source is not clear, but may involve heterogeneous reactions of halogen compounds with surface-bound oxides of nitrogen (NO_y). Most of the chlorinated products are rapidly converted into chlorine atoms, highly reactive towards man-made and/or natural organic compounds. This commonly leads to increased formation of tropospheric ozone — a toxic air pollutant and a potent greenhouse gas[5]. This is a prime example of synergistic interactions of anthropogenic and natural emissions[7], increasingly recognized as potentially important. Although these atmospheric processes are incredibly intricate and difficult to study, elucidating their chemistry is critical to quantitative predictions of processes, and in turn reducing or overcoming undesirable effects.

In any case, we cannot avoid chlorine in our daily lives, for better or for worse. The challenge is instead to maximize the former and minimize the latter. ☐

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in your element

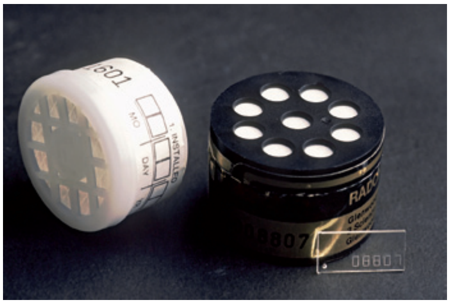
Recalling radon's recognition

Brett F. Thornton and **Shawn C. Burdette** look back at the discovery — and the many different names — of element 86.

In 1899, Pierre and Marie Curie noted an "induced radioactivity" — left behind by radium, distinct from its own radioactivity. Ernest Rutherford and Robert B. Owens also reported that year on a radioactive substance (^{220}Rn, $t_{1/2} = 55.6$ s) emitted by thorium, which they called emanation. In 1900, Friedrich Dorn realized that the Curies had observed a unique substance (^{222}Rn, $t_{1/2} = 3.8$ d), similar to emanation. In 1904, André-Louis Debierne found a third radioactive particle; this one produced from actinium (^{219}Rn, $t_{1/2} = 4$ s). These were at first regarded as elements and became colloquially known as thorium emanation, radium emanation and actinium emanation, but today we recognize them as radon isotopes. William Ramsay and J. Norman Collie suggested[1] a unique set of names (exradio, exthorio and exactinio) for these 'elements': "it appears advisable to devise a name which should recall its source, and, at the same time, by its termination, express the radical difference which undoubtedly exists between it and other elements."

The specific –io suffix names were largely ignored, but the concept of amalgamated names resonated within the scientific community. As experiments revealed similarities to the noble gases, Ramsay and Robert Whytlaw-Gray suggested niton (Nt), a name with the noble gas –on suffix, for the luminescent radium emanation. In 1911, the International Committee on Atomic Weights added the 'isotope' niton to their list of elements[2], inadvertently intertwining the linguistics of isotopes and elements. This was before 1913, the year Moseley showed that each element has a unique atomic number, and Frederick Soddy coined the term 'isotope', so this early misstep is understandable.

Names for the emanations that evoked both the noble gases and the emanations' parent elements eventually appeared, including Marie Curie's suggestion[3] of radion or radioneon. Eventually, in 1923, IUPAC adopted[4] the names radon (Rn), thoron (Tn) and actinon (An) for the three isotopes; names suggested by Elliott Q. Adams.



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An official statement on a name for all three isotopes — that is, a name for the element itself — would take seven more years. In a 1931 paper[5] that included Marie Curie, Rutherford and Debierne as co-authors, Rutherford's original 1899 element name emanation (Em) was finally formalized, in addition to the three isotope names. Despite this consensus of three early researchers of the element, periodic tables and lists of elements most often chose the name radon — the most stable isotope — instead of emanation. IUPAC's 1957 *Nomenclature of Inorganic Chemistry* elevated radon from isotope name to element name[6], an implicit change because only radon appeared on the element list. IUPAC's amended rules stated: "All isotopes of an element should have the same name. For hydrogen the isotope names protium, deuterium and tritium, may be retained, but it is undesirable to assign isotopic names instead of numbers to other elements."

Despite this declaration, radon had been designated an isotope for nearly four decades, and was a poor choice for an element name. Emanation was replaced by the awkward need to specify if the word radon referred to the element or the isotope. Using radon as the element name also muddled history. Dorn, who identified radium emanation (a specific isotope of radon) is today often mistakenly credited with discovering the element radon. Dorn's work even cited Rutherford and Owens' earlier discovery of thorium emanation, the radon isotope thoron.

Thoron, unlike radon, requires no such clarification, and ^{220}Rn is routinely called thoron today. Thoron is far easier to say than 'radon-two-twenty', perhaps explaining why the annual count of scientific papers mentioning thoron has increased over twenty-fold since thoron was 'disallowed' in 1957.

Distinguishing between ^{222}Rn (the isotope called 'radon') and ^{220}Rn (thoron) is not of idle linguistic and historic interest. ^{222}Rn can persist indoors, whereas the short-lived thoron cannot. Not all home radon detectors (pictured) are sensitive to thoron, and thoron-sensitive detectors must be placed with care because thoron does not travel far from its source. ^{222}Rn tests cannot necessarily rule out the presence of thoron[7], which occasionally leads to uncertainties in radon risk assessments.

Very few isotopes hold special names in modern chemistry: deuterium, tritium and thoron exist as near-element footnotes on the periodic table. Actinon has nearly vanished from the scientific literature, likely due to its short half-life and comparatively negligible health impacts. In 1948, the fourth natural isotope of radon was found (^{218}Rn, $t_{1/2} = 35$ ms). No one, apparently, thought of naming this final natural radon isotope — a β-decay product of ^{218}At — 'astaton'. ❐

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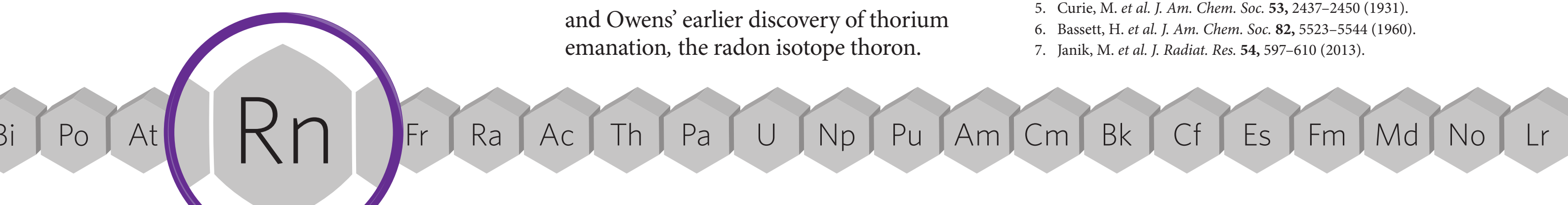


in your element

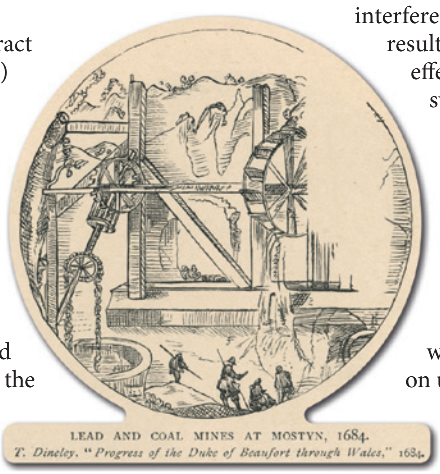
Lead between the lines

Somobrata Acharya explores the history, properties and uses of lead — an ancient metal that is still very relevant to today's technologies, but should be used with caution.

Lead was one of the first metals known to man. The history of element 82 can be traced back to as early as 6,400 BC from the Neolithic settlement Çatalhöyük (situated in the central part of modern day Turkey). The *opheret* of the Hebrews and *molybdos* of the ancient Greeks was referred to as 'lead' in the Old Testament[1]. Commonly used throughout the Antiquity, it is also believed to have been used in the 'Hanging Gardens' of Babylon, as sheets to retain moisture. Widespread applications — for example for water pipes throughout the Roman Empire — arose from the fact that this flexible and malleable heavy metal is abundant and easy to use; furthermore, its properties can be tuned by alloying it with other metals, such as copper or antimony. It played a crucial role during the Industrial Revolution.

Lead's symbol Pb originates from its Latin name, *plumbum* — which actually used to refer to soft metals more generally. In fact, lead and tin were not clearly distinguished until the sixteenth century, when lead was referred to as *plumbum nigrum* (black lead) and tin as *plumbum candidum* or *album* (bright lead). The Latin root name has persisted in other languages — for example it is 'plomb' in French — and in English through the words 'plumber' and 'plumbing', as lead was a popular material for pipes owing to its high corrosion resistance.

Pure lead is bluish-white in colour with a bright lustre, and crystallizes in a face-centred-cubic structure, with no known allotropic modifications[2]. On exposure to moisture this lustre is lost through the formation of an oxide coating that protects the underlying metal. Lead is found in nature, rarely in pure form but in ores with other metals — the most abundant one in the Earth's crust being galena (PbS). Natural formation of lead occurs by radioactive decay of uranium and thorium through radon (^{222}Rn). Four stable isotopes are known, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, the first three of which are used for estimating the ages of rocks. Lead compounds exist mainly in +2 or +4 oxidation states, the former being more common.



LEAD AND COAL MINES AT MOSTYN, 1684.
T. Dineley. "Progress of the Duke of Beaufort through Wales," 1684.

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An early route to extract lead from ores (pictured) involved roasting an ore in air, which converts its lead sulfide to oxide and sulfate forms, and subsequently smelting those with limestone and coke to obtain crude lead. Today about half of the annual production of lead comes from mining, and the rest from recycling.

Lead compounds are associated with several significant discoveries crucial to modern technologies. Rectifying properties were discovered at metal–galena point contacts by F. Braun in 1874[3]. In 1901 J. C. Bose detected an electromagnetic wave using galena — a key event for the development of the radio[4]. Infrared detectors based on lead chalcogenides (that is, sulfides, selenides and tellurides) represented a major advance in infrared technology, for example for night vision and for the spectroscopic analytical techniques that are now available to chemists. Lead chalcogenides are also characterized by low direct-bandgaps, which change depending on the sizes of the crystallites and cover a broad spectral range — a phenomenon called the quantum confinement effect, which forms the basis for devices such as field-effect transistors, solar cells and photodetectors.

The widespread production and consumption of lead continued until the twentieth century, through uses in petrol, lead-acid batteries, paint, radiation shielding and in the polyvinyl plastic industry as a stabilizer. However, humans are susceptible to lead poisoning by either acute or, more often, chronic exposure.

Lead accumulates in the body and interferes with various processes, resulting in neurotoxic effects with a variety of symptoms. Even as far back as the Roman period maladies were correlated with lead, through the use of 'lead sugar' (lead acetate) beverages and pipes for water supply. Yet these early warnings were not acted on until the mid-twentieth century, from which point the use of lead started being closely monitored in many countries — resulting in measures such as bans from petrol and paint.

Fortunately, lead poisoning can now be treated with chelating agents (typically ethylene diamine tetraacetate), using their greater affinity to the heavy metal to form complexes that can be expelled from the body. Sadly it is estimated that, at current use rates, the metal we've relied on for thousands of years will run out in about four decades. A more positive side of this situation is that these developments are generating renewed interest in recycling and thoughtful progress in fuel-cell technology. ❐

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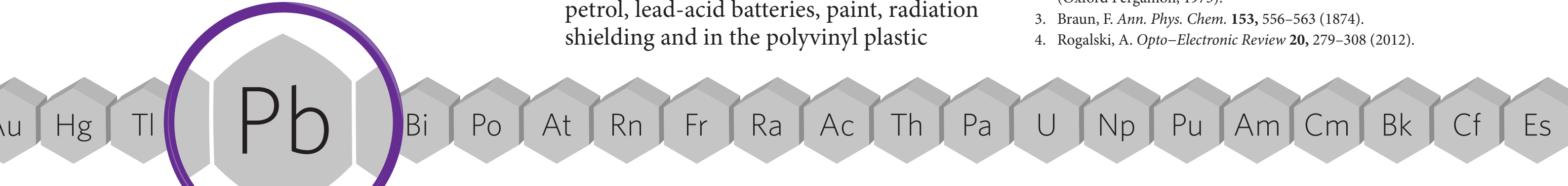

in your element

Manganese the protector

John Emsley looks at an element that is vital to life.

Manganese is an essential element for all species. It has a key role in protecting cells against the superoxide free radical O_2^-, and does this as the enzyme manganese superoxide dismutase (Mn-SOD) which converts O_2^- to H_2O_2. Manganese is also needed for other enzymes, and is involved in glucose metabolism, the utilization of vitamin B1, and the operation of RNA.

It was only realized in the 1950s that humans need manganese, partly because our requirement is so small: the average person contains only about 12 mg. The daily intake averages 4 mg, which is more than enough. Many foods provide this element, especially cereals and nuts. Beetroot has one of the highest levels, as has the French delicacy, snails. Too much manganese in the form of dust or fumes, however, can send you crazy, and miners of manganese minerals used to suffer the symptoms of 'manganese madness' with involuntary laughing or crying, aggression, delusions and hallucinations.

The power of Mn-SOD in protecting living cells was demonstrated in the 1950s by the microbe *Deinococcus radiodurans*. This organism is able to survive in meat subjected to intense radiation by accumulating manganese in preference to iron, and using it to destroy the devastating number of oxygen free radicals that the radiation produces. In so doing, it enables the DNA repair mechanism of cells to continue functioning and not be completely overwhelmed.


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Manganese was known long before it was isolated as an element. It occurs as the black ore pyrolusite (manganese dioxide), which was used by the cave artists of the Lascaux region of France more than 30,000 years ago. The Roman author Pliny the Elder, who perished when Pompeii was destroyed in 79 AD, wrote of a black powder that glass-makers used to make their products crystal clear — this was almost certainly pyrolusite, and it was also used as a black pigment by potters.

Manganese ores have also provided evidence of changes in planetary diversity over the millennia. The lack of manganese in sedimentary rocks in the period between 400 and 1,800 million years ago indicated a time when the oceans had low oxygen levels[1].

Pyrolusite is the most common manganese ore, of which around 25 million tonnes are mined every year. If the land-based deposits were ever to be exhausted then we would have to exploit the manganese nodules on the ocean floor. There are an estimated trillion tonnes (10^{12}) of these scattered over large areas, with the North East Pacific being particularly rich in them. In 1876 the sailing ship *Challenger* was sent to explore the deep oceans and it returned with curious, cone-shaped lumps that had been dredged up from the ocean floor. They turned out to be mainly manganese and seem to have formed around sharks' teeth, which are one of the few parts of living things capable of surviving at the bottom of the ocean.

Life has been intimately linked to manganese, and in parts of the ocean devoid of iron the success of marine diatoms relies on this element[2]. This microbial attraction to manganese might one day be the basis of an alternative source of the metal by using microbes to extract manganese from low-grade ores, as is currently done for copper and gold[3].

Manganese metal is not used as such because it is too brittle, and 95% of mined ore goes into alloys — mainly steel, to which around 1% is added to improve its strength, working properties and wear resistance. The alloy known as 'manganese steel' contains around 13% manganese, and a patent for this was granted in 1883 to a 24-year-old metallurgist, Robert Hadfield of Sheffield. This metal is extremely strong and is used for railway tracks, earth-moving machinery, safes, army helmets, rifle barrels and prison bars, and is still referred to as Hadfield steel.

Manganese compounds also find use, for example manganese(IV) dioxide (MnO_2) is added to rubber and is used as an industrial catalyst, and manganese(II) oxide (MnO), goes into fertilizers applied to manganese-deficient soils. Potassium permanganate ($KMnO_4$) — with the Mn(VII) oxidation state — is used to remove organic impurities from waste gases and effluent water. The characteristic purple of potassium permanganate is thus only a minor, albeit colourful, aspect of an element that plays a key part in our lives and that of planet Earth. ❐

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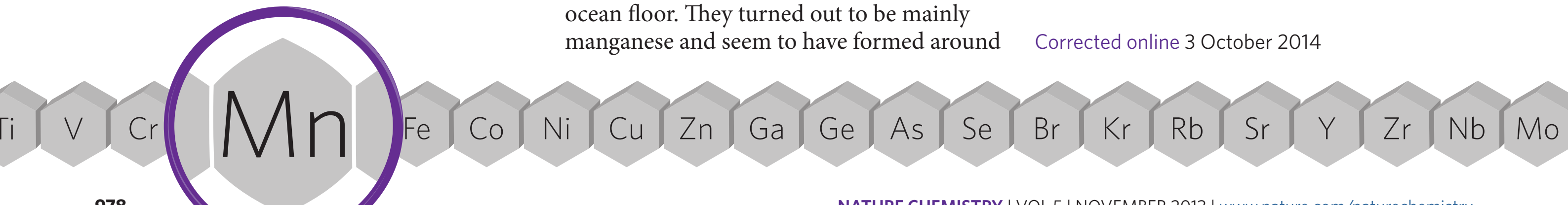

ADDENDUM

In Your Element: Manganese the protector

John Emsley

Nature Chemistry **5,** 978 (2013); published online 24 October 2013; corrected after print 3 October 2014.

In the version of this In Your Element article previously published, it should have stated that some passages in this essay are based on the manganese chapter in the author's book, *Nature's Building Blocks*.

in your element

Mesmerized by mercury

Joel D. Blum considers the two faces of mercury. It has many unique and useful properties in chemistry — yet it comes with a dark and dangerous side.

Mercury was central to the study of alchemy, the philosophical tradition that laid many of the foundations for both the principles and procedures of modern chemistry. European alchemists believed that mercury was a main ingredient in all metals and could be transmuted into gold by combination with other metals. Although we now know that this is not the case, mercury does dissolve fine flakes of gold and is widely used for this purpose in artisanal gold mining.

Its chemical symbol, Hg, comes from its former name hydrargyrum, which translates from Latin as 'water silver' and refers to its shiny liquid metallic form. This is also the origin of the nickname quicksilver — mercury is the only liquid metal at room temperature, a phenomenon recently shown to be due to the effects of relativity[1].

A dense liquid metal is a very useful material and mercury has widespread applications, from thermometers and barometers to electrical switches, batteries, dental amalgams, light bulbs and even for floating the mirrors of high-powered telescopes. It has also been widely used in electrolytic cells in chemical manufacturing.

Mercury may sound like a 'wonder element', but it also has a darker side. In the 1950s, much of the world supply of mercury was used to separate the ^{6}Li isotope by amalgamation for use in making hydrogen bombs. And in virtually all of its forms, element 80 is a highly potent neurotoxin. Exposure to mercuric nitrate by hat-makers during the treatment of fur, and the resulting symptoms of poisoning, led to the expression 'mad as a hatter'; similarly, a neurological disorder caused by exposure to methylmercury — a highly toxic and bio-accumulative compound — from consumption of fish contaminated by nearby industry in a Japanese coastal town became known as Minamata disease.


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Mercury occurs naturally in coal deposits; on combustion, gaseous elemental mercury is released. Because it can have an atmospheric lifetime of over a year, it is distributed to every corner of the globe. Some gaseous mercury reacts with tree foliage and is deposited directly into forests. Photochemical reactions in the atmosphere also oxidize elemental mercury and the oxidized form is then deposited in precipitation, reaching even the most remote lakes, oceans and terrestrial ecosystems[2]. Meanwhile, the widespread use of mercury in household products has also resulted in its presence in the waste stream.

The inorganic forms of mercury are generally deposited from the atmosphere in low enough concentrations that they do not represent a health concern. However, a number of anaerobic microbes have the ability to transform inorganic mercury into methylmercury. Earlier this year the genes responsible for mercury methylation were identified, and it has now become possible to screen microbes for their ability to methylate mercury[3]. Methylmercury biomagnifies up aquatic and terrestrial food chains, reaching levels high enough to be toxic for animals feeding at high trophic levels — including predatory fish, fish-eating mammals and insect-eating birds.

Microbial and photochemical reactions in the environment convert some methylmercury back to its inorganic forms, so the competition between methylation and demethylation reactions ultimately controls levels in the environment[2]. To better understand the behaviour of mercury in the environment, and the transformations that control its mobility and toxicity, researchers seek means of fingerprinting its various sources. In 2007, my research group identified a phenomenon whereby magnetic isotopes of mercury react during photochemical reactions at different rates from even-mass isotopes, leading to mass-independent isotope fractionation (MIF)[4].

The chemistry behind the MIF phenomenon is interesting in its own right. It can occur during reactions involving short-lived radical pairs (by the magnetic isotope effect) and also in equilibrium reactions (by the nuclear volume effect)[4,5]. The ratio of mass-independent to mass-dependent isotope fractionation, and the ratio of MIF between the two odd-mass isotopes ^{199}Hg and ^{201}Hg, can be used to determine reaction mechanisms and the ligands associated with mercury. Thus isotopes are proving to be a very useful tool in teasing apart the complex biogeochemistry of this element[5].

Many years ago when I began research on mercury, a wise senior colleague warned me that "once you delve into the chemical behaviour of mercury — there is no turning back." I dismissed this comment as not pertaining to me, but I have since learned that the rich chemistry of mercury, just like the shimmer of the liquid metal, catches one's attention and will not let it go. ❐

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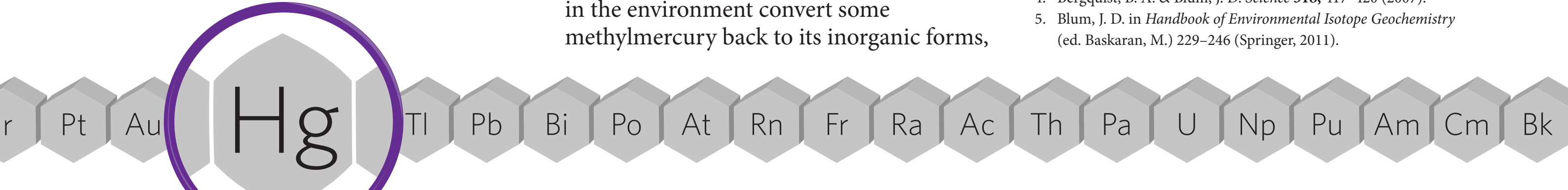


in your element

Argon out of thin air

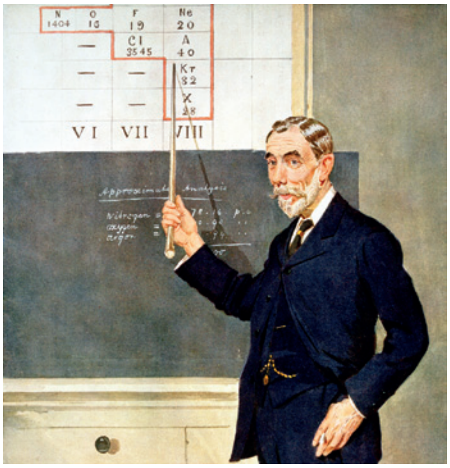
Markku Räsänen remembers making a neutral compound featuring argon, and ponders on the reactivity of this inert element.

The discovery of the noble gases shows how innovative researchers have been when it came to separating and identifying minor amounts of components from mixtures using relatively simple tools.

First indications of an inert component in air appeared in 1785 through Henry Cavendish's experimental studies, when he found about 1% of an unreactive component. He could not, however, identify the unreactive species, which turned out to be argon, and the names connected with its discovery are Lord Rayleigh and Sir William Ramsay (pictured). In 1892, Rayleigh and Ramsay's exceptionally skilful eudiometric measurements, after chemical separation of the constituents, revealed that the density of nitrogen prepared by removing oxygen, carbon dioxide and water from air with heated copper differed from the density of nitrogen prepared from ammonia.

The understanding that this meant another element, X, was present, and its identification through spectroscopy — not available at the time of Cavendish's studies — came two years later. Ramsay suggested[1] to Lord Rayleigh: "Seeing that X is very inactive, what do you think of argon *αργον* (idle) for a name?" They had been working separately but on very similar studies, and made a joint announcement. Their findings on noble gases were recognized in 1904 by the Nobel Prize in Physics for Rayleigh and that in Chemistry for Ramsay.

Argon didn't fit in the periodic table known at the time, and it was Ramsay who suggested including an additional column, group 18. Helium, and other elements subsequently discovered, were to find their place with the 'rare gases'. This name is somewhat misleading, however, with argon being the third most abundant atmospheric substance after nitrogen and oxygen (it makes up about 0.94% of our atmosphere). A preferred term for group 18 is 'noble gases', in reference to their reluctance to bond chemically. This idleness of argon finds many chemical and industrial uses, for example as a chemically inert atmosphere, in welding, food storage and insulating windows. Argon isotopes also serve in geological age determinations, and laser technology uses argon extensively, in the form of Ar^+ cations in gas lasers and excited ArF in exciplex lasers.



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Owing to the same inertness, it has been hard to coerce argon into forming neutral compounds. In 1995, noble gas (Ng) hydrides were discovered that have a general structure of HNgY, where Ng is Kr or Xe and Y an electronegative atom or fragment. These molecules consist mainly of a covalent bond between H and Ng and an ionic bond between Ng and Y.

Perhaps surprisingly, as early as 1995, low-level quantum chemical calculations suggested the existence of a chemical compound containing an Ar atom[2]: hydridoargon fluoride, HArF, that was predicted to be preparable at cryogenic conditions. The synthesis of HArF from H, Ar and F in solid argon was tried, in a similar manner to that of HXeI from H + Xe + I, but several attempts in my group failed. Still, during the following several years, more and more extensive computational studies strengthened the belief that HArF can exist. After learning the reasons for the failed experiments, mainly due to improper handling of the reactive precursor HF, the first signals of this new species were obtained in my group on 21 December 1999 — a time of the year conducive to experimentation, with no interfering students present in the lab. Conclusive experimental results were obtained from the vibrational spectral effects of H/D and ^{36}Ar/^{40}Ar isotopic substitutions[3]. A neutral molecule containing argon — I couldn't have wished for a better Christmas present.

A number of stable argon compounds have been computationally predicted, and are waiting for experimental verification. Recent extensions of this chemistry include, for example, the preparation and characterization of ArBeS (ref. 4) and ArAuF (ref. 5). Our chemical understanding of the group 18 elements is changing, as progress in noble gas chemistry has slowly started to enter schoolbooks, starting with xenon, which shows extensive bond formation.

The future will tell as to what extent noble gas hydrides and related species exist. At present, the number of experimentally characterized noble gas hydrides amounts to about 30, and it is easy to design more of such metastable molecules. Chemists want to explore the frontiers of chemistry for basic knowledge, and research of novel bonds between noble gases and other elements offers a challenging field for this. The excellent computational tools constantly being developed with experimental work offers very good possibilities for success. ❐

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P S Cl Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br

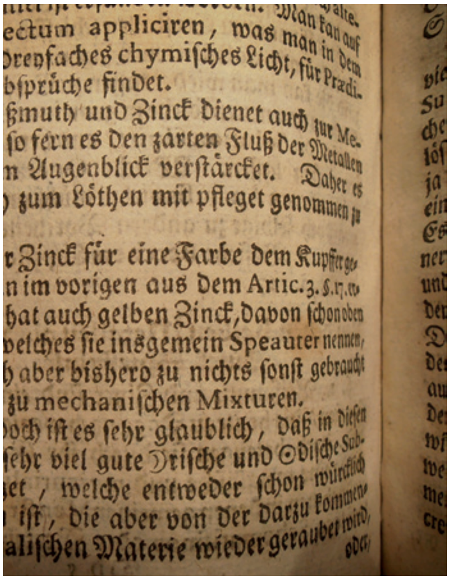
Zinc of unsuspected worth

Elements that are widespread in nature and have been used for thousands of years are not typically deemed exciting, but **Anders Lennartson** argues that we shouldn't take zinc for granted.

A professor once told me "You'll never impress me with zinc". Why are certain elements more spectacular than others? And why should zinc not be one of these? Sure, it does not exhibit extensive redox chemistry: zinc(I) species are rare, and calculations have recently suggested that we will never see a stable zinc(III) compound[1]. Element 30 holds on tightly to its *d* electrons, which is why its compounds do not display the vivid colours we have grown accustomed to with *d*-block elements. Actually, owing to their filled *d* shells, zinc and the other group 12 elements aren't strictly speaking 'transition' elements — they are sometimes referred to as post-, or 'honorary', transition metals.

We do not know who first discovered zinc[2,3], but zinc compounds have been used since ancient times; the Romans mixed zinc ores with charcoal and copper to produce brass. Its volatility, however, prevented its isolation until the Middle Ages and zinc was probably first obtained in India, whereas commercial production first occurred in China. Among chemists, it did not receive much interest until the eighteenth century, but from then it was soon found to be quite important: zinc protects countless tons of iron from rusting, it serves as a cathode in zinc–carbon and alkaline batteries, its oxide found its way into sunscreens, and zinc chloride is used as a flux for soldering.

Furthermore, element 30 is essential for human life; each of us contains about two grams of zinc. As numerous transcription factors and enzymes feature zinc ions in their cores, we would simply not survive a day without it —carbonic anhydrase, alcohol dehydrogenase and insulin protease are three enzymes that rely on the Lewis acidity of zinc. A well-known structural motif is the 'zinc fingers', where zinc ions both help fold peptide chains and provide a site for substrate coordination.



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© ANDERS LENNARTSON

Organic chemists also use their share of zinc. In 1849, Edward Frankland heated ethyl iodide with zinc powder in a sealed glass tube, with the idea of isolating free ethyl radicals[4,5]. To his surprise, he found that on adding a drop of water to the product, a blue-green flame of several feet shot out from the tube. Diethylzinc, the first main-group organometallic compound, was discovered! This essentially marked the birth of organometallic chemistry — in 1830, William Christopher Zeise had reported the compound $K[(CH_2{=}CH_2)PtCl_3]H_2O$, known as Zeise's salt, but it had only received modest attention. Diethylzinc inflames spontaneously in air and as dry nitrogen or argon were not readily available in those days, the brave pioneers of organometallic chemistry often used hydrogen as an inert gas; not exactly my first choice when working with pyrophoric substances…

The applications of organozinc compounds have ranged from attempts to prevent old documents from degrading by treatment with diethylzinc vapour (it actually works, but nobody dares to use the method!) to the Nobel Prize-winning use of organozinc derivatives in cross-coupling reactions. Organozinc reagents are typically milder and more selective than the popular magnesium-based Grignard reagents, and in recent years more and more complex functionalized organozinc reagents have been prepared[6].

An unusual example of selectivity in organozinc chemistry is the Soai reaction, described in 1995[7]. Dialkylzincs do not react with aldehydes without a catalyst; in the presence of a catalyst, however, diisopropylzinc reacts with prochiral pyrimidyl carboxaldehydes to give chiral alcohols. The reaction is autocatalytic, meaning that the product (a pyrimidyl alcohol) can catalyse its own formation. This is not bad in itself, but what makes this reaction unique is that the pyrimidyl alcohol produced will have a greater optical activity than the original catalyst. In effect, the catalyst can not only favour the formation of one optical isomer, but it also suppresses the formation of the opposite isomer. The small statistical bias in a virtually racemic catalyst is enough to trigger this amplification.

Based on its organometallic reactivity alone — how is zinc not impressive? ❐

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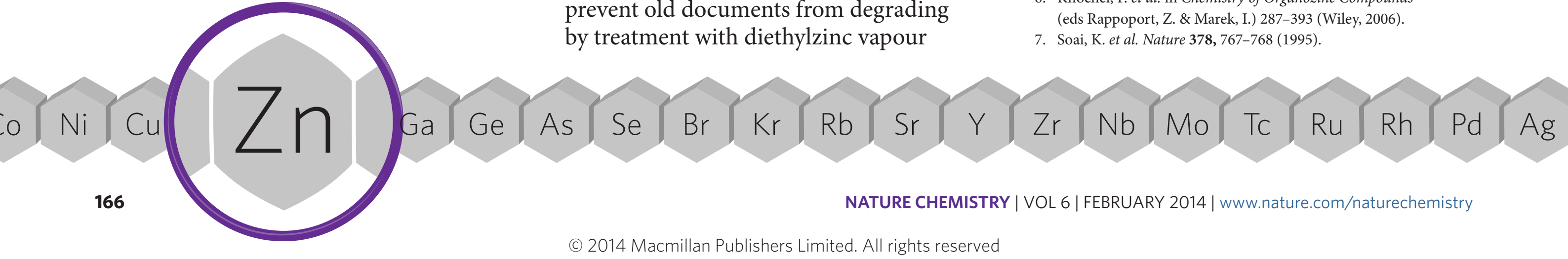


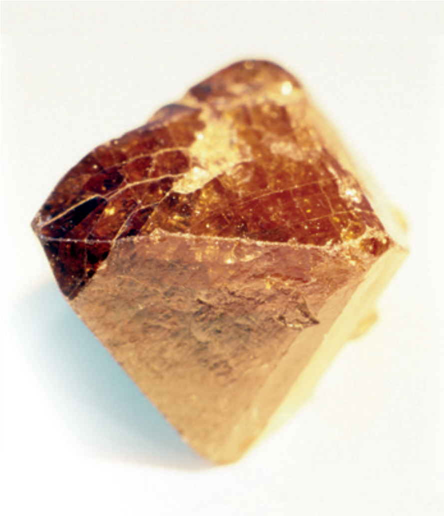
The A–Z of zirconium

From fake gems to a fixture of nuclear plants, **John Emsley** considers the many uses of zirconium.

Zircon — zirconium silicate ($ZrSiO_4$) to chemists — is a semi-precious gemstone (pictured) that has been known since ancient times. When cut and polished, a zircon crystal shines with an unusual brilliance because of its high refractive index; colourless specimens look like diamonds. The metal component of zircon was first identified by Martin Heinrich Klaproth when analysing a crystal of the substance in Berlin in 1789. In that same year, he also discovered uranium, and today both of these metallic elements are essential for nuclear power generation.

A zirconium–tin alloy, known as Zircaloy, is used as the cladding for uranium oxide fuel elements. Resistant to corrosion at high temperatures, this material does not absorb neutrons and so does not become radioactive. The nuclear industry buys almost all the zirconium metal that is produced and some nuclear plants have kilometres of zirconium-based tubing. Even so, corrosion can still occur in water-cooled reactors[1] and sometimes this has led to accidents. Although the metal is stable in contact with water below 900 °C, above this temperature they react to form the oxide and hydrogen gas. It was this process that led to the explosions at Three Mile Island in the US in 1979, and at Fukushima after the earthquake and tsunami there in 2011.

The chief source of zirconium is zircon and more than 1.5 million tonnes of this mineral are extracted each year, mainly in Australia and South Africa. Zircon sand is traditionally a refractory material — it maintains its strength at high temperatures — and, as such, is used to make heat-resistant linings for furnaces, giant ladles for molten metal, and foundry moulds. Other zirconium compounds, such as its oxide (ZrO_2), also have high-temperature applications. Better known as zirconia, this material only melts above 2,500 °C and is used to make heat-resistant crucibles — a red-hot zirconia crucible can be plunged into cold water without cracking.



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World production of pure zirconia is almost 25,000 tonnes per year, and it ends up in cosmetics, antiperspirants, food packaging, and even fake gems. The most unexpected use of zirconia is in ultra-strong ceramics. Research in this area was driven by the military who sought a tank engine that was not made of metal, and so would need neither lubricating oil nor a cooling system. Consequently, a new generation of tough, heat-resistant ceramics were developed that are stronger and sharper than toughened steel and which make excellent high-speed cutting tools for industry. Zirconia is found in some everyday objects too, such as knives, scissors and golf irons and, because of its durability and biocompatibility, is also used to make dental veneers.

Zirconia can adopt three different crystallographic forms; monoclinic, tetragonal and, the most admired of all, cubic zirconia (often referred to as simply CZ), which has the same crystal structure as diamond and even out-sparkles it. Fake gems made of CZ can be coloured by incorporating other metal oxides; traces of chromium produce green gems, cerium gives red ones, and those with neodymium are purple. Less frivolously, zirconia makes a useful barrier coating that is both tough and resists chemical attack. A ceramic layer of zirconia is used to protect the blades of jet engines and gas turbines and it also acts as a thermal barrier.

When it comes to matters of life and death, zirconium also plays its part. Zircon in rocks found in Australia in 2000 showed that life might have started much earlier than once thought. Dated to be 4.4 billion years old, the oxygen isotope ratio of O^{16}/O^{18} in these samples showed they could only have been formed when there was liquid water on the surface of the Earth, and this was nearly 500 million years earlier than previously assumed[2]. Turning to its darker side, ultrafine zirconium powder is used in some cluster bombs to produce burning particles that saturate a target area.

The metallic element itself is used in alloys — zirconium makes steel stronger and improves its machinability. It is also used for surgical implants and prosthetic devices because it is biocompatible — it has no known biological role or toxicity. The metal remains stable at high temperatures, so it is used for space-vehicles that heat up on re-entry to the Earth's atmosphere. Zirconium is more than twice as abundant as copper and zinc, and over ten times more abundant than lead. Because zirconium is regarded as completely non-toxic and environmentally benign, its use will probably continue to grow. For example, it is being added to paints to replace the small amounts of lead compounds that are still needed. ❐

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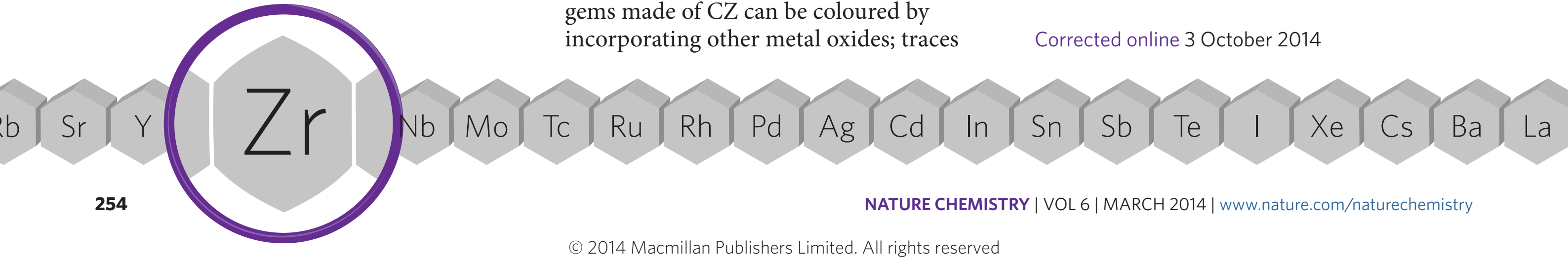


ADDENDUM

In Your Element: The A–Z of zirconium

John Emsley

Nature Chemistry **6,** 254 (2014); published online 20 February 2014; corrected after print 3 October 2014.

In the version of this In Your Element article previously published, it should have stated that some passages in this essay are based on the zirconium chapter in the author's book, *Nature's Building Blocks*.

in your element

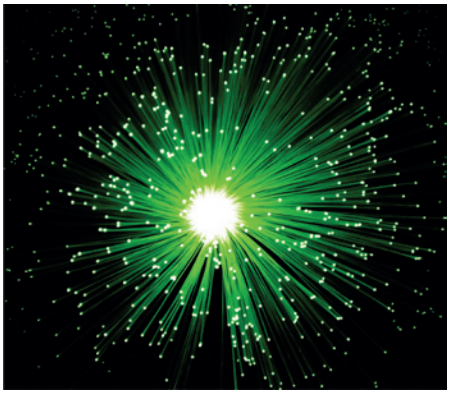
Extricating erbium

Claude Piguet reflects on the history of erbium, which is very much intertwined with its rare earth cousins yttrium, ytterbium and terbium.

The discovery of erbium did not come in a single 'eureka' moment, but rather in a series of steps, inextricably linked to the discovery of more new elements than the residents of one small town in Sweden could have ever anticipated. It started in 1787 when a lieutenant in the Swedish Royal Army named Carl Arrhenius collected a curious black stone in the town of Ytterby, ten miles away from Stockholm. Chemical analysis of the mineral revealed that it contained a new earth (a metal oxide, in modern terminology, but considered an element at the time), later named yttria after the town in whose quarry it was found.

Concurrently, in France, the revolutionary policy that '*La République n'a pas besoin de savants ni de chimistes*' (the French republic needs neither scientists nor chemists) sent Lavoisier to the guillotine, his discovery of oxidation reactions not enough to spare him. It was, however, enough to force his contemporaries to reconsider the concept of an element, abandon phlogiston theory and investigate the extraction of metallic elements from oxides. Back in Sweden, Carl Mosander applied newly developed reduction techniques to transform the oxide yttria into yttrium. Only then was it realized that this 'single species' contained not only yttria (a colourless oxide), but also two other oxides that could be isolated from the original sample: a yellowish substance that he named erbium oxide and a pale amethyst-coloured powder he called terbium oxide.

Pushed by his mentor for rapid dissemination of his results, Mosander published the discovery of erbium and terbium in 1843, but with severe reservations concerning the purity of these two new elements[1]. Submitted to systematic investigations by a dream team of chemists, geologists and spectroscopists in Geneva over the next few decades, Mosander's erbium and terbium proved to be mixtures of no fewer than seven elements: not only erbium and terbium, but also ytterbium, scandium, thulium, holmium and gadolinium. Ytterby had turned out to be quite the element mine, with four elements eventually named after it, out of eight new elements extracted from minerals collected there. The difficulty in separating these elements from each other was further underlined by the simultaneous extraction, in 1907, of yet another element from a sample of ytterbia: lutetium, or cassiopeium, depending on whether one is a turn-of-the-century French or German chemist.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Unequivocal proof for the existence of the elements yttrium, terbium and erbium was obtained by optical spectroscopy in 1864. In one final twist, however, the spectroscopist Delafontaine, in confirming their existence, erroneously switched Mosander's original names and called the amethyst-coloured compound erbium oxide and the pale yellow substance terbium oxide. This historical reversal has been carried through until the present day, so what we now know as the sesquioxide Er_2O_3 is characterized by a pale pink colour, rather than the yellow that Mosander would have recognized as erbium oxide.

The reconciliation of atomic theory with the periodic table at the turn of the twentieth century finally placed erbium and its fellow lanthanides in the 4*f*-block, after which erbium research dwindled for fifty years. In 1959, however, interest in erbium was reawakened in association with the nascent field of photonics. The plethora of regularly spaced and long-lived excited states found in Er^{3+} resulted in it becoming the perfect candidate for an experimental demonstration of a theoretical infrared detector, in which photons could be detected and counted through sequential absorptions in the successive excited levels of a given ion in a solid — that is, using superexcitation as a photon detector[2].

While the proposed upconversion pathway strictly relied on linear absorption from the ground state through successive excited states for detection, the direct absorption of photons by an Er^{3+} ion remained inefficient. A breakthrough came in 1966, when François Auzel demonstrated that superexcitation could greatly benefit from indirect light harvesting carried out by partner ions, followed by energy transfer to an erbium activator[3], a mechanism similar to that operating in erbium lasers, which are used today in dentistry and some skin treatments.

Returning to upconversion, the introduction of small amounts of trivalent ytterbium impurities into erbium-containing solids is now exploited for the design of highly efficient upconverters of near-infrared to green light used in laser pointers, in solar cell technologies and as dopants for visible-light-emitting optical fibres (see illustration). Given the great ingenuity and effort required to separate and purify these elements by early chemists, the fact that we now willingly contaminate erbium with ytterbium is, perhaps, somewhat ironic. ❐

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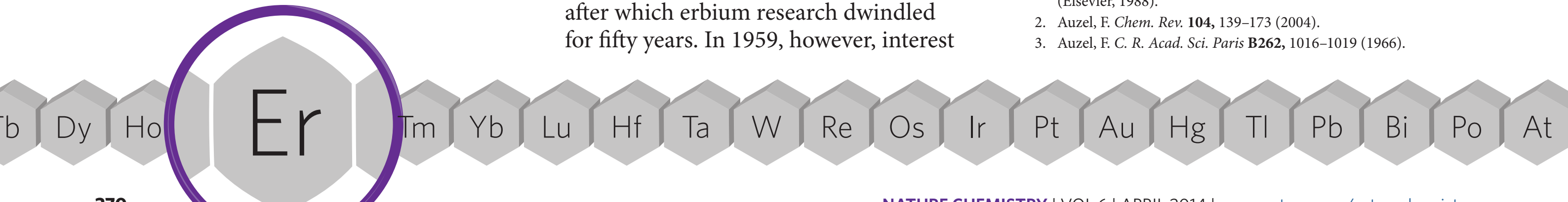

Poisonous polonium

Eric Ansoborlo considers the disproportionate potency of polonium compared with its relative scarcity on Earth.

Polonium is the 84th entry in the periodic table and is a natural radioelement present in the environment at extremely low concentrations. The discovery of polonium was published[1] by Pierre and Marie Curie in July 1898. It was the first element discovered using their newly developed radiochemical separation method, where each product isolated from primary pitchblende ore was detected using an electrometer constructed by Pierre. They cautiously wrote "we believe that the substance we recovered from pitchblende contains a heretofore unknown metal, similar to bismuth in its analytical properties. If the existence of this new metal is confirmed, we propose that it be named polonium in honour of the native land of one of us."

This discovery led to the first controversy[2] in radiochemistry, in this case between the Curies and a number of German scientists — including Willy Marckwald and Friedrich Giesel — who thought that this new element was nothing other than 'inducedly activated bismuth'. In 1901 Marckwald isolated, using a different method, what turned out to be the same 'new substance' and provisionally renamed it radiotellurium. For several years, controversy over both the identity of the material and its location in the periodic table continued, and it was only in 1910 that Marie Curie and André-Louis Debierne unequivocally identified, by a spark spectrum technique, 0.1 mg polonium in 2 mg of separated sulfide residue. In 1911 Marie Curie received the Nobel Prize in Chemistry for the discoveries of both polonium and radium.

Polonium has 41 isotopes, with masses ranging from 187 to 227. The predominant naturally occurring isotope is ^{210}Po, which is a radioactive decay product in the natural uranium decay series. Nowadays the two main methods for producing significant quantities (that is, a few milligrams) of ^{210}Po are to neutron-irradiate a ^{209}Bi target in a nuclear reactor, or to bombard a ^{209}Bi target with a 37 MeV beam of alpha particles. Isotope ^{210}Po is almost exclusively an alpha emitter with a half-life of 138.4 days. Consequently, it is both highly radioactive and highly toxic[3]. Because of its radiotoxicity, the fact that it volatilizes at low temperature (~50 °C) and that it sticks rather avidly to glass, it is difficult to handle, and therefore its chemistry remains only poorly known[4].

THINKSTOCK/TORSTEN LORENZ

Belonging to the chalcogenide family of the periodic table, along with oxygen, sulfur, selenium and tellurium, polonium can also be compared to bismuth, its neighbour to the left in the periodic table. Of several oxidation states (-II, +II, +IV and +VI), the tetravalent Po(IV) is the most stable in aqueous solution, and this gives rise to its most important chemical property: its tendency to hydrolyse and form colloids of $Po(OH)_4$, in analogy with most tetravalent elements. It also forms soluble salts with chlorides, acetates, nitrates and other inorganic anions, but precipitates with sulfides, and this is the property that was originally exploited by the Curies in separating and identifying it. With organic ligands, however, the coordination chemistry of Po(IV) is much more complicated and leads to mixed oxide and hydroxide complexes.

Elemental ^{210}Po has a few specific uses, such as studying the effects of alpha particles and for the calibration of radiation detectors. It is also a concentrated source of heat, and small neutron sources can be prepared by mixing it with beryllium. It is perhaps most widely known, though, as a rare but highly toxic poison that targets the liver[3] and also affects the bone marrow, gastrointestinal and central nervous systems. The lethal dose for humans is estimated to be fewer than 10 µg, and its radiotoxicity was demonstrated soon after its discovery, when the accidental release of polonium from a distillation vessel in the Curie lab caused the death of a technician.

More recently, Alexander Litvinenko, a former member of the Russian security services, was thought to have been poisoned[5] with ^{210}Po-contaminated tea in 2006, and the involvement of polonium has been suggested in Yasser Arafat's death. Polonium is over 10,000 times more toxic than hydrogen cyanide and, alongside the botulinum toxin, it is one of the most toxic substances known. In soils, ^{210}Po is absorbed by clay minerals and organic matter. In particular, it is known to accumulate in tobacco plants, which results in a surprisingly significant presence of polonium in cigarettes. Not good news for smokers then, considering that only a few studies have been carried out into treatments for polonium poisoning, with thiol-based chelating agents the only recommended ones thus far. ❐

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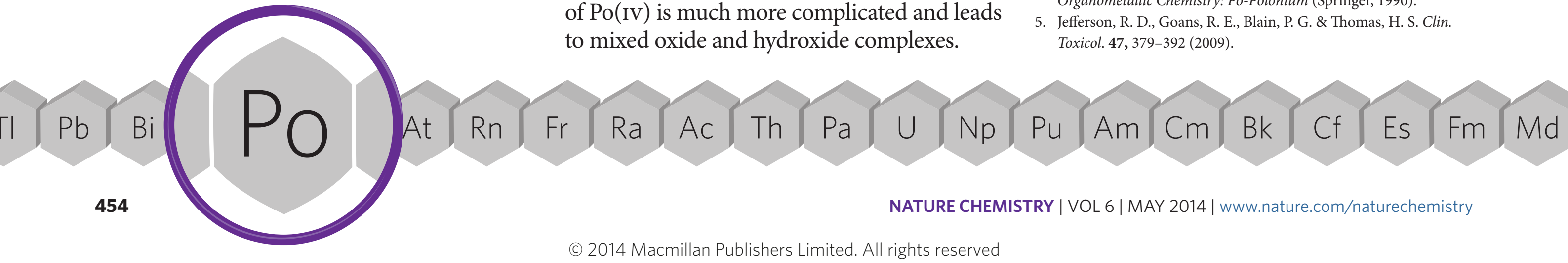

Thorium lends a fiery hand

John Arnold, **Thomas L. Gianetti** and **Yannai Kashtan** look back on thorium's chemistry, and look forward to harnessing its nuclear potential.

In 1828, the chemist Jöns Jacob Berzelius received for inspection an unusual ore, which he named thoria, after Thor, the Scandinavian god of thunder and war. The metal later isolated from it was named thorium, which has persisted to the present day, even though the ore has changed its name slightly to thorite. Although natural thorium is radioactive, almost all of its present uses exploit its chemical, rather than its nuclear, properties.

The first practical use for thorium was found 63 years after Berzelius's discovery. Carl Auer von Welsbach found that a 'mantle', made of 99% ThO_2 and 1% CeO_2, surrounding a gas flame would radiate white light more efficiently than an open flame, and this gas-lamp technology quickly spread throughout Europe. Although these lamps have since been superseded, thorium compounds are still used today as catalysts for petroleum cracking, sulfuric acid synthesis and in the Ostwald process for nitric acid synthesis. Thorium also features, because of its strength and creep resistance at high temperatures, in the Mag–Thor alloy used in aircraft and rocket engines. Additionally, ThO_2 has a high refractive index and low dispersion and is therefore used in high-quality optical lenses[1].

Among its remarkable chemical and physical properties, thorium metal is liquid over the widest temperature range of any element, and ThO_2 has the highest melting point of any known oxide[2]. Being the first true actinide, thorium still has an empty 5*f* orbital, and therefore Th(IV) is the most stable and plentiful oxidation state. Because of its large size, thorium's coordination chemistry is also quite remarkable, with $Th(NO_3)_4{\cdot}5H_2O$ being the first recorded example of an 11-coordinate complex[3]. Additionally, Th(III) is also an accessible oxidation state and has been reported[4] as free Th^{3+} in an aqueous solution of $ThCl_4$ and HN_3. Ligand-stabilized Th(III) complexes are also known and include $ThCp_3$ and the bis(trimethylsilyl) Cp analogue[5].


ALEX WING

Interestingly, experimental and computational evidence suggests the single unpaired electron in the $ThCp_3$ complex resides not in a 5*f* orbital, but in the $6d_{z^2}$ (refs 6,7). Unfortunately, despite the existence of a formally trivalent species, no redox chemistry has yet been observed with thorium.

Recent research has led to promising thorium-based materials — such as thorium- and copper-doped magnetite — to catalyse the activation of small molecules. These materials could eventually replace the more traditional chromium- and copper-doped magnetite catalysts used to form carbon dioxide and hydrogen from carbon monoxide and water[8]. Along similar lines, several research groups have synthesized well-defined thorium complexes to study their bonding and reactivity. Recent reports include the synthesis and characterization of thorium complexes using corrole ligands[9] and a dihalide thorium complex supported by trans-calix[2]benzene[2]pyrrolide, which on reduction undergoes double aryl metallation of the ligand[10].

Although most of the current research is focused on its chemical characteristics, perhaps thorium's most revolutionary potential use involves its nuclear chemistry. The theoretical feasibility of a thorium-based nuclear reactor has long been recognized. However, technical difficulties as well as prioritized interest in uranium reactors (which some posit stems from uranium reactors' greater ability to breed plutonium for fission bombs) have prevented the development of commercial thorium reactors. Natural thorium is almost exclusively ^{232}Th, thus no costly isotopic enrichment process would be necessary, and this would present a significant potential benefit over today's uranium-based reactors.

Perhaps the biggest advantages of thorium reactors are their safety and their relatively reduced environmental impact. Unlike uranium-based reactors, which produce waste that remains harmful for thousands of years, 83% of waste from a proposed liquid fluoride thorium reactor will become safe within 10 years, and the remaining 17% after 300 years. Thorium reactors aren't just an abstract concept either: the Indian government has a strong interest in thorium power because India has approximately a third of the world's thorium reserves, and in 2002 the government issued approval to start construction of a prototype thorium fast-breeder plant.

Thorium has proved itself as a catalyst and a great refractive material. With the effects of global climate change increasing with every passing year, hopefully more research and allocated resources will help thorium realize its great untapped potential and become a truly revolutionary material in our energy economy. ❐

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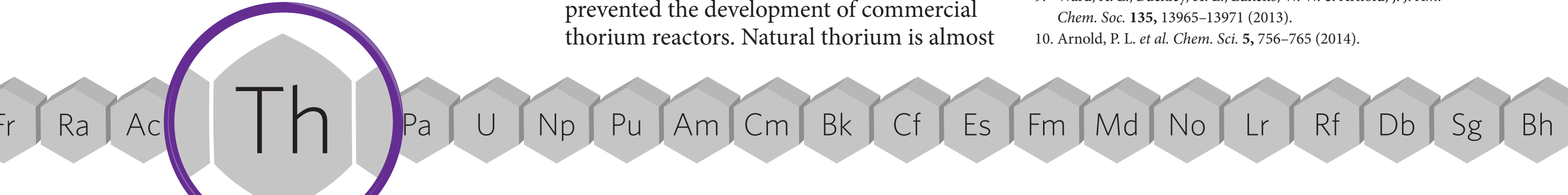

Nobelium non-believers

Alfred Nobel's eponymous element, nobelium, was 'first' discovered either in the 1950s or 1960s, in the USSR, Sweden or the USA. **Brett F. Thornton** and **Shawn C. Burdette** delve into the ensuing decades of internecine strife over the discovery of element 102.

In 1956, a research team in Moscow led by Georgy Flerov bombarded ^{241}Pu with ^{16}O using recently developed heavy-ion beam techniques. The Moscow team may have produced element 102, and contemplated the name joliotium (Jo) to honour 1935 Chemistry Nobelist Irène Joliot-Curie, who had died earlier that year. As Flerov noted later, the early data was inconclusive, and not widely disseminated. Cold War politics may have made joliotium a controversial name elsewhere because Irène Joliot-Curie and her husband were outspoken supporters of the Soviet Union.

In July 1957, researchers working at the Nobel Institute of Physics, now part of Stockholm University, claimed[1] to have synthesized either ^{251}102 or ^{253}102 by fusing ^{244}Cm and ^{13}C. The team, including collaborators from the UK and Argonne National Laboratory in the US, proposed the name nobelium (No) to recognize the institute's namesake, Alfred Nobel. The name was immediately popularized.

The nobelium report attracted the attention of the superheavy-element group at Lawrence Berkeley Laboratory. After months of unsuccessful attempts to replicate the Stockholm results, the group led by Glenn Seaborg and Albert Ghiorso wondered privately if 'nobelievium' would be a more apt name. Consequently, they initiated new experiments to produce other isotopes of element 102. In 1958 they reported[2] producing ^{254}102 by fusing ^{244}Cm and ^{12}C.

By the early 1960s, the Moscow group had moved to the new Joint Institute for Nuclear Research in Dubna. Results with their new accelerator led to suspicions that the Berkeley team had misidentified the reaction product and therefore had claimed incorrectly to have produced ^{254}102 in 1958. If an experiment generated an element, but the isotope and/or half-life assignments were incorrect, was the discovery valid? The Dubna group believed not, declaring IUPAC's acceptance of 'nobelium' hasty, and asserted their discovery of — and preference for — joliotium.

ALEX WING

Agitated by the repudiation of their work and competing discovery claim, Ghiorso and colleagues initiated new experiments and re-examined the earlier Berkeley data. They soon realized some of their earlier half-life and isotope identifications had been wrong and the revised analysis of the data aligned more closely with the Dubna findings. In their rebuttal, the Berkeley group emphasized their 'right according to tradition' to name the element, but conceded that they would be content with nobelium[3]. This was ignored in the Soviet Union, where the local discovery of element 102 was lauded officially.

Decades passed without détente. In the early 1990s, spurred by the still unresolved conflict over the names of several super-heavy elements, IUPAC re-evaluated the discovery of all transfermium elements. Meanwhile, the Dubna group published[4] an account of element 102's discovery — notably avoiding 'nobelium' and calling the credit given to Berkeley 'groundless'. After a long review, IUPAC attributed the definitive discovery of element 102 to two 1966 reports from Dubna[5]. The Berkeley group never relinquished their claims, and accused IUPAC of *ex post facto* meddling with discovery priority.

Although the Berkeley team contradicted the 1957 Stockholm ^{244}Cm + ^{13}C results in 1958, in 1967 they produced ^{253}No using the identical reaction and improved methods. Despite the synthesis being the same, the Stockholm group had isolated a product with a different half-life[6]. So, element 102 may have been produced in Stockholm first; but why had they not been able to isolate it convincingly?

Actinide purification protocols that the Stockholm group used to differentiate the common 3+ actinide ions with cation exchange columns were well established in the 1950s. Unfortunately, No^{2+} is more thermodynamically stable in aqueous solution[7]; any nobelium produced by the Stockholm group would have eluted at an unexpected, unnoticed time. In hindsight, this provides another example of the predictive power of the periodic table. Analogous to the filled *d*-shell electron configurations of Cu^+ and Ag^+, promotion of the $6d^1$ electron fills the 5*f* shell and yields a stable No^{2+}.

No known isotope of element 102 has a half-life greater than the 58 minutes of ^{259}No, precluding its inclusion in the famed medals that share the same etymological root. Nevertheless, after all the discord, it's still called nobelium and that is something that will not change over time. ☐

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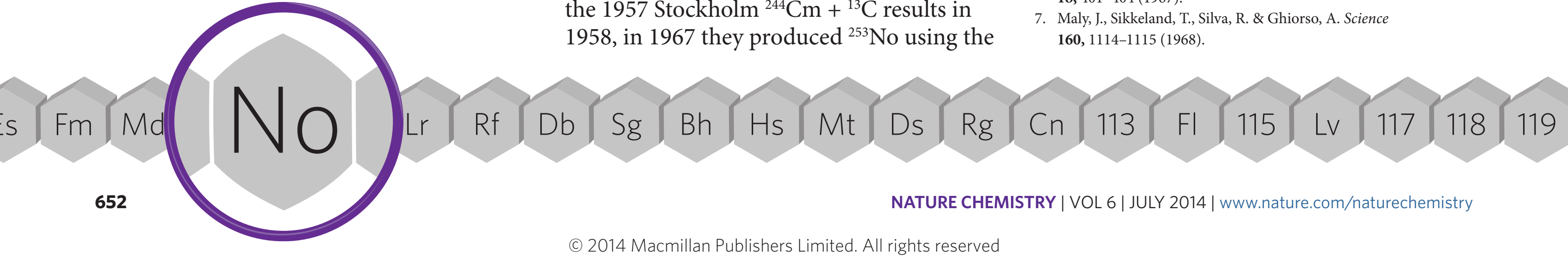


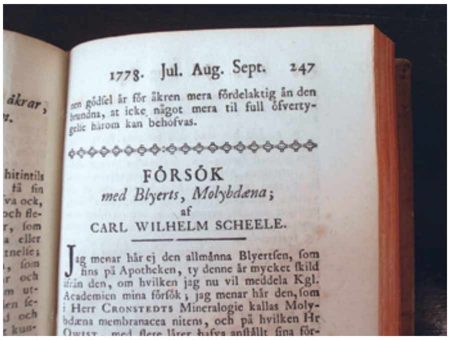
Made by molybdenum

Anders Lennartson muses on molybdenum and its essential role in catalysing reactions from the bacterial to the industrial scale.

The three minerals historically named galena, molybdena and plumbago have several common features — they are all soft, dark materials with a metallic lustre. Before the advent of modern chemical methods, these three substances were often mistaken for one another. Because galena (lead(II) sulfide) was known to be a useful lead ore, it was commonly believed that molybdena and plumbago also contained lead. However, molybdena (which we call molybdenite today) was actually molybdenum(IV) sulfide, and plumbago was what we now call graphite. This historical misunderstanding is why, even today, the graphite–clay mixture in pencils is often referred to as 'lead'.

Needless to say, early attempts to produce lead from molybdena or plumbago invariably failed, and attention instead turned to further investigating the content of these minerals. In 1776, a small sample of molybdena was presented to Carl Wilhelm Scheele, a pharmacist in the small Swedish city of Köping. Aged just 33, Scheele had not only discovered hydrofluoric acid, chlorine, tartaric acid, arsenic acid and uric acid, but had also characterized the first manganese and barium compounds. If anyone was going to be able to sort out the confusion over these minerals, it was probably him.

The molybdena sample was indeed similar in appearance to the plumbago Scheele had in his shop, but still different enough to warrant further investigation. He asked his friends for more of this substance until he had acquired enough for a thorough chemical study. In the molybdena sample he found no lead, but what he did find came as a surprise; he was able to isolate[1] a previously unknown substance, molybdic acid ($MoO_3{\cdot}H_2O$). Once on the right track with molybdena, he also showed that plumbago was a form of carbon, but that's another story altogether.



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en gödſel år för åkren mera fördelaktig ån den brundna, at icke något mera til full öfverty-gelſe hårom kan behöfvas.

* * *

FÓRSÓK

med Blyerts, Molybdæna;

af

CARL WILHELM SCHEELE.

Jag menar hår ej den allmånna Blyertſen, ſom finns på Apotheken, ty denne år mycket ſkild ifrån den, om hvilken jag nu vil meddela Kgl. Academien mina förſök; jag menar hår den, ſom i Herr CRONSTEDTS Mineralogie kallas Molybdæna membranacea nitens, och på hvilken Hr QWIST med flere lårer hafva anſtållt ſina för-

Reducing molybdic acid to molybdenum itself required more sophisticated equipment than a small pharmacy store could supply. Scheele turned to Peter Jacob Hjelm in Stockholm, who mixed molybdic acid with charcoal and linseed oil and heated it in an intense fire. After opening the sealed crucible he found the first sample of metallic molybdenum, in the form of small grains. Molybdenum metal produced in this way has a high carbon content, making it brittle and close to useless, and so throughout the nineteenth century it remained on the shelves of chemistry labs. In the early 1900s, methods of obtaining pure molybdenum in larger quantities were developed, enabling molybdenum steels to become increasingly important. These materials found their way into car frames and tools, and during the two world wars large amounts were also used for armour plating. More recently, molybdenum metal has been used as a target in X-ray tubes, both for medical applications and research purposes; Mo-K_α radiation is used extensively by crystallographers.

Not only is molybdenum useful in materials science, it is also very important in catalysis. Modern gasoline and diesel fuels have far less impact on the environment than they did a few decades ago because of the removal of sulfur from petroleum using molybdenum sulfide catalysts. Molybdenum-oxide-based catalysts are used by industrial chemists to selectively oxidize alcohols to aldehydes, reactions that otherwise suffer from competing carboxylic acid formation. In 2005, Richard Schrock shared the Nobel Prize in Chemistry for the development of olefin metathesis catalysts, including those based on molybdenum carbenes.

The use of molybdenum compounds for catalysis was, however, not a discovery first made by man. Long before humans roamed the Earth, several crucial processes were already being catalysed by molybdenum-containing enzymes — and still are. One such process is the conversion of atmospheric nitrogen gas to ammonia. When this reaction is performed industrially, it requires temperatures above 300 °C and pressures of about 200 bar. In contrast, nitrogen-fixing bacteria living in symbiosis with certain plants carry out the same process under physiological conditions, by exploiting the power of nitrogenase enzymes. Most nitrogenases have a molybdenum atom in their active site, which consists of a cluster of seven iron atoms, nine sulfur atoms, one molybdenum atom capped by a homocitrate ligand, and a histidine residue.

Not only can some molybdenum enzymes reduce dinitrogen to ammonium ions, certain anaerobic microbes — so-called acetogens — use other molybdenum-containing enzymes to convert carbon dioxide and hydrogen to formate ions, and eventually to acetyl-coenzyme A. It has been estimated that these organisms produce around 10^{11} tons of acetate from CO_2 gas annually[2]. Put another way, our world would be quite different without molybdenum! ❐

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in your element

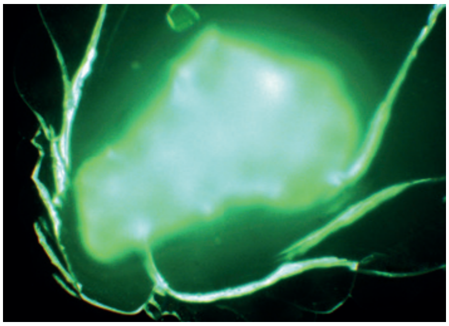
Californium gleaming

Thomas Albrecht-Schmitt explains the origin of element 98's striking green glow, and why the future for californium chemistry is just as bright.

A late actinide with twenty known isotopes, californium is a man-made transuranic element that does not occur naturally. It was first identified by Glenn Seaborg and co-workers in February 1950 in an experiment that used a 60-inch cyclotron to bombard curium-242 targets with helium ions. Although named primarily for the State of California, it also recognizes the University of California at Berkeley where many elements beyond uranium in the periodic table were first discovered. We now know that this was not the first observation of californium; late actinide elements up to fermium had been previously identified in debris from the first nuclear detonations in the 1940s, but this information was classified for many years.

Isotopes of elements beyond californium have half-lives much shorter than one year, meaning that it is the last element in the periodic table that macroscopic chemistry can be reasonably conducted on. Even einsteinium, its immediate neighbour in the periodic table, has only been made in microgram quantities. The majority of californium synthesized today is ^{252}Cf, although the hazards associated with this isotope makes chemistry — beyond tracer levels — essentially impossible. Owing to an unusually high rate of spontaneous fission, one microgram of ^{252}Cf releases 2.3 million neutrons every second.

Fortunately, ^{249}Bk is also generated during the production of ^{252}Cf and can be separated with high chemical and radiochemical purity from the other neutron-capture products. ^{249}Bk is short-lived, with a half-life of 320 days, and it undergoes β decay to ^{249}Cf, which has a much more chemically useful half-life of 351 years. Nearly all of the chemical studies on californium have been conducted with this isotope, but the truly desirable isotope — with a half-life of nearly 900 years — is ^{251}Cf. Unfortunately, ^{251}Cf is difficult to synthesize.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Although the first californium compounds (containing mixtures of Cf isotopes) were prepared on microgram scales in the 1960s[1], it was not until the High Flux Isotope Reactor located at Oak Ridge National Laboratory started to produce meaningful quantities of isotopically pure ^{249}Cf that single-crystal X-ray diffraction studies and detailed physical property measurements could take place[2]. This work really came to fruition in the early 1970s with the work of John Burns and Richard Haire, both unsung heroes of actinide chemistry.

Burns established that Cf(III) had an ionic radius similar to that of Gd(III). This is notable because it results in fluxional behaviour in solution whereby eight- and nine-coordinate aqua complexes rapidly equilibrate, a property exploited when using Gd(III) as an MRI contrast agent. As a result of this, Cf(III) is similar to Gd(III) in its ability to adopt both hexagonal and orthorhombic structures for trichloride compounds[2]. Some californium compounds are also self-luminescent — they emit green light as the consequence of their intense radioactive emission causing the excitation of *f*-electrons. The green glow (pictured being emitted by $^{249}\mathrm{Cf[B_6O_8(OH)_5]}$) is beautiful to behold and harmless — it is the invisible emissions that you have to be extremely cautious of. ^{249}Cf emits γ-rays (388 keV) that have sufficiently high energies that they are detectable through more than 2 cm of lead. Holding a 5 mg sample of ^{249}Cf in your hand would result in exceeding your yearly radiation threshold in less than 10 minutes. Hence, californium chemistry can only be conducted in purpose-built radiological facilities, and experiments have to be carefully choreographed to minimize exposure times.

Today, the chemistry of californium and the related actinides, curium and americium, is undergoing a renaissance[3] because of the increased use of commercial nuclear reactors to generate electricity. Most nations are determined to develop ways to recycle used nuclear fuel, a complex mixture of elements and isotopes that includes curium, americium and californium, and this requires the development of sophisticated chemistry to separate these elements from each other on an industrial scale.

The Manhattan Project in the 1940s produced data to suggest that valence orbitals of actinides might be involved in covalent bonding, in contrast to the ionic nature that would be expected for late actinides. Recently, a combination of theory and experiment has provided strong evidence that the 6*d* and 5*f* orbitals of mid-to-late actinides can be deliberately utilized to form covalent bonds, and that such bonding can differ substantially between neighbouring actinides, even if they are in the same oxidation state[4,5]. This ability to control bonding is the key to designing selective extractants and materials for trapping and differentiating radionuclides from nuclear waste, and shows that californium chemistry has a glowing future. ❐

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m Cm Bk Cf Es Fm Md No Lr Rf Db Sg Bh Hs Mt Ds Rg Cn 113 Fl 115

in your element

The colours of chromium

From rubies to Rolls-Royce, **Anders Lennartson** explores the colourful history of chromium and its coordination compounds.

As a boy, I set up my own makeshift laboratory in my parents' basement. During my early chemical investigations, I acquired some chromium(III) chloride hexahydrate, a green salt that gave an equally green solution when dissolved in water. When I came back the next day, however, to my great surprise I found that the solution was now a violet colour. How could that be, I wondered?

An important property of chromium(III) complexes is that ligand exchange is slow. When I dissolved $CrCl_3{\cdot}6H_2O$ — which is more properly represented by the formula $[CrCl_2(H_2O)_4]{\cdot}Cl(H_2O)_2$ — in water, it slowly reacted with the solvent to give the violet-coloured $[Cr(H_2O)_6]^{3+}$ complex and free chloride ions. If I had had some chromium(III) sulfate to hand, I would have observed the opposite colour change; it exists as $[Cr(H_2O)_6]^{3+}$ in the solid hydrate, but when an aqueous solution of this compound is heated, it turns from violet to green because of the slow dissociation of water ligands and coordination of sulfate ions. This property of Cr(III) makes it possible to isolate a wide variety of chromium(III) coordination compounds, and is why Cr^{3+}, along with Co^{3+}, was a big favourite amongst early coordination chemists like Alfred Werner.

In contrast to chromium(III), chromium(II) complexes can exchange their ligands rapidly, and addition of acetate to blue $CrCl_2$ solutions precipitates red $Cr_2(OAc)_4$, a compound that has a Cr–Cr quadruple bond. Chromium also exists in higher oxidation states: black chromium(IV) oxide was used extensively in the good old days of magnetic tapes because of its ferromagnetic properties; unstable CrF_5 (Cr(V)) is a volatile red solid. If chromium(III) oxide (also known as chrome green) is heated with potassium carbonate and potassium nitrate, the mixture slowly turns yellow. This colour change stems from the formation of potassium chromate, K_2CrO_4, in which chromium is found in oxidation state VI.

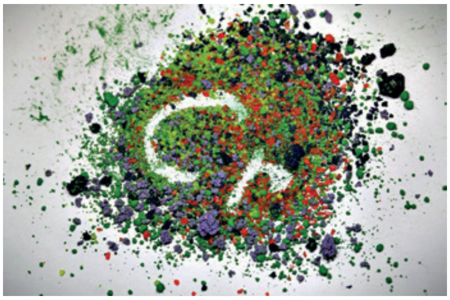
IMAGE COURTESY OF PETRA RÖNNHOLM

Other chromium(VI) compounds include the beautifully orange potassium dichromate, $K_2Cr_2O_7$, red potassium trichromate, $K_2Cr_3O_{10}$, and red chromium(VI) oxide, CrO_3. The latter is an acidic oxide, and its aqueous solutions are referred to as chromic acid — with the addition of dilute sulfuric acid this becomes Jones reagent, used to convert alcohols to ketones or carboxylic acids. Acidic potassium dichromate is also used by organic chemists for the same reaction, with the added bonus that if a synthesis fails, a solution of $K_2Cr_2O_7$ in sulfuric acid can be used to clean the dirty glassware, such is its oxidizing power.

It is now known that chromium(VI) compounds are toxic and may cause cancer, but previously they were popular in pigments such as $PbCrO_4$ and Pb_2OCrO_4 (chrome yellow and chrome red, respectively). The colours of chromium have been highly admired since ancient times — rubies are nothing but crystalline aluminium oxide doped with chromium, and pink hues in sapphires also originate from traces of chromium in an aluminium oxide lattice. Emeralds, a form of beryl, $Be_3Al_2(SiO_3)_6$, derive their green colour from small amounts of chromium.

It seems more than appropriate, therefore, that chromium was named after the Greek word *chroma* — which means colour — by Louis Nicholas Vauquelin, who discovered the element in 1797. The metal was not an immediate commercial success. Fifteen years after its discovery, Sir Humphrey Davy did not know much about chromium or its compounds when he wrote his famous text book *Elements of Chemical Philosophy*, but he did remark that chromic acid has a sour taste[1]. Tasting chemicals was obviously the order of the day, because in that very same year Jöns Jacob Berzelius wrote in his textbook that the aftertaste of the toxic chromic acid was harsh and metallic[2]. Berzelius also noted that the metal, although brittle, was very resistant to both acids and oxidation in air. We now know that this property comes from the fact that, when exposed to air, metallic chromium forms a very thin, but dense, oxide layer on its surface.

In the 1820s it was found that addition of chromium to steel made it resistant to rusting, but unfortunately the high carbon content of the chromium available at the time made these alloys brittle and useless for practical applications. When methods developed such that carbon-free chromium was produced in the 1890s, the situation changed. Stainless steel, which typically contains 8% chromium and 18% nickel, soon became widely used, and it remains one of the main applications of chromium today. The discovery, in the 1920s, that a thin layer of shiny chromium could be electrolytically deposited on steel came as a delight to the automotive industry. What would a 1930s Rolls-Royce Phantom II be without its chrome plating?

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Unsporting scandium

From Earth to the stars and back again, **John Emsley** surveys the uses, occurrences and mysteries of an element that is playing an increasing role in human affairs.

When Dimitri Mendeleev first presented his periodic table in 1869, he did so noting that there were larger than expected differences between the atomic weights of several elements, and left gaps for them. One such gap was between calcium and titanium, and from this he speculated that there should exist a metal with an atomic weight of approximately 44 — which he called 'ekaboron'. Just ten years later, Lars Fredrik Nilson at the University of Uppsala was analysing the brown lustrous mineral euxenite — which actually contains no fewer than eight metals — when he found that a metal extracted from it exhibited lines in its atomic spectrum that had not been previously reported. This metal, whose atomic weight he calculated to be 44, was indeed the missing element anticipated by Mendeleev. Ekaboron is not to be found in modern-day periodic tables though, as Nilson named his newly discovered element 'scandium' after the Latin for Scandinavia.

On Earth, scandium is not particularly abundant, and is found in similar quantities to lead. Unlike lead, however, it is widely dispersed throughout the Earth's crust because there are no geological processes to concentrate it, which is why it is present in small amounts in hundreds of minerals. Minerals made purely of scandium compounds are highly prized by collectors. Samples of the greenish-black thortveitite ($Sc_2Si_2O_7$) from Iveland in Norway were worth more than their weight in gold at some points during the 1950s, and a specimen less than 10 cm in length is currently on the market for $1,500. There are samples of thortveitite of such crystalline purity that they have been cut as gem stones, which may explain why similar specimens fetch such a high price.


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The strong lines in the atomic spectrum that enabled Nilson to first identify scandium also allow its relative abundance in stars and the interstellar medium to be probed. In 1908, Sir William Crookes used these spectra to report that scandium is, unexpectedly, more abundant in other stars than in our Sun. This stellar anomaly is still being studied, as is a curious scandium-rich nebula that surrounds the Eta Carinae star system 8,000 light years away. It has been observed over the centuries to brighten and dim quite inexplicably[1], and the role of scandium in this observation is still under investigation.

Although its function and fate in interstellar space has yet to be clarified, scandium has no role in the biosphere on Earth, and no living organism has yet been found that requires it. Only minute traces of scandium enter the food chain and the average person's daily intake is likely to be less than a tenth of a microgram. Rather strangely, tea leaves contain comparatively more scandium than other plants — although, as this is on average only 140 ppb, tea lovers need not be concerned. One explanation for this unusual concentration is that tea bushes do not discriminate between absorbing chemically similar aluminium — which they are known to require — and scandium.

Even though there are no scandium mines, and so it is only extracted as a by-product of tantalum and uranium mining, scandium is still valued for use in alloys with aluminium. Adding 0.5% scandium to aluminium greatly increases the metal's strength while maintaining its light weight, as well as raising its melting point by 800 °C so that, unlike ordinary aluminium, it can be welded. Russia has even stockpiled scandium for strategic reasons because several parts for advanced MiG jet fighters (pictured) are manufactured from this alloy. Meanwhile in the USA, scandium alloys are often used to make sports equipment such as baseball bats, lacrosse sticks and bicycle frames. It was also discovered that using such alloys to make cricket bats also improved their hitting power, but this was deemed 'unsporting' and scandium was immediately banned.

The primary form of refined scandium, the oxide, Sc_2O_3, also has a few specialized uses, even though world production amounts to only a few tonnes per year — and even less is converted to the metal itself. Scandium oxide provides a specialized optical coating for UV detectors[2], transparent to wavelengths between 0.25–5.0 μm, and is also used in neutron filters for nuclear reactors.

Other potential uses of scandium continue to be found. It is added to mercury vapour lamps to create a softer glow more akin to sunlight, and these lamps are often used in floodlights at sports venues. Scandium complexes show potential as hydroamination catalysts[3], and scandium sulfate does likewise as a seed germinating agent. Whether these applications of scandium become as prized as its use in fighter jets or as frowned upon as its use cricket bats remains to be seen. ❐

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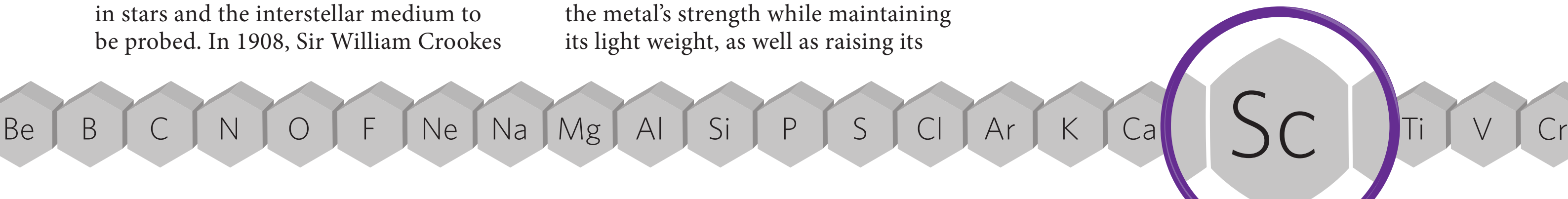

Gregarious gallium

Trick cutlery and mobile phones have one peculiar element in common, as **Marshall Brennan** explains.

The periodic table is arguably the most recognizable tool in chemistry. In 1869, Dmitri Mendeleev arranged the elements known at the time from lightest to heaviest, starting a new row whenever the properties of the elements appeared to resemble those in the row above. Mendeleev was by no means the first to try and organize the elements like this, but perhaps the reason his table is the one that hangs in classrooms and laboratories worldwide comes from the fact that he initially left gaps in it to be filled later. Wherever he reasoned that there should be an as-yet undiscovered element that better emulated the members of a given group than those known, he left placeholders named after congeners of the closest element in their group — ekaboron, ekaaluminium, ekamanganese and ekasilicon — and predicted some of their properties and characteristics based on their position in the table.

In 1875, the French chemist Paul-Émile Lecoq de Boisbaudran detected the first of these hypothetical elements in a sample of the mineral sphalerite. Spectroscopic examination revealed a pair of violet lines, which denoted the signature of ekaaluminium. De Boisbaudran collected the first pure sample of the element by electrolysis later that year, naming it 'gallium' after his home country of France. He went on to describe the element and its properties, and so similar were most of the experimental findings to the predicted properties of ekaaluminium that Mendeleev felt compelled to write to de Boisbaudran to suggest that his measured density of 4.5 g ml^{-1} for the metal was incorrect (Mendeleev had predicted a density of 6 g ml^{-1}). Indeed, the value was subsequently corrected to 5.9 g ml^{-1}, in stunning agreement with Mendeleev's prediction, and vindicating his placement of the eka- elements in his periodic table.

Gallium is a soft, silvery metal with modest conductivity; its properties are intermediate between those of aluminium and indium, as expected given its place in the fourth period[1]. Due to poorer shielding from its *3d* shell compared with aluminium's filled *2p* shell, gallium's ionization energies are greater than those of aluminium, and, perhaps more importantly, its atomic radius is much smaller than might be expected — at 130 pm, it is nearly identical in size to aluminium. This unusually small atomic radius is one factor that gives rise to gallium's most familiar property: at room temperature, gallium is a soft metal, but a mere 9° C higher — the equivalent of a warm day in Illinois, or a few degrees below body temperature — the metal melts. This property was the subject of a classic prank among nineteenth century chemists, where a spoon would be fashioned from gallium and given to an unsuspecting guest with his or her tea (pictured). Upon stirring the tea, the spoon rapidly melts, much to the victim's surprise. More practically, its low melting point means that gallium exhibits metallic properties in the liquid phase across a useful and accessible temperature range.


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Perhaps the most important characteristic of gallium is the ease with which it can alloy with various metals, as its small radius allows it to diffuse relatively easily into the lattice of many metals. Gallium's low melting point is often conferred on the final alloy, which makes the resulting material more easily workable, more stable and, as a result, more cost-effective. Most applications for gallium are in the semiconductor industry. GaAs — far and away gallium's most common alloy — is used in high-speed logic chips and preamplifiers in mobile phones, while AlGaAs and InGaAs are the light-emitting materials in the 405 nm laser diodes for Blu-ray disc players.

In addition to enabling technological advances, gallium chemistry has started tackling fundamental problems in fuel and energy science. Early work showed that gallium-doped zeolites effectively catalyse the ring opening and scission of methylcyclohexane into small alkanes[2] — used to recycle the pyrolysis products of gasoline. Gallium zeolites can also aromatize *n*-decane[3] and emerging work indicates that nanowires of GaN can even catalyse the production of benzene from methane[4]. Cleaving a C–H bond in methane is no small feat, and these reactions are important steps to convert relatively unreactive methane deposits and unwanted byproducts of gasoline production into useful petrochemicals, which has important implications for fuel storage and fine chemical synthesis.

Gallium itself holds few records on the periodic table, with middle-of-the-road properties including its melting point and density. It is likely to be these characteristics that allow it to be so fundamentally important in the semiconductor industry, where its cohesion with other elements and phase transition properties are highly valued. From its role in confirming early chemical theories to the most cutting-edge technologies, gallium has had a profound impact on all of chemistry, and perhaps its importance will only increase as further applications are explored. ☐

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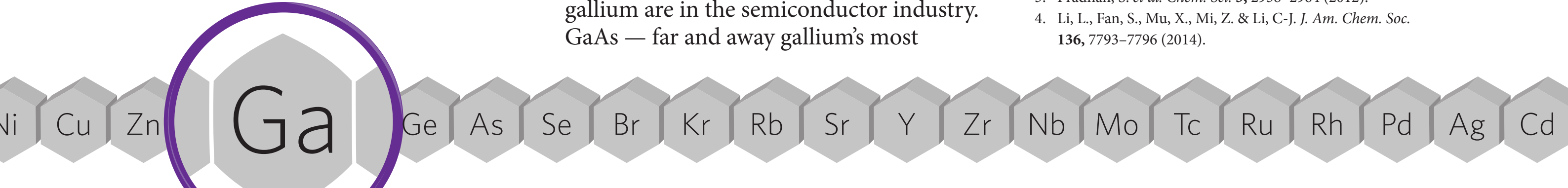

in your element

All manner of antimony

Claire Hansell surveys the uses, past and present, for antimony, including an unusual method for ‘recycling’ it.

Traversing the periodic table, there are few elements whose chemical symbols are not derived from their full (English) name. Most are from the handful of metals known since antiquity. Whilst iron, gold or silver might spring immediately to mind, antimony is also part of this venerable ‘old world’ of elements. Its symbol Sb comes from the Latin *stibnum*, which also lends its name to the mineral in which antimony is most commonly found: stibnite (Sb_2S_3), used by Ancient Egyptians as an eye cosmetic owing to its rich black colour.

Ancient Greek and Latin authors referred to it using variants of the name *stibium*, so where did ‘antimony’, the medieval term that has stuck until the present day, come from? A popular, but most likely fanciful, etymology is that it is derived from the French *antimoine* meaning anti-monk. Many early alchemists were monks who believed it was possible to transform antimony into gold — but were unfortunately unaware of its toxicity and conducted alchemical experiments with not a lab coat or safety goggles in sight. More likely though is that the name derives from the Greek ἀντίμόνος (*antimonos*), meaning against aloneness, reflecting the fact that element 51 is rarely found naturally in its metallic state.

A metalloid, rather than a true metal, antimony exists in four allotropes: the most stable is metallic and grey; with a non-metallic yellow, a black and an explosive white form also known. Unusually, metallic antimony expands slightly upon freezing, one of only four elements known to do so. It generally forms compounds in its trivalent and pentavalent states. One example is the powerful Lewis acid SbF_5, which in combination with HF forms fluoroantimonic acid ($[H_2F][SbHF_6]$), the strongest known superacid (pH −31.3), which is even able to protonate hydrocarbons to form carbocations and molecular hydrogen.

Orange deposits of antimony pentasulfide (Sb_2S_5) at Champagne Pool, Rotorua, New Zealand.
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Antimony is poisonous by inhalation and ingestion, and it has also been found to be carcinogenic[1], although the exact mechanisms of its toxicity are still unclear. This, however, hasn’t prevented element 51 from finding a role in medicine throughout history. As well as eye make-up, stibnite was used as a skin medication in Ancient Greece. In the Middle Ages, it was widespread practice for pellets of antimony to be swallowed whole to induce vomiting and as a laxative; this was in tune with the medical belief of the times that ‘bad humours’ needed to be expelled from the body. It was an expensive metal, and so pellets were often retrieved for re-use, and even passed on from generation to generation — whilst not the best medicine, this was certainly an innovative recycling method! A more refined alternative, generally used in the 1600s after the pellets were outlawed, was to drink wine that had been left standing in an antimony cup overnight.

Far from being an effective medical treatment, it has been suggested[2] that excessive use of antimony therapy may have contributed to Mozart’s early death at just 35. Today some pentavalent antimony compounds have found proper medical use as treatments for leishmaniasis[3], a parasitic disease mostly found in the developing world.

One of the major current uses for element 51 is the incorporation of antimony trioxide as a flame retardant into plastics and other materials[4]. Alloying antimony with other metals has also long been used as a tactic to improve hardness and tensile strength; when Gutenberg invented the printing press in the 1400s, the metal type blocks were made from a lead–tin–antimony alloy. Today similar alloys are used for the plates in lead–acid batteries. Elemental antimony is also considered to be a promising anode material for high-energy density lithium ion batteries, owing to its high theoretical capacity when lithiated to Li_3Sb.

With the ever-increasing interest in more efficient semiconducting materials to further miniaturize transistors in integrated circuits, doping non-metals with antimony has also found use. Doped zinc oxide has been shown to act as a p-type (electron-conducting) semiconductor, and under certain oxidizing conditions can also result in a ceramic with variable resistance properties. Doping silicon to increase its hole-conducting properties (as an n-type semiconductor) is also under investigation[5].

From ancient times to the present day, from use of both the bulk metal and stibnite through to the careful incorporation of tiny amounts in alloys and ceramics, antimony has found all manner of applications. Future developments in electronics may well hinge on the precise location and environment of antimony atoms, arranged with just as much care as an Ancient Egyptian queen applying stibnite-based make-up. ❐

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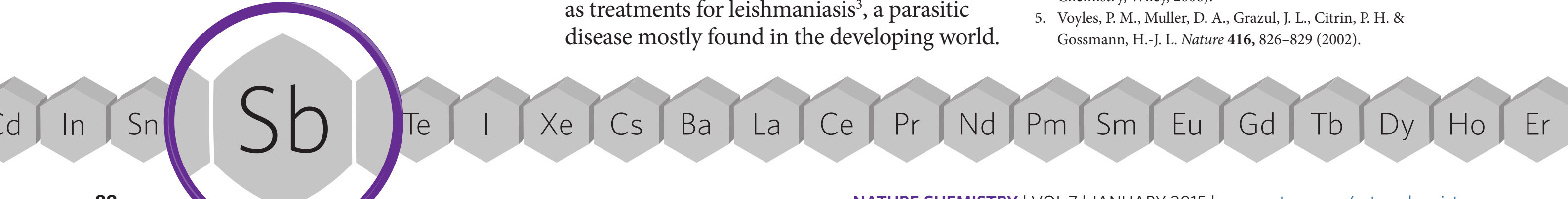

in your element

Subtle niobium

Michael Tarselli reflects on the intriguing characteristics of a rather underrated element, niobium, in its 'missing' and existing forms.

Pity poor niobium — it's suffered identity crises for the better part of the past two centuries. Originally dubbed columbium by discoverer Charles Hatchett in 1801, niobium was exceedingly difficult to separate from its group 5 neighbour tantalum, as they possess very similar chemical properties. Nearly 50 confused years passed before Heinrich Rose 'rediscovered' niobium in the mineral tantalite in 1844. He named it after the goddess Niobe, whose father, the mythical king Tantalus, is the namesake of its elemental cousin. The name columbium, however, was to linger alongside niobium until the 1950s. Several other elements believed to have been isolated from tantalite were later shown to be either niobium or mixtures of niobium and tantalum. In fact, Hatchett's columbium itself was also probably an Nb–Ta mixture.

Much of the niobium believed to exist on Earth — from compositional comparison with meteorites — is actually 'missing'; geologists theorize[1] that it may be contained in deep silicate reservoirs in the planet's core. Unequal distribution in the Earth's crust of the remainder — mostly in Brazil and Canada — has prompted a vigorous search for new deposits. Many have recently been found in geopolitically sensitive areas, such as southern Afghanistan[2] and the Democratic Republic of the Congo.

Despite this avid interest, niobium manages to fly under the very radars it helps to build. In practical applications — for example as a steel strengthener, a refining additive or a mineral acid for metalwork — it always plays second fiddle to some other transition metal. Yet element 41 endows many materials with noteworthy properties. Niobium–zirconium alloys[3] have been incorporated in non-toxic, non-immunogenic dental amalgams and bone implants. Benzyl alcohol-modified niobium nanoparticles can initiate reversible addition–fragmentation chain transfer (RAFT) polymerizations under irradiation with visible light, yielding well-controlled chains of the versatile poly(methyl methacrylate) polymer. Doped niobium oxides, called 'niobates', serve as thin-film capacitors for solar cells and promote biofuel refining on zinc supports. Alloyed with tin or strontium, niobium exhibits superconductor-like behaviour promising for energy storage materials. Your mobile phone may well contain niobium nitride, a superconductor used in some tiny piezoelectric devices.

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With five electrons in its outer valence shell, niobium enjoys rich redox chemistry through oxidation states ranging from −1 to +5. This shell can be plucked away to reveal a highly oxophilic [Kr] core, useful as a halide transfer agent, oxidant, or even to activate C–H bonds. In a recent catalytic effort, a Nb(III) complex has been shown to activate fluoroarenes' C–F bonds[4] — probably through two niobium complexes arranging in an 'inverted sandwich' around the benzene ring, twisting it with η^6 coordination into an almost cyclohexane-like geometry, thus removing its aromaticity and facilitating C–F cleavage.

Ask most organic chemists about niobium-promoted reactions and you'll get blank stares — its organic chemistry just hasn't been widely explored. But niobium still finds synthetic use in surprising places. For example, the niobium(V) to (III) reduction can promote reductive couplings[5] of alkynes and various electrophiles — much like that of manganese, titanium, or nickel. In heterogeneous catalysis, niobium nanoparticles and clays serve as solid supports for oxidative transformations. Homogeneous catalysis with niobium(V) chloride can deprotect methyl ethers, perform Friedel–Crafts cyclizations and snap together multicomponent reactions. A recent study[6] capitalizes on niobium(V)'s highly oxidizing nature to decontaminate warfare agents: combined with hydrogen peroxide, niobium–saponite clays can readily convert mustard gas simulants into non-toxic products.

Niobium also inspires beautiful chemical artistry. Pamela Zurer wistfully describes[7] how refractive, shimmering surfaces can be 'dialled in' on the surface of bare niobium metal using anodizing baths to generate thin coatings of niobium oxide. Different layer thicknesses produce different colours. This technology has served both art and commerce, with Austria minting green, pink, or purple collectable Euro coins (pictured).

What does the future hold for this underappreciated metal? No doubt its uses in energy storage and organic synthesis will increase, but perhaps most exciting is its role in building novel inorganic frameworks — zeolites, semicrystals and core–shell particles — for biomass conversion and harvesting solar power. After two centuries, niobium may finally receive some long overdue recognition. ❐

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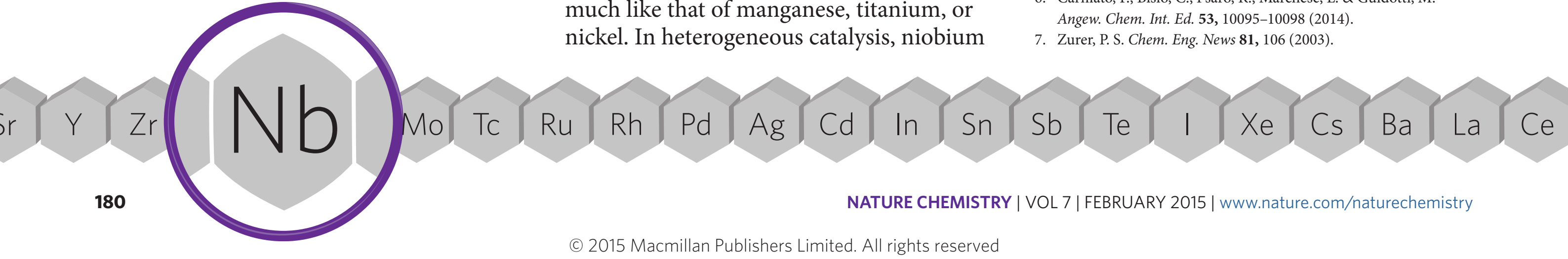

in your element

First there was hydrogen

Wojciech Grochala describes how the oldest, lightest and most abundant element in the universe continues to play an essential role on today's Earth.

The history of hydrogen — the element that fills the world as we know it — consists of a most dramatic set of events. Hydrogen and helium atoms emerged a measly 379,000 years after the Big Bang. As the hot, dense plasma of protons, electrons and photons that was the universe began to cool and expand, electrons and protons gathered to form atoms. Four hundred million years later stars — such as our very own Sun — evolved from gravitationally collapsed clouds of hydrogen gas, providing the heat necessary to sustain life in an otherwise giant, freezing, cosmic abyss at 2.7 kelvin. The third colossal breakthrough in hydrogen history came some 4.4 billion years ago, when the temperature on Earth dropped below 100 °C and dihydrogen oxide began to condense at its surface, allowing the emergence of life in the new aqueous environment.

Today hydrogen is estimated to account for 90% of all atoms in the universe, and it is essential to the material world. That includes ourselves: close to two-thirds of the atoms in our bodies are hydrogen. By no means an unproductive mass, the first element of the periodic table makes for an excellent chemical fuel — one that has been attracting increasing attention. The early Earth's atmosphere was rich in hydrogen, and bacterial enzymes called hydrogenases evolved to generate energy from molecular H_2 or H_2O (ref. 1). Microorganisms proliferated under reducing conditions, and many of those have survived on hydrogen fuel to this day.

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Van Helmont was the first to find out that although hydrogen was combustible in air, it could not support combustion by itself. In 1671 Robert Boyle described the formation of gas bubbles from the reaction of iron filings with acid, but it was Cavendish who recognized H_2 (which he referred to as 'inflammable air') as a substance distinct from other gases, which, when it was burnt in 'dephlogisticated air' (oxygen) produced water. This discovery inspired Lavoisier to call the substance 'hydro-gen', meaning water-former, in 1783. Conversely, in 1800 Nicholson and Carlisle (shortly followed by Ritter) managed to decompose water into its elemental constituents using electrolysis. It is this process that we try to achieve today, although with a much smaller electric bill, through a photochemical process[2]. The evolved H_2 gas is an excellent, ultra-light energy carrier, and very promising as a fuel — abundant and environmentally friendly as its oxidation produces water. Molecular H_2 filled one of the first balloons used to carry people in 1783 (pictured), and the fuel tanks of rockets two centuries later, permitting the inquisitive to explore further and further.

For practical applications, however, it must be stored in either a compressed, liquefied or solid state[3]. In 1970 in the Philips Research laboratories it was accidentally discovered that hydrogen could be reversibly taken up by intermetallic compounds in the form of a hydride[4]. This led to spectacular success for electrochemical hydrogen storage, and the first mass-produced nickel–metal-hydride battery-powered vehicles hit the roads of Japan in 1997. Together with vigorous development of hydrogen–oxygen fuel cells and solid proton conductors[5], these advances bring us closer to fulfilling Jules Verne's dream that "hydrogen and oxygen … will furnish an inexhaustible source of heat and light", mentioned in *The Mysterious Island* as early as 1874.

Because H and H_2 constitute the prototypical atom and molecule, respectively, they have been extensively used by theoreticians for over a century — since the birth of quantum mechanics. These two species have served as test beds for rigorous critical evaluations of diverse quantum mechanical models and approximations[6]. The oxidation states of hydrogen span from −1 (hydride), through 0 (elemental), to +1 (proton), with very different physicochemical properties for each species. The H_2 molecule — isoelectronic to the closed-shell He atom in the unified atom model — is quite inert. It was only in 1984 that Kubas described the coordination of molecular H_2 to transition metals[7]. On the contrary, the H^- anion is a very strong base and a strong reducing agent, whereas H^+ is a voracious acid and a powerful oxidizer; non (or very slightly)-hydrated protons present in a superacidic environment readily convert alkanes into carbocations[8]. Indeed, hydrogen has been a key element in establishing quite reasonable theories of acidity and basicity, which came to be viewed as proton transfer reactions in the Brønsted-Lowry theory.

The first element has never ceased to be of prime importance to many aspects of our world, and this is poised to continue with its major role in sustainable energy strategies. ❐

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Corrected after print 18 March 2015

Correction

In the In Your Element article 'First there was hydrogen' (*Nature Chem.* **7,** 264; 2015), the image was incorrect and did not depict a hydrogen balloon. The sentence referring to the image should have read 'Molecular H_2 filled one of the first balloons used to carry people in 1783 (pictured), and the fuel tanks of rockets two centuries later, permitting the inquisitive to explore further and further.' These errors have been corrected in the online versions after print: 18 March 2015.

Quantum caesium

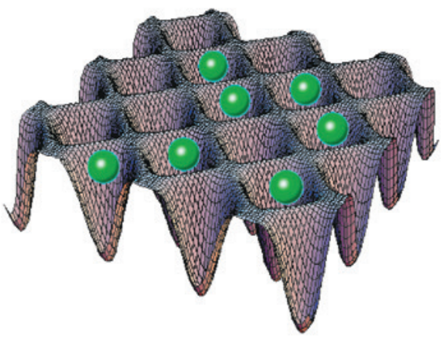
Eric Ansoborlo and **Richard Wayne Leggett** discuss the chemical and radiological characteristics that make caesium a captivating element but also a troublesome contaminant.

The fifty-fifth element in the periodic table, caesium, is an alkali metal and a close physical and chemical analogue of neighbours rubidium and potassium. As a soft ductile element with a low melting point of 28.4 °C, it is one of the few elemental metals to be liquid near room temperature. It is extremely reactive, pyrophoric and explosive in contact with water — thus unsurprisingly hazardous. With its large atomic radius, it readily loses its only valence electron to adopt the +1 oxidation state. It also tends to form covalent bonds and exhibit high coordination numbers (6 to 8), which serves in chemical separation from other cations, such as K^+ in nuclear waste remediation.

Element 55 was discovered in 1860 by Robert Bunsen and Gustav Kirchhoff while analysing a sample of mineral water with their recently invented spectroscope. They named the new element from the Latin word *caesius,* meaning sky blue, for the bright blue lines in its emission spectrum.

Among caesium's 40 known isotopes, with mass numbers ranging from 112 to 151, only one is stable (^{133}Cs). The most common radioisotope is the uranium and plutonium fission product ^{137}Cs, which has a half-life ($T_{1/2}$) of 30 years. ^{137}Cs decomposes by β decay to ^{137m}Ba, a short-lived ($T_{1/2}$ = 2.6 min) radionuclide that emits high-energy γ radiation. This makes ^{137}Cs a long-lived source of high-energy γ radiation, which has found uses in industry, such as in logging devices and levelling gauges, and in medical therapy for cancer treatment. Unfortunately, these same radiological properties make ^{137}Cs a troublesome environmental contaminant — even more so because of its high mobility.

Caesium can migrate long distances in the air before depositing on the ground. It mainly concentrates in the topsoil (~95%), although it is predominantly internalized by plants through their leaves. Its mobility in fresh water depends on its ability to adsorb certain particles and colloids from the soil[1]. Caesium then enters the animal and human food chain by consumption of contaminated water, plants, mushrooms, meat, fish and milk.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A considerable amount of ^{137}Cs has been released into the environment over the years: ~10^{18} Bq were dispersed in nuclear test fallout from 1950 to 1963, ~10^{17} Bq in the 1986 Chernobyl accident, and an estimated 10^{16} Bq in the 2011 Fukushima accident. It was also caesium, albeit in much smaller quantity, that led to one of the most tragic radiological incidents in history. In 1987 Goiânia, Brazil, scavengers — unaware of what the substance was — opened a sealed ^{137}Cs source they had found at an abandoned medical clinic. The fascinating blue glowing powder was sold to a junkyard owner, who shared it with many family members and acquaintances. When the source of sudden illnesses among those who had handled the sample was finally identified, an investigation found that about 250 people had been subjected to readily measurable contamination, and about 20 had received dangerous radiation levels. Four, including a four-year-old child, died soon after exposure.

The biological behaviour of caesium in animals and humans is similar to that of potassium, although caesium generally traverses cell membranes more slowly than its lighter analogue[2]. Soluble forms ingested or inhaled are almost completely absorbed to blood and distributed throughout soft tissues, with skeletal muscle accumulating most of the body's content within 1–2 days. Caesium then leaves the body within a few months in adults and a few weeks in young children. The recommended treatment for decorporation of radiocaesium is orally administered Prussian blue (ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$), which binds to caesium atoms secreted into the gut and prevents their reabsorption to blood.

On a different note, a novel application of stable caesium uses an inherent time-keeping ability that is quantum mechanical in nature. In 1967, the International System of Units (SI) defined the second as 9,192,631,770 periods of the wavelength of light associated with the transition between two 'hyperfine' energy levels of the ground state of the ^{133}Cs atom (pictured). Since then, caesium has been widely used in atomic clocks[3].

In an interesting turn of events, the ubiquitous anthropogenic isotope ^{137}Cs generated in recent decades by nuclear fallout has found an unexpected use. Measurement of its characteristic γ emissions serves as a non-destructive method of determining whether a purportedly extremely old wine was indeed produced before the nuclear age.

Thus, caesium has proved to be a mixed blessing to mankind, a potentially hazardous environmental contaminant yet also a beneficial industrial and medical tool that keeps the time for clocks and wine. ❐

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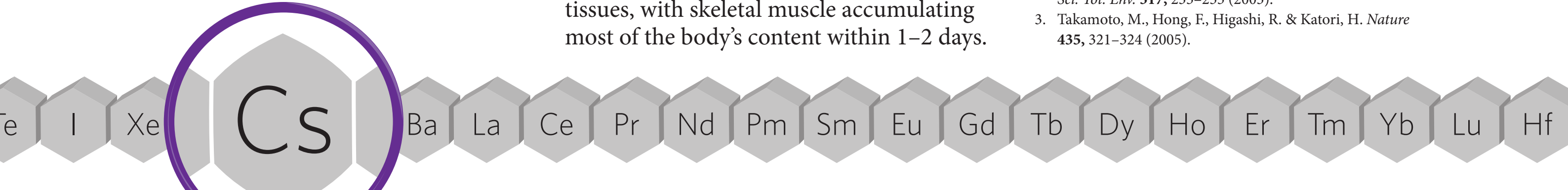
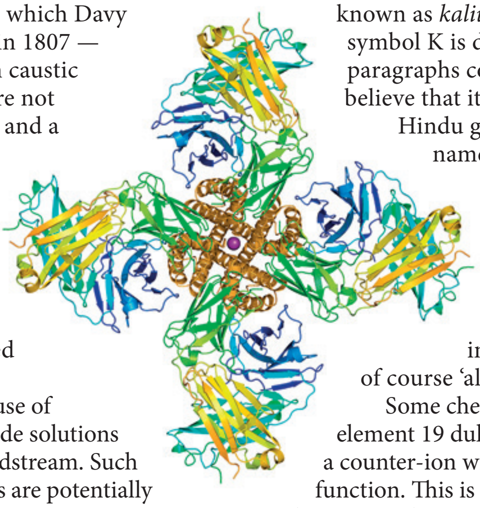


in your element

Potent potassium

Lars Öhrström ponders the importance of potassium in matters of life and death.

As an essential element (we need to consume 1–5 grams per day), potassium is life-preserving, but it is also intimately associated with danger and even death. The electrochemical experiments through which Davy isolated the element in 1807 — electrolysis of molten caustic potash (KOH) — were not for the faint-hearted, and a year later young Gay-Lussac got first-hand evidence of the reactivity of the pure metal in an explosion that left him with damaged eyesight for life[1].



LAGUNA DESIGN/SCIENCE PHOTO LIBRARY

The most sinister use of potassium is as chloride solutions injected into the bloodstream. Such intravenous injections are potentially lethal and serve for executions in some US states, although they are also used to treat potassium deficiency. KCl(aq.) has been implicated in tragic medical errors, as well as gruesome serial killings, because it is difficult to detect and the cause of death often seems deludingly natural[2]. A rapid analysis is required to identify potassium poisoning — anecdotally, this makes using it in crime novels awkward, as the prompt analysis would force writers to divulge the plot too early[3].

In our bodies there is a fine balance between the K^+ and Na^+ concentrations inside and outside the cells, and it is the disruption of this balance that makes KCl injections lethal. Potassium ions are transported across the biological membranes through proteins known as potassium channels (pictured). Studies on these ion channels afforded Roderick MacKinnon the 2003 Nobel Prize in Chemistry, but the detailed mechanism at play is still under debate; the predominant idea of water co-transport was recently challenged by the suggestion of a direct K^+–K^+ 'Coulomb knock-on' mechanism[4].

Element 19 comes with two aliases: variations of 'potassium' are common in many languages and it is also known as *kalium*, from which its symbol K is derived. The previous paragraphs could lead one to believe that it derives from the Hindu goddess Kali, whose name is associated with death, but just as 'potassium' it comes from one of the early compounds, K_2CO_3 known as potash or *al-qalyah* in Arabic, which is of course 'al-kaline'[5].

Some chemists may consider element 19 dull, as it often is merely a counter-ion without specific function. This is far from the case however. Saltpetre (KNO_3) for example, once the most important potassium compound, was a superior oxidant in gunpowder for ancient firearms compared with its more hygroscopic analogue $NaNO_3$.

The source of potassium ions had traditionally been potash, historically an important export from northern Europe, obtained by the extraction of wood ashes and subsequent crystallization in pots. Today potassium is mined primarily as KCl in North America and Russia. Its main use is as a macronutrient in 'NPK' fertilizers, along with nitrogen and phosphorus as the name implies. Operations are on a huge scale, as the uptake in crops is large and demands that potassium constantly be replaced in the soil, yet we do not risk depleting resources as it is the eighth most abundant element in the Earth's crust[6].

The chemistry of potassium is dominated by the K^+ cation and its mainly electrostatic interactions. Significant coordination chemistry also arises from the introduction of crown-ethers and related compounds[5]. Some of these hosts have helped shed light on the biological role of potassium; others have been used to promote disproportionation into complex-bound K^+ and K^- counter ions, demonstrating a small but significant electron affinity of this very electropositive element.

The crown-ether complexes of the alkali metals also nicely illustrate the trend in sizes within this group. The reactivity trends are also very regular; reacting sodium with water is a classic demonstration, but the larger size and lower ionization energy of potassium make the corresponding experiment dangerous as the generated hydrogen gas will invariably ignite and explode. Thus, although organic solvents are typically dried by distillation over pieces of Na, the use of potassium metal as a substitute is not advisable. Yet this is exactly what chemistry student Primo Levi did when given the task of distilling benzene, and could not find sodium metal in Turin's war-depleted stock rooms. Although he handled his piece of potassium "like a holy relic" the lab still caught fire, but luckily for himself — and literature — he was able to extinguish the blaze[7].

Whether in biological systems or laboratory settings, rather than a mere spectator counter-ion potassium often assumes a role that is a matter of life and death. ❒

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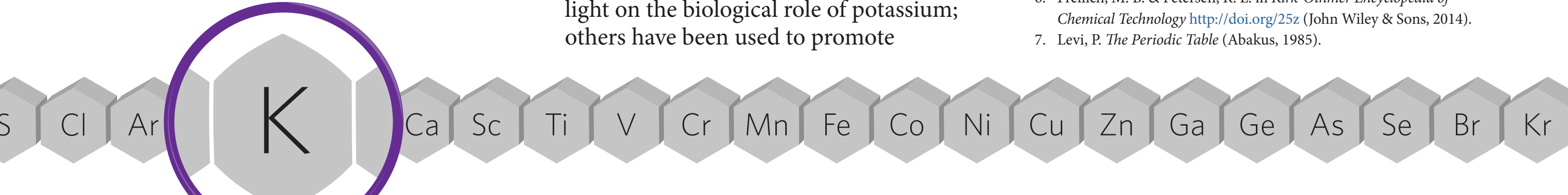
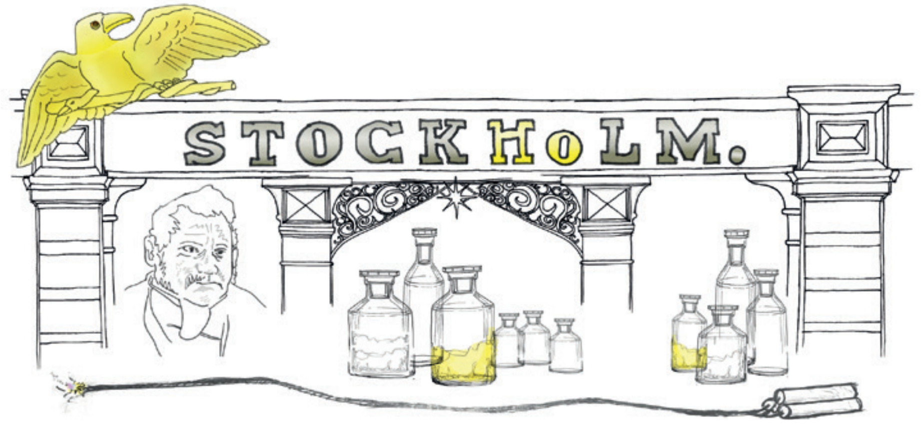


Homely holmium

Brett F. Thornton and **Shawn C. Burdette** consider holmium's hotly contested discovery and later obscurity.



EMMA S. KARLSSON, OXYRIA NATUR, STOCKHOLM

In 1878 Marc Delafontaine, a Swiss native working in Chicago, noticed previously unknown emission lines when studying a solution extract of samarskite ore. This observation alone was not enough to claim that element 67 had been discovered — newly observed spectral lines often heralded the identification of a new element, but it was not unusual for the same element to be 'discovered' multiple times with different spectral lines. Such spurious element discoveries appeared frequently in the late nineteenth century.

Nevertheless, Delafontaine's observations were confirmed by Jacques-Louis Soret, who was working in Switzerland with solutions extracted from gadolinite ore. Delafontaine suggested the name philippium (after the Swiss chemist-physician Philippe Plantamour), but uncertainties about the element's identity lingered; both he and Soret became embroiled in a priority dispute with the American chemist J. Lawrence Smith. Smith claimed to have discovered the same element (he named it mosandrum after Carl Gustaf Mosander, discoverer of three lanthanoids). The dispute fulminated in French-language journals[1,2].

During this period, Per Teodor Cleve in Uppsala, Sweden was analysing erbia-containing residues from Lars Fredrik Nilson's recent separation of scandium from erbium ores. A spectroscopic analysis of erbia (erbium oxide) by physicist Tobias Robert Thalén led Cleve to propose the presence of additional undiscovered elements in erbia, and he went on to separate two new oxides from a sample of it. A brown oxide he named *thulia* (hence, thulium) and a green oxide *holmia* — the medieval Latin name for Cleve's hometown of Stockholm[3]. Because Cleve had more comprehensive and convincing data, Cleve's claim gained precedence, and the new element became known as holmium.

Stockholm's chemistry pedigree is legendary. Berzelius worked in the city and helped discover at least four elements (his students, including Mosander, found five more). Former Stockholm pharmacist Carl Wilhelm Scheele found oxygen before Priestley, even though the latter published his results first. Many other famous chemists hail from the city including solution chemist Svante Arrhenius (who studied under Thalén and Cleve) and, of course, Alfred Nobel. Stockholm county boasts Ytterby, the periodic table's most-honoured suburb (namesake of Y, Yb, Er and Tb), and the original source of several elements, including holmium.

Delafontaine later attempted to obtain a purer sample of philippium, but holmium had already become elemental dogma. Modern texts often acknowledge Delafontaine, Soret and Cleve for finding holmium, but Thalén could share credit for the discovery because Delafontaine and Soret also used spectroscopy to identify the element.

Holmium's chemical similarity to its neighbouring elements made it difficult to discover; today this similarity often leads to few compelling reasons to select it for a given purpose from a choice of other similar — and often cheaper — lanthanoids. Holmium's high magnetic susceptibility means that it is occasionally used in high-strength magnets, especially as a magnetic-flux concentrator; however, elemental holmium's magnetic properties only manifest themselves at cryogenic temperatures.

Holmium is now commonly used in surgical lasers, where holmium-doped aluminium garnet (Ho:YAG) is the lasing material, with an infrared emission around 2,100 nm. This wavelength is particularly useful for surgery because water-laden tissues absorb the laser energy within half a millimetre, allowing for precise cutting. Cuts made with Ho:YAG lasers generally self-cauterize, minimizing bleeding. In urology, Ho:YAG lasers are used for removal of urinary stones[4] and the treatment of an enlarged prostate[5].

137 years after its discovery, holmium languishes as one of the most underutilized elements on the periodic table. Although medical uses of Ho:YAG lasers account for an order of magnitude increase in mentions in the scientific literature beginning in the late 1980s, holmium remains one of the least-discussed elements — perhaps some fascinating holmium chemistry may yet be discovered[6]. ☐

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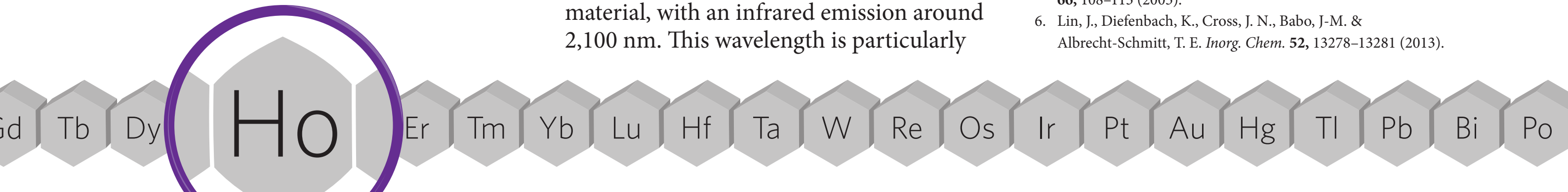

in your element

Toxic thallium

Anders Lennartson ponders on the contribution of thallium to society, since its main characteristic is its toxicity.

The lightest member of group 13 in the periodic table, boron, has been used in medicine for centuries and serves a wide variety of industrial applications; what would a chemist do without borosilicate glass? Aluminium, the next family member, is used for everything from wrapping chocolate bars to constructing space craft. Then follow gallium and indium, two elements that are indispensable in modern electronics — for instance, InGaN is used as the emitting layer in blue light-emitting diodes. At the end of the group comes thallium, the black sheep. Its compounds have found some use, for example in photoresistors, optical glass and in a class of high-temperature super conductors, yet element 64 has no real widespread application in consumer products and it appears that we could live very well — and perhaps even be better off — without it altogether.

The story begins in 1861 when Sir William Crookes used the newly invented spectroscope to search for tellurium in a residue from a sulfuric acid plant. He did not find any, but instead noticed a green, as-yet-unknown spectral line flashing by. Crookes named the new element thallium, after the Greek *θαλλός* meaning green branch. Whether it was Crooks or the French chemist Claude-Auguste Lamy — also working, independently, on materials obtained from a sulfuric acid plant — who first prepared metallic thallium is disputed[1]. At the time this led to a major controversy across the Channel, which seems to have died down after both scientists received recognition.

In contrast to the lighter group 13 elements, thallium prefers the +1 rather than the +3 oxidation state. Due to a similar ionic radius to K^+ our bodies readily take up Tl^+, with an often fatal result as it disrupts important processes involving K^+, although the exact mechanisms are not yet known. Ingestion of usually innocent-looking, colourless, nearly tasteless thallium salts gives rise to gastric and neurological disorders and rapid organ degradation. At low doses, symptoms are slow to appear and can easily be attributed to other ailments, which makes thallium rather discreet and why it is dubbed the poisoner's poison. A characteristic effect of thallium poisoning is massive loss of hair.


DOROTA NOWAŃSKA / ALAMY

Soon after its discovery, thallium's toxicity became apparent and it found widespread use as rat poison, but has since been deemed unsafe and banned in many countries due to numerous tragic accidents as well as murders. Agatha Christie made use of thallium in her 1961 novel *The Pale Horse* — and in doing so actually saved a life. In 1977, a 19-month-old girl from Qatar was admitted to Hammersmith Hospital, London, suffering from a serious, unknown sickness. Without a diagnosis, the doctors could not do much. One of the nurses, however, was reading *The Pale Horse* and realised the similarities between the symptoms of her patient and Agatha Christie's fictitious victim. A urine sample revealed high levels of thallium and an antidote could be administrated — Prussian blue, which binds to the metal and helps expel it from the body. The subsequent publication[2] describing the case includes the following acknowledgement: "We are indebted to the late Agatha Christie for her excellent and perceptive clinical descriptions and to Nurse Maitland for keeping us up to date on the literature."

English serial killer Graham Young (1947–1990), 'the teacup poisoner', also built his fame on thallium[3]. Aged 14 he killed his step-mother with thallium acetate, but was found out when he started to treat his father in a similar fashion, and ended up at the Broadmoor psychiatric hospital. Released at the age of 23, he took up his old hobby and it didn't take long until a mysterious disease started to spread among his colleagues, eventually killing two. It was Young himself who suggested thallium poisoning to the company doctor, thus putting investigators on the right track. He spent the remainder of his life behind bars.

Considering thallium's non-selective toxicity and limited applications, perhaps it would have been no great loss if, rather than causing a tussle over the credit for its discovery, the green spectral line had remained unnoticed. ❐

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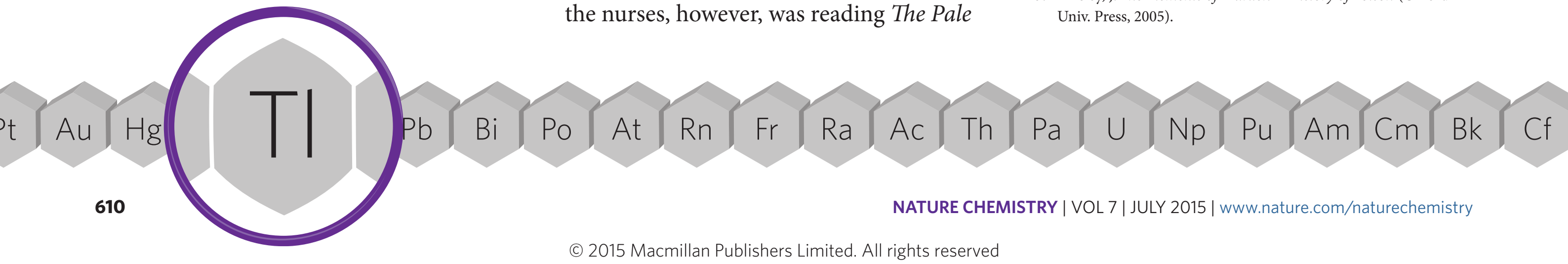


Magically magnetic gadolinium

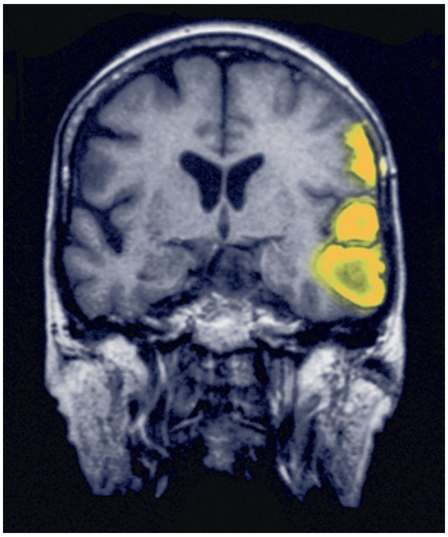
Pekka Pyykkö discusses the history and characteristics of gadolinium.

The lanthanides run from lanthanum to lutetium across the periodic table, and together with the chemically similar yttrium and scandium they form a family dubbed the rare-earth elements. An unspecified mixture of their oxides was isolated in 1794[1–3] by Johan Gadolin (1760–1852) from a mineral that had been discovered in Ytterby, near Stockholm, Sweden by Carl Axel Arrhenius, and described in 1788 by Geijer[4]. Gadolin cautiously stated that this oxide, or 'earth', could contain a new element. This would be a pity he said[1–3], because the elements were already "becoming far too numerous" — an interesting twist for an element that would be named after him. Gadolin's analysis was confirmed in 1797 by A. G. Ekeberg[5], and the original mineral was soon named gadolinite.

The oxide of gadolinium (symbol Gd) was discovered by repeated recrystallization by Marignac[6], who also determined its atomic weight, but it was Boisbaudran (with Marignac's approval) who suggested the name in 1880[7]. Although it is not known whether he was thinking of the mineral or the man, or both, gadolinium remains the only element with a name derived from Hebrew. Its root 'gadol' (pictured), meaning 'great', was chosen by Gadolin's grandfather as his surname and comes from a translation of Maunula, the name of the Finnish farm he lived on.

גדל

The chemical behaviour of most lanthanides is fairly similar, which explains why, in all, it took more than a century to split them into the individual elements. Despite their chemical similarities, their optical and magnetic properties are distinct. The magnetic properties of gadolinium in particular are unique, and underscore many of its applications. Element 64 is located halfway through the lanthanide 4*f* series and the trivalent Gd^{3+} ion can organize its seven 4*f* electrons in a half-filled shell with all spins parallel — a magic number, as it were. This gives Gd(III) the largest possible total spin $S = 7/2$, and a correspondingly very large spin magnetic moment. This characteristic can be used to improve permanent magnets. The 4*f* shell of lanthanides has electron binding energies in the valence range, making it possible to chemically vary the 4*f* occupation, but the compact 4*f* radial size is typical of the outermost core electrons and prevents most 4*f* electrons from directly participating in bond formation.


SCOTT CAMAZINE / ALAMY

Despite their name, the rare earths are not particularly rare; €111 per 10 g of metallic gadolinium (99.9% purity) is the going rate, though in metallurgy a much cheaper, unseparated *mischmetal* is normally used. An important current use is in medicine, as a 'contrast agent' in magnetic resonance imaging (MRI). The MRI signal comes from certain nuclear spins, such as the ubiquitous protons. That nuclear spin system, however, is heated by the radiofrequency field used for the magnetic resonance. This heating typically weakens the MRI signal. The large electronic magnetic moment of Gd(III) helps to couple the nuclear spin system to the 'lattice' and to keep it cool. This is called nuclear spin–lattice relaxation. To avoid health hazards, because Gd^{3+} is somewhat toxic, the gadolinium ion is surrounded by chelating ligands that prevent it from entering tissues. New ligands are under development to improve safety.

Both gadolinium and some of its alloys or salts play a prominent role in magnetic cooling. In this refrigeration process, a magnetic substance becomes hotter when placed under certain external magnetic field, owing to the orientation of its magnetic dipoles. Inversely when the field is removed, and the substance thermally isolated, it cools down. By varying the magnetic field, and the sample's insulation, one shuffles entropy between the material's electronic spin system and other degrees of freedom.

The conspicuous luminescence colours of certain other lanthanides are used in fluorescent lamps and in displays — both the old-style picture tubes, and the current flat screens. The compounds of element 64 itself are colourless, but they can be used to absorb UV radiation and to transfer its energy to other lanthanides that have emissions in the desired optical range. Moreover, the ^{155}Gd and ^{157}Gd nuclei have unusually large neutron absorption cross sections, which can be used in nuclear technology for reactor control rods.

Gadolin may have wished for fewer elements to exist, but gadolinium offers a rich history spanning over two centuries, intriguing characteristics, and a variety of practical applications. ☐

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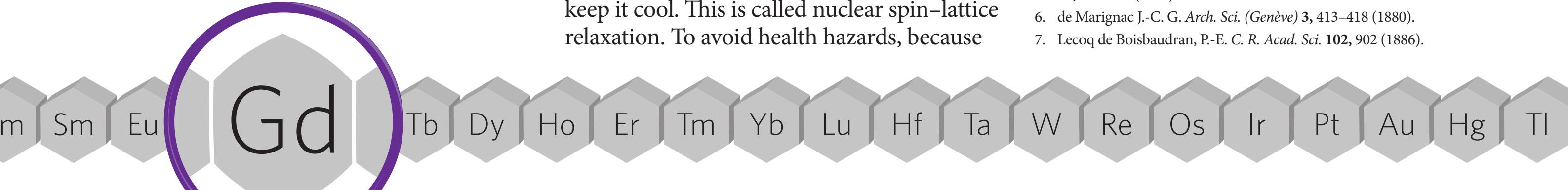

in your element

Seaborgium's complex studies

Christoph E. Düllmann reflects on the excitement, and implications, of probing the reactivity of heavy element seaborgium.

The periodic table of elements devised by Mendeleev well over a hundred years ago has become a prime tool for chemists, as well as a widely recognized symbol of chemistry — such that it is easy to forget it remains a live document. The addition of a new element every now and then stirs up much interest, in particular with regards to whether its properties conform to the table's established structure and trends.

This isn't necessarily a given, especially for heavy elements. Indeed, the many protons inside the nucleus accelerate proximal electrons to a substantial fraction of the speed of light, causing the electrons' mass to increase owing to relativistic effects, and their orbits to deviate from the hypothetical ones they would otherwise follow. This is hardly noticeable in lighter elements, but the transactinide series, with atomic numbers ≥104, makes for an ideal 'laboratory' for studying these effects.

Studies are hindered, however, by the small quantities and short lifetimes of these elements, generally single atoms existing for seconds or minutes at most. Still, elaborate automated set-ups for performing gas-chromatography volatility measurements of single atoms or molecules have enabled studies on compounds of all elements up to hassium, and recently also on copernicium and flerovium (elements 108, 112 and 114, respectively)[1]. Comparisons with analogues of lighter homologues in their respective groups allowed conclusions to be drawn about the validity of trends established in the periodic table.

Element 106 — named seaborgium (Sg) after Glenn T. Seaborg (pictured) — was discovered in 1974. The first chemical studies, of SgO_2Cl_2, showed its volatility conformed to the trend established in group 6 by MoO_2Cl_2 and WO_2Cl_2, in agreement with relativistic quantum chemical calculations. These results, together with later studies on the oxide–hydroxide system and two liquid-phase experiments, constitute our current knowledge on seaborgium's chemistry and establish it as a full member of its group.


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Despite these successes, compounds featuring transactinide atoms have remained poorly available. Atoms of transactinides are formed in fusion reactions of lighter atomic nuclei using intense high-energy ion beams and are thus often only available for study in an environment hostile to most chemical systems: a beam-induced plasma.

Our efforts to overcome this technical limitation started about 10 years ago, and have recently shown some success: seaborgium ions have been separated from the ion beam in a magnetic field[2], then collected in a gas-volume at ambient conditions, enabling the synthesis of seaborgium hexacarbonyl — the first transactinide complex in which the metal is in a reduced oxidation state. This technique was pioneered with zirconium and hafnium[3], and the focus was subsequently set on group 6 hexacarbonyl complexes.

Experiments worked marvellously with molybdenum and tungsten ions stopped in CO-containing gas[4]. We teamed up with researchers from RIKEN, Wako-shi, Japan, who had perfected seaborgium's synthesis and separation. In over two weeks of around-the-clock experimenting, our detection system registered the decay of 18 atoms of seaborgium and its decay products — a high-statistics experiment by transactinide chemists' standards. Passing the volatile Sg species over progressively colder surfaces allowed us to measure the temperature at which they immobilize — owing to physisorption, as our data show. The deduced adsorption enthalpy is similar to those of $Mo(CO)_6$ and $W(CO)_6$, corroborating our assignment[5] of the species to $Sg(CO)_6$ as also supported by theoretical work[6].

Fascinating perspectives for further studies arise: syntheses of other complexes featuring a metal–carbon bond appear feasible, paving the way towards transactinide organometallic compounds. $Sg(CO)_6$ currently represents the heaviest element carbonyl, adding to the riches of carbonyl chemistry over a hundred years after the discovery of a carbon monoxide complex[7], $Ni(CO)_4$. After the $Sg(CO)_6$ identification, a next step may include measuring the seaborgium–carbon bond strength, for which theoretical data are available[8]. Not least, carbonyl complexes of yet heavier elements appear in reach as well.

Forty years after seaborgium's discovery, twenty years after its first chemical study, a hexacarbonyl compound with seaborgium in a reduced oxidation state has been synthesized and will be scrutinized. We feel honoured to continue Glenn Seaborg's legacy by expanding transactinide chemical studies to new systems, and measuring previously inaccessible characteristics. $Sg(CO)_6$ is an exciting step on this path. ❒

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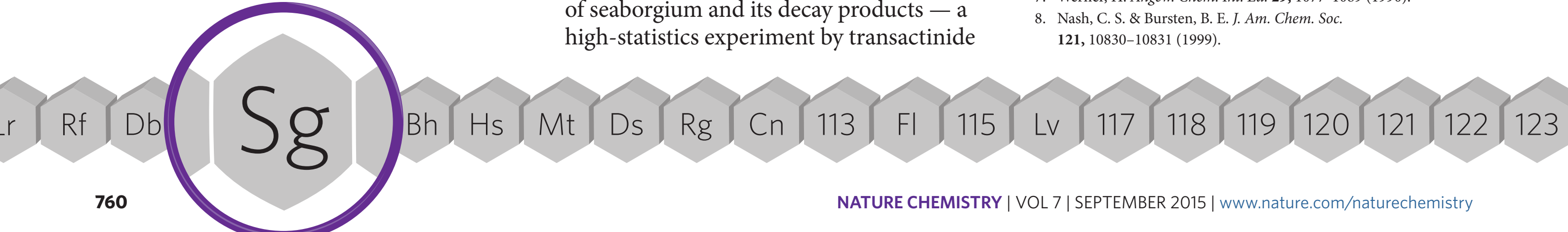

Tantalizing tantalum

Giovanni Baccolo relates tales of tantalum, an element known, and named, for its inertness, yet one that holds some surprises, such as a naturally occurring nuclear isomer.

Element 73 was first extracted from mineral samples and described in 1802 by the Swedish chemist Anders Ekeberg. He chose the name tantalum because "when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them", in a manner reminiscent of the Greek mythological king Tantalus (pictured) who couldn't eat or drink anything despite being surrounded by food and water[1].

For over six decades tantalum and its neighbour in the periodic table, niobium — discovered in 1801 by Charles Hatchett and initially named columbium — were thought to be one and the same. They share very similar chemical and physical properties, and are always found together in nature. The discoveries of columbium, tantalum, pelopium, niobium and ilmenium were all repeatedly claimed between 1801 and 1866, however, these proved to be just tantalum, niobium and mixtures of the two.

It was the French scientist Jean Charles Galissard de Marignac who first succeeded in separating tantalum from niobium, by exploiting the different solubilities of their fluorinated compounds[2]. Tantalum belongs to the refractory metals along with — perhaps unsurprisingly — niobium, as well as molybdenum, tungsten and rhenium. These elements have extremely elevated melting points (tantalum melts at 3,290 K), and notoriously high mechanical and chemical resistance.

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This inertness is what makes tantalum useful for a variety of practical purposes. Its first applications date from the beginning of the twentieth century, on the heels of new extraction and purification methods. In 1905 engineers employed by Ernst Werner von Siemens designed an incandescent light bulb based on a tantalum filament, in the first commercial attempt to replace fragile carbon filaments with a metal. Tantalum bulbs however were soon replaced by another refractory metal, tungsten, more suitable because it is less volatile and has an even higher melting point (3,695 K). Tantalum has also been used to make fountain pen nibs that were very resistant to ink, but was soon replaced with osmium- and iridium-based alloys. Modern applications of tantalum span from the production of alloys, to electronics — mobile phones and similar devices often rely on tantalum capacitors — to surgical implants, where inertness ensures that it doesn't interfere with biological tissues or processes.

The most peculiar features of element 73 involve some of its nuclear properties. Tantalum was initially believed to have only one natural isotope, ^{181}Ta, but in 1955 a second was identified[3], ^{180}Ta. Its relative abundance is estimated to be only 0.01201% of natural tantalum, making it the rarest naturally occurring isotope observed so far. The half-life of ^{180}Ta is about 8 hours, which means that it should be radioactive — so how is it possible to observe it in natural samples?

This isotope exists as ^{180m}Ta, in which the 'm' denotes a metastable state, called isomer in nuclear physics. An isomer thus lies in the excited state of an atomic nucleus, in the same manner as excited electrons do. They are typically radioactive species that decay quickly to the ground state emitting characteristic gamma rays. But sometimes they take longer times to decay. This is the case with ^{180m}Ta, which is the most stable and the only naturally occurring nuclear isomer known. Despite several attempts, its spontaneous decay hasn't been observed yet; only lower limits of half-life have been posed, in the range of 10^{12}–10^{16} years. Astrophysicists tried to shed some light on the origin of this peculiar isotope by investigating the classical nucleosynthesis pathways occurring in the stars, as well as extreme events such as supernova explosions, nuclear captures and disintegrations — but a consensus has yet to be reached. Understanding this elusive process will be an important test for nucleosynthesis models.

Another important aspect of ^{180m}Ta, and the other long-lived nuclear isomers, is that it may be possible to force their decay to the ground state, inducing the release of energy in the form of gamma ray emission. Some successful attempts have already been carried out with ^{180m}Ta, but the process is far from energetically efficient[4]. Improving this process may lead to the development of gamma ray lasers, or perhaps a new kind of nuclear battery[5].

It may be better known for its inertness and chemical and mechanical resistance, but element 73 also poses intriguing questions. ❐

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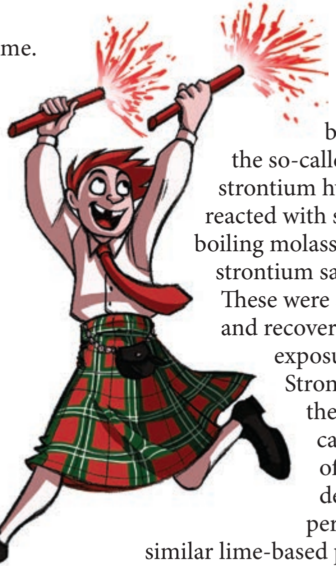
Strontium's scarlet sparkles

From sugar beets to TV screens, **François-Xavier Coudert** explores the history, applications and perils of the Scottish element, strontium

Strontium takes its name from the Scottish village of Strontian (*Sròn an t-Sìthein*), making it the only element named after a place in the United Kingdom. Adair Crawford in 1790 recognized that the ore extracted from the lead mines of Strontian, and sold as 'aerated barytes', had different chemical properties from the barium minerals known at the time. This was confirmed by other chemists, in particular Friedrich Gabriel Sulzer in 1791 and Thomas Charles Hope in 1793, who named this mineral 'strontianite' and 'strontites', respectively.

The isolation of strontium in its metallic form is credited to Sir Humphry Davy in 1808. Earlier that year, Jöns Jacob Berzelius and Magnus Martin af Pontin had performed an electrolysis of calcium oxide at a mercury electrode to produce a calcium–mercury amalgam. Learning of this result, Davy applied the new technique to four different alkaline earths and subsequently proceeded to distil the mercury off, thus isolating a small quantity of the elements that he named barium, strontium, calcium, and magnium (now known as magnesium).

Strontium is a soft silvery or yellowish metal that behaves in a similar manner to the other alkaline earth metals in group 2. Although abundant in the Earth's crust — ranking 15th at 340 ppm, very close to barium — relatively few strontium minerals are known. The most common are celestine (strontium sulfate, $SrSO_4$, named for its delicate blue color) and strontianite (strontium carbonate, $SrCO_3$). The former occurs in large sedimentary deposits, from which 300,000 tons of celestine are mined annually, mostly from China.



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The first industrial use of strontium was in the production of sugar from sugar beet in the nineteenth century. Beet molasses, a by-product of sugar production from sugar beet, contains 50% sugar by weight. This sugar was extracted by desugarization using the so-called strontian process: strontium hydroxide $Sr(OH)_2$ reacted with soluble sugars in near-boiling molasses to form poorly soluble strontium saccharate compounds. These were subsequently filtered and recovered by cooling and exposure to carbonation. Strontium hydroxide was then regenerated by calcination in the presence of steam. Nowadays, desugarization is instead performed using a similar lime-based process, or through ion-exclusion chromatography.

The second large-scale application of strontium was in colour television cathode ray tubes, accounting for up to 75% of US strontium consumption in the latter part of the twentieth century. It was used in the faceplate glass to block X-ray emissions without compromising the transparency of the tube. Strontium carbonate was added to the glass melt, where it was converted to strontium oxide. With replacement of cathode ray tubes by flat-panel displays, the largest remaining consumer of strontium compounds is the production of ferrite ceramic magnets. Strontium ferrite, $SrFe_{12}O_{19}$, is among the most common ferrite permanent magnets, used for devices such as refrigerator magnets, loudspeakers and small electric motors. Other uses of strontium in our daily lives correspond more to niche applications, including imitation diamonds (strontium titanate), glow-in-the-dark toys (europium-doped strontium aluminate), and toothpastes for sensitive teeth (strontium chloride).

One application of element 38, however, has stood the test of time: the use of its red flame, described as crimson, scarlet or carmine, depending on the author. *Chemical News* noted in 1918 that strontium's sole employment in the UK was in the manufacture of signal lights, flares and fireworks. Today, pyrotechnics still accounts for 30% of the use of primary strontium compounds, in the form of chloride, sulfate, carbonate, nitrate or oxalate. If you see purple fireworks, they also likely contain strontium salts, in combination with copper salts (which emit blue light).

In the human body strontium is absorbed in the same manner as its neighbour in group 2, calcium, and mostly deposited in the bones. This makes strontium fairly innocuous, and it has even been investigated for the prevention and treatment of bone diseases such as osteoporosis. Concurrently however this also makes its longest-lived radioactive isotope ^{90}Sr — generated by nuclear reactors and nuclear tests — dangerous as it promotes bone cancer. In controlled amounts, ^{89}Sr and ^{90}Sr have also found use in radiotherapy for the treatment of cancers that have spread to the bone.

Aside from anthropogenic applications, element 38 is also involved in a biological riddle. The Acantharea class of protozoa have skeletons made of celestine, puzzling scientists as to the evolutionary benefits behind this peculiar choice of building material. ☐

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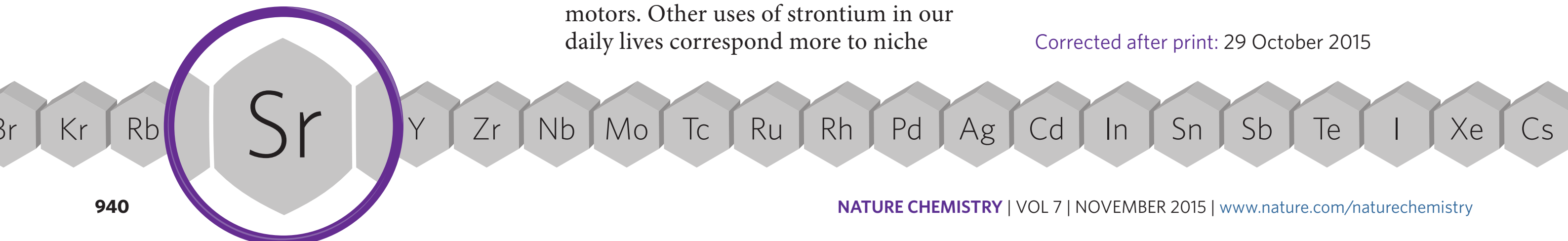


Correction

In the In Your Element article 'Strontium's scarlet sparkles' (*Nature Chem.* **7,** 940; 2015), the years in the first paragraph were incorrect. These were corrected in the online versions after print on 29 October 2015.

Rubidium round-the-clock

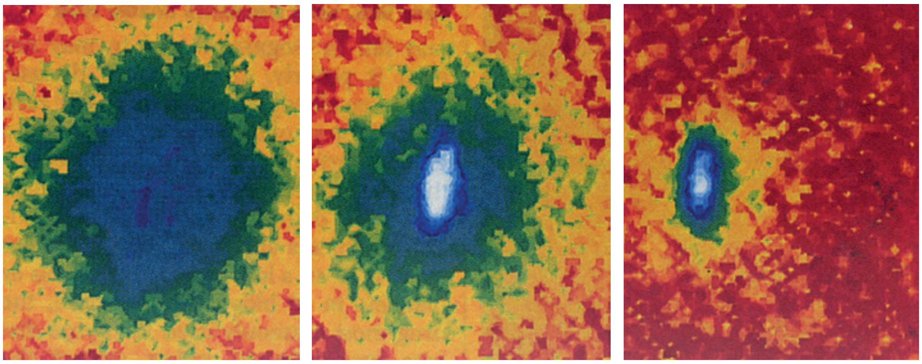
Iulia Georgescu explains why rubidium is atomic physicists' favourite chemical element.

Rubidium (Rb) was discovered in 1861 by physicist Gustav Kirchhoff — perhaps better known for his work on electrical circuits — together with chemist Robert Bunsen, in Heidelberg. Using their newly invented spectroscope to investigate the composition of a variety of samples they came across new elements: first caesium (Cs) in mineral water and then rubidium in the mineral lepidolite. Both were named after the colour of their emission lines — sky blue (*caesius*) and red (*rubidius*), respectively.

Element 37 firmly belongs to group I of the periodic table, with characteristics similar to those of the other alkali metals. A soft metal with a low melting point (39.3 °C), it reacts violently with water — even more so than sodium (typically used in high-school demonstrations) and potassium (already too dangerous for this purpose) in agreement with the increasing energy of the valence electron as one goes down the column. The hydrogen gas produced during the reaction of rubidium with water ignites in air; in fact, rubidium itself can spontaneously ignite in air.

Rubidium proved well suited to low-temperature experiments. In the 1990s cheap commercial laser diodes — such as those used in CD players — operating close to the wavelength used to laser-cool rubidium (780 nm) became readily available. The rubidium vapour required for these experiments is generated at accessible temperatures, just above that of the human body. These factors, together with rubidium's laser-cooling-friendly atomic energy level structure, made it the atom of choice for many atomic physics experiments.

In the early summer of 1995 Eric Cornell and Carl Wieman first managed to cool ^{87}Rb vapour down to 170 nK (pictured), thus observing the strange state of matter predicted to arise near absolute zero temperatures by Satyendra Nath Bose and Albert Einstein seventy years beforehand. Any number of bosons — particles obeying Bose–Einstein statistics — can occupy the same quantum energy state. When cooled close to absolute zero, bosonic atoms collectively huddle into the lowest energy state, forming a 'Bose–Einstein condensate' — a single quantum mechanical entity observable at the near-macroscopic scale. Cornell and Wieman shared the 2001 Nobel Prize in Physics with Wolfgang Ketterle, who a few months later made the first sodium Bose–Einstein condensate.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In the past twenty years, rubidium Bose–Einstein condensates have enabled amazing progress in our understanding of quantum many-body phenomena and our ability to mimic exotic physics, like radiation emitted from black holes. Ultracold atomic gases are also key to technologies such as atomic clocks or sensors (gravitational, rotational, magnetic) with excellent sensitivity that exploit quantum mechanical effects.

Discovered together spectroscopically, caesium and rubidium currently both set our standards for time. The International System of Units' definition of the second is 9,192,631,770 periods of the transition frequency between two energy levels of ^{133}Cs. For sixty years, since the first atomic clock, caesium has been the primary time and frequency standard. Rubidium clocks also make use of a hyperfine transition in the microwave region, and serve as secondary standards. However, their low cost, smaller size and greater stability make rubidium clocks ideal for many commercial applications including the Global Positioning System (GPS). Nowadays, rubidium clocks have been miniaturized to the size of a matchbox and still have uncertainties of just 10^{-12}. To put things into perspective, the current record is held by the strontium-87 (^{87}Sr) optical lattice clock at 10^{-18}, meaning that the clock should be accurate to within a second in 15 billion years.

That may be a long time on the human timescale, but not for rubidium. It only has two naturally occurring isotopes, ^{85}Rb and ^{87}Rb, the latter is radioactive with a half-life of 48.8 billion years. It decays to stable ^{87}Sr, which turns out to be a very useful process as it gives us another rubidium clock — a geological one, used in rubidium–strontium dating.

Because rubidium is reasonably abundant in the Earth's crust, to determine the age of a rock one can compare the ratios of both ^{87}Rb and its decay product ^{87}Sr to the naturally occurring ^{86}Sr. First used by Otto Hahn in the early 1940s, this rubidium–strontium dating method is very reliable for very long timescales, for instance 4.5 billion years — the age of the Earth.

I hope you now agree that rubidium rocks. ❐

IULIA GEORGESCU is a Senior Editor of *Nature Physics*.

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in your element

Rhodium roles

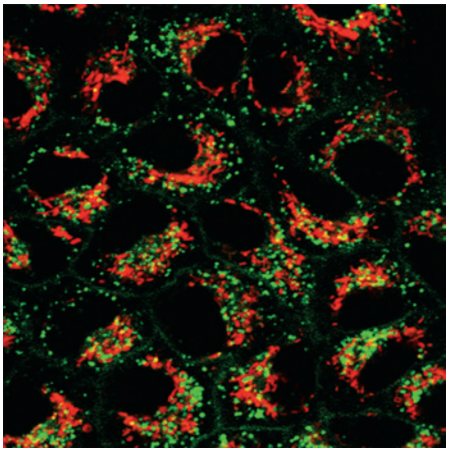
Lars Öhrström relates the various roles played by rhodium in our daily lives, ranging from car components to drugs.

Once the thin electroplated rhodium coating that makes new pieces of jewellery extra bright and shiny wears off, most of us are likely to come across rhodium mainly as a crucial component in catalytic converters for cars. In these devices, metallic particles of element 45 are embedded in the porous ceramic structure of the catalyst, and its specific role is to help break down nitrogen oxides to innocuous O_2 and N_2.

In 1988, a year before catalytic converters became compulsory for new cars in Sweden, I encountered this otherwise silver-white noble metal in a very different form: 50 grams of a purple powder, worth half a year's pay for a graduate student. This price reflected both the fact that element 45 is typically the most expensive of the platinum group metals (PGMs), as well as the difficulty of oxidizing it into a molecular compound. Rhodium's price fluctuates according to external factors, increasing for example if car sales go up or environmental legislation gets tougher. Moreover, as its production is dominated by a few countries, notably South Africa, mining strikes or local politics may also significantly affect the world market.

The purple powder was rhodium(III) chloride, the compound that incidentally also gave the element its name, from *rhodon* (Greek for rose). I used it over the next five years to make various coordination compounds, including catalysts, a main use for this metal in laboratories — new organic reactions catalysed by rhodium complexes are reported every year.

Such rhodium catalysts are also used industrially, notably for making menthol (found in many consumer products such as lip balm, cough remedies, toothpaste and aftershave), as well as L-DOPA (L-3,4-dihydroxyphenylalanine) used to treat Parkinson's disease. A noteworthy aspect of these catalysts is their enantioselectivity, which is crucial for applications, and the reason behind William S. Knowles and Ryoji Noyori sharing half of the 2001 Nobel Prize in Chemistry.



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A notable feature of coordination compounds containing rhodium in oxidation state +3 is their slow release and recapture of ligands. For example, for rhodium(III) chloride dissolved in water, ten different species may form and the interchange in the octahedral coordination environment around the rhodium centre — say between *cis*-$[RhCl_2(H_2O)_4]^+$ and *trans*-$[RhCl_2(H_2O)_4]^+$ — is very slow. So slow in fact that it may take a year or more for such a solution to reach chemical equilibrium. This is in sharp contrast to, for example, the Fe(III) analogue *cis*-$[FeCl_2(H_2O)_4]^+$ for which the corresponding *cis–trans* isomerization takes milliseconds.

There is a peculiar way to observe this: rhodium NMR spectroscopy[1]. Rhodium is one of the few elements that comes with only one isotope in nature, ^{103}Rh. This isotope has the same nuclear spin (½) as that of protons, and is thus excellent for NMR studies. Its poor sensitivity means that impractical amount of sample and time are often required to get a signal, which has hampered widespread use, yet it is not without proponents as Rh-coupling with other nuclei can allow valuable information to be extracted by 2D NMR spectroscopy techniques.

Several artificial radioactive isotopes are also known, including meta-stable nuclear isomers. One of those, ^{103m}Rh — produced by decay from ^{103}Ru — has been investigated as a cancer therapy agent[2]. In light of its short half-life (59 min) and the slow ligand exchange rates for Rh(III) complexes, however, the synthesis and use of ^{103m}Rh compounds require careful planning.

A variety of complexes based on the Rh_2^{4+} core have also shown promise as anticancer compounds. Recently, in an exciting development, a dirhodium(II) compound featuring a ligand endowed with an organic fluorophore has been shown to be taken up by cancer cells in a different manner than the free ligand[3] (the dirhodium compound shows a scattered distribution in the cytoplasm, pictured). This points to new possibilities for these kinds of M–M bonded compounds and may encourage big pharmaceutical companies to step outside their organic comfort zone, just as they did 40 years ago with the development of cisplatin-type drugs based on rhodium's diagonal neighbour in the periodic table, platinum.

Although it may be in the shadow of its better-known PGM cousins, palladium and platinum, on the road of chemical applications, rhodium is gaining ground and shows no signs of slowing down. ❐

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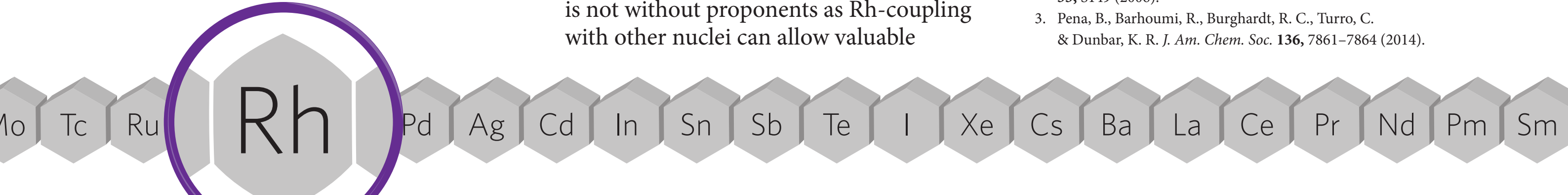


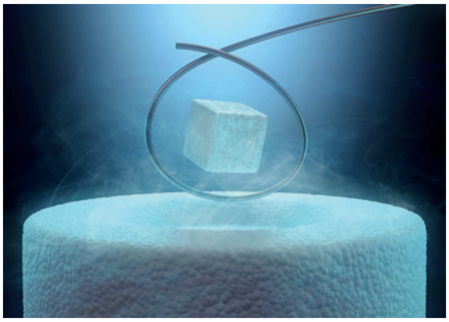
Yttrium from Ytterby

Peter Dinér describes the journey of yttrium from its discovery in a remote mine to high-temperature superconductors and light-emitting diodes.

If you find yourself in Stockholm with some time to spare for a piece of science history, I recommend making a short visit to the village of Ytterby on the nearby island Resarö. It is still possible to visit the abandoned and refilled mine that was the birthplace of four rare-earth elements, whose names all derive from Ytterby: yttrium, erbium, terbium and ytterbium.

The village's scientific story started in 1789 in a quarry, which at the time produced quartz for ironworks and feldspar for the porcelain industry, when Carl Axel Arrhenius — a young lieutenant in the Swedish army with a keen interest in minerals acquired during his time at the Royal Mint's laboratory — discovered a black piece of stone among the leftover gangue. The peculiar black mineral, first presumed to be tungsten, was shipped off to Arrhenius's friend Johan Gadolin, a chemistry professor at the Royal Academy of Turku in Finland (known in latin as *Regia academia aboensis*).

Gadolin identified that the mineral 'ytterbite' (which would later be renamed gadolinite in his honour) contained the oxide of a new rare-earth element[1]. The Swedish chemist Anders Gustaf Ekeberg subsequently confirmed these findings and named the oxide yttria[2]. Elemental yttrium, in an impure form, was first isolated in 1828 by Friedrich Wöhler by passing chlorine gas over the gadolinite mineral to form anhydrous yttrium chloride (YCl_3), which was in turn reduced to yttrium using potassium[3]. In 1843, Carl Gustaf Mosander discovered that yttria was in fact a mixture of a number of metal oxides, which he separated into three parts: yttria (containing yttrium oxide, Y_2O_3), erbia, and terbia[4]. In the end, the black mineral found by Arrhenius was shown to contain oxides of eight rare-earth metals — erbium, terbium, ytterbium, scandium, thulium, holmium, dysprosium, and lutetium. In the 1920s, element 39 saw a change in its symbol, when Y replaced the older Yt in the periodic table.



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Along with above-neighbour scandium in group 3 of the periodic table, yttrium is chemically similar to the lanthanides and together they form the rare-earth elements. This means that, in the same manner as the lanthanides, yttrium is produced by separation from a mixture of oxides in ores such as monazite sand and bastnäsite. It can then be purified by the preparation of yttrium fluoride, and its subsequent reduction with calcium metal.

Yttrium has a silver-metallic luster and is relatively stable in air. Again, like the lanthanides, it usually exists as a trivalent ion, Y^{3+}, and is abundant as yttrium oxide (Y_2O_3). It has many isotopes, with mass numbers ranging from 79 to 103, but the naturally occurring element consists of only one stable isotope, ^{89}Y.

Organic chemists are very familiar with trivalent yttrium complexes, which are used as Lewis acid catalysts for a wide range of reactions. For example, a recent highly enantioselective ring-opening reaction of aziridines was catalysed by a bimetallic yttrium complex[5].

Element 39 also serves in various optical devices, through yttrium aluminate garnets (YAGs). In these materials, a small portion of the yttrium atoms have been replaced by lanthanides, introducing lattice strains that change the optical properties of the material. For example, cerium-doped YAGs (Ce:YAGs) are used as phosphors in combination with blue light emitting diodes (LEDs). Blue radiation from the LED 'bleeding' through a Ce:YAG phosphor is down-converted to a yellow emission, which in turns combines with the LED's blue radiation to produce white daylight-like light. Other devices include the so-called Nd:YAG lasers that are commonly used both in medical and industrial applications.

Yet perhaps the most important impact of yttrium has been its role in the discovery of high temperature superconductors — those materials with no electrical resistance. In 1986, Bednorz and Müller discovered superconductivity in a lanthanum-based cuprate perovskite material (La_2CuO_3) at a temperature of 35 K, for which they were awarded the Nobel Prize in Physics the following year[6]. Also in 1987, physicists in the United States found that yttrium-based $Y_{1.2}Ba_{0.8}CuO_4$ (often referred to as YBCO) was superconducting at 93 K — a temperature increase of practical importance as this is above the boiling point of liquid nitrogen (77 K), which makes it a practically feasible cooling temperature[7]. The discovery invigorated research efforts in the quest for superconductivity at even higher temperatures — ideally, above room temperature, though this has remained elusive.

A transition metal close to the lanthanides, element 39 has found its way from a now-abandoned mine to a variety of high-tech devices. ❒

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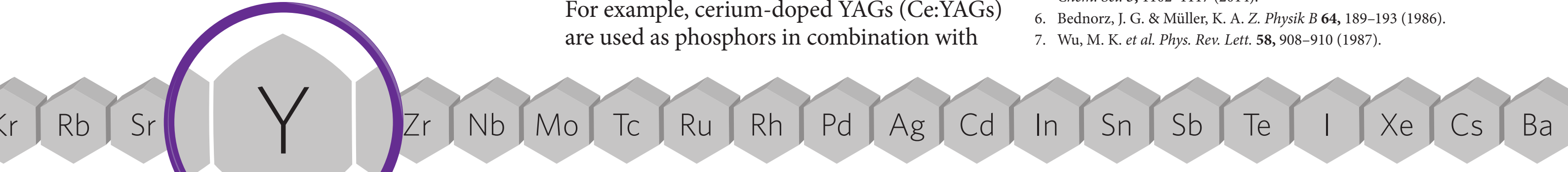


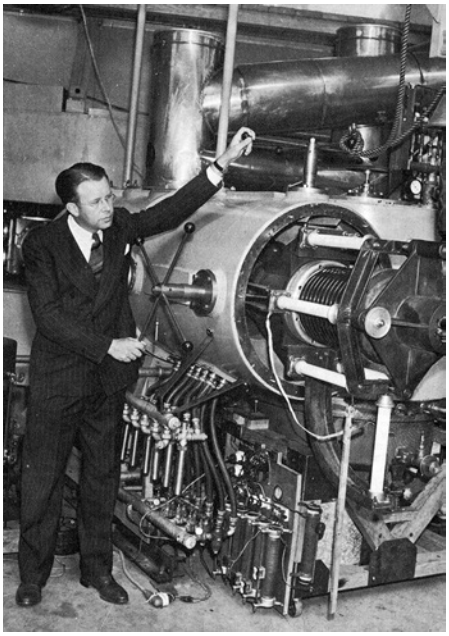
Lawrencium's place at the table

Yuichiro Nagame ponders on the steps it took to make lawrencium, and its location in the periodic table.

The discovery — or, rather, the synthesis — of lawrencium spanned several years and several experiments from two research teams, in Berkeley, USA, and in Dubna, Russia[1]. In 1961, the US-based team first reported the synthesis of an isotope of element 103. Mixed californium isotope targets ^{249,250,251,252}Cf were bombarded with boron beams; the reaction products were caught by a metalized Mylar tape and moved past a series of α-particle detectors. A new α-emitting nuclide with an energy of 8.6 MeV and a half-life of approximately 8 s was assigned to the isotope ^{257}Lr.

Subsequent identification of element 103 — though one that conflicted with the mass assignment of the Berkeley team — came from Dubna in 1965, from bombarding a ^{243}Am target with a beam of ^{18}O ions. After sustained efforts on both sides, conclusive identification of isotopes with mass numbers 255 through 260 finally came from Berkeley in 1971, from bombardments of ^{248}Cm with ^{14}N and ^{15}N ions, and ^{249}Cf with ^{10}B and ^{11}B ions. These results also confirmed most of the previous reports, apart from the identification of the first isotope created, which was in fact ^{258}Lr.

The recognition of the new element also occurred in several steps. It was the Berkeley team who suggested the name lawrencium, with the symbol Lw, in honour of Ernest O. Lawrence, inventor of the cyclotron particle accelerator (pictured). The International Union of Pure and Applied Chemistry (IUPAC) approved the name in 1971, though changed the symbol to Lr. In 1992, however, a Transfermium Working Group set up by IUPAC and IUPAP (International Union of Pure and Applied Physics) re-evaluated all the reported data and recommended that both the Berkeley and the Dubna teams should share credit for the discovery of element 103 (ref. 2), leading to their official recognition as co-discoverers in 1997. The name, by then commonly accepted, remained unchanged.



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At present, twelve isotopes are known with mass numbers 252–262 and 266 — the longest-lived one with a half-life of 11 h — as well as two metastable nuclear isomers with mass numbers 253 and 255.

Chemical studies of heavy elements with atomic numbers $Z \geq 100$ are extremely difficult because the atoms exhibit short half-lives and must be produced at accelerators, in quantities of a few atoms, or often even one atom, at a time. Thus experimental procedures must be repeated hundreds or thousands of times to give statistically significant results. The first chemical characterization came with ^{256}Lr as early as 1970, through a fast solvent extraction technique[1]. Over 200 individual experiments, overall involving approximately 1,500 lawrencium atoms, showed that it exhibits a stable +3 oxidation state in solution, as expected for an actinide. The ionic radius of Lr^{3+} was first evaluated in 1988 through cation-exchange chromatography with the longer-lived isotope ^{260}Lr, and its accuracy was later improved to 0.0881 ± 0.0001 nm.

According to the actinide concept formulated by Seaborg, which placed the 5*f* elements ($Z = 89$–103) in the periodic table as a new transition series directly below the lanthanides, lawrencium is the last of the actinides and sits directly under lutetium. Yet despite — or owing to — recent advances in understanding lawrencium and lutetium, a debate[3] has emerged over their place in the table: is it in the *f*-block, *d*-block or *p*-block?

By analogy with lutetium, which has an electronic structure of $[\mathrm{Xe}]4f^{14}6s^{2}5d^{1}$, the electronic configuration of lawrencium would be expected to be $[\mathrm{Rn}]5f^{14}7s^{2}6d^{1}$. These configurations may place both elements below scandium and yttrium in the *d*-block — a move supported by some chemical similarities between the four elements. Because of relativistic effects, however, the $7p_{1/2}$ orbital of lawrencium is expected to be stabilized below the 6*d* orbital, giving instead a revised configuration of $[\mathrm{Rn}]5f^{14}7s^{2}7p_{1/2}^{1}$, which suggests it would also not be out of place in the *p*-block.

Recently, in our group, the first ionization energy of lawrencium was measured using an efficient surface ion-source and a single-atom detection system coupled to a mass separator[4]. A surprisingly low energy of 4.96 eV — lower than that of sodium — was found to be required to remove one electron from a neutral atom. This makes element 103 the easiest actinide to ionize, and is in excellent agreement with the predicted $[\mathrm{Rn}]5f^{14}7s^{2}7p_{1/2}^{1}$ configuration.

Nevertheless, these measurements can be taken to support lawrencium's place as an *f*-block actinide, a *d*-block transition metal or a *p* element, such that they have not allowed the question of its location to be unambiguously settled, and lawrencium continues to create controversies. ❐

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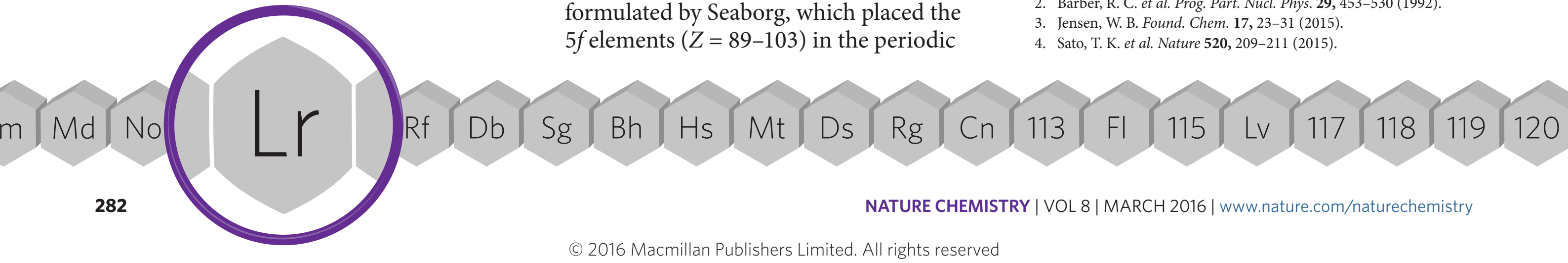

Iridium's impact

David Payne relates iridium's role in two very different ages.

The story of iridium is both modern and prehistoric. It was discovered along with osmium in 1803 by the British chemist Smithson Tennant, born in 1761 in Selby, Yorkshire. Tennant studied medicine but after graduating found it unsuitable for his temperament, and focused on chemistry instead. In 1785, despite not having yet published any scientific papers, he was elected a Fellow of the Royal Society at the young age of 23. Although he published few papers during his career, they were of great significance — he demonstrated for example that diamond consisted solely of carbon[1].

Tennant discovered elements 76 and 77, osmium and iridium respectively, by collecting insoluble black impurities derived from the treatment of platinum ore with *aqua regia*. He treated them with caustic soda before carrying out an extraction step with hydrochloric acid, which was repeated a number of times. From this he obtained red crystals, most probably $Na_2[IrCl_6]\cdot nH_2O$, that when heated gave a white powder, which Tennant stated was "not capable of being melted, by any degree of heat I could apply"[2]. He named the element iridium after Iris, messenger of the gods in Greek mythology and the personification of the rainbow, owing to, in his own words, the "striking variety of colours it gives" when the metal is dissolved in hydrochloric acid[2,3].

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Insulating states of iridium oxides are predicted to display exotic physics.

The physical properties of iridium were apparent from the moment of its discovery with a very high melting point (2,447 °C), hardness (1,760 MPa) and density (22.56 g cm^{-3}) — over twice that of lead and only just beaten by osmium. It is one of the least abundant elements in the Earth's crust — about forty times less abundant than gold. It is thought to have sunk to the Earth's core during the formation of the planet, owing to its siderophilic (iron-loving) nature. Only three tonnes are produced annually, mainly as a by-product of the electrorefining process of copper and nickel, therefore making iridium an expensive commodity.

Despite its rarity, iridium has found uses in technology — albeit limited ones. Its high resistance to corrosion, including under high temperatures, makes it a desirable constituent in spark plugs and engine parts, for example, in aviation applications. Iridium is also commonly found in homogenous catalysis, with organoiridium compounds finding use in the carbonylation of methanol to acetic acid. Vaska's complex, $IrCl(CO)[P(C_6H_5)_3]_2$, used in oxidative addition reactions, has the unusual property of being able to reversibly bind diatomic oxygen.

The oxides of iridium have also attracted great interest in the last 10–15 years. As a heavy transition metal with partially filled 5*d* orbitals, the oxides would be expected to display metallic conductivity, yet relativistic effects (spin–orbit coupling to be precise) on the electronic structure, drive a number of the oxides into an insulating state. It is these insulators that have been predicted to display exotic magnetic and electronic physics[4].

Recently element 77 had also made the news[5] in chemistry through the isolated compound $[IrO_4]^+$, which features iridium in the highest oxidation state observed so far, +9. This makes iridium the element that displays the widest range of oxidation states (from −3 to +9).

Its modern developments are counterbalanced by the (literal) impact of iridium in the much older history of our planet: one of the great global catastrophic events. Sixty five million years ago, the Cretaceous–Paleogene (K–Pg) extinction event occurred, and marked the loss of 70% of the plant and animal species on Earth including all non-avian dinosaurs. The geological record is marked by the K–Pg boundary, a thin layer of sediment, which was found to contain very high levels of iridium — much higher than the natural abundance in the Earth's crust. Asteroids are notably rich in iridium, and Luis Alvarez and colleagues[6] postulated that the K–Pg extinction was caused by an asteroid impact; subsequently a suitably sized crater was discovered in the Yucatán Peninsula, Mexico. The theory that the extinction of the dinosaurs was caused by an iridium-rich asteroid strike is further backed up by the fact that no dinosaur fossils are ever found above the K–Pg boundary. A significant amount of iridium present in the Earth's crust today came from this asteroid strike.

Element 77, which participated in the end of one age, finds applications and still holds surprises in the modern age. ☐

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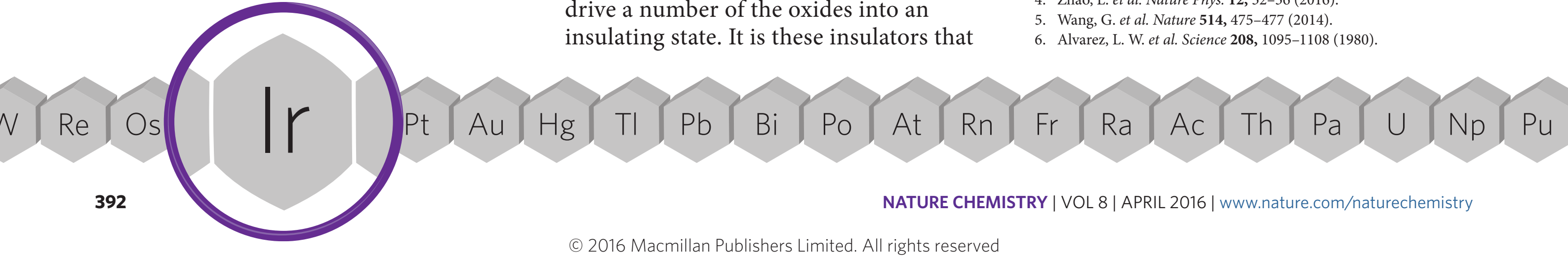


Curious curium

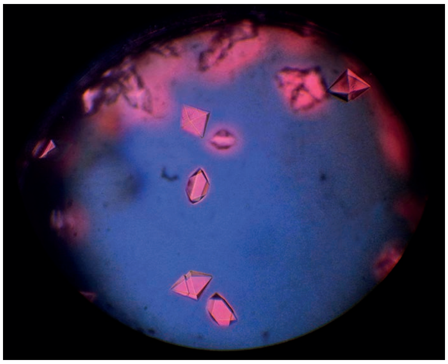
From secretive beginnings to serving in missions on Mars, **Rebecca J. Abergel** and **Eric Ansoborlo** take a look at the glowing mark curium has left on contemporary science and technology.

Although perhaps not as renowned as its actinide siblings plutonium and uranium, the fourth transuranic element — named in honour of Pierre and Marie Curie — has a story that is intertwined with that of the twentieth century.

The first isotope of element 96, ^{242}Cm, was prepared in 1944 by Seaborg, James, and Ghiorso through bombardment of ^{239}Pu with helium nuclei. This finding was quickly followed by that of element 95 (americium) but the news of both discoveries were kept under wraps during the war and only announced by Seaborg himself on 11 November 1945, Armistice Day, in a somewhat impromptu manner on the 'Quiz Kids' American radio program.

Today curium is mostly produced by irradiation of uranium and/or plutonium oxides with neutrons in nuclear reactors: about 20 g of curium can be produced from 1 ton of spent nuclear fuel. We now know over twenty isotopes of curium with mass numbers ranging from 232 to 252, all of which are radioactive and primarily α-particle emitters, with ^{242}Cm and ^{244}Cm (respective half-lives of 163 days and 18.1 years) accounting for 90% of those produced in the nuclear fuel cycle.

Because of their high specific activities (10^{12} to 10^{15} Bq g^{-1}), ^{242}Cm and ^{244}Cm were investigated as heat sources for power generation in spacecraft programmes, but abandoned as costs and shielding requirements proved prohibitive. ^{244}Cm still went on to be sent to space, as a source of α-particles in alpha particle X-ray spectrometers for analysis of rocks and soil on Mars. ^{242}Cm served to produce the more stable ^{238}Pu for thermoelectric generation in devices including cardiac pacemakers. Although less common, isotopes ^{245}Cm and ^{248}Cm recently made headlines as targets in the synthesis of one of the newest elements of the periodic table, livermorium.



DAHLIA AN, 2016

Despite these uses, the high activity of curium isotopes has mainly been considered an issue because it significantly contributes to the radiotoxicity of nuclear waste. Most curium research has therefore focused on characterizing its physico-chemical properties in the quest for actinide separation, recovery, and recycling processes.

In most compounds and solutions curium is present in the trivalent oxidation state +3, the stability of which is attributed to the half-filled $5f^7$ electron shell configuration — although a few +4 and +6 compounds are also known, such as CmO_2 and CmO_3. The similarities between curium and the other lanthanides, which stem from the predominance of this +3 state, make their separation a challenging task. In fact, elements 95 and 96 were so difficult to separate from each other, and from the rare-earth metals, that the Seaborg group nicknamed them 'pandemonium' (demons or hell in Greek) and 'delirium' (madness in Latin).

Setting curium aside from other actinides is its inherent strong fluorescence (attributed to relaxation through *f*–*f* electronic transitions), which gives rise to bright orange luminescence[1]. Because the energy and intensity of curium emission depend on the coordination of the metal ion, time-resolved laser-induced spectroscopy has been used extensively to characterize curium compounds. The high sensitivity of this technique is important for the detection and analysis of different species of curium in environmental and biological media[2], especially relevant to current issues involving waste storage, remediation and potential transport in terrestrial and freshwater ecosystems. As hard Lewis acids, curium ions form strong hydrolysis complexes in neutral to basic solutions and very stable compounds with hard bases such as oxygen or fluoride donors. Sorption studies of Cm^{3+} at the hydrated Al_2O_3 surface using an $Al_{31}O_{60}H_{21}$ model cluster have evidenced bonding with both ionic and covalent character[3].

Even on a small scale, accidental release of curium into the environment would be disastrous because it is extremely hazardous to humans, and is in particular strongly retained by the liver and skeleton. The high radioactivity of its isotopes would result predominantly in radiation-induced injury rather than chemical toxicity: the lethal ^{244}Cm dose for a 70 kg human is only ~250 MBq, or ~80 µg. Fear of such an event has sparked the use and development of hard oxygen-donor, high-affinity ligands that may serve as sequestering agents[4].

Its radioactive properties and its ability to form fluorescent complexes have inspired much curiosity about curium, and will no doubt continue to do so, perhaps in particular towards curium remediation and decontamination strategies. ❐

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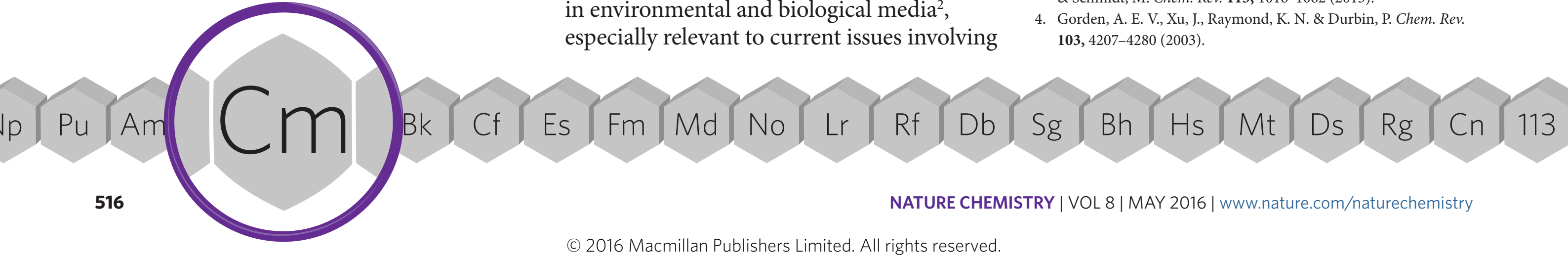


in your element

Probing bohrium

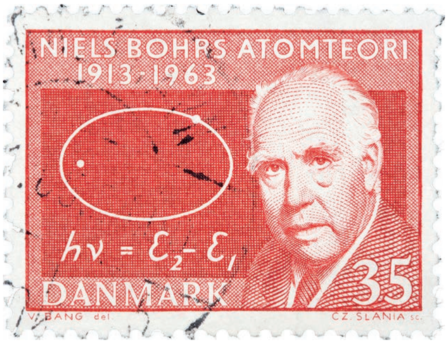
Bohrium behaves just as a group 7 element should — but this is in fact surprising, **Philip Wilk** explains.

The superheavy element bohrium was first identified in 1981 at the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany[1] and was named after one of the founders of modern atomic and nuclear physics, Niels Bohr. Simply placing bohrium in group 7 of the periodic table would suggest a chemical behaviour similar to its above neighbour rhenium — that is, if periodic trends were to continue at the extreme end of the table. However it is not obvious that they should and, in fact, theory suggests that they must not.

The now ubiquitous periodic table as proposed by Dmitri Mendeleev in 1869 was arranged by increasing atomic weight, this original form was expanded to include the noble gases and the lanthanides. It was then modified in 1913 by Henry Moseley to arrange the elements by their X-ray energy (proportional to the square of the atomic number), which solved the vexing problems of a few elements appearing out of sync with their chemical properties. Tellurium and iodine, for example, swapped position, thus falling into place with the groups they were expected to belong to.

The next — and so far final — change to the table was made in 1944 when Glenn Seaborg postulated the existence of the actinide series analogous to the lanthanide series[2] instead of a uranium-like group, which was the prevailing wisdom of the time. By this date, the basic chemistries of neptunium and plutonium were fairly well understood, and the initial chemical experiments on as-yet-unnamed elements 95 and 96 were being carried out. Seaborg interpreted the existing evidence as indicating decidedly non-transition-metal-like behaviour, which pointed toward the filling of the 5*f* orbitals instead of the 6*d* ones.

With the end of the actinide series comes a transition metal series characterized by filling these previously discarded 6*d* orbitals. The behaviour of these 'superheavies' is expected to be greatly influenced by relativistic effects, due to the tight binding of the inner electrons that have velocities not far-removed from the speed of light. These effects should have such a profound effect on chemical bonding that traditional extrapolation of chemical properties down and across the periodic table will be misleading at some point. Chemical studies on the heaviest members of the table are therefore important, to test these theoretical predictions and determine the influence of the relativistic effects. Such investigations have shown that the chemical behaviour of dubnium (element 105), for example, does not rigorously follow trends down the fifth group.



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Those chemical studies at the extreme end of the periodic table are challenging to perform, due to the low production rate of these elements. To reach the superheavy elements, heavy elements are bombarded with lighter ones, resulting in (on rare occasions) the complete fusion of target and projectile nuclei with production rates of an atom a day, or less.

Starting in the late 1990s, Robert Eichler, Heinz Gäggler, and a host of international collaborators set upon the task of elucidating the chemistry of bohrium and other superheavy elements. The only chemical or physicochemical method that has the sufficient speed and efficiency to achieve a chemical determination on these ultra-rare elements is gas chromatography[3]. Over the course of many years and a few different device iterations, the researchers constructed and tested a purpose-built gas-phase chromatographic separator at the Paul Scherrer Institute in Switzerland.

During seminal investigations in 1999 and 2000, five atoms of ^{267}Bh were identified by observing their distinctive pattern of decay and chemically analysed[4]. Although reaction parameters were selected that favoured the longest-lived isotope, this isotope still decayed with a half-life of only ~17 s. Over two dozen scientists were involved in this scientific marathon to perform a volatility analysis on five individual atoms of bohrium. The volatility was measured as adsorption enthalpy of the oxychloride, and ultimately determined that bohrium does in fact form an oxychloride — like the other group-7 elements technetium and rhenium. These experiments further showed that the bohrium oxychloride is less volatile than rhenium oxychloride, which is in turn less volatile than its technetium analogue.

What is rather surprising is that this result is thoroughly in line with predictions based purely on bohrium's position at the bottom of group 7 in the periodic table — despite the expected breakdown of periodic trends as the relativistic effects dominate the chemical behaviour of the heaviest of elements, supported by the peculiar behaviour of other transactinide elements, such as the previously mentioned dubnium. ❐

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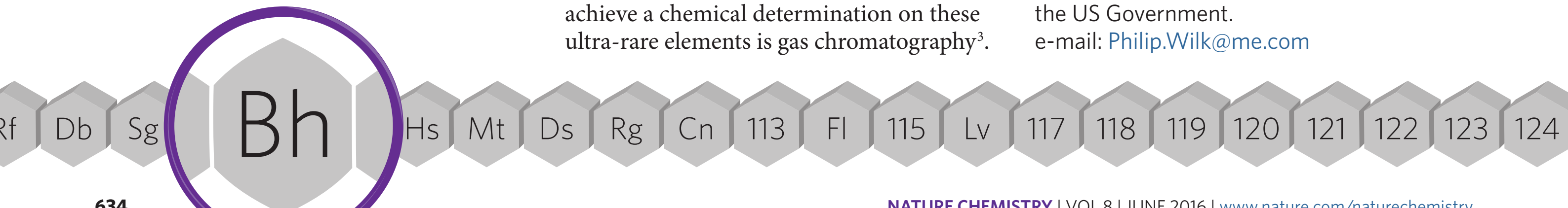


in your element

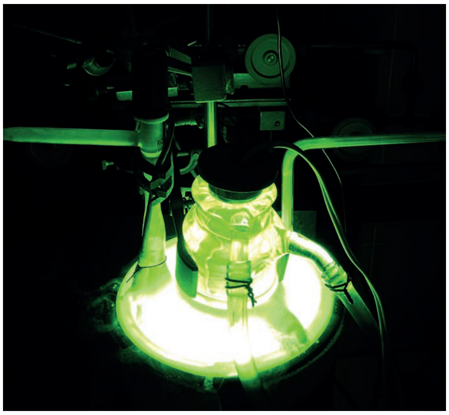
The world of krypton revisited

Matic Lozinšek and **Gary J. Schrobilgen** consider krypton — namesake of Superman's home planet — its superoxidant compounds, and their roles in coaxing elements into their highest oxidation states.

Element 36 takes its name from the Greek word, *kryptos* meaning hidden. Like all other members of group 18 (the noble gases), it is colourless, odourless, and occurs in only minute amounts in the Earth's atmosphere (1.14 ppm in dry air). It was Sir William Ramsay who, following the 1894 discovery of argon with Lord Rayleigh, suggested that a new family of elements would now need to be accommodated within the periodic table. In 1898 Ramsay, together with Morris Travers, went on to discover krypton, and two weeks later neon and xenon in residues remaining after evaporating nearly all components of liquid air.

Krypton gas is commercially produced by fractional distillation of liquefied air. Its only other notable source is uranium fission from nuclear reactors. It produces ^{85}Kr (fission yield ~0.3%), a radioisotope with a half-life of 10.8 years, which decays into non-radioactive ^{85}Rb, and which has been used to detect clandestine military-based nuclear activities.

For a time (1960–1983), the metre was defined as 1,650,763.73 wavelengths of the red-orange (605 nm) emission line of ^{86}Kr. Element 36 serves in high-performance incandescent light bulbs to retard the evaporation of the tungsten filament, improving efficiency and enhancing the brightness and lifetime of the bulb — although these are now being superseded by LED technology. The krypton–fluoride laser, a type of excimer or exciplex (excited complex) laser, is widely employed in photolithography, which has enabled further miniaturization of semiconductor devices and an increase in their densities on silicon chips. In addition to its lighter noble-gas neighbour argon, krypton may also be found in homes where it serves as a high-efficiency thermal insulator in double- or triple-pane glass windows. Liquid krypton electromagnetic calorimeters employed in particle physics research hold up to ~30 tonnes of krypton and are the largest known concentrations of this rare gas.



MATIC LOZINŠEK

Synthesis of KrF_2 by UV-irradiation of liquid-N_2-cooled solid Kr and liquid F_2 with a Hg lamp.

Krypton is the lightest noble gas to form compounds that are isolable in macroscopic amounts. The synthesis and isolation of the first krypton compound, KrF_2, was reported in 1963 shortly after the syntheses of the first xenon compounds in 1962 — 65 years after the discovery of these noble gases[1,2] — although unfortunately at the time it was erroneously described as KrF_4 instead[1]. Krypton difluoride has so far remained the only isolated binary krypton compound. Unlike xenon compounds, which have been characterized for xenon in the +½, +2, +4, +6, and +8 oxidation states, krypton chemistry is limited to the +2 oxidation state and all known compounds have been derived from KrF_2 (ref. 3).

Owing to its thermodynamic instability, KrF_2 is a better source of $F^•$ radicals and a much stronger oxidizer than elemental fluorine, F_2. Its synthesis in gram quantities is challenging and only a few low-temperature methods[3] based on the generation of $F^•$ radicals are in use, such as hot wire, electric glow discharge, and UV photolysis (pictured) methods. Derivatives of KrF_2 are often prepared by utilizing its fluoride-ion donor abilities, which in reaction with strong Lewis acids such as SbF_5 or AsF_5, forms salts of the KrF^+ and $Kr_2F_3^+$ cations[4]. With weak fluoride acceptors, KrF_2 forms fluoride-bridged adducts where the KrF_2 ligand coordinates through fluorine to either metal or non-metal centres, for example MOF_4 (M = Cr, Mo, W) and $BrOF_2^+$. The Lewis acidity of the KrF^+ cation has been exploited for the synthesis of $[HCNKrF]^+[AsF_6]^-$, which features the first example of a krypton–nitrogen bond[5]. Krypton is, however, rather selective in its choice of bonding partners and will only bond under the right conditions to the most electronegative atoms — fluorine, oxygen, and nitrogen — with only one example of a Kr–O bond known thus far, in $Kr(OTeF_5)_2$.

The extreme oxidizing abilities of KrF_2 and KrF^+ have been exploited for the syntheses of otherwise hard-to-attain high-valent compounds containing Ag(III), Ni(IV), Au(V), and exotic species such as $Tc^{VII}OF_5$, $Os^{VIII}O_2F_4$, $Cl^{VII}F_6^+$, and $Br^{VII}F_6^+$. These applications demonstrate that the original krypton compound, KrF_2, is not simply a chemical curiosity in the scientific cabinet of wonders but also a part of the chemist's toolbox.

In 1938, the name of this element inspired the naming of Krypton, Superman's birth planet, as well as the powerful material originating from this planet called kryptonite. The analogy between the 'superoxidants' KrF_2, KrF^+, and $Kr_2F_3^+$, which rob other strong oxidant species of their electrons, and kryptonite, which robs Superman of his powers, is, of course, pure coincidence. ❐

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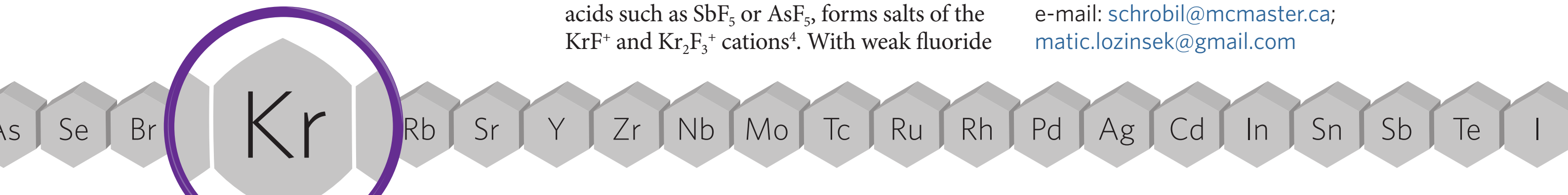

Salute to samarium

Stanislav Strekopytov relates the history of rare-earth element samarium, from its geological origins to its geochronological uses.

Many years ago while studying for a degree in mineralogy, I was privileged to visit the Russian Ilmen Mountains, host to two minerals from which several rare-earth elements were discovered — monazite ((Ce, La, Nd, Th)PO$_4$), and another mineral that was first described in 1839 by the German mineralogist Gustav Rose. He found uranium and tantalum in its composition and thus proposed the name uranotantalite. Gustav's chemist brother Heinrich Rose conducted his own analysis a few years later and found that in fact it contained mostly niobium — an element that was initially named columbium, but that Heinrich 'rediscovered' in 1844 and coined a name for.

To avoid a mismatch between name and composition, Heinrich renamed the mineral 'samarskite', after Colonel Samarsky-Bykhovets, who had provided him with specimens[1]. Whilst at least two other people had provided samples, those from Samarsky were of superior quality — though I do wonder whether it was actually his high status as chief of Russian Mining Engineering Corps that ultimately determined the choice of name.

Samarskite, found in large quantities in North America in 1878, became the raw material of choice for isolating new rare-earth elements. Lecoq de Boisbaudran isolated a new metal oxide in 1879, and proposed the name samarium, deriving it from the same root as that of the mineral[2]. A year later an oxide of yet another element (later named gadolinium) was separated by Galissard de Marignac, and in 1896 Demarçay found that the samarium oxide prepared by Lecoq de Boisbaudran contained substantial amount of 'radical Σ', now known as europium.

In 1900, the French pharmaceutical company Chenal, Douilhet & Co. presented a unique collection of rare-earth compounds at the Paris *Exposition Universelle*. These had been prepared from monazite by Leon Séquard through fractional crystallization — a method developed by Demarçay based on the differences in the solubility of double magnesium nitrates[3]. Only cerium and yttrium had a commercial use at the time, but the display at the *Exposition* still attracted much interest and represented a great achievement for the French chemical industry. These salts — the purest rare-earth compounds available in those days — were used in a number of chemical studies. However, the authors of *A Treatise on Chemistry* claimed that samarium compounds were only obtained in pure form in 1904 by Urbain and Lacombe[4]. I was fortunate enough to obtain a sample of samarium oxide produced by Chenal, Douilhet & Co. (pictured) and, to settle the argument myself, analysed it by inductively coupled plasma mass spectrometry. It proved to be 97.6% pure with respect to other rare-earth elements — with the main admixtures being Gd (1.9%), Eu (0.4%) and a little Nd (0.08%).

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An important use of rare-earth elements is in high-strength magnets. In the 1970s and 1980s, element 62 was particularly important because of its use in samarium–cobalt permanent magnets (SmCo$_5$ and Sm$_2$Co$_{17}$). At that time, the production of these magnets was limited by the availability of Sm produced from bastnäsite ((Ce, La)CO$_3$F) and monazite. Since 1985, the high raw materials cost of SmCo magnets lead to their rapid replacement by $Nd_2Fe_{14}B$ magnets. However, the former are much more resistant to demagnetization at higher temperatures and to corrosion — as a result they are still critical in the aircraft industry and in military applications.

Samarium also serves in nuclear reactor control rods (since ^{149}Sm is a strong absorber of neutrons) and in organic synthesis, as samarium diiodide, a very common reducing and coupling agent. For example, SmI$_2$ is used in three separate ways to synthesize paclitaxel (Taxol), a drug used to treat several forms of cancer[5]. In another medical setting, a radioactive ^{153}Sm ethylene diamine tetramethylene phosphonate (Quadramet) is used to treat pain when cancer has spread to the bone[6]. The α-decay of ^{147}Sm to ^{143}Nd with a half-life of 1.06×10^{11} years is used to determine the dates and origin of rocks, be it terrestrial or extra-terrestrial. Since both are isotopes of rare-earth elements, the samarium–neodymium geochronometer is barely affected by sedimentary and metamorphic processes, which means it can be used to date rocks that are not suitable for dating by the rubidium–strontium or other methods[7].

Little could the colonel have imagined that his namesake mineral would give its name to an element that is now used for such diverse purposes. ❐

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in your element

Uuh? No. It's livermorium!

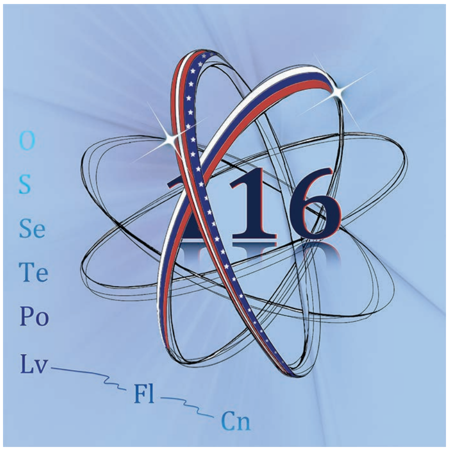
Alpha decay into flerovium? It must be Lv, says **Kat Day**, as she tells us how little we know about element 116.

At the end of last year, the International Union of Pure and Applied Chemistry (IUPAC) announced the verification of the discoveries of four new chemical elements, 113, 115, 117 and 118, thus completing period 7 of the periodic table[1]. Though now named[2] (no doubt after having read the Sceptical Chymist blog post[3]), we shall wait until the public consultation period is over before In Your Element visits these ephemeral entities.

In the meantime, what do we know of their close neighbour, element 116? Well, after a false start[4], the element was first legitimately reported in 2000 by a collaborative team following experiments at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia. There, scientists bombarded a ^{248}Cm target with accelerated ^{48}Ca ions. Just by simple summation of the respective atomic numbers, 96 and 20, one might predict that element 116 would make an appearance; and so it proved, as the team successfully detected the alpha decay of a single such atom. The results were later repeated by the same group, and have since been confirmed by other laboratories[5].

Element 116 was officially named livermorium (Lv) in May 2012, having been known previously by its systematic designation, ununhexium, with the symbol Uuh. The new name recognized the Lawrence Livermore National Laboratory in California — host to some of the original team responsible for the discovery, provider of the curium target, and an institution that has contributed much to the advancement of nuclear science generally. It was said in 2011 that the Russian vice director of the team at JINR favoured the name moscovium, after the Moscow region, for the new element. It now seems that this suggestion will be employed for element 115.

Like all of the superheavy elements, livermorium is very unstable. The isotopes ^{292}Lv, ^{291}Lv and ^{290}Lv all have half-lives of less than twenty milliseconds. Even its longest-lived isotope, ^{293}Lv, has a half-life of only about sixty milliseconds before decaying into flerovium (Fl, element 114), and in turn copernicium (Cn, 112) (ref. 6). As a consequence, scientists have been unable to collect a significant quantity for determination of its physical properties. Indeed, only about 35 atoms of it have ever been observed.



EMMA SOFIA KARLSSON, STOCKHOLM, SWEDEN

That said, thanks to its position in the periodic table, we can perhaps make some predictions. It falls into group 16 — known as the chalcogens — which also contains oxygen, sulfur, selenium, tellurium and polonium. Like the others in its group, it's predicted to have six electrons in its valence shell, with an electronic configuration of $7s^2\ 7p^4$. However, electrons in superheavy elements move much faster than those in lighter atoms. As a result, the 7*s* and 7*p* electron energy levels are expected to be very stable, the 7*s* particularly so due to the inert pair effect. Two of the 7*p* electrons are also expected to be more stable than other four.

The upshot is that the +2 oxidation state is likely to be favoured[7]. There should also be an accessible +4 oxidation state, although it would probably only be achievable with very electronegative ligands such as fluorine (for example, LvF_4). Conversely, the +6 oxidation state — observed for all the other elements in this group bar oxygen — is unlikely to occur due to the difficulty of removing the 7*s* electrons. We see comparable patterns of behaviour in polonium, which we'd expect to have very similar chemistry. The most stable class of polonium compounds are polonides, for example Na_2Po (ref. 8), so in theory Na_2Lv and its analogues should be attainable, though they are yet to be synthesized.

Experiments carried out in 2011 showed that the hydrides $^{213}BiH_3$ and $^{212m}PoH_2$ were surprisingly thermally stable[9]. LvH_2 would be expected to be less stable than the much lighter polonium hydride, but its chemical investigation might be possible in the gas phase, if a sufficiently stable isotope can be found.

Despite the considerable challenges posed by the short-lived nature of livermorium, scientists are keen to explore its chemistry experimentally. As Robert Eichler, head of the heavy elements research group at the Paul Scherrer Institute in Switzerland concludes, more model studies will be required to establish the most efficient way to produce these new superheavy element species, but "chemistry has arrived on the island of stability of superheavy elements"[9]. It seems unlikely that scientists will ever carry out experiments on test tubes full of livermorium, but new insights may not be that far away. ❐

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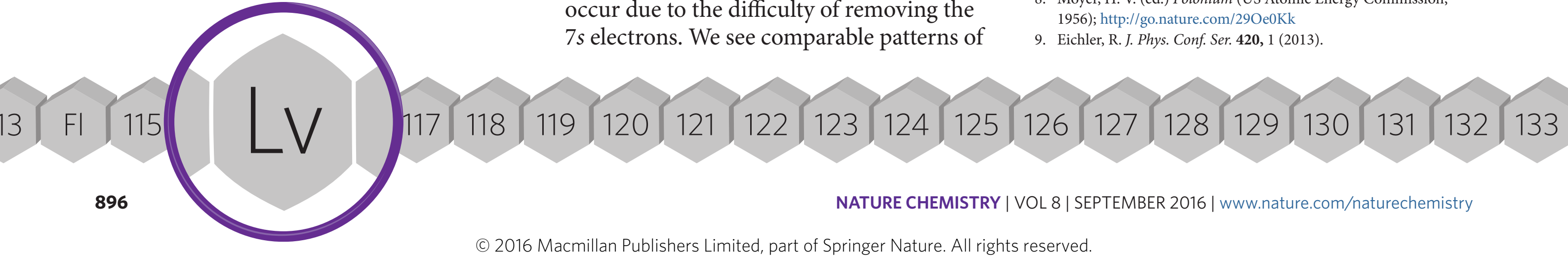

Brief encounters with dubnium

Lars Öhrström tells of the fleeting, but still tangible, chemistry of dubnium, the heaviest of the group 5 elements.

Now you see me, now you don't, this might be a fitting exit line for a dubnium atom slipping through our hands as it decays by sending out an alpha particle. However, the chemist gets the last laugh, as it is this very vanishing act that makes the one-atom-at-a-time chemistry experiments on element 105, a heavier analogue of tantalum, feasible.

As one of the most hotly disputed elements during the transfermium name dispute, when the Cold War cast a dark shadow on science, dubnium initially went under many names. It was synthesized by groups in the Soviet Union and the United States in the late 1960s, starting in Dubna — the science city outside Moscow that was to eventually give its name to the element. There, scientists smashed ^{243}Am with ^{22}Ne producing a mixture of ^{260}Db and ^{261}Db ($t_{1/2}$ = 1.5–1.8 s) after the loss of five and four neutrons, respectively, and announced the discovery of nielsbohrium. Around the same time, their principal rivals from Berkeley used ^{15}N to hit a ^{249}Cf target and formed ^{260}Db, proposing the name hahnium[1]. The dispute was eventually resolved[2] and the name dubnium was adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1997.

One often meets with the opinion that the transfermium elements are of limited use on account of their short lifetimes. On the contrary, take radiopharmaceuticals used in diagnostics for example. These must decay relatively quickly to provide an image for the physician in a timely manner. For this purpose, the ^{99m}Tc isotope is routinely employed; it has a half-life of 6 hours, which is approximately four times shorter than that of ^{268}Db — the longest-lived Db isotope known.

The real problem for dubnium use is its slow production rate. One atom of the most studied dubnium isotope, ^{262}Db ($t_{1/2}$ = 34 s), can be prepared in less than 1 minute, whereas for the ^{268}Db isotope — the final alpha-decay product from the synthesis of elements 113, 115 and 117 — we are talking about atoms per week. Thus with current technology, the chances of accumulating any meaningful amount of dubnium is nil.

Legendary transuranium and transactinide scientists Georgy Flerov (1913–1990), Yuri Oganessian (1933–) and Glenn Seaborg (1912–1999) on the Volga River bank in Dubna, Russia. Photo reproduced with permission from the Joint Institute for Nuclear Research, Dubna.

So, we cannot expect to prepare dinuclear compounds characteristic of the group 5 elements, such as the analogues of the dimeric Ta_2Cl_{10}. Luckily, the gas-phase chemistry of Ta_2Cl_{10} is that of the pentacoordinated mononuclear complex. As a result $DbCl_5$, $DbBr_5$, and also $DbOCl_3$ — the latter of which is expected from the reaction with traces of oxygen in the carrier gas — have been inferred from one-atom-at-a-time experiments.

These techniques are becoming increasingly sophisticated such that investigation of dubnium's aqueous chemistry is now possible[3]. Both $[DbOCl_4]^-$ and $[Db(OH)_2Cl_4]^-$, and even complexes with the chelating α-hydroxyisobutyric acid, have been suggested, based on where in the chain of chromatography, extraction and surface detection a characteristic Db alpha decay is observed. Crucial for these experiments is comparison with lighter analogues under the same circumstances. For example, radioactive isotopes of Hf and Ta, produced by neutron activation, were recently used to develop an extraction system for the separation of dubnium from its group 4 neighbour rutherfordium[4].

One has to be aware that a simple extrapolation from the properties of the lighter group members (Nb and Ta in this case) is not an adequate way of predicting the properties of the 6*d* elements. As the nucleus gets heavier, relativistic effects come into play, so the experiments need to be complemented by advanced quantum chemistry. In this case, such calculations suggest an increased stability of the +5 oxidation state and an electron configuration of $[Rn]5f^{14}6d^37s^2$, concurrent with Db being the heaviest member of group 5 (ref. 1).

This intricate interplay between theory and experiment is of interest and importance not only to chemists, but also to nuclear physicists trying to establish the identity of new elements. When these decay into unknown isotopes, as for elements 113, 115 and 117 where many alpha-decay chains ended in ^{268}Db, it is vital to establish the identity of these isotopes so that the back-calculation will give the right atomic number of the new element[5].

So, in this borderland where chemistry meets physics, nothing should be taken for granted and one does well to remember that even after a new superheavy element has obtained its place in the periodic table, isotopes with higher stability may yet be discovered, as indeed was the case for dubnium. ❐

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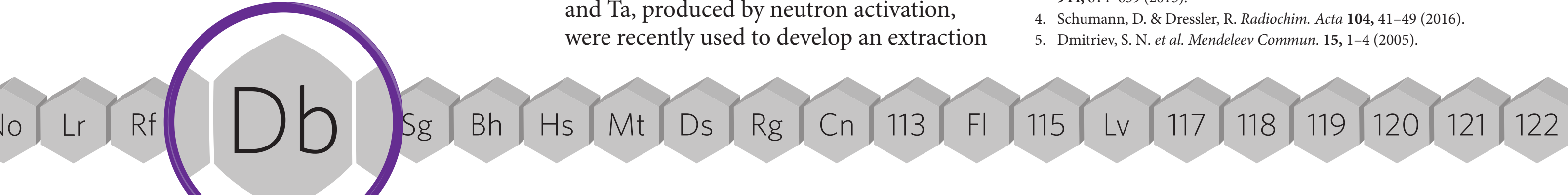


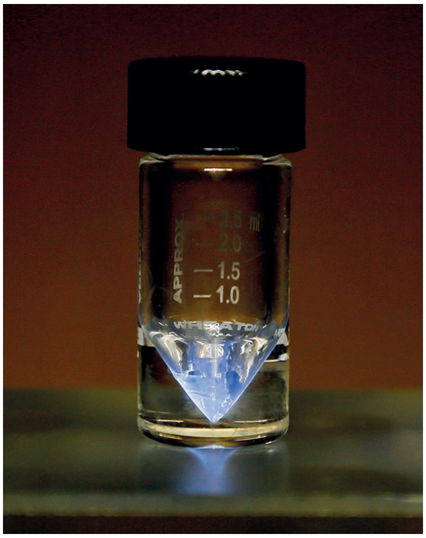
Active actinium

Naturally scarce but synthetically accessible, **Gauthier J.-P. Deblonde** and **Rebecca J. Abergel** discuss element 89 and its emergence as a candidate radio-theranostic metal for cancer treatment.

In 1899, during the aftermath of Marie and Pierre Curie's resounding discovery of both polonium and radium, André-Louis Debierne — one of their French research fellows — partially isolated another new element. Ambiguities in Debierne's purification procedure from pitchblende residues almost cost him the credit for the discovery of element 89, with Friedrich Oskar Giesel independently managing to isolate the same isotope just three years later. After some discussion, Debierne's actinium (for the Greek *aktinos*, meaning ray) was preferred to Giesel's emanium; although both names highlight its active alpha-particle emanations.

The discovery of Ac was a continuation of the work of the Curies, but never had the same impact as its freshly discovered radioactive neighbour, Ra. Indeed contrary to radium-based therapies, actinium had no commercial applications at the time, and its extreme rarity in nature made it almost impossible to extract from ores — a process that is still difficult even with today's technologies.

Unlike ^{226}Ra, which has a relatively long half-life ($t_{1/2}$) of 1,600 years, the only naturally occurring isotopes of actinium are ^{227}Ac ($t_{1/2}$ = 21.8 years), which comes from the decay of the already rare ^{235}U, and ^{228}Ac ($t_{1/2}$ = 6.1 hours), a furtive decay product of ^{232}Th. The elusive nature of Ac, combined with two world wars in the first half of the twentieth century, resulted in the knowledge of no new isotopes until 1947, though 32 have now been identified and 60 more are expected to exist. Unfortunately, this profusion of new man-made Ac isotopes synthesized since the 1950's has not produced any long-lived actinium atoms, they all actively decay in a few hours at best, with the exception of ^{225}Ac ($t_{1/2}$ = 10 days). Bulk chemical studies on actinium are therefore still dependent on the original ^{227}Ac (ref. 1). Nonetheless, progress in particle accelerators and nuclear reactions made both ^{227}Ac and ^{225}Ac more accessible through neutron or proton irradiation of ^{226}Ra or ^{232}Th targets.


COURTESY OF OAK RIDGE NATIONAL LABORATORY, US DEPT. OF ENERGY

Purified ^{225}Ac emitting Cerenkov luminescence.

Beyond credit for discovery, the debate on the position of actinium in the periodic table is still highly active[2]. Although the name actinium would unambiguously make it the first member of the actinide family, Ac is still placed below Sc, Y and La in most periodic tables. Recent arguments tend to support its reassignment as an actual *f*-block member with irregular electronic configuration, whereas the current heaviest actinide, Lr, would be drafted to the *d*-block below Sc, Y and Lu. Regardless of whether Ac is an *f*- or *d*-element, its chemistry has experienced a revival in the past few years[3]. Indeed, actinium may supersede radium due to its ongoing development in alpha-emitting radionuclide therapies. If chelated and targeted adequately, the tremendous energy released by the fourfold alpha disintegrations of ^{225}Ac could be used to surgically strike prostate, breast and bone marrow cancer tumours. In contrast to very short-lived isotopes such as ^{213}Bi ($t_{1/2}$ = 46 minutes) and ^{211}At ($t_{1/2}$ = 7.2 hours) that have been evaluated for these applications, the day-scale decay of the now easily accessible ^{225}Ac makes it a seemingly ideal candidate for destroying tumour cells. Its final decay to the stable and non-toxic ^{209}Bi is also beneficial when compared with competitors under clinical evaluation, namely ^{227}Th, ^{228}Th and ^{230}U, all of which alpha-decay to stable, but toxic, Pb isotopes.

A rising challenge for chemists resides in the handling of ^{225}Ac intermediates and potentially harmful recoiling daughters — ^{221}Fr, ^{217}At, and ^{213}Po. The design of *in vivo* stable carriers able to scavenge both actinium and its alpha cascade raises hope for highly efficient cancer therapies with no side effects. Various strategies are under development, among which the encapsulation within nanoparticles seems most promising, whereby tumour delivery of ^{225}Ac through a lanthanide-based 'nanosafe' could neutralize metastases without leaving radioactive traces in the patient[4]. Finally, Cerenkov luminescence imaging of targeted tissues using the *in situ* decay of ^{225}Ac and its daughter products has recently brought to light the formidable theranostic potential of ^{225}Ac-based radiopharmaceuticals[5].

The quest for an efficient and silent, but traceable cancer treatment could turn into reality thanks to an element that has been largely overlooked since its discovery. Studies of actinium have taken researchers through the realms of radiochemistry, nuclear science, particle physics, medicine, and more recently nanomaterial design, underlining how Ac chemistry is as highly active as ever. ☐

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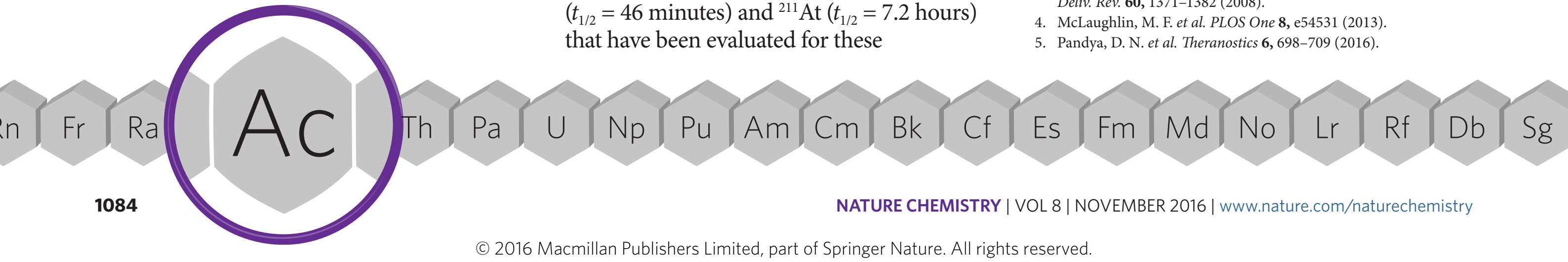


Einsteinium declassified

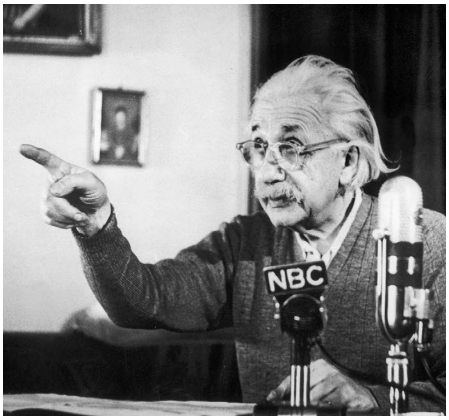
Discovered during secret testing by the United States, **Joanne Redfern** tells us about element 99 and why its namesake cautioned against the very technology that led to its creation.

On the first of November 1952, in a top secret test known as Mike, the United States detonated the 'Sausage' — the world's first hydrogen bomb. The explosion annihilated the entire Pacific island of Elugelab, but it wasn't all devastation; at the same time it created two new elements that their discoverers would later name einsteinium and fermium. The explosion was colossal, being more powerful than all of the high explosives used in World Wars I and II combined[1]. In an instant, an enormous number of neutrons (around 10^{24}–10^{25} cm^{-2}, ref. 2) blasted into the uranium atoms used in the bomb. Some of these atoms captured 15 neutrons each — resulting in very heavy uranium isotopes — before rapidly undergoing seven beta decays. The result was a new element with an atomic number of 99 and an atomic mass of 253.

Radioactive debris — including element 99 — mushroomed out of the explosion in a 60-mile-wide cloud. Keen to understand more about the science of thermonuclear explosions, the US Government sent fighter jets flying through the cloud to sample the radioactive fall-out by using special filter papers attached to their wing tanks[2]. The detailed analysis fell to Albert Ghiorso and colleagues at the University of California, Berkeley — according to Ghiorso, the results were entirely unexpected[3].

The team detected a unique radiation signal that they deduced must have come from the hitherto unknown element 99. They later detected the same signal (and that of element 100) from radioactive coral debris gathered from neighbouring islands. The miniscule amount of element 99 (fewer than 200 atoms in total[4]) made the discovery all the more remarkable. Frustratingly, the team were not allowed to say a word as the details of the Mike test remained classified.

To get around this, Ghiorso's team set about making element 99 by other means. They discovered that bombarding ^{238}U with nitrogen ions produced a short-lived isotope of element 99, and they published their findings in 1954 with a note to acknowledge that prior work on the element existed[5]. A few months later the Mike test was declassified, allowing Ghiorso to report his team's earlier discovery in 1955[6]. He also had the honour of choosing the name, einsteinium (Es).



Einstein warns of the dangers of developing the hydrogen bomb (12th February 1950).

KEYSTONE-FRANCE / GAMMA-KEYSTONE / GETTY IMAGES

Today scientists produce einsteinium by bombarding plutonium with neutrons in a nuclear reactor, then allowing the resulting isotopes to undergo beta decay. This is a slow process. Indeed, it took until 1961 (nine years after its initial discovery) before scientists managed to make enough einsteinium to observe its form as a silvery metal[4].

As well as being scarce, einsteinium is difficult to study because it self-destructs. It has nearly 20 different isotopes, all of which are radioactive. The most stable, ^{252}Es, has a half-life of about 472 days, but it is difficult to produce and is only available in tiny amounts. ^{253}Es is the most common isotope, but it has a half-life of only 20 days. It releases gamma rays and X-rays when it decays, damaging its crystal lattice and hampering any X-ray crystallographic analysis. The intense release of energy (1000 W per gram) also causes einsteinium to glow[7]. Furthermore, because it decays rapidly into berkelium and californium, samples of einsteinium are nearly always contaminated.

Einsteinium is mainly used to make heavier elements, such as mendelevium — first discovered by Ghiorso's team when bombarding ^{253}Es with alpha particles. In addition, scientists have used its radiation to study accelerated aging and radiation damage, and have examined its potential for medical treatments, although not commercially[7]. Outside of basic research, einsteinium has no practical use. So although its name lends it a familiarity, most of us will never come across even a single atom of einsteinium in our lifetimes.

Einsteinium kicked off a trend for naming new elements after famous scientists, and it is hard to imagine a scientist who would not appreciate this honour. But for Einstein, this particular element seems like an ironic choice; he was a pacifist, vehemently opposed to the development of the hydrogen bomb. He even recorded a statement for US television show *Today with Mrs. Roosevelt* (pictured) in which he warned that the hydrogen bomb could annihilate life on earth. So how did he feel about a bomb-born element being named after him? We will never know. He died just a few months before Ghiorso announced einsteinium to the world. ❐

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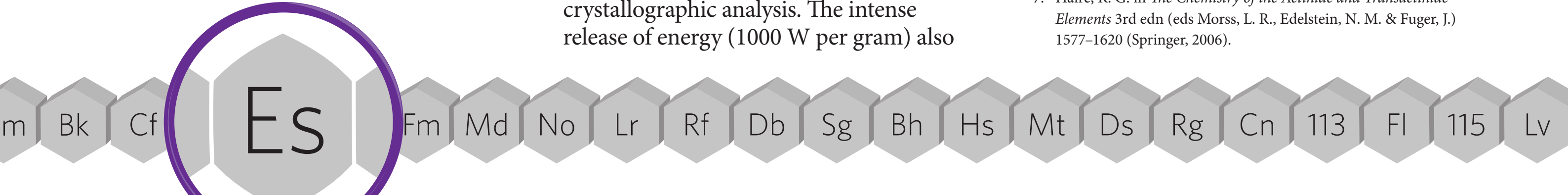

A portrait of cadmium

Nadezda V. Tarakina and **Bart Verberck** explore the colourful history and assets of element 48.

In early-nineteenth-century Prussia, quality control of pharmaceuticals was entrusted to government-appointed physicians. In 1817, one such physician, Johann Roloff, became suspicious of a batch of zinc oxide that could be traced back to the factory of Karl Hermann. Roloff's preliminary tests suggested that the samples contained arsenic, and so Hermann — worried about the reputation of his business — investigated further. He and others soon discovered that arsenic had nothing to do with it, but that an unknown metal was involved.

Meanwhile, Friedrich Stromeyer, Inspector-General of the apothecaries in the neighbouring Kingdom of Hanover and professor at the University of Göttingen, was investigating some puzzling zinc carbonate samples that, upon heating, left behind a yellow oxide. He managed to isolate the source of the yellowness down to the oxide of a new metal.

The entangled roles of Roloff, Hermann and Stromeyer — who corresponded and wrote about their findings — make it virtually impossible to give someone sole credit for the identification of the new element[1]. Furthermore, others also published reports on the discovery. Different names for the element were suggested, including klaprothium, in memory of the chemist (and element-discoverer) Martin Klaproth, and melinum, from the Latin *melinus*: referring to the colour of a quince. However, the name cadmium — originally proposed by Stromeyer — stuck. His proposal came from the root *cadmia*: Latin for calamine, which is an umbrella term referring to various zinc-based minerals.

Cadmium partners vividly with sulfur: CdS is a yellow solid — hence the suggestion of melinum — and has long been a fixture on painters' and graphical artists' colour palettes under the name 'cadmium yellow'. Solid solutions with selenium (cadmium sulfoselenides) serve as pigments covering orange to red; mixing CdS with ZnS produces a yellow–green tone. As such, cadmium pigments have been embraced by artists since the nineteenth century. They are known for their outstanding hiding power, light-fastness and stability — qualities that also make them excellent industrial paints. Indeed, thanks to their resistance to temperatures up to 3,000 °C, cadmium pigments can be used for painting hot pipes or glass — for example in red traffic lights or the lit stars on the Moscow Kremlin (pictured).


MIHAIL CHEKALOV / ALAMY

The physical reason for this plethora of colours is that these II–VI cadmium compounds are semiconductors with a bandgap in the visible spectrum. CdS has a bandgap of 2.42 eV (512 nm) and therefore absorbs blue, indigo and violet: the spectral complement is thus perceived by the human eye as yellow.

CdS and CdSe nanoparticles are popular quantum dots. On the nanoscale, due to quantum confinement effects, the absorption threshold of semiconductors becomes size dependent: the smaller the dot, the higher (bluer) the energy threshold. The size of such nanoparticles therefore provides a handle for tuning their optical properties, handy for use in display screens — modern pigments, if you like.

Cadmium has no known biological function in higher organisms. In fact, it is highly toxic and regulations on its use have become increasingly stringent — cadmium salts are gradually being replaced by azo compounds in commercial paints.

Because of its ability to capture neutrons, cadmium played an instrumental role in the development of the very first nuclear reactor — cadmium-coated rods were being used to control the nuclear reaction[2].

From 1907 to 1960, cadmium moonlighted as a metrology standard. During that time, the ångström was defined by fixing the wavelength of a distinct, red spectral line of cadmium at 6438.4696 Å — a choice put forward by physicist Albert Michelson[3]. In 1960, the ångström became coupled to the metre, and the latter was redefined in terms of a particular spectral wavelength of ^{86}Kr.

But cadmium is perhaps best known for its use in battery technology. The invention of the rechargeable nickel–cadmium battery goes back to 1899, and has played a major role in electrical technology throughout the twentieth century. A cell built from cadmium and NiO(OH) electrodes delivers a potential of 1.2 volt; Ni–Cd batteries have superb characteristics, including robustness, stability and long life. However, because of cadmium's toxicity, the use of Ni–Cd batteries has been progressively banned in recent years, for example by the European Union's Battery Directive[4], encouraging adoption of less hazardous alternatives such as nickel–metal hydride and lithium-ion batteries.

According to Greek mythology, Cadmus brought the (Phoenician) alphabet to Hellas. Over the past 200 years, cadmium has also brought us plenty. Its toxic nature has somewhat caught up with it colourful past, seeing it replaced here and there. But when handled with care, the element's unique merits in chemistry's alphabet can still be put to good use. ❐

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in your element

The neodymium neologism

From grand challenges of nineteenth century chemistry to powerful technology in small packages, **Brett F. Thornton** and **Shawn C. Burdette** explain why neodymium is the twin element discovered twice by two Carls.

In 1838, Swedish chemist Carl Mosander isolated lanthanum, a new metal that had been hiding in Berzelius' cerium since 1803[1]. Two years later, he found yet another metal in cerium — this third component was responsible for a purplish hue in his samples[2]. He named this metal didymium, from a Greek word meaning twin. Didymium shared many chemical properties with lanthanum and thus appeared to be a fraternal twin derived from the same zygotic ore. After 1878, when didymium's visible spectrum was noted to vary depending on its geological source, suspicions grew that didymium contained more than one element[3]. Didymium would remain on element lists for over four decades, and it is the only element on Mendeleev's 1869 periodic table that does not appear on our modern version.

In the early 1880s, Austrian chemist Carl Auer von Welsbach was separating rare earth elements by repeatedly performing fractional crystallizations — a tedious and time-consuming method that relies on tiny solubility variations of lanthanide double ammonium nitrate salts. In 1885, Welsbach's hard work paid off and led him to a new element. Announcing that didymium had been shown to consist of two elements[4], he triumphantly proposed two new names — in contrast to the established practice of only naming the less-abundant component. The minor fraction that produced green salts he named praseodymium; the major fraction he renamed neodymium.

No other acknowledged element has ever been renamed because a new element was separated from it. Nor did any contemporary chemists challenge this discovery grab — Mosander died in 1858 and so could not defend didymium. In recent years, however, some voices have been raised: it has been suggested[1] that Welsbach acted pretentiously and because only one new element was separated from didymium, that name should have stuck for one of the two elements in question[5]. Nevertheless, Welsbach was not alone in using the 'neo-' prefix during the rush of rare earth element discoveries (many of which were spurious) in the late nineteenth century, but only his neologism stuck.

EMMA S. KARLSSON, OXYRIA NATUR, STOCKHOLM

Welsbach was regarded as a master of commercializing his discoveries, but the difficult separation of rare earth elements limited his options in this area. These elements are often found together because even Mother Nature finds them hard to separate. Neodymium is second only to cerium in crustal abundance amongst the rare earth elements and is far more common than many better-known elements, including lead and tin. In ores such as monazite and bastnäsite, neodymium can account for 12–16% of the ore.

The main application for neodymium in the nineteenth century was mischmetal — a blend of cerium and lanthanum containing small amounts of neodymium and praesodymium — a component of ferrocerium, which was used as the sparking flints for lighters. After mischmetal, colouring glass was one of the first popular applications for neodymium. Melting neodymium oxides into glass induces tints that vary from hot pinks to blues depending on the ambient light source. In lasers, neodymium-doping of the glass lasing medium became important for high-power applications, including laser fusion research.

The most powerful known permanent magnets are produced from the alloy $Nd_2Fe_{14}B$. Since their invention by industry in 1982, these magnets have become commonplace in speakers, headphones, hard drives, high-performance electric motors and generators, and even superstrong refrigerator magnets. Their ubiquity belies their uniqueness: no other permanent magnets come close to the strength of the $Nd_2Fe_{14}B$ alloy.

Owing to its uses in modern technologies, concerns about the supply of neodymium have grown in recent years. It is generally not recycled from consumer products because of the lack of industrially feasible recovery methods and the small mass percentage present in each product. Moreover, some uses of neodymium (such as in ferrocerium flints, fireworks and phosphors) are dispersive. The readily available small, powerful $Nd_2Fe_{14}B$ magnets in cast-off electronic detritus has even led to creative recycling uses — including building equipment for chemistry education in schools[6]. ❐

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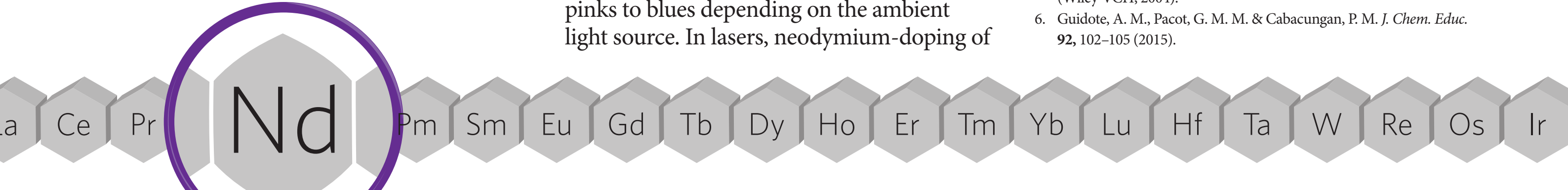


in your element

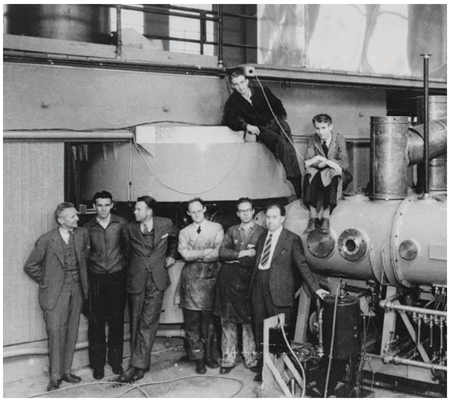
The unveiled states of americium

Made under a cloak of wartime secrecy, yet announced in the most public of ways — a radioactive element that governments insist we take into our homes. **Ben Still** explains how element 95 is one of real contradiction.

The Manhattan project gave rise to the world's first atomic bombs, which relied on the chain reaction of two particular fissile isotopes of uranium and plutonium. ^{235}U, having been enriched from its natural abundancy, was used for the first atomic weapon. Little Boy, as it was codenamed, was dropped on Hiroshima on the 6th of August, 1945. Three days later the second atomic bomb, Fat Man, was detonated over Nagasaki: for this bomb, high densities of neutrons in nuclear 'breeder' reactors transformed abundant ^{238}U into ^{239}Pu.

It was realized early in the project that if the ^{239}Pu in the Fat Man bomb were to be transportable and only reach criticality (the point at which nuclear chain reaction can be self-sustained) when desired, then any and all impurities had to be carefully studied and understood[1]. It was the task of those working in the Metallurgical Laboratory (Met Lab) at the University of Chicago (now the Argonne National Laboratory) to identify and analyse the properties of these new synthetic elements.

Some isotopes were notoriously difficult to extract and so scientists at Berkeley Laboratory used Ernest Lawrence's atom smasher — a 60-inch cyclotron — to create them in a controlled environment. Samples of ^{238}U and ^{239}Pu were bombarded with high-energy alpha particles (helium nuclei) to recreate environs present in breeder reactors. With ^{239}Pu this process resulted in element 96, now named curium, whereas with ^{238}U it produced element 95. Using this method, the Berkeley scientists were able to obtain a large enough quantity of both new elements to enable the team at the Met Lab to identify their properties.



Ernest Lawrence (third from the left) and his team in front of the 60-inch cyclotron that produced the first measureable sample of americium.

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After irradiating ^{238}U with ^{4}He nuclei they discovered a hitherto unseen low-energy emission — the β-decay of ^{241}Pu. This process, transforming one neutron into a proton, resulted in an element with atomic number 95 and mass number 241. In the autumn of 1944 this observation was the first confirmed sighting of element 95 (ref. 2). Further experiments produced other isotopes, of which the ^{243}95 isotope was found to be the most stable. The very existence of the element was classified and would remain secret until the war came to a close.

Once the cloak of secrecy was shed in late 1945, the discovery of elements 95 and 96 was announced to the world in an unexpected way. Their unveiling was planned for the American Chemical Society's national meeting, scheduled for the 16th of November. Instead, Glenn T. Seaborg told a national audience live on radio during a show called *Quiz Kids* five days before the conference[3]. He was asked by a child contestant if any other elements, aside from plutonium and neptunium, had been discovered at the Met Lab during the war. Seaborg disclosed the discovery of elements 95 and 96, telling his young audience "now you'll have to tell your teachers to change the 92 elements in your schoolbook to 96 elements".

Element 95 was named americium (Am) by Seaborg and his team[2], giving recognition to the location of its discovery, but also mirroring its lanthanide opposite number: europium. It is the only radioactive element that governments insist we keep in our homes. AmO_2 is a key component of smoke detectors: around 0.3 μg of the isotope ^{241}Am sits inside a sealed metal box at the heart of the device, spitting out alpha radiation. The small electric charge arising from ionization of air by the alpha radiation lets the detector know everything is just fine. However, large smoke particles absorbing the alpha radiation reduce the amount of ionization and thus electric current, which triggers the detector to sound the alarm.

Americium is most commonly trivalent in solution, with tetravalency also frequent in solids such as the oxide mentioned above. However, states +2 to +7 have been reported experimentally, and even Am(VIII) has been suggested as being potentially accessible — albeit somewhat speculatively[4].

Although the radioactivity of plutonium is used to provide thermonuclear energy to deep space exploration satellites, there are ever tighter regulations around its sale and use on account of its fissile nature. Americium on the other hand is non-fissile, which is enticing European space scientists to consider using it as a plutonium alternative for future missions[5].

Ever since its discovery was announced on live radio, element 95 has found its way into our homes, and it could soon be powering our exploration to the furthest reaches of the cosmos. ❐

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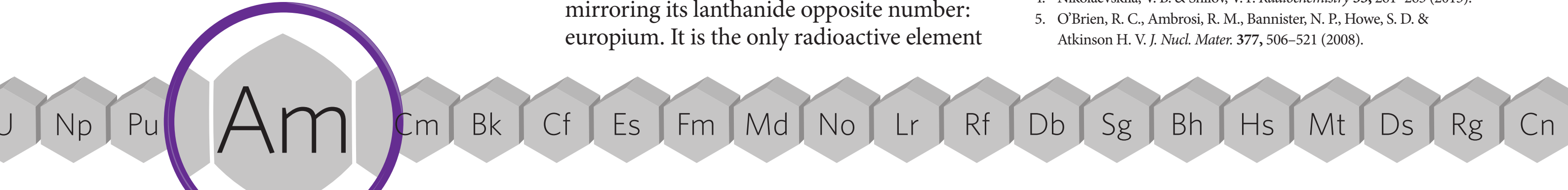

Iterations of ytterbium

Alasdair Skelton and **Brett F. Thornton** examine the twisting path through the several discoveries of ytterbium, from the eighteenth century to the present.

Although ytterbium was named by the Swiss chemist Jean de Marignac in 1878, his 'element' was subsequently split into two in 1905: ytterbium and lutetium. The atomic weight of the 'new' ytterbium was later published in 1907 — so when was ytterbium actually discovered? The story begins on 13 June 1726, more than 150 years before it first received its name. On that date an agreement was signed allowing the Dutch tin-glazed imitation of porcelain (faience) to be produced in Sweden, which led to German alchemist, Johann Wolff, establishing a 'porcelain' factory in Rörstrand Castle in Stockholm. In the late 1700s, the factory began producing flintware (an improved product invented by Josiah Wedgwood), leading to a need for feldspar. Rörstrand purchased a quartz and feldspar mine located 20 km away in Ytterby, a village probably named for its location on the seaward (*den yttre*) side of Resarö, a small island in Stockholm's archipelago.

In 1788, Reinhold Geijer: chemist, mineralogist and then owner of Rörstrand porcelain factory published a letter[1] describing a black non-magnetic mineral with a specific gravity of 4.223, which had been found in the Ytterby mine by an amateur geologist, Carl Axel Arrhenius. Arrhenius had also sent a sample of this mineral to Johan Gadolin, professor at Åbo Akademi in Finland. Gadolin performed a series of experiments on this mineral and found that it contained 31 parts silica, 19 parts alumina (in reality beryllia), 12 parts iron oxide and 38 parts of an unknown earth (or oxide, in modern terms)[2].

In 1797, Anders Gustaf Ekeberg, a chemist from Uppsala, re-analysed a purer sample and showed that Gadolin had overestimated the silica and alumina content and underestimated the proportion of new earth, of which he found 47.5 parts — he also noted its disgusting taste[3]! He proposed the name *yttersten* (ytter-rock) for the mineral, and the Swedish and Latin names *ytterjord* (ytter-earth) and *yttria* for the new earth.

Ytterby mine minerals. Bottom-left: rare earth containing black biotite veins in quartz. Bottom-right, 20 cm orange feldspar crystal. Photographs courtesy of Emma Sofia Karlsson.

Yttersten, or gadolinite, is now known to have the general formula $FeBe_2Y_2Si_2O_{10}$, though the 'Y' would prove to be quite complex.

In the decades that followed it became clear that yttria was much more than an oxide of yttrium. In 1843 it was found to contain oxides of erbium and terbium too. Then, in 1878, Marignac isolated ytterbia from yttria[4], which he claimed to be the oxide of a new trivalent element, ytterbium, with an atomic weight of 172 g mol^{-1}. However, in Austria in 1899, Franz Exner and Eduard Haschek presented spectroscopic evidence suggesting that ytterbium was not one substance. Six years later, also in Austria, Carl Auer von Welsbach used fractional crystallization to split Marignac's ytterbium into two elements, which he distinguished on the basis of emission spectra and called aldebaranium and cassiopeium. He published[5] atomic weights of 172.90 and 174.23 g mol^{-1} for these elements in December 1907.

Forty-four days before Welsbach published his finding, Georges Urbain announced[6] to the Paris Academy that he had separated ytterbium into two elements, which he called neo-ytterbium, and lutecium — after *Lutetia*, the Latin name for Paris — with atomic weights of approximately 170 and 174 g mol^{-1}, respectively. Urbain claimed that Welsbach had no more than rediscovered these elements, referring to Welsbach's 1905 discovery as non-quantitative and lacking proof. In 1909, the International Committee on Atomic Weights — which included Urbain — favoured Urbain's nomenclature, listing[7] neo-ytterbium and lutetium with atomic weights of 172 and 174 g mol^{-1}, respectively. The neo-ytterbium name was short-lived, however, and Marignac's original 'ytterbium' was soon reinstated. Considering that Welsbach had earlier turned one element discovery into two (neodymium and praesodymium) by renaming the major component of didymium 'neodymium', it must have been frustrating for Urbain that he was prevented from doing the same.

Like many lanthanides, ytterbium is a relatively lesser-studied element. It is used as a strengthening agent in stainless steel; and because it becomes semi-conductive at high pressure, ytterbium has been used to make stress gauges. Also, its radioactive isotope (^{169}Yb) is used in portable X-ray machines. A more recent application is in atomic clocks, where using ultra-cold ^{174}Yb promises an accuracy exceeding one second in 50 billion years[8] — over ten times the age of the Earth. Thus, Marignac's ytterbium from Ekeberg's yttria may find its way into global navigation and communication systems, and might ultimately aid in redefining the SI second[8]. ❐

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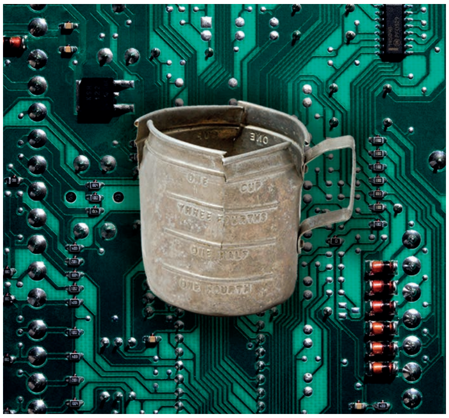
Ho Er Tm **Yb** Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr

in your element

Tin can

Tin has been ubiquitous throughout the course of human history, from Bronze Age tools to lithium-ion battery components, yet **Michael A. Tarselli** warns it should not be deemed pedestrian. Its tendency to linger in human tissues presents a dangerous side that steers researchers towards greener chemistries.



CIRCUIT BOARD: JULIAN JAMES WARD / MOMENT / GETTY
TIN CUP: STEVEN SANDERS / ALAMY STOCK PHOTO

Tin hides everywhere in our culture, often in plain sight. Consider movie relics: from *The Wizard of Oz*'s Tin Man to the tin-can radio often spotted in treehouses. Element 50, whose symbol 'Sn' comes from the Latin *stannum*, has been mined all over the world for centuries. Its tendency to alloy with other metals such as copper or antimony gave the Bronze Age weapons and pewter tableware. Today, tin compounds live inside antifouling paint, PVC pipes and probably even in your bones, where tin compounds often accumulate in the human body. The lustrous silvery metal has a role to play, for good or ill, in the oncoming rush of battery science and electronics.

Metallic tin mainly occurs in two phases. The 'tin pest' — conversion of the strong, crystalline β form into a brittle α form at low temperatures — is recounted[1] as the apocryphal cause of disaster of the Russian campaign, through failure of Napoleon's buttons in the cold winter of 1812. Two other allotropes exist under high temperatures and pressures. Anyone observing a printed circuit board has seen solder: a tin–lead alloy extremely facile to melt and used to join contacts in a complex electronic circuit. Mass-produced tin cans have held a great variety of products — from food to oil to shoe polish — since the late nineteenth century, though today they often comprise the less costly, more malleable aluminium instead.

In its elemental form, tin poses no threat to human health. Organotin toxicity, on the other hand, has been epidemiologically linked to several markers of impaired health and growth in animal models. If there were a poster-child molecule for these studies, it's tributyltin chloride ($(C_4H_9)_3SnCl$, TBTC). A former antifouling compound for naval vessels and a PVC additive, TBTC has been shown to have multiple endocrine-disrupting effects. Chief among these: triggering apoptosis, interrupting metabolism, and 'obesogen' interactivity — rendering TBTC capable of influencing fat storage in animal models and increasing the likelihood of weight gain in later life[2].

Given their tendency to bioaccumulate and to affect multiple enzymatic pathways, are tin compounds worth the risk in any application? From organometallic and synthetic organic chemists' viewpoints over the past century, yes! Organotin has long been used to trigger radical additions, form polymers and serve as cross-coupling partners for palladium catalysis. This latter technology has recently been expanded to aniline-derived quaternary ammonium salts as coupling partners under nickel catalysis, using trimethyltin aryl species, through Ni–F–Sn complexes[3] The coupling proceeds in high yields despite the presence of functional groups — silyl ethers, nitriles, esters and ketones — that might have interfered with its Pd-catalysed cousin.

Yet many synthetic practitioners now also see tin compounds as a potential liability — a troublesome impurity, and former of potentially toxic byproducts. Efforts are underway to develop a mild, tin-free generation of radical precursors[4] from xanthates and organic peroxides. In the green-chemistry movement, element 50 has also slowly waned in popularity relative to organometallic precursors such as boron or copper. To limit tin byproducts, especially in late-stage synthesis where ppm levels must be explicitly controlled, a variety of polymer- and solid-support-immobilized reagents have also been proposed[5]. These reusable precursors can serve as catalytic generators of organotins or radical precursors.

Yet tin has hardly become obsolete. Its unique conductivity, electronic structure and tendency to readily form alloys have landed it a new role in solar energy and next-generation electronic devices. Traditional alloys such as nitinol (nickel titanium) have given way to Ni–Sn–Sr and tin oxides, which harvest a wider range of available wavelengths of light and are often more highly conductive. Tin-based nanoparticles hold promise as next-generation anodic materials for lithium-ion batteries, spurring interest in their formation and characterization. A three-layered Sn/SnO/SnO_2 core-shell nanoparticle, for example, was recently probed through a combination of spectral techniques[6].

Time will tell whether synthetic and solar services can outweigh tin's involvement in toxins and endocrine disruptors. For now, governments and environmental agencies are looking into ways to limit it in manufacturing processes and monitor organotins in potable water (http://go.nature.com/2meRuOq) — so as to keep the Tin Man firmly in the realms of fantasy. ❐

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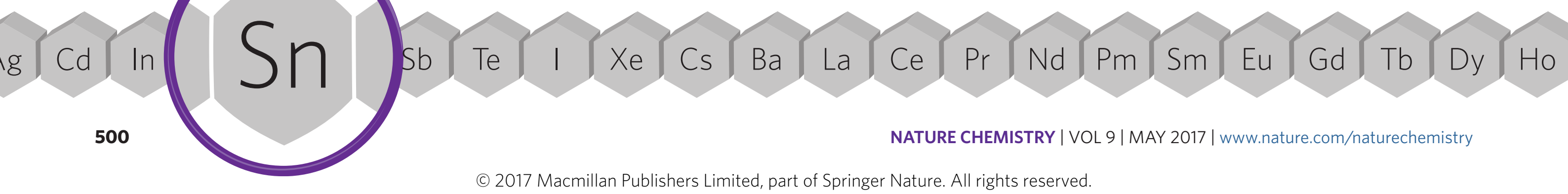

in your element

V for vanadium

Andrea Taroni shares his experience with vanadium — a colourful element with a rich chemistry (and physics!) that is emblematic of all transition metals.

Quite why I chose to study chemistry at university is a mystery, even to me. I mostly got the general principles, but it was as if its details — oxidation, reduction; *cis*, *trans*; *R*, *S* — or rather which way around those details went, had been designed to consistently make me feel like I couldn't tell my right hand from my left. It is fair to say I wasn't a natural at the subject.

One of the first elements I remember encountering in the lab — by attempting to work with it, as opposed to simply acknowledging its existence — is vanadium. My inorganic chemistry lab practical involved the synthesis and analysis of the five-coordinate complex VO(acac)$_2$ (where acac is acetylacetone) and I soon got a vivid demonstration of just how colourful chemistry could be.

> The fascinating chemical and physical properties of vanadium all stem from the rich behaviour of its *d* electrons.

Like most transition metals, vanadium exists in a wide range of oxidation states — most commonly from +2 to +5, but all states from –1 to +5 exist and even the rare –3 is known, in $V(CO)_5^{3-}$ — and can therefore take part in all manner of electron-transfer processes. In a coordination complex, these can occur in the form of charge-transfer transitions from the metal ion to the ligand (or vice versa). As the excitation energies of these transitions occur in the visible region of the electromagnetic spectrum, absorption of light produces a characteristic intense colour — blue in the case of VO(acac)$_2$.

Changing a metal's oxidation state, typically by adding or swapping a ligand, affects its coordination environment, in turn altering the energetics of the charge-transfer transitions it is involved in, thereby changing the colour of the complex. The rest of my undergraduate practical required me to determine the oxidation states of vanadium upon reducing my solution with various agents. I vividly recall the sudden changes in colour that came with each oxidation state switch, and I like to think this gave me a greater appreciation for the inspired decision to name the element after Vanadis, the Norse goddess more commonly known as Freyja, whose attributes include beauty.

In fact, many transition metal compounds have spectacular colours (pictured), making them ideal for pigments. Their rich redox chemistry is also key to their application in biological systems (think manganese in photosynthesis). Redox reactions are also, of course, central in electrochemistry, and vanadium flow batteries have been devised that store energy in liquid electrolytes instead of electrodes. These work using V^{4+}/V^{5+} and V^{2+}/V^{3+} aqueous sulfate solutions as cathode- and anode-side electrolytes separated by an ion-exchange membrane.

Transition metals give rise to exciting physics too. When bound together in the solid state, forming what condensed-matter physicists call a strongly correlated electron system, remarkable properties become manifest.

The conductivity and ferromagnetic nature of iron — an element that has been exploited to the extent that an entire epoch of human history is named after it — are two examples that have been used since antiquity; for example in magnetite-based compass needles. In the mid-1980s, it was realized that certain copper oxides can be made to superconduct when cooled with liquid nitrogen, a discovery for which J. Georg Bednorz and K. Alex Müller were awarded the 1987 Nobel Prize in Physics. In the same decade, thin Fe–Cr films were found to display a giant electrical response to applied magnetic fields, an effect now known as giant magnetoresistance, which underpins much of the memory storage technology in use today

ANDREW LAMBERT PHOTOGRAPHY/ SCIENCE PHOTO LIBRARY

(earning Albert Fert and Peter Grünberg the 2007 Nobel Prize in Physics in the process). All of these properties arise from the different choreographies that the electrons of these systems can be made to arrange in — a seemingly limitless set that material scientists are becoming ever more adept at manipulating.

Naturally, element 23 also displays its own set of intriguing, yet useful, properties in the solid state. Vanadium dioxide, for instance, is the textbook example of an oxide that undergoes a transition from a conducting metal to a non-conducting insulator as it is cooled below room temperature. In fact, this metal–insulator transition can be controlled using a range of external parameters such as pressure, doping and applied electric fields, and as it is accompanied by huge changes in resistivity and opacity, VO$_2$ is widely used in coatings and sensors.

Like the rest of the transition metal elements, the fascinating chemical and physical properties of vanadium all stem from the rich behaviour of its *d* electrons. Back in my undergraduate chemistry days, where I got a small, albeit spectacular demonstration of this, I never would have guessed that these strongly correlated electron systems would go on to dominate my own research interests as a physicist. ❐

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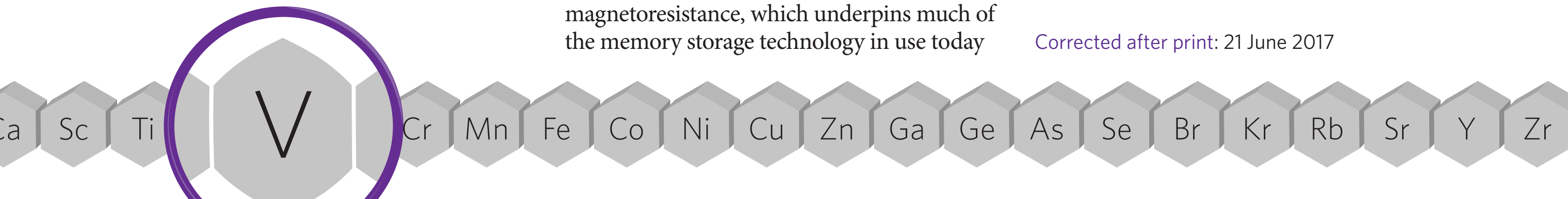
Corrected after print: 21 June 2017



Correction

A sentence in the fifth paragraph of the In Your Element article ‘V for vanadium’ (*Nat. Chem.* **9,** 602; 2017) incorrectly mentioned magnesium, it should have read: “Their rich redox chemistry is also key to their application in biological systems (think manganese in photosynthesis)”. This has been corrected after print 21 June 2017.

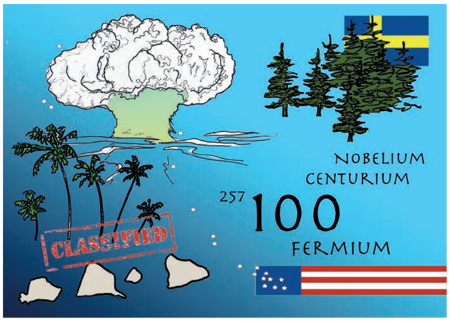
Frantically forging fermium

Brett F. Thornton and **Shawn C. Burdette** relate how element 100 was first identified in a nuclear weapons test, but that was classified information, so researchers had to 'discover' it again using other methods.

When the circumstances surrounding a discovery mean that its publication is blocked by external forces, how do you ensure that you can claim appropriate credit for your findings? This was the case with the discovery of element 100 — fermium — which was named for Enrico Fermi who, among many other things, developed the first nuclear reactor. Fermium was first produced in the Ivy Mike thermonuclear weapons test at Enewetak Atoll in November 1952; this led to a rush to produce the element by different means in order to circumvent a publication embargo on results associated with the tests on that group of islands in the Pacific Ocean.

Undiscovered heavy transuranium isotopes had been postulated as by-products of large nuclear explosions because the high neutron flux might cause uranium to undergo multiple neutron captures almost instantaneously. A research group led by Albert Ghiorso at the University of California Radiation Laboratory (UCRL) found element 99 in atmospheric filter samples collected from the Ivy Mike test. In larger fallout samples from a nearby atoll they found several other neutron-rich isotopes, including ^{255}100. The formation of ^{255}100 was attributed to the β-decay of ^{255}99, which itself originated from multiple β decays of uranium that had absorbed many neutrons in the explosion to yield ^{255}U. ^{255}100 eluted from an ion-exchange column at the expected time[1,2]; however, the UCRL team was barred from reporting a discovery from the classified weapons test. Ghiorso knew his team had discovered element 100, but fretted about losing credit if scientists elsewhere produced the element independently and published first.

Ghiorso's concerns were valid. At the Nobel Institute of Physics (NI) in Stockholm, a cyclotron had been recently upgraded to produce heavy-ion beams[3]. On 19 February 1954, NI scientists produced ^{250}100 by bombarding a uranium target with ^{16}O^{6+} ions for several hours[4]. Due to the numerological significance, the name centurium for element 100 had been circulating in the scientific community. NI director Manne Siegbahn wrote to Glenn Seaborg at UCRL to inform him of the discovery and suggested the name nobelium.



EMMA SOFIA KARLSSON, STOCKHOLM, SWEDEN

The UCRL group, realizing they were in a discovery race, had been conducting similar experiments with oxygen- and nitrogen-ion beams on uranium and plutonium targets. After producing ^{253}99, the UCRL team coaxed another neutron into the nucleus, hoping to obtain ^{254}99, which would then undergo β-decay to form ^{254}100. Their success was published[5] on 1 March 1954 — a mere ten days after the production of ^{250}100 in Stockholm — in a paper in which they took care to overtly mention the existence of earlier "unpublished [classified] information". The NI article would appear just a few months later, on 15 July[4].

The earlier classified information — the production of element 100 in the Ivy Mike test — was not publicly reported until June 1955 in a joint paper by UCRL, Argonne National Laboratory and Los Alamos Scientific Laboratory, the last of which was credited with building the weapon[2]. In the paper, the UCRL group unequivocally argued this earlier discovery in fallout should take precedence. The first sentence of the paper makes that claim crystal clear: "This communication is a description of the results of experiments performed in December, 1952 and the following months". To cement their discovery priority, they suggested the name fermium in the paper's title.

Typically in science, two independent, near-simultaneous discoveries are afforded recognition. Oxygen was independently found by Joseph Prisetley in 1774 and Carl Wilhelm Scheele around 1773. Lutetium was independently discovered by Georges Urbain and Carl Auer von Welsbach in 1907. Nevertheless, the Stockholm group is rarely, if ever, credited with a shared discovery of element 100. The Stockholm experiments reported in 1954 probably represent an independent discovery of element 100: with Cold War secrecy, the NI group was unlikely to have known about the UCRL group's earlier discovery before its publication in 1955.

Element 100 was not the last bit of element-discovery controversy for the NI. A few years later, they reported the production of element 102, a claim challenged by both UCRL and a Soviet group. Assigning discovery credit of element 102 took decades. This time, however, the name provided for element 102 by the NI group — nobelium — stuck, even though their discovery claim did not[6]. ❐

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in your element

Meitnerium in tribute

Adrian Dingle tells the story of how the name of element 109 represents the lasting recognition that one of the greatest nuclear physicists was in danger of never receiving.

While the furious and well-documented bickering between Cold War adversaries over the discovery priority for many of the transfermium elements was raging in the 1950s and 1960s (mostly involving the Lawrence Berkeley National Laboratory and the Joint Institute for Nuclear Research in Dubna), a new player in super-heavy synthesis was emerging: the GSI Helmholtz Centre for Heavy Ion Research, founded in Darmstadt in the old West Germany in 1969.

It wasn't long before the team there, led by Peter Armbruster and Gottfried Münzenberg, laid claim to the syntheses of new elements, starting with element 107 in 1981, and 109 a year later. In the original experiment that yielded a single atom of what came to be known as meitnerium, a ^{209}Bi target was bombarded with atoms of ^{58}Fe. Analysis led to the detection of an unusual α-decay — determined to have been from an atom of ^{266}109 — which was followed by a second α-decay event from the resulting ^{262}107 daughter nuclide[1].

At the time of element 109's discovery, IUPAC had stepped in to dissuade the premature suggestion of names for new elements, which conspicuously reflected discovery disputes. But the main reason meitnerium managed to avoid the transfermium naming wars was because nobody else had claimed priority for its discovery, which left the GSI group unchallenged in their suggestion, formally accepted by IUPAC in 1997[2]. Peter Armbruster described it in words that clearly allude to two major aspects of the intriguing life of nuclear physicist Lise Meitner (pictured): "to render justice to a victim of German racism and to credit in fairness a scientific life and work"[3].

Meitner's story is one of persecution (she faced discrimination as a woman then as a Jew, and was forced to flee Nazi Germany), and one of a bitter quarrel with her long-time colleague and erstwhile friend, Otto Hahn.

EVERETT COLLECTION HISTORICAL / ALAMY STOCK PHOTO

She played a pivotal role in understanding nuclear fission and giving the first theoretical explanation of the process together with her nephew Otto Frisch, accounting for the puzzling chemical findings of Hahn and Fritz Strassmann that bombarding uranium with neutrons had produced lighter elements. She was largely marginalized, however, notoriously by Hahn, who despite decades of productive collaboration, publicly excluded her from the story of nuclear fission's discovery.

Even though it did not seem like it at the time — with Hahn being solely awarded the 1944 Nobel Prize in Chemistry "for his discovery of the fission of heavy nuclei" — history has perhaps been kinder to Meitner: her Nobel exclusion is now widely regarded as unfair, and those who have an element named after them are part of a far more exclusive club than that of the Nobel laureates. A further fitting tribute would be a significant, real-world application of meitnerium.

For now, any utility clearly remains in the future. The bismuth/iron nuclear fusion that had produced the original, single atom of ^{266}Mt in 1982 was replicated in both 1988[4] and 1997[5], producing two and twelve atoms, respectively. In addition Dubna and Berkeley each confirmed the existence of ^{266}Mt through another reaction, this time between ^{208}Pb and ^{59}Co, with the Americans reporting it in 2009[6]. Current research has identified a number of isotopes ranging in mass from 266 to 278 — almost exclusively α-emitters — with ^{277}Mt undergoing spontaneous fission. Those isotopes have half-lives ranging from just milliseconds to up to a few seconds, the heavier ones being the longest lived.

Thus, it has not been possible to carry out chemical studies on meitnerium (even at the one-atom-at-a-time level), and its chemical and physical properties remain largely those of educated speculation through theoretical calculation and by analogy with other group 9 and period 7 elements. These point to an incredibly dense solid metal element that resembles iridium in terms of its most likely oxidation states, with +3 being the most stable in aqueous solution. A more recent study published in 2016 suggests the existence of a further isotope of meitnerium, ^{282}Mt (ref. 7), that may have a more workable half-life (in excess of one minute), providing potential for further research.

At this time, meitnerium's significance thus remains peripheral in terms of efficacy — but it should not be underestimated as it reminds us of an important part of history, scientific and otherwise. ❐

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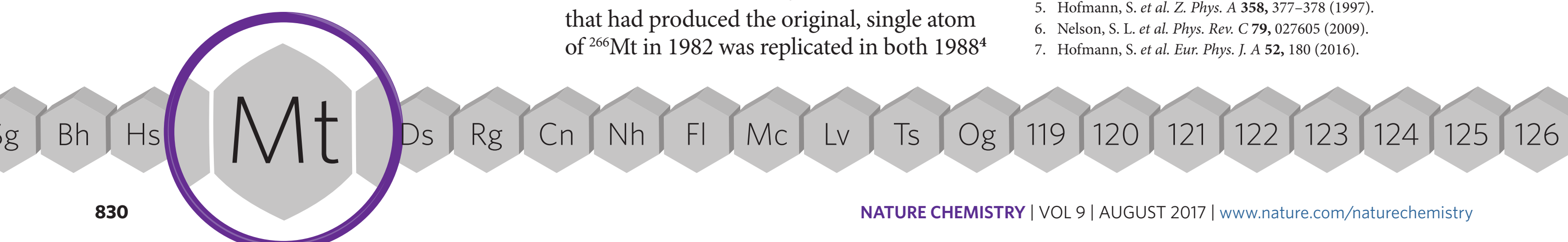

Peaceful berkelium

The first new element produced after the Second World War has led a rather peaceful life since entering the period table — until it became the target of those producing superheavy elements, as **Andreas Trabesinger** describes.

If nomenclature were transitive, element 97 would be named after an Irish bishop whose philosophical belief was that material things do not exist. But between the immaterialist George Berkeley and the element berkelium stands, of course, the fine Californian city of Berkeley (pictured), where the element was first produced in December 1949. The city became the eponym of element 97 "in a manner similar to that used in naming its chemical homologue terbium […] whose name was derived from the town of Ytterby, Sweden, where the rare earth minerals were first found"[1].

A great honour for the city? The mayor of Berkeley at the time reportedly displayed "a complete lack of interest when he was called with the glad tidings"[2]. There was every reason to take pride though. Berkelium was already the seventh new element discovered in which the city's University of California Radiation Laboratory (later renamed the Lawrence Berkeley National Laboratory) was critically involved. And by 1974, nine more elements would follow.

Though an effort of many, one name came to stand out in these elemental endeavours: Glenn Seaborg. A contributor to the Manhattan project, he played a central role in the first synthesis of plutonium. The procedures developed for its chemical isolation became crucial for the discovery of further transuranium elements. Elements 95 (americium) and 96 (curium) were still produced during the war, but the next step would prove tricky.

AF ARCHIVE / ALAMY STOCK PHOTO

Work towards synthesizing element 97 started around Christmas 1945, but was rendered difficult by the fact that only minute amounts of target materials were available for irradiation, and those were intensely radioactive. Nevertheless, Seaborg's recently postulated actinide concept (which posits that elements 89–103 form a series of their own that mirror the lanthanides) served as a helpful *leitmotif*. By the end of 1949, the team around Seaborg, including Albert Ghiorso and long-time collaborator and schoolday friend Stanley Thompson, had finally succeeded and obtained trace amounts of 243-berkelium by bombarding 241-americium with helium ions. The path to the new kid on the *f*-block had been tedious, so much so that Thompson and Ghiorso initially suggested assigning berkelium the chemical symbol Bm — evoking an association with 'bum' — "because it had been such a stinker in resisting identification for so long"[2]. In the end though, Bk was adopted.

Since its identification, berkelium led a mostly tranquil life. The element has found no practical uses, although it can be formed in nuclear detonations and in nuclear reactors. This makes understanding its chemistry relevant, in particular with a view to nuclear-waste management. Yet, studying berkelium remains a challenge. Only one isotope is available in bulk quantities: ^{249}Bk, with a relatively short half-life of 330 days.

Very early tracer experiments[3] had shown that berkelium has stable +III and +IV oxidation states, but further properties of berkelium have only started to transpire in the past few years. In 2016, the first single-crystal structures were presented[4], together with the finding that in Bk(III) compounds spin–orbit coupling leads to a mixing of the first excited state and the ground state. This gives rise to unexpected electronic properties not present in analogous lanthanide structures containing terbium. Even more recently[5], a combined experimental and computational study revealed that berkelium can have stabilized +III and +IV oxidation states also under mild aqueous conditions, indicating a path to separating it from other lanthanides and actinides.

The main use of berkelium, however — arguably one that wouldn't have met with Bishop Berkeley's approval — remains a distinctly material one: as the target for the synthesis of other transuranium and superheavy elements. For the production of element 117, which is currently the latest addition to the periodic table, ^{249}Bk samples were produced at the Oak Ridge National Laboratory, Tennessee (US) in a procedure that takes well over a year[6]. Targets were then shipped to Dubna (Russia) and later to Darmstadt (Germany), where they were bombarded with 48-calcium to synthesize element 117. So crucial was the berkelium target in these experiments that the name of element 117 references the place where the target — not the element itself — was produced: tennessine.

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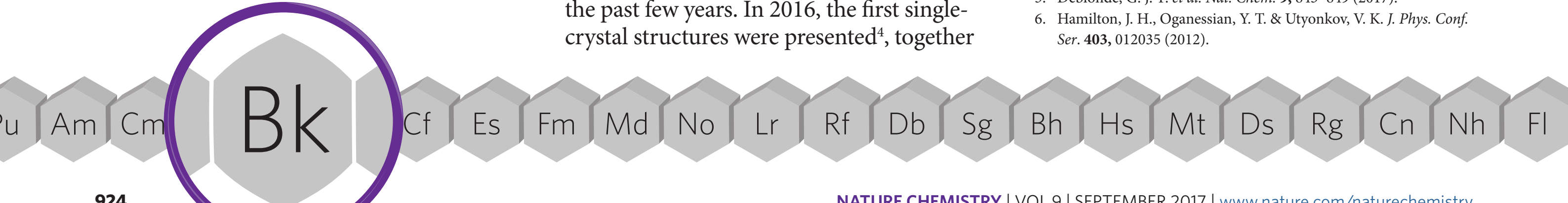

The darmstadtium cornerstone

Dieter Ackermann explains why element 110 occupies a significant place in the superheavy corner of the periodic table.

The first isotope of darmstadtium to be synthesized was ^{269}Ds, in November 1994, through a cold fusion reaction between ^{62}Ni and ^{208}Pb (ref. 1). The concept of cold fusion, where a nucleus is formed in a fusion process at low excitation energy, had already been exploited successfully in the hunt for superheavy nuclei by the team working at the accelerator laboratory GSI in Darmstadt, Germany — the city that gave its name to this element.

The team at GSI had already successfully synthesized elements 107 (bohrium), 108 (hassium) and 109 (meitnerium) in 1981, 1984 and 1982, respectively. Ten years had elapsed, during which the group had improved the efficiency of their experimental set-up to cope with ever-lower probabilities for the synthesis of ever-heavier elements. To attempt the synthesis of element 110, it was crucial to first measure the 'excitation function' — a production probability as a function of energy — of the hassium isotope ^{266}Hs ($Z = 108$). An extrapolation then allowed the team to successfully predict the correct energy needed for the synthesis of darmstadtium.

The targeted isotope ^{269}Ds was indeed produced by fusion between ^{62}Ni and ^{208}Pb, followed by 'cooling down' of the fused system through a one-neutron emission. But there was more: the team had enough time to change the projectile to ^{64}Ni and synthesize a second isotope, ^{271}Ds, and to then go one step further. They exchanged the ^{208}Pb foil that had served as the target for the previous two reactions to a ^{209}Bi one, featuring one more proton, thus producing element 111 (roentgenium) in the same exciting run.

An earlier attempt to synthesize ^{271}Ds at higher beam energy had failed in 1985, despite having applied a beam dose that was three times higher[2]. One of the reasons for the choice of the higher energy had been a concept called 'extra push', according to which an additional amount of energy may push the fusing system across a complex potential energy landscape. This concept — which had also constituted part of a controversial debate within the GSI group during measurement of the ^{266}Hs excitation function[3] — had failed here, however.


PETER SCHICKERT/ALAMY STOCK PHOTO

The Darmstadtium conference centre in Darmstadt holds a copy of the publication reporting the discovery of its eponymous element in its cornerstone.

Experimental superheavy-element chemistry is an extremely challenging undertaking and other, even heavier elements seem to promise more exciting features than darmstadtium. Therefore, this chemistry has not been attempted yet and only theoretical predictions of the chemical properties of darmstadtium exist. They point to a different ground-state configuration than that of its lighter homologues in group 10, but nevertheless a rather similar chemical behaviour. As for all the superheavy elements, relativistic effects are of major importance here. These effects arise from the acceleration of the inner electrons to the highest velocities in the strong Coulomb field created by the many protons (here 110) in the heavy nucleus[4].

In contrast to its chemistry, the physical properties of darmstadtium — or rather of its isotopes — have been experimentally studied, revealing some exciting nuclear structure features. The known darmstadtium isotopes sit on the edge of a region of deformed nuclei in the Segrè chart — the representation of nuclides as a function of their proton and neutron numbers. This region is characterized by enhanced nuclear stability at atomic number 108 (hassium), and at neutron numbers 152 and 162, which are often called deformed sub-shell closures[5]. Towards higher atomic numbers and higher mass, theory predicts that nuclear deformation vanishes and the area of spherical nuclei, which should be stabilized by quantum mechanical effects — referred to as the 'island of stability' — will be reached[6].

Its nuclear deformation is also the cause of a striking feature of one of its isotopes, ^{270}Ds, which represents the heaviest case of a metastable state — referred to as a *K* isomer. This state resembles a wobble stone with an axis of total spin, which is inclined with respect to its symmetry axis, and whose decay is 'forbidden' by quantum mechanics. It is more stable than the ground state — an uncommon feature for nuclei. This is possibly a first hint of some interesting physics, yet to be discovered, at the onset of the development towards the nuclear sphericity predicted to occur in this area. In addition, these metastable states, depending on deformation, have the potential to be tracers guiding us towards the 'island of stability'[7].

These interesting features make ^{270}Ds one of the cornerstones in the arc leading to the superheavy elements. ☐

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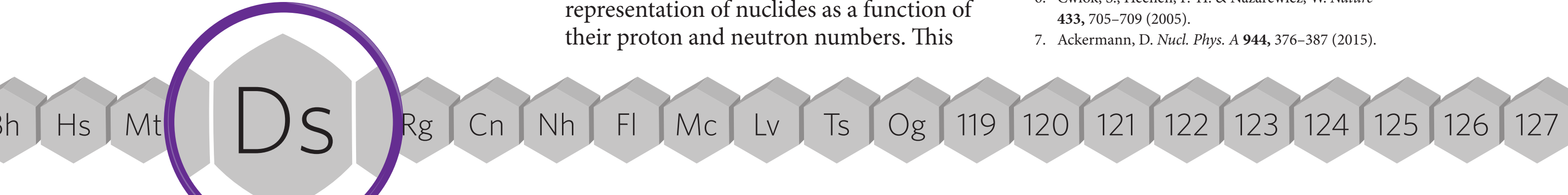


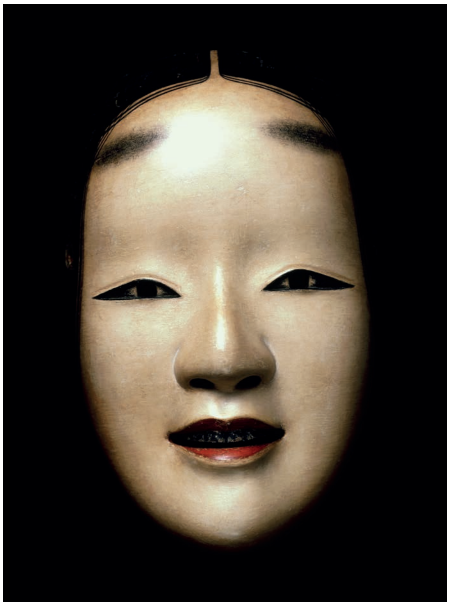
in your element

Nihonium the obscure

Iulia Georgescu explains her fascination with the elusive element 113.

Confused by the empty boxes at the bottom-right corner of the periodic table, my friend and I bugged our high-school chemistry teacher until she produced a newer version from a back cabinet. There, those boxes were filled with obscure element symbols such as Uut, Uuq or Uup, associated with near-unpronounceable latinized placeholder names that simply stood in for the atomic numbers: Uut for ununtrium, which just means 1-1-3-ium, Uuq for ununquadium, or 1-1-4-ium, and so on. None of this did anything to help illuminate us. We were then sent away with a brief mention that these were short-lived man-made elements created in a nuclear reactor. This not-entirely-accurate explanation was rather unsatisfying. Undeterred, we went straight to the bookshop, purchased a periodic table poster, stuck it on the wall of my room and promptly proceeded to fill in the empty boxes with new elements shamelessly named after our ourselves, our surnames germanized for good measure.

My career did not live up to my exalted teenage expectations and unsurprisingly there is no element named after me, but years later I was working as a postdoc at RIKEN (Rikagaku Kenkyūsho, or the Institute of Physical and Chemical Research) in Japan and met Kosuke Morita, who led the team that discovered element 113 — the Uut that had intrigued me back in school. For a long time I had no idea that the jovial, unassuming man that I was regularly meeting at the Go club playing the popular strategy board game was actually a well-known superheavy element hunter. But this is not the only reason I have a special affinity for element 113. I associate it with the exotic and sometimes misunderstood culture of its eponymous country.



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Element 113 — named nihonium (Nh) after Nihon, which means Japan in Japanese — was the first element discovered and correctly identified in Asia. We need "and correctly identified" because of its problematic cousin nipponium (named after Nippon, synonym of Nihon). At the beginning of the twentieth century the Japanese chemist Masataka Ogawa was studying with William Ramsay in London. They suspected some new element could be found in a mineral called thorianite. Ogawa managed to isolate what was indeed a new element and published his results in 1909, naming it nipponium — he had misidentified it as element 43 (now technetium), however, when it was in fact element 75 (rhenium), right below it in the periodic table. Element 43 was mistakenly claimed for another time by German chemists Walter and Ida Noddack and Otto Berg, who all actually went on to discover rhenium in 1925 — completely independently from Ogawa's unrecognized element. Finally, element 43 was discovered — and correctly identified — by Emilio Segrè and Carlo Perrier in 1937.

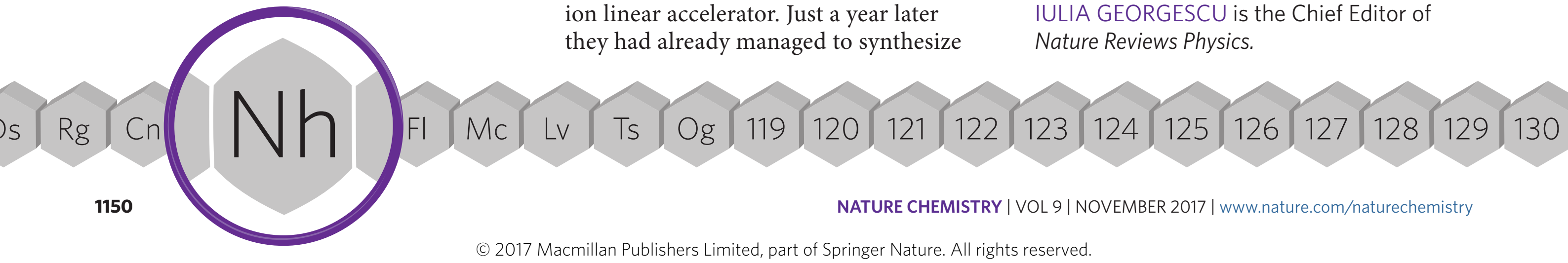
Nihonium's discovery was perhaps less dramatic, but element 113 was arguably far more difficult to spot and identify. In 2003 Morita's team started looking for superheavy elements at RIKEN's heavy-ion linear accelerator. Just a year later they had already managed to synthesize the first nihonium atom by smashing bismuth-209 and zinc-70 nuclei. The atom decayed after a mere 0.34 milliseconds and the challenge was to identify it through a forensic analysis of its decay products. Nihonium decays sequentially to dubnium-262 through four α-decays, which in turn further breaks down into two smaller fragments. In 2005 the RIKEN team managed to identify the remains of another nihonium atom.

To fully characterize the dubnium decay chain the RIKEN team still had two α-decays to understand, from bohrium-266 to dubnium-262 and lawrencium-258. For this, they bombarded curium with a sodium beam to obtain bohrium and dubnium, and once this process was clear they then 'just' had to wait for another nihonium atom to be generated. It took seven years and a lot of patience, but in 2012 Morita's team finally identified a chain of six α-decays from element 113, this time not to dubnium but further down to lawrencium-258 and mendelevium-254. The existence of nihonium was finally nailed down.

Meanwhile, a Russian–US collaboration between the Dubna Joint Institute for Nuclear Research and the Lawrence Livermore National Laboratory had also identified element 113 as a decay product of element 115, which they would name moscovium, and made a discovery claim for these two elements. By 2005 the collaboration had strengthened their case for the observed decay, but the IUPAC still found the evidence insufficient and the discovery of element 113 was attributed to the RIKEN team, who were given the privilege of naming it.

Although it's now been produced, identified and named, we still haven't learned an awful lot more about element 113 since my school years. Nihonium makes me think of a Japanese Noh mask (pictured): mysterious and somewhat disturbing. We don't know what is hiding behind it; for example, in terms of its properties or behaviour, but perhaps that is where its charm lies. ❐

IULIA GEORGESCU is the Chief Editor of *Nature Reviews Physics.*



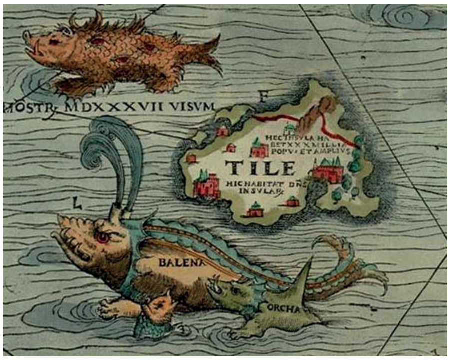
Thoroughly enthralling thulium

Named after a mysterious place, thulium — one of the rarest rare earths — has some exotic chemistry in store for us, says **Polly Arnold**.

Thulium — isolated by a Swedish chemist like so many of the other rare earths — is named after a mysterious place in the far northern corners of Europe. The Thule of medieval geography (and its variations such as Tile, as seen in the 1539 map by cartographer Olaus Magnus, pictured) has since been attributed to a variety of places including Iceland, islands north of Scotland, and Scandinavia. It is the latter that Per Teodor Cleve referred to when he proposed a name for element 69, which he identified in 1879 while studying the mineral 'erbia' from the Swedish town of Ytterby, working on isolating different rare-earth trications from each other — a notoriously challenging endeavour, given their very similar behaviours.

Thulium is relatively expensive and has only found commercial application in low-volume uses in the medical field as a dopant to the yttrium aluminium garnet (YAG; $Y_3Al_5O_{12}$) used in surgical lasers, and its radioactive isotope ^{170}Tm serves as a source of X-rays for portable devices. Its sharp inter-4*f*-orbital electronic transitions are also exploited in anti-counterfeiting inks in Euro currency banknotes, whose blue fluorescence under UV light arises from Tm^{3+} ions.

Rare-earth chemistry in solution mostly occurs in the +3 oxidation state. Nevertheless, divalent rare-earth halides (REX_2, with RE a rare-earth element, X a halide F–I) are accessible for europium, ytterbium and samarium, which approach or achieve a full- or half-full *f*-shell in this oxidation state. Indeed, samarium diiodide and its solvates (which help tune its solubility and reducing power) have been used for around fifty years now by organic chemists for controlled one-electron reduction reactions of a range of functional groups, including carbonyl, alkyl halide and nitro groups[1].



DETAIL FROM THE *CARTA MARINA*, OLAUS MAGNUS, 1539, COLOURED BY ANTONIO LAFRERI, 1579

Although textbooks stipulate the absence of the +2 oxidation state for the other rare earths in solution, research chemists know of three others — neodymium(II), dysprosium(II) and thulium(II). Although they are extremely difficult to reduce, and can only be isolated with the right ligands, they can be accessed by comproportionation ($2REX_3 + RE = 3\ REX_2$), or through REX_3 reduction by a very strongly reducing metal such as potassium.

In 1997, with the report that TmI_2 could be dissolved and solvated in the ether solvents dimethoxyethane (DME) and tetrahydrofuran (THF)[2], Bochkarev made the breakthrough that launched the reactivity of compounds of all of the rare earths(II) in solution. Until then, formally zero-oxidation-state complexes (with strong colours arising from metal–ligand charge transfers[3]) made using metal vapours had been the only known low-oxidation-state complexes of these 'non-reducible' rare earths.

As one of the rarest rare earths, thulium will not be replacing samarium as organic chemists' reductant of choice any time soon due to its high cost[4]. Yet its potential for exotic new chemistry is enormous. Using organometallic ligands and techniques, we can make compounds that do not follow the well-established rules of the *d*-block metals. Studying their fundamental electronic structures and bonding subtleties can then help us gain a better understanding of — and in turn a better ability to manipulate — the heavy, relativistic and often radioactive metals of the *f*-block metals, whose reactivities are critical to renewable energy, magnet technologies and nuclear waste management.

The capacity for ligands to tune organometallic species is phenomenal — ligand choice for example can shift the formal potential of a particular metal redox couple by as much as 1.5 eV. The first organometallic thulium(II) complex reported was isolated by replacement of the iodides of $TmI_2(THF)_3$ by a silyl-functionalized cyclopentadienyl anion, which is well-known for its capacity to stabilize formally low-oxidation-state metal cations through electron-density acceptance from the metal (back-donation). At low temperatures, dark purple crystals of the THF solvate were grown and characterized. These colours are typical of rare-earth(II) systems; at room temperature these slowly react to deoxygenate the solvents, returning to the pale-yellow colours of $5d^0$–RE(III) ions.

The high reactivity of these complexes means that no suitable method to record the potential of the metal's redox couple in solution has yet been developed. However, pleasingly, there has been a resurgence in the development of new ligands that can shift these redox couples by manipulating geometries and orbital overlap[5–8], and in the search for other metals in the *f*-block — including even the highly radioactive transuranic elements[9] — that can exhibit new, low formal oxidation states. New data suggest different *d*/*f* electron configurations are now achievable[10]; future undergraduates may be disappointed to have to learn ligand-field theory for the *f*-block as well as the *d*-block. ❐

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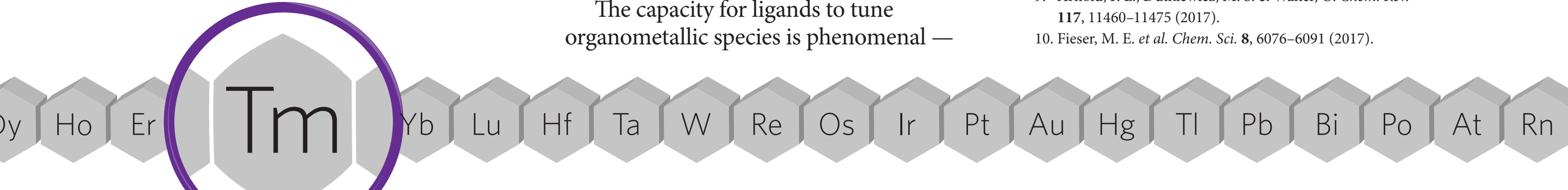

in your element

Terbium glows green

Geng Deng relates how terbium, a garden-variety lanthanide, has found its way into our daily lives owing to its green phosphorescence.

It may be one of the rarer rare-earth elements in the Earth's crust, but terbium is actually quite common around us. Despite their name, the rare-earth elements (which consist of the lanthanides as well as scandium and yttrium) aren't all that scarce; element 65 for example is more abundant than mercury, and as numerous lights and monitors of modern life have made use of green terbium-based phosphors, it has seeped into our homes and working environments.

The story of terbium discovery started in Ytterby, a prolific small village in Sweden that has no fewer than four rare-earth elements named directly after it — yttrium, terbium, erbium and ytterbium — and from whose earths (as oxides were then called) several other elements were also isolated (scandium, thulium, holmium, gadolinium and lutetium). It took decades to identify the composition of a black mineral found in Ytterby by Carl Axel Arrhenius in 1787, first referred to as ytterbite. It was later renamed gadolinite after Johan Gadolin, who realized it contained an unknown earth; that is, the oxide of a new element, which he called yttria.

In 1843 Swedish chemist Carl Gustaf Mosander separated an yttria sample into three components: yttria (mostly consisting of yttrium oxide), as well as erbia and terbia, each of which, he believed, contained a new element. He was right — but a mix-up of Mosander's samples during their spectroscopic analysis means that terbium was isolated from his original erbia, while erbium was found in his terbia. This was just too confusing, so the minerals later also swapped names to match those of their principal components.

Like the other lanthanides, terbium's most common oxidation state is +III. The green (or light-lime) phosphorescence under ultraviolet light of its trivalent salts, such as $Tb_2(SO_4)_3$ (pictured), has long been known — it is so intense that it can be seen with the naked eye. It arises from several excited-to-ground electronic-state transitions[1], with one transition contributing the main emission peak at 545 nm. Many of its rare-earth cousins also luminesce brightly in different colours; for example, europium(III) is a red emitter while its reduced form europium(II) is a blue one. But although those emissions were well-known, it wasn't until the second part of the twentieth century that they were taken advantage of for practical applications in lighting.

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The incandescent lamp, invented by Thomas Edison in 1879, had been widely used for over a century. But it is inherently energy-inefficient: heating a wire with an electric current to the point that it will glow means that most of the energy used is dissipated in the form of heat and only a small fraction is converted into light. In the 1960s, rare-earth salts came into focus[2,3] as they waste little energy during the emission process. Furthermore, the green-emitting terbium compounds could be combined with the red- and blue-emitting europium ones to make white-light fluorescent lamps. The first commercial such rare-earth-based energy-efficient lamp was made in 1974, and this type of lighting soon spread across the world.

Meanwhile, traditional colour television sets and monitors were also being developed that used cathode ray tubes, in which electron beams are sent to the screen to excite phosphors and in turn generate images. Here as well the combination of terbium and europium compounds in the red–green–blue (RGB) additive colour model allowed a wide range of colours to be produced. Between the 1950s and 1990s, those monitors delivered terbium compounds to millions of households around the globe. Although the advent of flat-panel technologies in the late 2000s has curbed that application, terbium-containing compounds have also found use as probes in the biomedical field, such as in fluoroimmunoassays[4] and supramolecular luminescent sensors[5].

A perhaps more exotic use of element 65 is in an alloy called terfenol-D, which consists of terbium, iron and dysprosium: it is a magnetostrictive material that contracts and expands in a magnetic field. Because it is able to withstand high strains, terfenol-D has been used in actuators and underwater transducers. It also serves in the portable system 'SoundBug', which can be attached to any resonant flat surface (such as, wood, glass or metal) to turn it into a speaker: the magnetostrictive material converts electrical input into vibrations by changing the applied magnetic field, which are then amplified by the resonant surface.

Located in the middle of the lanthanides — a part of the periodic table that has remained relatively unexplored — terbium has shone through owing to its distinctive green phosphorescence and found exciting uses. ❐

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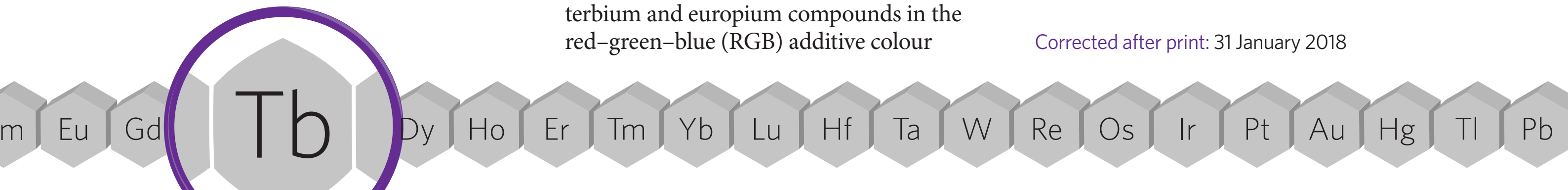
Corrected after print: 31 January 2018



Correction

In the In Your Element 'Terbium glows green' (*Nat. Chem.* **10,** 110; 2018), phosphorescence was mistakenly described as fluorescence in three instances: the standfirst, the fourth paragraph, and the final paragraph. Furthermore, the line from the fourth paragraph "Many of its rare-earth cousins also fluoresce" was changed to "Many of its rare-earth cousins also luminesce". This has been corrected after print 31 January 2018.

The germination of germanium

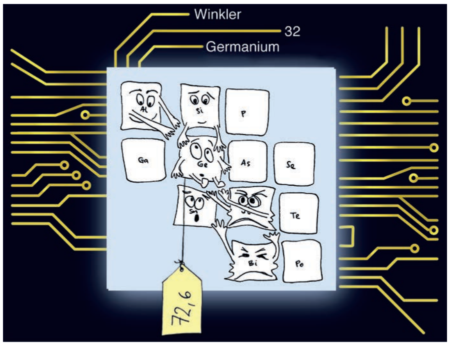
Shawn C. Burdette and **Brett F. Thornton** explore how germanium developed from a missing element in Mendeleev's periodic table to an enabler for the information age, while retaining a nomenclature oddity.

When German chemist Clemens Winkler analysed the mineral argyrodite that had been excavated from a mine near his hometown of Freiberg, he could not account for 7% of the total mass[1]. The balance of the contents was identified as silver (75%), sulfur (18%) and some minor impurities. In 1886, after many failed attempts to isolate the elusive substance, Winkler finally precipitated a sulfide complex using a large excess of hydrochloric acid, and rigorously interrogated the material[2].

These investigations coincided with an era of confusion and clarification about the then-relatively-new periodic table. Mendeleev's seminal proposal for element organization had appeared in 1869, and an important part was the empty spaces he had left for elements yet to be discovered. Two of those predicted elements, gallium and scandium, were discovered in 1875 and 1879 respectively, and corroborative evidence was mounting. Nonetheless, some scientists still had doubts about Mendeleev's periodic table.

Recognizing that the missing component in argyrodite was a new element, Winkler dubbed it 'germanium' and proposed placing it between antimony and bismuth, based on chemical similarities with these known elements[1]. One look at the modern periodic table makes this placement appear incongruous — but Mendeleev's table did indeed have such an opening for 'eka-antimony' between antimony and bismuth. After Mendeleev learned of Winkler's discovery, the two scientists, together with German chemist Julius Lothar Meyer, corresponded at length about the new element's anticipated and actual properties. Mendeleev doubted some of the initial hypotheses, even suggesting that the element might be eka-cadmium.

These seemingly bizarre suggestions arose because Mendeleev's tables wrapped the blanks for the then-unknown lanthanides into the same groups as lighter main-block and transition elements. Only four elements were known between barium and tantalum, and the arrangement at the time made Winkler's suggestion of eka-antimony and Mendeleev's of eka-cadmium seem eminently reasonable. Obtaining the atomic weight of germanium, as Winkler noted in his first report[1], would resolve the positioning problem. Ultimately it was Meyer, with his assertion that germanium was in fact eka-silicium, who was proven right by analyses of the physical properties of germanium, which perfectly matched nearly all of Mendeleev's 1869 predictions for eka-silicium — including an atomic weight of 72.



EMMA SOFIA KARLSSON, STOCKHOLM, SWEDEN

In his extensive follow-up report on the identification and characterization of germanium[2], Winkler reported having received objections to his proposed name because it had too much of 'un goût de terroir' — that is, it was too nationalistic. He resisted any change, citing that both gallium and scandium paid homage to their discoverers' homelands. Although it was its root that was begrudgingly accepted, another aspect of the name could have invited scrutiny. Germanium, along with selenium, tellurium and helium, is one of the few non-metallic element to carry the '-ium' suffix in English[3]. This can seem an odd choice as the title of Winkler's original report, entitled 'Germanium, Ge, a new non-metallic element', plainly states he did not believe it was a metal[1]; yet it is consistent with the German name of the other group 14 metalloid, silicium.

With the invention of the point-contact transistor in 1947, germanium played a key role in solidifying the definition of metalloids as well as ushering in the information age[4]. The same characteristics that contributed to the challenge in isolating element 32 and placing it on the periodic table are also the attributes that impart it with semiconducting properties. For a time, the moderately uncommon element (~1.5 ppm in the Earth's crust) became a vital commodity, because it was easier to obtain in the necessary purity for the electronics industry than silicon until the 1960s. Although improvements in silicon refining temporarily reduced the industrial demand for germanium, recent years have seen a resurgence in its uses. Germanium now finds uses in optical fibres, polymerization catalysts, and Si-Ge alloys in microchip manufacturing, with feature sizes on the chips reaching 7 nm (< 60 Ge atoms).

Over 100 years after its discovery, the placement of germanium with the other metalloids along the dividing line between the metals and non-metals seems prosaic, even if its metallic nomenclature remains an aberration. ❐

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Rounding up lutetium

Lars Öhrström suspects that as time goes by, we may see more of lutetium — the last of the lanthanoids.

"We'll always have Paris" Rick says to Ilsa in their final goodbye on the foggy airstrip of Casablanca in the eponymous film. However, the question among chemists about the element lutetium, named after Lutetia, as the French capital was known in Roman times, is not so much about having it (it is more abundant than silver in the Earth's crust), but rather where to place it on the map.

With its valence electron configuration $[\mathrm{Xe}]4f^{14}6s^{2}5d^{1}$, element 71 seems to belong to group 3, but we often see it placed at the very end of the lanthanoid series. Its downstairs neighbour lawrencium, for which experimental data are much more difficult to obtain, is in the same ambiguous situation. So which elements should come below scandium and yttrium — lutetium and lawrencium, or lanthanum and actinium?

Many periodic tables — including the one presented by the International Union of Pure and Applied Chemistry (IUPAC) — are a bit vague on this point, and the question of group-3 membership is currently under thorough investigation by an IUPAC project[1]. Meanwhile, the chemical closeness of the group-3 and 4*f* blocks are widely recognized and reflected through collective names approved by the IUPAC: the 'lanthanoids' designate the 15 elements from lanthanum to lutetium, and the 'rare-earth metals' include those 15 as well as the unambiguous members of group 3, scandium and yttrium.

In any case, lutetium was isolated independently by three chemists in 1907, from samples composed of mainly an oxide of ytterbium, one of the later lanthanoids — so it seems fitting for lutetium to also be considered part of this gang. There appears to have been a heated argument over priority between two of the discoverers, Georges Urbain and Carl Auer von Welsbach, from France and Austria, respectively. The third — uncharacteristically for the field — kept a low profile, though the US chemist Charles 'King' James now has a National Historic Chemical Landmark dedicated to him at the University of New Hampshire.

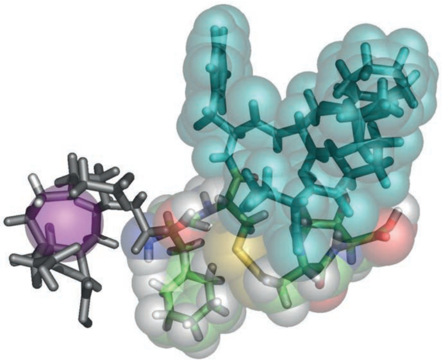

Illustration of a radiolabelled somatostatin analogue built using PyMOL (https://pymol.org) with a DOTA derivative (PDB: 1NC2[6], shown in black) enclosing lutetium (in lilac), and Tyr^{3}-octreotate (PDB: 1YL8[7]); the part of octreotate that binds to the receptor is shown in turquoise. PDB, protein data bank.

BRITTA LANGEN, UNIVERSITY OF GOTHENBURG, SWEDEN

The International Atomic Weights Commission under its chair Frank Clarke settled the dispute in 1909. The discovery credit was attributed to Urbain and his suggested name — lutecium, later to be spelled lutetium — was adopted over Welsbach's cassiopeium. Oddly, this was not the end of element 71's role in the naming game. In 2009, the name copernicium was proposed for the new element 112, but its suggested symbol Cp was rejected by IUPAC because it had already been used for cassiopeium — which, although not official, was used in the German-speaking world for a long time; copernicium instead got the symbol Cn.

Lutetium is mined together with the other rare-earth metals from oxides, but is much less abundant, with an average yield that is in the range 0.01–1.00%. Water solutions will contain colourless Lu^{3+} ions, the only stable oxidation state, with seven to nine water molecules coordinated. This means that to be useful, coordinating ligands need to support high coordination numbers, and that is exactly the case for motexafin (based on the 'texaphyrins'), a sub-class of porphyrin-like macrocycles with five instead of four nitrogen atoms in an approximately planar ring. Motexafin lutetium, which features Lu^{3+} and two acetate counter-ions coordinated on either side of the macrocycle, is potentially a good photosensitizer in dynamic phototherapy and has been going through phase I trials against prostate cancer[2].

Uses of the naturally occurring element are otherwise scarce, but its isotope Lu-177 is successfully used in experimental and clinical treatments against some severe cancers by hooking it up to a tetraazacyclododecane-tetraacetate (DOTA) ligand grafted to octreotate, a small peptide (pictured). DOTA acts as a seven- or eight-coordinating chelator whereas octreotate binds to receptors on the surfaces of a number of neuroendocrine tumour cells, thus directing the ionizing radiation of the lutetium isotope into the tumour and killing it[3,4].

Lutetium is also used, together with hafnium, in geological radioactive dating, and trace amounts can be analysed by neutron activation. This was recently used in quantifying rare earths, including lutetium, in the sediments of the Bou Regreg River in Morocco — not far from Casablanca[5]. Here's looking at Lu, kid! ❐

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r Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra

Corrected: Author Correction

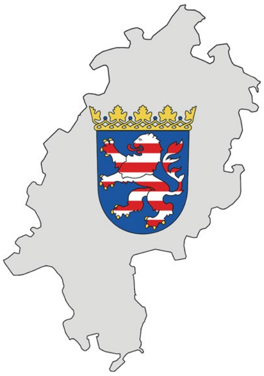
Hidden hassium

From its scarcity to political intrigue over naming conventions, element 108's story describes how international cooperation overcame the limits of nuclear science, says Michael Tarselli.

A casual aside uttered by Nottingham Professor Sir Martyn Poliakoff during his *Periodic Table of Videos* series (http://www.periodicvideos.com/videos/108.htm) reflects a general feeling: "Hassium … I know nothing about hassium. Shall we make something up?". Among the already little-known super-heavies, element 108 doesn't have the controlled reactivity of a seaborgium atom, or the relative stability of fermium — the longest-lived isotope is ^{257}Fm with a net 100 day half-life, and ^{252}Fm is believed to resist spontaneous fission rather well[1], though it undergoes α-decay. In contrast the half-life of hassium's most stable isotope, ^{270}Hs, is only a few seconds. Estimates for the total number of hassium atoms created so far run from a few dozen to as many as 100 atoms. Ever.

How were those lone atoms produced? Let's rewind to 1984. Major nuclear research was emerging from three countries, two of which had outmoded names: West Germany, the USSR and the USA. Back then, element 108 was simply known as Uno for 'unniloctium', literally meaning 'one-zero-eight' according to a system of numerical roots adopted in 1979[2]. Since the 1940s, scientists had prepared novel transactinides by bombarding uranium with neutron beams. This approach, however, only works up to element 100 (fermium). The team at the Joint Institute for Nuclear Research (JINR) in Dubna, USSR (now Russia), led by actinide heavyweight Yuri Oganessian, then pioneered the techniques of 'cold' fusion (collisions of two early elements such as iron and bismuth) and 'hot' fusion (using actinide radionuclides as the targets).

In hot fusion, researchers bombard a heavy target such as einsteinium or plutonium with a beam of lighter elements such as carbon or oxygen. This early technique, according to Peter Armbruster[3] from Germany's GSI Helmholtz Centre for Heavy Ion Research, worked fine up to element 106 (seaborgium). New equipment later allowed beams of heavier nuclei such as calcium or iron to be fired, pushing back the limit to 118…so far. The first hassium atoms were synthesized by bombarding a lead target with iron atoms. The process was later optimized, and firing ^{26}Mg at a target made of ^{248}Cm gave ^{270}Hs — which was dubbed the doubly magic isotope[4].



Credit: michal812 / Alamy Stock Photo

Along with new elements came numerous priority disagreements, and thus naming controversies — so much so that the International Unions of Pure and Applied Chemistry and Physics (IUPAC and IUPAP) created the Transfermium Working Group, in which scientists from the three main heavy-element-discovering nations first oversaw the recognition process for elements 101–109. In 1994, this group advanced the names hahnium and meitnerium for elements 108 and 109, for nuclear fission discoverers Otto Hahn and Lise Meitner, respectively. Meitnerium was adopted, but for 108 the suggestion of the German team, led by Peter Armbruster and Gottfried Münzenberg, was the one ratified in 1997: hassium, which honours the German state of Hesse (whose map and coat of arms are pictured).

Perhaps the most tantalizing aspect of hassium is that it's nearly unexplored. We still don't know many of its physical properties — melting point, boiling point, pressure or heat capacity. Looking at its group 8 cousins iron, ruthenium and osmium one expects it might be a solid, but this is tough to tell from a handful of atoms stuck to a silicon detector. When you have only traces of a specific element, how do you investigate its properties? Invent some fairly specialized lab equipment. Hassium is tough to separate away from other super-heavies and by-products of the fusion reaction; specialized detectors were built to study its characteristic α-decay and probe its reaction chemistry. In 2002 the GSI, JINR, the Lawrence Berkeley National Laboratory and seven other institutions joined forces to create seven atoms of hassium. Those were then pushed through a stream of oxygen to yield a highly volatile oxide with similar properties to ruthenium and osmium tetroxides — "presumably HsO_4", whose single ^{269}Hs atom was identified by α-decay[5]

In a 2011 *Science* Perspective[6], nuclear physicist Walter Greiner wryly suggested that neutron-rich nuclei, such as hassium, might be feasibly made by setting off "two or three nuclear explosions near a suitably protected target buried deep underground." As multiple global treaties prohibit this, we will have to keep relying on technologies such as bombarding accelerator targets with neutron-rich beams of ^{48}Ca or ^{58}Fe. Even if we have to wait a few more decades for the next generation of nuclear scientists to produce enough hassium to fill in the blank spaces of our knowledge, it's probably for the best. ❐

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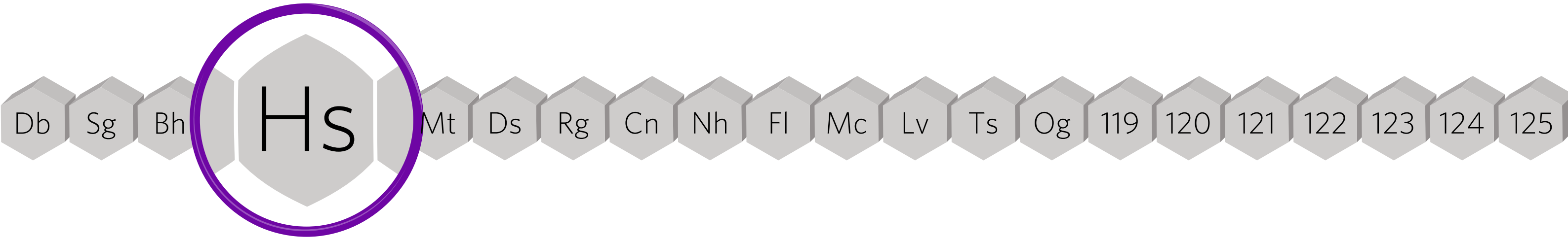

in your element

Praseodymium unpaired

Adrian Dingle relates how one ‘element’ that fell off the periodic table was eventually replaced by two.

If there’s a single thread that runs through the history of the lanthanoids, it’s the manner in which they persistently resisted easy distinction from one another. The similarity in the chemistry of the 4*f* elements confounded nineteenth-century chemists for decades, and it took a new analytical technique to finally tease praseodymium from its hiding place.

The story of element 59 starts with Carl Gustav Mosander in 1841, and his discovery of what he thought was a new element in cerite. He named it didymium[1], Greek for ‘twin element’, because it so closely resembled lanthanum. As it turned out, his choice of name could hardly have been a better one, although for an entirely different reason.

In addition to didymium (which turned out to be fictional), by 1843, the actual elements cerium, lanthanum, erbium and terbium of the modern 4*f* series had all been discovered. There then came a pause in the discovery of the remainder of the lanthanoids. The traditional analytical method of the time — the extraordinarily tedious fractional precipitation and crystallization — had reached the end of its useful life as a technique able to, on its own, distinguish between elements so similar to each other: they looked the same and behaved in similar ways. Further discoveries would only come with a new impetus, which came from both practice and theory.

The advent, and subsequent perfection, of Bunsen and Kirchhoff’s spectroscopy[2] throughout the early 1860s coincided with an increased understanding of patterns in the properties of elements, which culminated with Mendeleev’s first periodic table of 1869. At the time didymium was sufficiently well established as an ‘element’ to appear on Mendeleev’s table with the symbol Di — it is the only one from the original table that does not appear on the contemporary version.

The advances in spectroscopy enabled chemists to finally distinguish lanthanides from each other thanks to their unique spectral fingerprints. Taken together with the fractional precipitation and crystallization method and the development of the periodic system, they led to a new surge of rare-earth discovery between 1878 and 1886, yielding holmium, ytterbium, samarium, thulium, gadolinium, praseodymium, neodymium and dysprosium.

Credit: imageBROKER / Alamy Stock Photo

It is Carl Auer von Welsbach who is credited with the separation of didymium into neodymium and praseodymium. Long before his successful fractional crystallization of the double ammonium nitrates[3], though, the potential for didymium to be something other than the singular substance Mosander proposed was recognized by several chemists. Jean-Charles Galissard de Marignac, Paul-Émile Lecoq de Boisbaudran, and Per Teodor Cleve were among the prominent names of the time to believe didymium was not pure. Two others went further and embarked on spectroscopic studies: Marc Delafontaine in 1878, and in 1882 Bohuslav Brauner, who like Auer von Welsbach was a student of Bunsen’s in Heidelberg.

But despite apparently having written a note to the Austrian newspaper *Wiener Anzeiger*[4], it seems that Brauner never formally published his work. In 1885, Auer von Welsbach announced to the Vienna Academy of Sciences his successful separation of didymium into two ‘earths’ (as oxides were then known): neodymia and praseodymia, from which the elements neodymium (the new twin) and praseodymium (the green twin) would ultimately be isolated.

Despite the death of didymium as an element, the name lives on in the specialized glass used in the lenses of goggles worn by welders and glassblowers. The combination of praseodymium and neodymium allows the filtering out of both yellow light and infrared wavelengths, thus protecting the wearer’s eyes from potentially harmful radiation without affecting their vision.

As is the same for all of the lanthanoids, the chemistry of praseodymium is dominated by the +3 oxidation state — but its electronic configuration of [Xe]$4f^3 6s^2$ makes it a good candidate for creating higher oxidation states, including that of +5. In 2016, a Pr(v) centre was reported[5] in PrO_2^+. One year later, NPr(v)O was described, together with NPr(iv)O$^-$ — both featuring a Pr≡N triple bond and a Pr=O double bond[6].

Another oxide of praseodymium has found use as a spacer layer in a potentially super-conducting material[7]. The compound $Pr_4Ni_3O_8$, whose structure can be described as three layers of a nickel oxide separated by two layers of praseodymium oxide, represents a chance for high-temperature superconductors to become a reality — and one where praseodymium is literally at the centre of things. ❐

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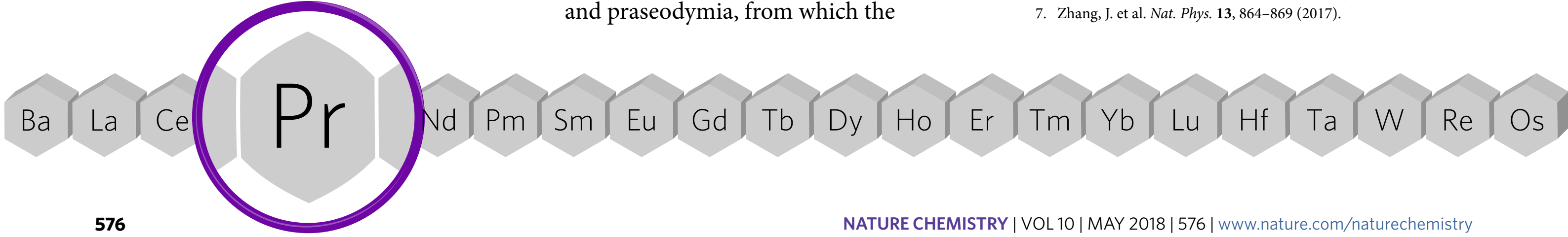


Tritium trinkets

Scientists take nomenclature seriously, but tritium was named in a casual aside. Brett F. Thornton and Shawn C. Burdette discuss the heavy, radioactive hydrogen isotope that is available for purchase online.

Why is ^{3}H called tritium and not simply hydrogen-3? More specifically, why have ^{2}H and ^{3}H been named as if they are elements, when thousands of other isotopes are not deemed worthy? In the early 1900s, a number of radioactive isotopes held individual names, but these fell out of use long ago. IUPAC formally disallowed isotope names, except those of hydrogen, in 1957. Only a few unsanctioned exceptions — such as radiocarbon for ^{14}C, thoron for ^{220}Rn and ionium for ^{230}Th — persist in specialized fields.

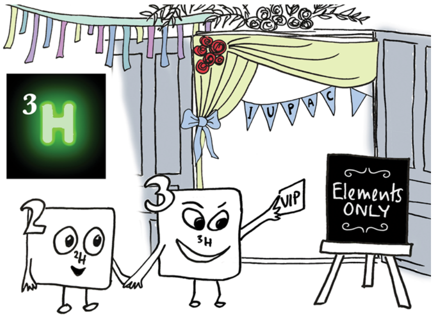
When the concept of isotopy was realized, many isotopes that had previously been seen as unique elements were grouped together as single elements on the periodic table due to their apparently identical chemistry. Although slight chemical differences had been observed for some isotopes, the discovery of hydrogen isotopes was a significant inflection point. ^{2}H and ^{3}H clearly did not behave exactly like 'ordinary' ^{1}H in chemical reactions, which provided a clear rationale for naming them separately. Soon after the discoveries of ^{2}H and ^{3}H, chemistry teachers were told[1] to exercise "caution in stating that the chemical properties of the isotopes of an element are identical" — a caution that even today is not always heeded.

American scientists Harold Urey, George Murphy and Ferdinand Brickwedde, who had discovered deuterium in 1932, proposed the name tritium for the not-yet-discovered ^{3}H in their 1933 report[2] in which the name deuterium was suggested for ^{2}H. This pre-emptive proposal for ^{3}H added further controversy to what soon became an acrimonious public debate over the appropriateness of the name deuterium[3]. Across the Atlantic, Ernest Rutherford endorsed diplogen for ^{2}H and diplon for its nucleus. His fame provided visibility to these alternatives. Soon thereafter, in early 1934 at Cambridge University, Mark Oliphant, Paul Harteck and Ernest Rutherford reported[4] producing ^{3}H by 'diplon' bombardment of 'diplogen'. The article conspicuously did not mention, or suggest, a name for the new isotope.

The initial Cambridge report incorrectly claimed ^{3}H was stable, because the other reaction product, ^{3}He, was believed to be the source of radioactivity[3]. By the time the opposite was shown to be true[5], the name tritium was already in common use. Shortly before his death in 1937, Rutherford penned a retrospective on ^{3}H advocating for the name triterium (ref. [6]). Despite his efforts, triterium did not displace Urey's tritium, and triplogen, the counterpart to diplogen, gained even less support.

Tritium occurs naturally on Earth, although in vanishingly low concentrations. It is produced in the stratosphere, where cosmic ray spallation releases neutrons that impact ^{14}N to yield ^{12}C and T. The natural amount of tritium in the entire atmosphere may be less than 2 kg, but testing of fusion weapons produced about 200 kg more by the early 1960s. Its decay (12.3 year half-life) has proven useful for many geophysical tracer studies, especially in surface and groundwater systems, as well as the oceans. Tritium is an extremely weak β-emitter, not harmful unless inhaled or ingested in unlikely large quantities. Furthermore, its decay product is the stable ^{3}He. These characteristics make tritium one of the most widely available radioactive substances. A wide selection of keychains, necklaces and watches can be easily purchased online that incorporate a minuscule amout of tritium, whose decay excites a phosphor, such as copper-doped ZnS, providing self-luminescence for years without batteries or external power.

Tritium remains special amongst the isotopes — and not just on account of its name. The T + D reaction is the most promising one for fusion energy in the future. As the isotopes of an element differ only by their number of neutrons, the relative mass difference between an element's isotopes is greater for lighter elements, and greatest by far for hydrogen. Vast fields of research now depend on slight variances in isotope chemistry, often driven by the differing masses. But although ^{208}Pb is about 0.5% heavier than ^{207}Pb, and ^{13}C is about 8.5% heavier than ^{12}C, T is about 200% heavier than ^{1}H. With this huge relative mass difference, T versus ^{1}H is an extreme outlier compared to isotope pairs of other elements. A pity, perhaps, that the relatively short half-life and rarity make its bulk chemistry more difficult to study, as tritium is truly in a class of its own for isotope effects. ❐



Credit: Emma Sofia Karlsson, Stockholm, Sweden

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The oganesson odyssey

Kit Chapman explores the voyage to the discovery of element 118, the pioneer chemist it is named after, and false claims made along the way.

Having an element named after you is incredibly rare. In fact, to be honoured in this manner during your lifetime has only happened to two scientists — Glenn Seaborg and Yuri Oganessian. Yet, on meeting Oganessian it seems fitting. A colleague of his once told me that when he first arrived in the halls of Oganessian's programme at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia, it was unlike anything he'd ever experienced. Forget the 2,000 ton magnets, the beam lines and the brand new cyclotron being installed designed to hunt for elements 119 and 120, the difference was Oganessian: "When you come to work for Yuri, it's not like a lab," he explained. "It's like a theatre — and he's the director."

For 60 years, with his very own blend of creativity, scientific skill and leadership, Oganessian has pushed the boundaries of the periodic table. Born in Rostov-on-Don of Armenian descent, the young Oganessian wanted to be an architect before he joined the Moscow Engineering Physics Institute. There, he elected to join the USSR's element hunters under Georgy Flerov. He went on to pioneer the 'cold fusion' technique, which would lead to elements 107–113, and the 'hot fusion' reactions with the neutron-rich ^{48}Ca that would give the world flerovium and beyond. A large part of modern science is about partnerships; Oganessian builds and cultivates them with warmth, insight and insatiable scientific curiosity.

The element that bears his name, oganesson, is similarly unique. It was first produced in 2002, firing ^{48}Ca at a ^{249}Cf target, by Oganessian's team from JINR and colleagues at the Lawrence Livermore National Laboratory, US[1]. There is currently only one known isotope, ^{294}Og, made in reactions so rare that it took ten years to obtain four confirmed atoms. The fourth in particular was a lucky discovery: it came from an attempt to make element 117 by bombarding a ^{249}Bk target with a beam of ^{48}Ca, but 28% of the target had decayed into ^{249}Cf, thereby producing element 118 instead[2].

Credit: ITAR-TASS News Agency / Alamy Stock Photo.

An earlier claim[3] for element 118 had come not from Russia, but the Lawrence Berkeley National Laboratory, in 1999. Soon after the death of Glenn Seaborg, who had led or taken part in the discovery of ten elements including plutonium, three decay chains were reported, products of a krypton beam into a lead target. It somewhat seemed too good to be true.

It was. Other groups around the world, along with the Berkeley team itself, were unable to reproduce these decay chains — prompting the Berkeley team to reanalyse the original data. When evidence of the chains couldn't be found, the article was retracted[4] by all authors except for Victor Ninov, the first author, who had been in charge of analysing the raw data. By the time the retraction appeared, in July 2002, Ninov had been dismissed from Berkeley for scientific misconduct in May[5], and had filed a grievance procedure[6].

Today, the discovery of the last element of the periodic table as we know it is undisputed, but its structure and properties remain a mystery. No chemistry has been performed on this radioactive giant: ^{294}Og has a half-life of less than a millisecond before it succumbs to α-decay.

Theoretical models however suggest it may not conform to the periodic trends. As a noble gas, you would expect oganesson to have closed valence shells, ending with a filled $7s^27p^6$ configuration. But in 2017, a US–New Zealand collaboration predicted that isn't the case[7]. Instead the relativistic effects — discrepancies between expected and observed behaviours caused by relativity — may result in the loss of shell structure. These effects are seen across the periodic table, increasing as nuclei get larger. Oganesson seems to have reached the point where electrons form an evenly distributed gas of charge. Such changes affect an element's properties: oganesson may well be a solid at room temperature, and more reactive than its noble family as the electrons in its p orbitals can be removed more easily.

If the models hold true, it could be the end of periodicity as we know it: a turning point at the join of chemistry and physics. Just like its maverick father, oganesson could be very interesting indeed. ❐

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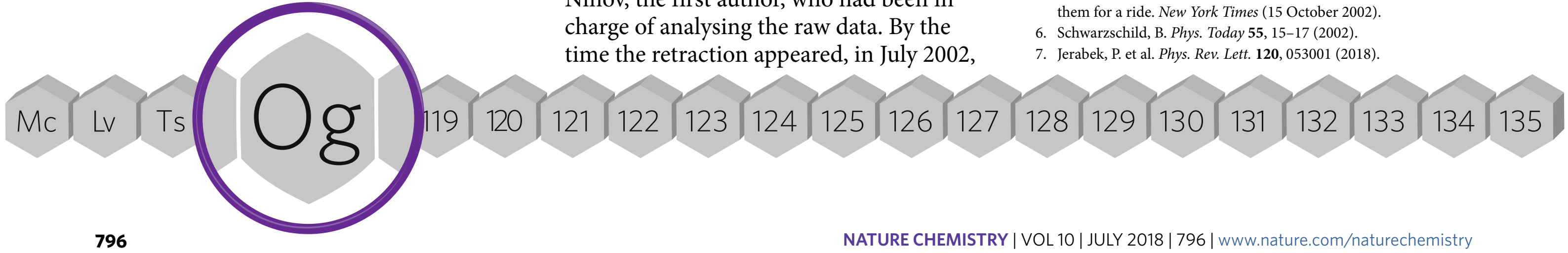

in your element

The realities of radium

Vikki Cantrill tells the story of element 88's discovery and how its glowing reputation eventually faded.

In a report describing a new substance, Marie and Pierre Curie noted[1] on 26 December 1898: "This radioactive substance contains a large proportion of barium; despite this, the radioactivity is considerable. The radioactivity of radium must therefore be huge". The finding came as part of their studies into the mineral ore pitchblende (now known as uraninite), from which they had discovered polonium just a few months before. The substance contained a new element; chemically very close to barium, it glowed with a faint blue light, which earnt it the name radium from the Latin 'radius' that means ray.

The Curies extracted a few milligrams of highly radioactive radium chloride from several tonnes of pitchblende. It was not until 1910 that Marie Curie and André-Louis Debierne isolated the pure metal by electrolysis of its chloride salt with a mercury cathode. The procedure — which produced a radium–mercury mixture — involved distillation of the mercury that would require quite the risk assessment today. In the same year, the importance of element 88 was set when it was chosen as the benchmark to define the original unit of radioactivity: the curie, with 1 Ci being equivalent to the decay activity of one gram of pure ^{226}Ra. The SI unit, the becquerel, was introduced in 1975. One Bq corresponds to one disintegration per second, and 1 Ci is equivalent to 37 GBq.

Only one year after the successful isolation of elemental radium, Marie Curie was awarded the Nobel Prize in Chemistry for her discoveries of both polonium and radium. Element 88 sits beneath barium in the periodic table, and like the other members of Group 2 it is a soft, shiny, silvery-white metal. A decay product of uranium, it has over 30 isotopes, all of which are radioactive with half-lives that range from mere nanoseconds to 1,600 years.

Entrepreneurs were quick to cash in on the glowing element. Radium soon became hailed as an all-around health and beauty elixir, and added to everyday items such as water, coffee, beer, chocolate, toothpaste, face creams (pictured) and suppositories. It was also used as a treatment for male impotence — through the careful, and presumably eye-watering, insertion of radioactive wax rods (bougies) into the urethra — and was even added to chicken feed to try to obtain self-incubating eggs.

Credit: Musée Curie (Coll. imprimées)

By 1921 the price of radium was so high (US$100,000 per gram) that Curie could no longer afford to purchase it for her research at the Institut du Radium in Paris. Fortunately, Mrs Marie Mattingly Meloney, an American editor, heard about the situation and raised the necessary funds to buy one gram of pure radium, which was presented to Curie during a visit to the USA — cautiously housed in a lead-lined mahogany box, as by then some suspected it to have harmful effects, even in small doses that had been deemed safe.

Most notoriously[2], radium was widely used in paints for clock and watch dials to make them glow in the dark. The women employed to do this detail work had to regularly shape their brushes to a sharp point by using their lips. The small amount of radium that they ingested each time caused severe anaemia, tooth loss, jaw decay, bone cancer and ultimately death. Although their deteriorating health was disregarded for far too long, the Radium Girls, as they became known, brought a lawsuit against the dial manufacturers in 1927 and settled out of court; eventually radium's popularity declined.

Radium's current annual production — by extraction of spent nuclear fuel rods — is less than 100 grams. Element 88 has become a focus in environmental monitoring, in which its contamination levels in soil are quantified and its radiation levels in watercourses assessed. In medical treatments its use has mostly been superseded by safer alternatives, such as ^{60}Co, although ^{223}Ra is still used in radiotherapy to treat prostate cancer that has spread to the bone[3,4]. It acts as a calcium mimic and is incorporated into the bone matrix at sites of active mineralization. Once inside the bone, the α-particles emitted can kill cancerous cells.

Today, the thought of Marie Curie with radium vials in her pocket is terrifying. The warming blue glow she liked to watch at night turned out to be a warning about radium's intense radioactivity.

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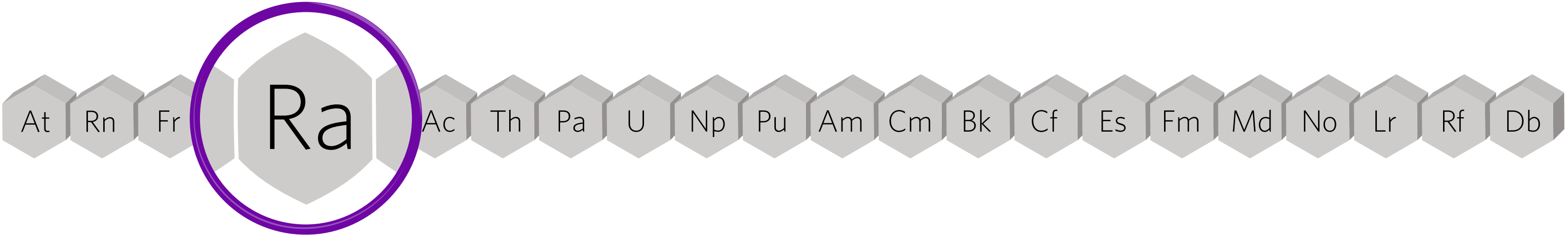
Competing interests

Vikki Cantrill is married to Stuart Cantrill, who is the Chief Editor for *Nature Chemistry*. Stuart Cantrill has not been involved in any way with the commissioning or editorial handling of this article.



Roentgenium generation

Taye Demissie relates unununium's unusually smooth route to roentgenium, and how predicting its properties relies on relativistic calculations.

The heaviest elements of the periodic table do not occur naturally, they are created in nuclear fusion reactions that are either carefully carried out in a few laboratories around the world or take place in thermonuclear reactions — einsteinium and fermium, for example, were first found in the radioactive debris of weapon tests before being made in high-flux neutron reactors. Among these superheavy-element-hunting laboratories is the GSI Helmholtz Centre for Heavy Ion Research (GSI) near Darmstadt, Germany, where element 111 was first synthesized in December 1994[1]. Officially, it went for a decade by its temporary name 'unununium' (for 1-1-1-ium), according to the naming system of the International Union of Pure and Applied Chemistry (IUPAC). In reality, along with the other superheavy elements, it was more commonly referred to by its atomic number.

The GSI team led by Sigurd Hofmann bombarded a target of ^{209}Bi with a beam of ^{64}Ni nuclei and successfully detected three ^{272}111 nuclei. Another element-hunting team at the Joint Institute for Nuclear Research in Dubna, Russia, had previously attempted to generate the element in 1986 — using the same reaction — but no data supporting the formation of 111 had been gathered. In 2002, the GSI team observed the detection of another three ^{272}111 nuclei[2]. Taken together, the six decay chains, among which three proceeded through the known nuclei ^{260}Db and ^{256}Lr, represented strong enough evidence for the IUPAC and IUPAP (International Union of Pure and Applied Physics) Joint Working Party (JWP) to attribute the priority of discovery of element 111 to the GSI team. Independent confirmation came from researchers at the RIKEN linear accelerator facility in Japan, who reported fourteen decay chains of the ^{272}111 isotope[3].

In contrast to the intense debate that some of the other superheavy elements were the subject of (so intense that the period was referred to as the 'transfermium wars'), the recognition and naming process was straightforward for element 111. Keeping with tradition, the discoverers proposed a name and symbol that were swiftly accepted, and in 2004 unununium became roentgenium[4] in honour of the German physicist Wilhelm Röntgen, who discovered the X-rays (the first X-ray image, of his wife's hand, is pictured). Just over a century before that, this finding had already earned Röntgen the first ever Nobel Prize in Physics in 1901.

Credit: World History Archive / Alamy Stock Photo

Roentgenium is extremely radioactive. All of its isotopes are very unstable, with half-lives ranging from a mere few minutes to milliseconds, and decay by α-emission or spontaneous fission. In the unlikely event that roentgenium could be observed, it is predicted to look silvery and be even denser than osmium, the densest known element (with densities of 28.7 versus 22.6 g cm^{-3}, respectively).

Artificial, extremely unstable transactinides do not lend themselves well to experimental chemistry. Scientists, undeterred, have developed sophisticated specialized technology for careful single-atom investigations, but it has not yet been possible to probe roentgenium. Element 111 has been explored instead using quantum-mechanical methods: the relativistic Dirac equation, instead of its non-relativistic Schrödinger counterpart, provides an exciting route to predict the chemical properties of the superheavies.

Towards the bottom of the periodic table, as nuclei become bigger and more highly charged, electrons approach relativistic speeds, making the atoms behave differently than what would otherwise be expected. Relativistic effects are known to be important already for understanding the electronic structure — and, in turn, the properties — of gold, roentgenium's above neighbour in group 11; they are crucial for superheavy elements.

The aqueous chemistry of Rg(I) was probed alongside that of the other group 11 ions: Au(I), Ag(I) and Cu(I). Using density functional theory, the formation of monoamine complexes from aquo ions was studied in the gas phase, and extrapolated to aqueous solutions[5]; Rg(I) was predicted to be a strong Lewis acid, even softer than Au(I). Its halide, cyanide and isocyanide species are among those investigated[6–8]. RgCN is predicted to feature a shorter bond than that of AuCN, with a covalent character that arises from the relativistic stabilization of the 7*s* orbital.

Although roentgenium has not yet been probed experimentally — and this may become possible if some of the less unstable isotopes can be generated directly — it is proving to be good playground for exploring relativistic effects. ❐

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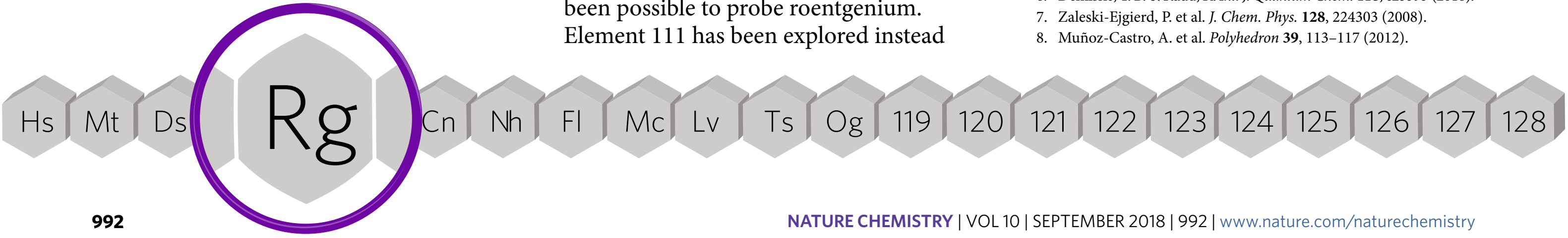


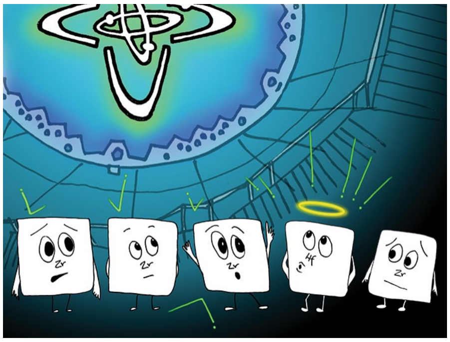
Hafnium the lutécium I used to be

Shawn C. Burdette and Brett F. Thornton examine hafnium's emergence from ores containing a seemingly identical element to become both a chemical oddity and an essential material for producing nuclear energy.

Mendeleev's periodic table was particularly notable for making predictions about undiscovered elements expected to be placed in several open positions. These elusive elements were ultimately found in rare ores, or by detecting the tiny quantities found as impurities in other minerals. Element 72 was no exception. Like many elements discovered in the twentieth century, it was also the subject of disproven discovery claims[1].

Believing element 72 would be a rare earth rather than a transition metal — an unusual position at the time[2] — Georges Urbain began searching in the ytterbia mixtures that had yielded element 71, now known as lutetium, which he had co-discovered. In 1911, he published optical spectroscopy data attributed to a new element, along with the proposed name celtium[3]. On learning of Henry Moseley's new X-ray emission techniques to determine an element's atomic number, Urbain went to England to confirm his discovery in May 1914. However, their experiments[4] failed to produce any evidence that Urbain's celtium was indeed element 72. Undeterred, Urbain later asserted to Rutherford that the failure to verify his discovery was due to deficiencies in Moseley's methods during this brief visit.

Accounting for newly proposed ideas about atomic structure, Georg von Hevesy assumed that element 72 would be a transition element and initiated a new search with colleague Dirk Coster. X-ray analysis of zirconium silicate materials revealed evidence for small amounts of an unknown substance with spectral lines consistent with those predicted by Moseley for element 72. Subsequent fractional crystallizations after treatments with acidic potassium fluoride and hydrogen fluoride led to an enrichment of the unidentified material dissolved in the mother liquor, as evidenced by the intensification of these emission lines. Coster and von Hevesy published their results and suggested the name hafnium from the Latin name for Copenhagen, Hafnia, the place of discovery[5]. Although Urbain would continue to defend the celtium claim for years, hafnium and celtium simply produced different X-ray emission spectra, and the latter was eventually confirmed, as Moseley suspected, to be purified lutetium[1].



Credit: Emma Sofia Karlsson, Stockholm, Sweden

Both the successful and failed discoveries are reflective of the unique chemistry of hafnium, which is directly related to its position on the periodic table. Sitting beneath zirconium, element 72 would be expected to share some of its properties, such as number of valence electrons and accessible oxidation states. Unlike many other analogous pairs of elements, however, hafnium is the first element with a filled *f*-shell, and the lanthanide contraction results in the zirconium and hafnium atoms being nearly identical in size. Because of their matching sizes, hafnium can easily substitute for zirconium in many minerals, although it seldom accounts for more than 5% of the metal content. Furthermore, their separation by chemical means is very inefficient — in fact, nearly impossible — because of their similar reactivities. Despite their frequently identical chemistry, differences have recently been observed in polymerization efficiencies in the production of polypropylene and polyethylene copolymers using zirconium or hafnium catalysts[6].

The starkest contrast between zirconium and hafnium is found in nuclear chemistry — zirconium has a low neutron-absorption cross-section, whereas hafnium readily absorbs neutrons. Nuclear fuel rods are clad in zirconium alloys to prevent escape of fission products, whereas hafnium in control rods mediates the neutron flux to control the energy output of the reactor. These opposing neutron-absorbing properties necessitate the complete removal of hafnium from zirconium materials to be used in fuel rods, and the majority of hafnium produced globally is isolated as a by-product of zirconium purification. Hafnium can also be found in high-temperature ceramics, because like its neighbour tantalum it produces extremely refractory borides, nitrides and carbides with melting points exceeding 3,000 °C (even above 3,800 °C for HfC)[7].

Hafnium and lutetium share more than a connection in their discovery story. About 2.6% of natural lutetium is the ^{176}Lu isotope, which has a half-life exceeding 37 billion years. The β-decay of ^{176}Lu to ^{176}Hf is the basis of the Lu-Hf geochronometer. Minute amounts of hafnium, formed and trapped for aeons in stable zircons, allow the dating of events in planetary development[8].

Although hafnium may seem to be only an extravagant, redundant alternative to zirconium, time has shown that even seemingly identical peas come in different pods. ❐

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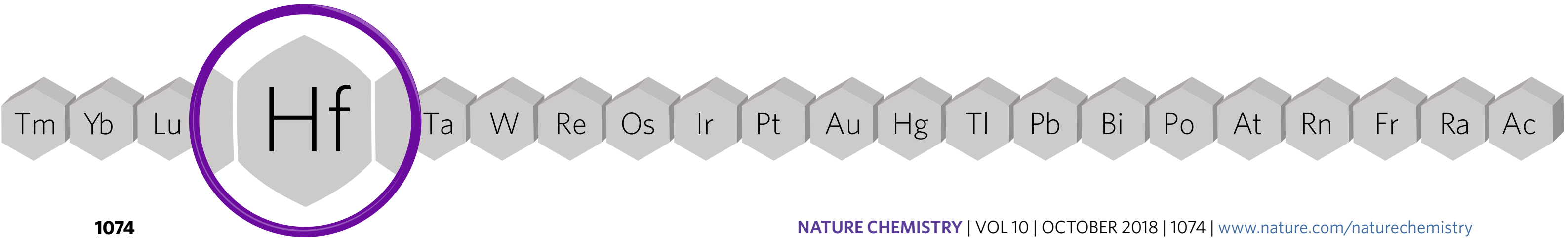


in your element

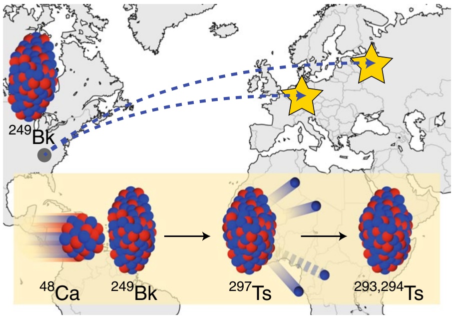
Targeting tennessine

Liz Williams explores the synthesis of tennessine, a story in which elements in supporting roles play a crucial part.

All experiments have their struggles. In the quest to create new superheavy elements, there is a lot of anxious waiting. Weeks, even months can go by without a single piece of evidence that an element exists. The time between the first day of beam time and an initial promising event can feel like eternity. Is the experiment set up properly? Were the calculations correct?

The first few syntheses of element 117 were full of such moments. The penultimate element of the periodic table as we know it was first discovered by a Russian–US collaboration at the Flerov Laboratory of Nuclear Reactions (FLNR) at the Joint Institute for Nuclear Research in Russia[1,2]. Their findings were later confirmed by a GSI-led international collaboration at the GSI Helmholtz Centre for Heavy Ion Research in Germany[3]. The independent verification of an element by a different team may not carry the same prestige as its initial synthesis, but for superheavy elements it is an important part of the discovery process. In the case of element 117, this second synthesis was also valuable in its own right, as it lifted some uncertainties in the GSI team's quest for the even-heavier element 119.

In 2009, the FLNR team was running an experiment using a technique called hot fusion, in which a radioactive actinide nucleus (in this case, berkelium-249, with 97 protons) reacts with, typically, calcium-48 (20 protons). Hot fusion reactions are capable of producing nuclei close to where we think we might find the 'island of stability' — a cluster of relatively stable nuclei (in comparison to their neighbours) predicted to exist either around elements featuring 114, or between 120 and 126 protons, and 184 neutrons. If it does indeed exist, the exact locations and the decay properties of the island's nuclei will be powerful tools for refining our understanding of nuclear structure.



During 70 days of beam time, the FLNR team saw evidence[1,2] that six atoms of element 117 had been created by first forming tennessine-297, which rapidly emitted three or four neutrons to form two isotopes (pictured). This evidence came in the form of α-decay chains that went down to dubnium and roentgenium. Cross-sections — a measure of the probability of creating a particular element for a given reaction — are incredibly small, and the detection of only a handful of such chains makes an experiment a successful one. On a second run in 2012, the FLNR team saw evidence for[4,5] another seven atoms. Both experiments confirmed a rise in stability for elements with more than 110 protons, supporting the existence of the island of stability.

Meanwhile, the GSI team had embarked on a hunt for element 119 by colliding titanium-50 (22 protons) with berkelium-249. They had put a lot of effort into refining their experimental set-up for this purpose by creating a very intense titanium-50 beam, introducing a digital data acquisition system, and working to reduce background radiation. But, four months into the experiment, element 119 remained undiscovered.

The radioactive berkelium target was decaying away and tension was running high in the team, so in 2012 they switched to a calcium-48 beam to check their experimental set-up by trying to detect a rare but known superheavy element. In doing so, they confirmed[3] the existence of element 117 through independent synthesis, and established that their observation of nothing in the element 119 experiment was simply a sign that the fusion cross-section for this reaction was smaller than expected. A year after the GSI team published their results, element 117 — along with 113, 115, and 118 — were officially welcomed onto the periodic table by the International Union of Pure and Applied Chemistry and International Union of Pure and Applied Physics joint working party.

When the FLNR team was asked to propose a name for element 117, they made an unconventional suggestion: tennessine, whose suffix identifies the element as a halogen, is rooted in the state of Tennessee, USA. Rather than the location of discovery, this name — approved by the IUPAC in 2016 — honours the place where some of the FLNR collaborators came from, but also where the berkelium-249 material had been crafted. The state's Oak Ridge National Laboratory had successfully taken on the herculean task of producing the berkelium-249 target so essential to the element's discovery.

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Competing interests

The author collaborated with the GSI group on other superheavy element research (not $Z = 117$ or 119).

in your element

Promethium puzzles

Stuart Cantrill explains why looking to the heavens for element 61 — named after the Titan who stole fire from the gods — could extend the periodic table.

Based on his studies of atomic weights, in 1902 Czech chemist Bohuslav Brauner predicted[1] the existence of element 61 — as well as six others that hadn't been discovered at that point. Just over a decade later, Henry Moseley's work with X-ray spectroscopy confirmed that there was a gap in the periodic table between neodymium and samarium, and so then it was just a matter of finding the missing element. But it wasn't easy.

Initial work centred on trying to extract the element from samples of rare-earth minerals. In the 1920s, claims of discovery — supported by X-ray emission data — were made on both sides of the Atlantic, in the USA[2] and Italy[3]. With competing claims came competing names: would element 61 be illinium (Il) or florentium (Fr)? The debate reached the pages of *Nature* on a few occasions, with William Noyes, former head of the chemistry department at the University of Illinois and past president of the American Chemical Society (ACS), getting involved[4].

But no one had actually isolated element 61, and so doubts began to grow. In the 1930s, theoretical work that suggested the element would not have any stable isotopes came as a further blow. Then, in 1937, following the identification of technetium in a piece of molybdenum foil that had been bombarded for months with a deuterium beam in a cyclotron at the Lawrence Berkeley National Laboratory, it became clear that gaps in the periodic table could be filled in a new way. If elements couldn't be found in nature, perhaps they could be made in the laboratory instead.

As the decade ended the world descended into war — one that would see the power of the atom harnessed. An important part of the Manhattan Project was to analyse the fission products of uranium to better understand the processes involved, and this led to a team of scientists at Oak Ridge in Tennessee finally isolating[5] element 61 by using ion-exchange chromatography. The official announcement was delayed until after the end of the war, and was made at the 1947 national fall meeting of the ACS in New York City.

Statue of Prometheus near the Chernobyl nuclear power plant. Credit: kpzfoto / Alamy Stock Photo

The name 'prometheum' was proposed for the new element by Grace Mary Coryell — the wife of one of the Oak Ridge team. Prometheus stole fire from the gods and gave it to humanity, but was punished by being tied to a rock where each day an eagle would feed on his liver (which would grow back at night). The name, which reflects the power and peril of nuclear energy, was accepted in 1949 by the International Union of Chemistry, but the spelling was amended to promethium to be consistent with other metallic elements.

All 38 known isotopes of promethium are radioactive; the longest-lived is Pm-145, with a half-life of 17.7 years. As a consequence of its instability, at any given time there is estimated to be only roughly 500 g of promethium on Earth (from the natural decay of europium and uranium)[6]. Compare this with its neighbours in the lanthanide series, neodymium to the left and samarium to the right, of which there are roughly eight and two million tonnes respectively.

Unsurprisingly, the chemistry of promethium is not very well developed, but simple salts such as halides and oxides have been prepared. Pm-147 has been used in luminous paints, in which its beta emission causes a phosphor to produce light; some electrical switches in the Apollo Lunar Modules were illuminated this way. Although safer than radium, the relatively short half-life of this promethium isotope (roughly 2.5 years) means that radioluminescent materials are now typically based on tritium. Promethium has also been used to make nuclear (or 'betavoltaic') batteries that served as power sources for some pacemakers in the 1970s.

Not too long after promethium was made on Earth it was detected in the spectra of stars that have highly unusual elemental compositions. Considering the short half-life (particularly on an astronomical timescale) of even the longest-lived promethium isotope, its presence in these stars is puzzling. Various theories have been put forward, including the idea that such stars could contain as-yet unidentified super-heavy elements from the 'island of stability' that would decay into promethium and other radioactive elements[7]. Alternatively, of course, it could just be a sign of alien technology[8]. ❐

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