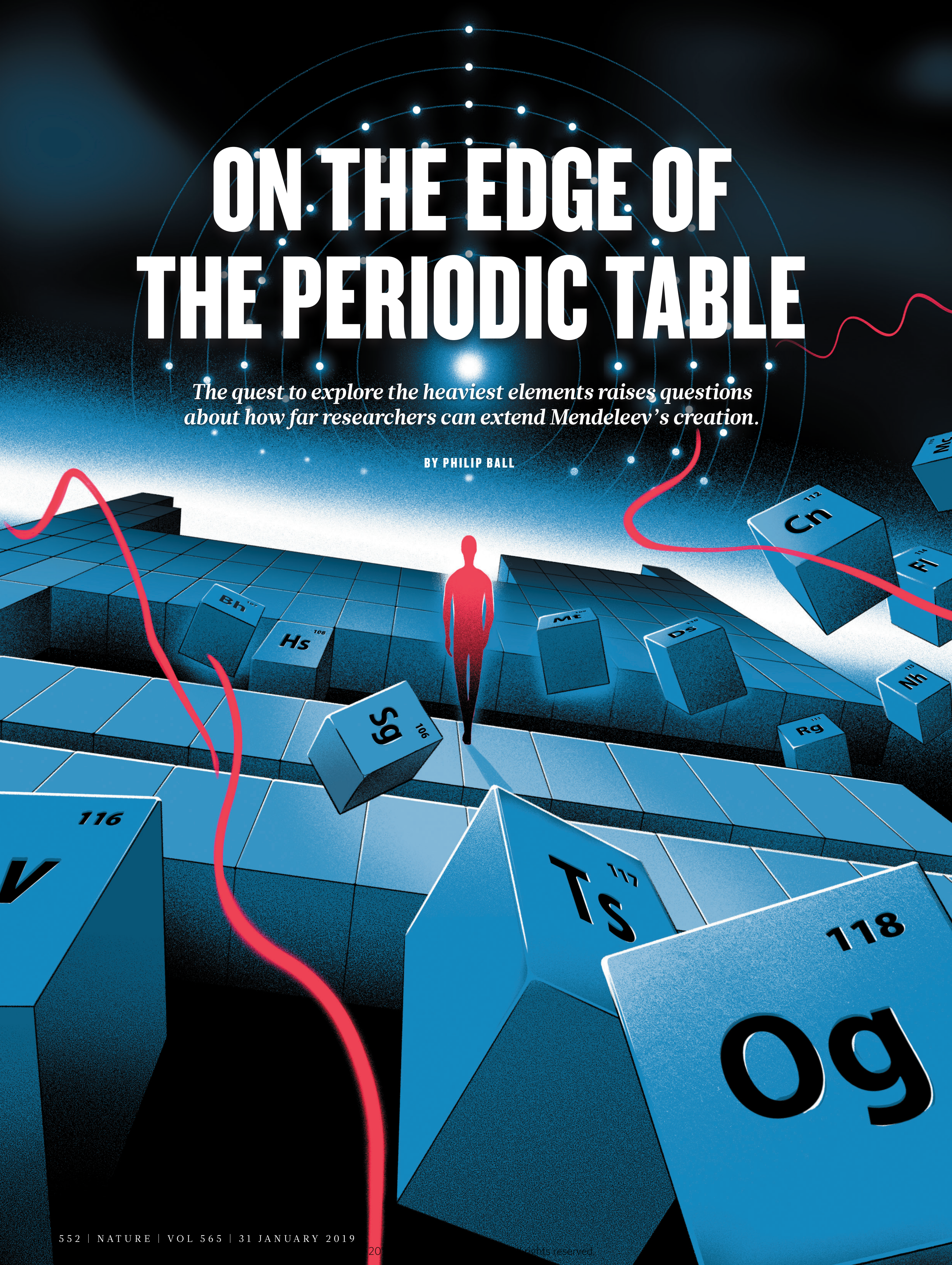
ON THE EDGE OF THE PERIODIC TABLE

The quest to explore the heaviest elements raises questions about how far researchers can extend Mendeleev's creation.

BY PHILIP BALL



If you wanted to create the world's next undiscovered element, number 119 in the periodic table, here's a possible recipe. Take a few milligrams of berkelium, a rare radioactive metal that can be made only in specialized nuclear reactors. Bombard the sample with a beam of titanium ions, accelerated to around one-tenth the speed of light. Keep this up for about a year, and be patient. Very patient. For every 10 quintillion (10^{18}) titanium ions that slam into the berkelium target — roughly a year's worth of beam time — the experiment will probably produce only one atom of element 119.

On that rare occasion, a titanium and a berkelium nucleus will collide and merge, the speed of their impact overcoming their electrical repulsion to create something never before seen on Earth, maybe even in the Universe. But the new atom will fall apart within perhaps one-tenth of a millisecond. As it decays, it will spit out α-particles and γ-rays, which hit silicon detectors placed around the target to verify that element 119, fleetingly, existed.

Researchers have tried this experiment. Chemists in Germany spent several months in 2012 on it, but gave up with no sightings. Scientists in Japan have tried other combinations of beam and target, and both they and a team in Russia have sought element 120, too, but with no luck.

The quest to extend the periodic table is not over, but it is grinding to a halt. Since Russian chemist Dmitri Mendeleev published his periodic table 150 years ago, researchers have been adding elements to it at the average rate of one every two or three years (see 'When elements were discovered'). Having found all the elements that are stable enough to persist naturally, researchers started to create their own, and are now up to element 118, oganesson. Although they still hope to find more, they agree that prospects of venturing beyond element 120 are dim. "We're reaching the area of diminishing returns in the synthesis of new elements, at least with our current level of technology," says Jacklyn Gates, who works on heavy-element chemistry at the Lawrence Berkeley National Laboratory in California.

As a result, research on the edge of the periodic table is shifting focus. Rather than chasing new elements, scientists are going back to deepen their understanding of the superheavy ones — roughly speaking, those with an atomic number above 100 — that they have already made. Studying the chemical properties of these elements could show whether the most massive ones obey the organizing principle of the table — which sorts elements into groups with similar behaviours on the basis of periodically recurring patterns of chemical reactivity. And although the heaviest elements decay in less than the blink of an eye, researchers still hope that they might arrive at the fabled 'island of stability': a hypothesized region of element-land where some superheavy isotopes — atoms that have the same number of protons in their nucleus, but differing numbers of neutrons — might exist for minutes, days or even longer.

Creating new elements is conceptually straightforward, if technically immensely difficult and slow. But studying the chemistry and nuclear physics of atoms that decay in less than a second pushes both computational and experimental work to their limits. The results that have been obtained so far are already raising questions about the concept of chemical periodicity at these extremes. "The discovery of superheavy elements sometimes reminds me of the opening of Pandora's Box," says Yuri Oganessian, an 85-year-old Russian nuclear physicist, who is only the second scientist in history to have an element (oganesson) named after him while still alive. "The problems that were flung out from the box are much more complicated than the discovery of one more element."

RARE FRUIT

Work on superheavies has its origins in wartime science in the 1940s. Some of the first non-natural elements were discovered in radioactive debris from the fallout of atom-bomb tests; others were made in particle accelerators. From the 1950s to the 1970s, when most of the research was conducted at either Berkeley or at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia — the group that Oganessian leads — it took place in an atmosphere of cold-war competition. In the 1980s, Germany joined the race; an institute in Darmstadt now named the Helmholtz Center for Heavy Ion Research (GSI) made all the elements between 107 and 112.

The competitive edge of earlier years has waned, says Christoph Düllmann, who heads the GSI's superheavy-elements department: now, researchers frequently talk to each other and carry out some experiments collaboratively. The credit for creating later elements up to 118 has gone variously, and sometimes jointly, to teams from Germany, the United States and Russia; a Japanese team at the RIKEN Nishina Center for Accelerator-based Science in Wako was credited with making element 113.

> "THE DISCOVERY OF SUPERHEAVY ELEMENTS SOMETIMES REMINDS ME OF THE OPENING OF PANDORA'S BOX."

The modern-day hunt for superheavy elements resembles particle-physics experiments on a miniature scale, in that it involves teams with diverse scientific expertise sifting through masses of collision data for very rare events, says Matthias Schädel, who has been involved in element synthesis at the GSI for four decades. "Sitting in a control room for hours, days, maybe weeks, just looking for the long-awaited signal from a detector can become very boring and tiring," he says. "However, observing the first event can be most exciting and joyful — and an enormous relief."

"The synthesis of artificial elements has always been difficult and painstaking work," says Oganessian. But expanding the periodic table beyond 118 consumes accelerator beam ime with diminishing returns. "Element 117 was obtained in the amount of one atom per week, and element 118 one atom per month. There is no reason to believe that the yield will increase for the still-unknown elements 119 and 120," he says. It would help if researchers could increase the intensity of atomic beams, or the thickness of the targets, but both tasks are "technologically very challenging", says nuclear physicist Dirk Rudolph of Lund University in Sweden.

The GSI has suspended its hunt for now, says Düllmann, because superheavy research at the German facility is being reined in during construction of an accelerator known as the Facility for Antiproton and Ion Research for studying astrophysical phenomena. Meanwhile, researchers at the JINR "practically stopped" searching for elements at the end of 2014, says Oganessian. Instead, over the past five years they have focused on building a laboratory, which Oganessian calls a superheavy-element factory, to churn out tens or hundreds of times more atoms of known elements, sometimes as new isotopes. The laboratory can accommodate five simultaneous experiments, says Oganessian; two 50-day demonstrations to make elements 114 and 115 are planned to start in April.

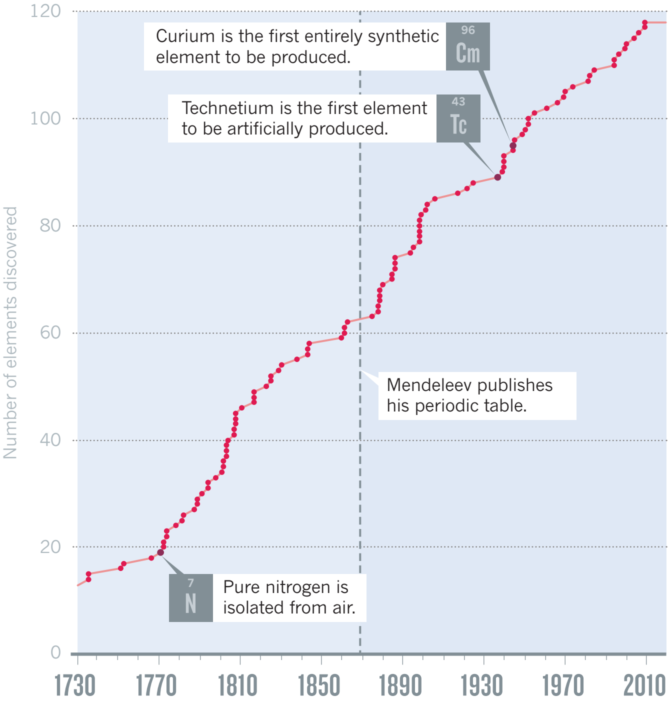
The group at Berkeley gave up element hunting some years back. "There are frequently discussions about whether or not we should try to make a new element," says Gates, "but I think that the available beam time is better used by performing more detailed studies on the presently known elements." RIKEN is still hunting for elements, but it is also consolidating what we know of existing ones: Hiromitsu Haba, who leads the centre's superheavy-element production team, says his group is going to study the chemical properties of elements 104, 105 and 106.

Most researchers have always felt that there is as much value in probing the chemistry and

ILLUSTRATION BY SEÑOR SALME

WHEN ELEMENTS WERE DISCOVERED

Since Dmitri Mendeleev published his periodic table in 1869, researchers have discovered, or created, new elements at an average rate of one every two or three years.



SOURCE: F-X COUDERT, CNRS

nuclear physics of known elements as there is in making new ones. A key question is how much the superheavy elements sustain the periodicity in chemical behaviour that underpins Mendeleev's table. The chemistry of an element depends on the reactivity of its outermost electrons. In atoms, electrons occupy discrete, fuzzy clouds called orbitals that surround the nucleus, and those with the highest energy are the ones involved in forming chemical bonds and ions. Elements in the same column in the periodic table ('homologues') share similar chemical properties because they have similar electron configurations, with the same number of electrons in their outermost shells.

So seaborgium (element 106), for example, would be expected to resemble elements above it in the periodic table (such as molybdenum and tungsten), in forming compounds in which the six outermost electrons have been shared or transferred to surrounding atoms. And by carrying seaborgium quickly to a reaction chamber so that its compounds can be produced and separated by both gas and liquid chromatography, chemists proved two decades ago that this is true[1,2]. The atoms can be tracked as they move between chemical phases because of their radioactive instability: they spit out α-particles as they decay. No one has managed to examine liquid-phase reactions beyond seaborgium, but hassium (element 108) has been shown to bind to four oxygen atoms like its homologue osmium — forming hassium tetroxide — while borne along within a carrier gas[3].

But it is extremely hard to conduct such experiments with the heaviest of the superheavies. Valeria Pershina, a theoretical chemist at the GSI, says that such experiments currently require isotopes that have a half-life no shorter than 1 second; their feasibility might also depend on the rate at which atoms can be produced. Although some isotopes for elements 109–111 are relatively long-lived — some lasting more than a minute — these are all formed in decay chains and are not suitable for chemical studies (see 'The superheavy realm'), although radiochemist Andreas Türler at the University of Bern in Switzerland says he is confident that they exist. "The difficulty is to produce them at a rate that would allow experiments," he says.

But some of the even heavier elements have turned out to be amenable to other kinds of chemical study. A relatively simple technique to probe superheavies, for instance, measures how strongly the atoms, carried along in a surrounding gas, become attached to surfaces. Experiments at the GSI have shown, for example, that flerovium (114) forms a metal–metal bond on a gold surface like its homologue lead, but that the bond is much weaker: in other words, the superheavy element is less reactive and more likely to stay in the gas phase[4]. Copernicium (112), meanwhile, interacts with gold much less strongly than its homologue mercury does — in fact, it behaves almost like a noble gas[5]. Nihonium (113) has been harder to study experimentally, but preliminary observations at the JINR[6], as well as Pershina's calculations[7], suggest that it forms relatively strong chemical bonds to a surface, albeit weaker ones than its homologue thallium.

This is somewhat as expected: the strength of chemical bonding tends to decrease down a periodic group, as atoms get larger. But to fully explain superheavies' chemistry, Pershina's calculations must also take into account relativistic effects. In very heavy atoms, which have super-strong interactions between the innermost electrons and the highly charged nuclei, the electrons are travelling so fast (potentially at more than 80% of the speed of light) that their mass increases, as special relativity predicts. This pulls them farther in towards the nucleus, which can mean that they screen the outer electrons from the nuclear charge more effectively. That alters the outer electrons' energies and, consequently, their chemical reactivity.

RELATIVISTIC EXTREMES

Relativistic effects are already understood — they are responsible for the yellowish colour of gold and the low melting point of mercury, for example. But superheavy elements display these effects in extreme form, whereby they are hard to calculate precisely from first principles. The 2002 discovery[8] of how relativistic effects cause dubnium (105) to behave rather differently from its homologue tantalum in group 5 of the periodic table was "so exciting for us that it created an enormous momentum to continue probing the chemistry of the superheavy elements", says Schädel.

Chemists don't think that the relativistic deviations observed so far destroy the broad idea that elements in the same group share similar properties that distinguish them from other groups, says Düllmann. In his opinion, researchers won't see a marked loss of chemical periodicity until they find elements beyond 120. Here, he says, "several orbitals start to be so close in energy that no regular pattern is expected anymore". That tendency seems already borne out by calculations last year, which suggest that oganesson might not be an unreactive noble gas like its homologues xenon and radon. Its outermost electron orbits are smeared together so that it might be more reactive than its position in the periodic table seems to imply[9].

> "MORE LONG-LIVED ISOTOPES JUST AWAIT DISCOVERY."

To measure electrons' energy levels directly, physicists and chemists have long used spectroscopy. Essentially, this involves firing light at atoms to measure the energies at which electrons absorb — and later emit — photons as the particles jump up to higher energy levels or relax down again. But doing this on single, short-lived atoms is extremely challenging: how do you do the measurement, with enough sensitivity, before your quarry has vanished? Still, in 2016, a team working at the GSI was able to measure the ionization potential of single atoms of nobelium, element 102, that had a half-life of 51.2 seconds[10]. The researchers made the nobelium atoms at a rate of around four per second by colliding a calcium ion beam into a lead target, before slowing down the atoms in argon gas to collect them on a filament of tantalum. Periodically, the researchers heated the filament to release the nobelium atoms into the gas phase and excited them with lasers, kicking off an electron in a two-step process — all in a matter of seconds. In later work, they used such spectroscopic measurements to infer the shape and structure of the nuclei of three nobelium isotopes, concluding that they are not spherical, but a rugby-ball shape: a distortion that affects electronic structure[11]. The group is now working to extend its measurements to lawrencium, element 103.

Researchers at the Japan Atomic Energy Agency (JAEA) in Tokai have developed a different approach for measuring ionization energies. In their set-up, atoms of a superheavy element recoiling out of a target are taken up in a jet of helium carrier gas passing through a heated tube of tantalum. The atoms transfer an electron to the metal surface, before being taken to an α-particle detector that verifies their identity. In this way "we can measure ionization energies of elements with a half-life of a few seconds", says Yuichiro Nagame, a member of the research group for heavy-element nuclear science at the JAEA. Nagame and his colleagues have used the method to measure this quantity for all elements from fermium (100) to lawrencium (103)[12,13]. As calculations had predicted, relativistic effects make the ionization potential of lawrencium even lower, relative to its lighter homologue lutetium, than the usual periodic trends would imply. Nagame says his group is now developing a new method for measuring ionization potentials of elements beyond lawrencium, which are not volatile enough for this surface technique to be used.

THINGS FALL APART

Observing the chemical behaviour of elements beyond 118, even if they can be made, will be an immense challenge because they are expected to fall apart so quickly. "I do not want to say that it is impossible, but just now I do not know how to approach this task," says Oganessian.

Yet nuclear scientists have speculated that long-lasting superheavy isotopes could exist. Like electrons, the protons and neutrons in atomic nuclei are also arrayed in shell-like configurations that make their structure more or less easy to disrupt. And particular 'magic numbers' of these particles, corresponding to filled shells, are predicted to confer stability, prolonging the time before an atom decays. (The effect is roughly analogous to how noble gases are relatively stable and unreactive because they have filled shells of electrons).

A leading candidate for a stable superheavy element is the isotope flerovium-298, with 114 protons and 184 neutrons. "Most reasonable models favour this proton and neutron number to be those that should give extra stability in the region," says Rudolph. Researchers dream that particular isotopes within this island of stability might last long enough for significant amounts of the element to be accumulated. Already, the longer half-lives of some isotopes of copernicium and flerovium offer "a first indication that this concept is correct, and that more long-lived isotopes just await discovery", says Düllmann. Although experiments support the existence of the island of stability, Sebastian Raeder, a nuclear chemist at the GSI, says that "it will be very difficult to reach it in the near future", because no one knows how to load that many neutrons into a nucleus.

At times, researchers discuss among themselves where the periodic table absolutely has to end. That might happen, for example, because the outermost electrons of a very heavy atom might not have any states in which they are actually bound to the nucleus, and so there will be no real chemistry to speak of. Or the nuclei themselves might fall apart as soon as they are formed. Last May, the governing body of chemistry, the International Union of Pure and Applied Chemistry (IUPAC), reasserted its position that an element should persist at least for 10^{-14} seconds. But some chemists question whether atoms that don't have time to interact can be meaningfully assigned chemical properties and so qualify as an element.

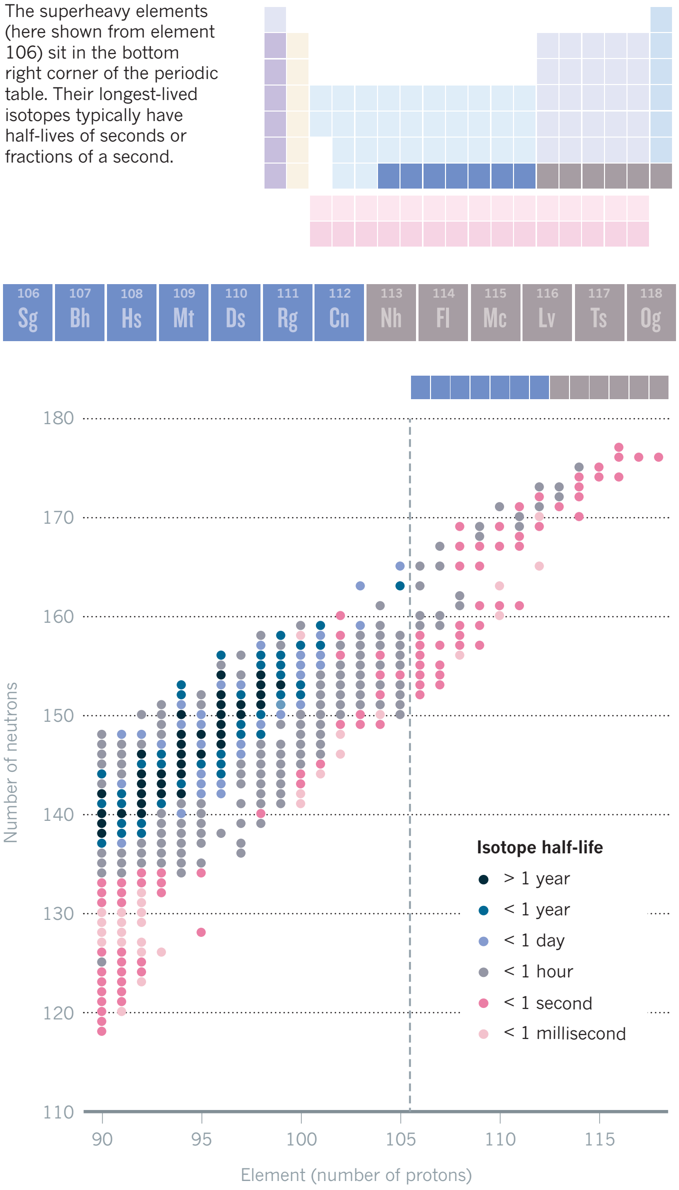
That is really a question about whether, at its farthest extremes, the periodic table will remain a scheme based on chemistry — as it was for Mendeleev — or whether it becomes about the physics of matter at very high nucleon densities. New elements have to be put somewhere in the table, but their positioning might become an empty formality, rather than indicating something useful about chemistry.

To reach that point, however, chemists will need to create those heavier elements. For all its technical difficulty, the hunt continues. "We started the search for element 119 last June," says RIKEN researcher Hideto En'yo. "It will certainly take a long time — years and years — so we will continue the same experiment intermittently for 100 or more days per year, until we or somebody else discovers it."

"I am quite optimistic that elements 119 and 120 will be found in the next ten years," says Düllmann. "The longer-term outlook may seem dim, but when I was a PhD student in the 1990s, papers were published by giants in the field that explained why 112 was close to the limit. Twenty years later, we have 118. I guess we should not underestimate the next generation." ■ SEE EDITORIAL P.535

THE SUPERHEAVY REALM

The superheavy elements (here shown from element 106) sit in the bottom right corner of the periodic table. Their longest-lived isotopes typically have half-lives of seconds or fractions of a second.



SOURCE: IAEA

Philip Ball *is a science writer based in London, UK.*

1. Schädel, M. *et al. Nature* **388**, 55–57 (1997).
2 Schädel, M. *et al. Radiochim. Acta* **77**, 149–159 (1997).
3. Düllmann, C. E. *et al. Nature* **418**, 859–862 (2002).
4. Yakushev, A. *et al. Inorg. Chem.* **53**, 1624–1629 (2014).
5. Eichler, R. *et al. Angew. Chem. Int. Ed.* **47**, 3262–3266 (2008).
6. Dmitriev, S. N. *et al. Mendeleev Commun.* **24**, 253–256 (2014).
7. Pershina, V. *Inorg. Chem.* **57**, 3948–3955 (2018).
8. Schädel, M. *J. Nucl. Radiochem. Sci.* **3**, 113–120 (2002).
9. Jerabek, P. *et al. Phys. Rev. Lett.* **120**, 053001 (2018).
10. Laatiaoui, M. *et al. Nature* **538**, 495–498 (2016).
11. Raeder, S. *et al. Phys. Rev. Lett.* **120**, 232503 (2018).

CORRECTION

The News Feature ‘On the edge of the periodic table’ (*Nature* **565**, 552–555; 2019) erred in saying that no isotopes have been found for elements 109–111 that live long enough for chemical studies. In fact, the problem is not the length of the half-lives, but that the isotopes are created in decay chains, not through collisions. The feature also mislabelled the Y-axis of the graph ‘The superheavy realm’.