follow the Madelung rule. Although scandium's extra electron lies in its 3d orbital, experiments show that, when it is ionized, it loses an electron from 4s first. This doesn't make sense in energetic terms — textbooks say that 4s should have lower energy than 3d. Again, this problem has largely been swept under the rug by researchers and educators.

Schwarz used precise experimental spectral data to argue that scandium's 3d orbitals are, in fact, occupied before its 4s orbital. Most people, other than atomic spectroscopists, had not realized this before. Chemistry educators still described the electronic structure of the previous element in the periodic table (calcium) carrying over into the next. In fact, each atom has its own unique ordering of energy levels. Scandium's 3d orbitals have lower energy than its 4s orbital[10]. Schwarz urged chemists to abandon both the Madelung rule and Löwdin's challenge to derive it.

Schwarz is correct in saying that the Madelung rule is violated when it comes to the progressive occupation of orbitals in any particular atom. But it is still true that the electron that differentiates an element from the previous one in the table follows Madelung's rule. In the case of potassium and calcium, the 'new electron' relative to the previous atom is a 4s electron. But in scandium, the electron that differentiates it from calcium is a 3d one, even though it is not the final electron to enter the atom as it builds up.

In other words, the simple approach to using the aufbau principle and the Madelung rule remains valid for the periodic table viewed as a whole. It only breaks down when considering one specific atom and its occupation of orbitals and ionization energies.

The challenge of trying to derive the Madelung rule is back on.

THEORIES STILL NEEDED

This knowledge about electron orbitals does not change the order or placement of any elements in the table (even the anomalous 20 cases). It does enhance its theoretical underpinning. It shows how resilient the periodic table continues to be, along with the rules of thumb that have developed around it, such as the Madelung rule.

Quantum mechanics does a great job of explaining specific properties of atoms. Yet something more is needed to see the big picture. Although Schwarz cautions against superficial quantum-mechanical accounts of chemical facts, a deep dive into quantum mechanics might reveal a fundamental explanation of the Madelung rule, or a new way of thinking about it.

Even 150 years on, theoretical chemists, physicists and philosophers still need to step in to comprehend the gestalt of the periodic table and its underlying physical explanation. Experiments might shed new light, too, such as the 2017 finding that helium can form the compound Na_2He at very high pressures[11]. The greatest icon in chemistry deserves such attention. ■

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The women behind the periodic table

Brigitte Van Tiggelen and **Annette Lykknes** spotlight female researchers who discovered elements and their properties.

The story of how dozens of elements were corralled into a periodic table reaches beyond one person and one point in time. Scientists classified and predicted elements before and after Dmitri Mendeleev's 1869 framework. And many more worked to find and explain these new substances. Noble gases, radioactivity, isotopes, subatomic particles and quantum mechanics were all unknown in the mid-nineteenth century.

Here we spotlight some of the women who revolutionized our understanding of the elements. Marie Curie is the most celebrated, for her double Nobel-prizewinning research on radioactivity and for discovering polonium and radium[1]. Stories of other women's roles are scarce. So, too, is an appreciation of the skills required, including tenacity and diligence in performing experiments, sifting through data and reassessing theories.

Proving the discovery of a new element is hard. The first step is finding unusual activity — chemical behaviour or physical properties that cannot be ascribed to known elements, such as unexplained radioactive emissions or spectroscopic lines. Then the element, or its compound, must be isolated in large enough quantities for it to be weighed, tested and used to convince others.

SEARCH AND SORT

Marie Curie wasn't looking for elements when she started her PhD on 'uranium rays' in 1897. She wanted to explore radioactivity, which had just been discovered by Henri Becquerel, in 1896. She came across pitchblende, an ore with radioactivity that was too strong to be explained by uranium alone. She suspected the presence of other elements, and brought in her husband, Pierre, to help.

In 1898, they identified spectroscopic lines of two new elements — radium and polonium. Yet it took them more than three years to grind, dissolve, boil, filter and crystallize tonnes of the mineral to extract just 0.1 gram of radium compound. (They struggled to do the same for polonium because of its short half-life.) Nobel prizes followed — the first shared by the pair and Becquerel in 1903 for discovering radioactivity, the second by Marie alone in 1911 for her discoveries of polonium and radium, and for the isolation and study of radium.

Positioning an element in the periodic ▶


THE PERIODIC TABLE
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table requires establishing its atomic weight and chemical properties. For example, radium behaves a lot like barium and has a heavier atomic weight, so it fits just below barium in the periodic table. Determining atomic weights is difficult because it demands pure substances.

Elements of similar weight and character are hard to distinguish. Just after Mendeleev prepared his table, Russian chemist Julia Lermontova took up the challenge — probably at Mendeleev's behest — to refine the separation processes for the platinum-group metals (ruthenium, rhodium, palladium, osmium, iridium and platinum)[2]. This was a prerequisite for the next step of putting them in order. The only account of her work (to our knowledge) is in Mendeleev's archives, along with their correspondence. Lermontova studied chemistry in Heidelberg, Germany, under Robert Bunsen (who discovered caesium and rubidium in 1860 with Gustav Kirchhoff, using their newly invented spectroscope), and was the first woman to be awarded a doctorate in chemistry in Germany, in 1874.

Securing values for atomic weights was also crucial for working out radioactive decay series, and for telling apart new elements and unknown versions of existing ones — isotopes. This solved the problem that many new elements seemed to be popping up, yet only a few gaps were left in the periodic table. Although the British chemist Frederick Soddy introduced the concept of isotopes in 1913, it was the physician Margaret Todd who suggested the term (meaning 'same place' in Greek) at a dinner party.

Experimental proof of isotopes was soon provided by Stefanie Horovitz, a Polish–Jewish chemist. Working at the Radium Institute in Vienna, she showed that even a common element such as lead can have different atomic weights, depending on whether it stems from the radioactive decay of uranium or thorium[3].

Another problem was the nature of a curious 'emanation' from radium. Was it a particle or a gas? Canadian physics graduate student Harriet Brooks solved it with her supervisor Ernest Rutherford at McGill University in Montreal, Canada[4]. In 1901, Brooks and Rutherford showed that the emanation diffused like a heavy gas, providing the first evidence that a new element could be produced during radioactive decay. In 1907, William Ramsay suggested that the gas, later named radon, belonged to "the helium group of elements" — now called the noble gases[5].

In 1902, Rutherford and Soddy announced their theory of radioactive disintegration: atoms decay spontaneously into new atoms while giving off rays. Rutherford was awarded the Nobel Prize in Chemistry in 1908 for his investigations; Brooks's radon contribution was a first, crucial step. She is rarely credited. Although the first paper was authored by both Brooks and Rutherford[6], the next one in *Nature* carried only Rutherford's name — with a credit line that Brooks assisted him[7]. As a woman, Brooks found it hard to get permanent appointments (especially once married) and to pursue a steady line of research.

German chemist Ida Noddack left industry to hunt for missing elements, and co-discovered rhenium.

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DEEPER INTO THE MATTER

Insights into the physics of the atomic nucleus continued to emerge. In 1917–18, physicist Lise Meitner and chemist Otto Hahn discovered element 91, protactinium, in Berlin[8]. Meitner was Austrian and had left for Germany after her PhD to improve her career opportunities. In 1907, she was admitted as Hahn's unpaid collaborator at the chemistry department at the University of Berlin. She had to work in the basement — women were not meant to be seen. In 1913, after Hahn relocated to the Kaiser-Wilhelm Institute for Chemistry in Berlin-Dahlem, she was made an 'associate' of the institute.

Hahn and Meitner discovered protactinium while they were looking for the 'mother substance' of actinium in the radioactive decay series. They were part of a wider race to find the element, and priority disputes inevitably followed. The pair's discovery was eventually acknowledged as the first because Meitner and Hahn had collected more of the substance and characterized it more completely than their competitors had.

Another element, number 75 — rhenium — was jointly discovered in 1925 by German chemists Ida Noddack and her husband Walter Noddack in Berlin, together with Otto Berg at the electrical-engineering company Siemens–Halske (later part of the firm Siemens)[9]. Ida Noddack, née Tacke, was a chemical engineer who left industry to hunt for missing elements. In 1925, she started as unpaid guest researcher at the Physikalisch-Technische Reichsanstalt (Imperial Physical and Technical Institute) in Berlin, where Walter headed the chemistry laboratory. The Noddacks struggled to produce weighable quantities of rhenium, which they named after the Rhine; it is one of the rarest elements on Earth, and is not radioactive.

The Noddacks also claimed to have found element 43, which they called masurium (after the Masuria region, now in Poland). But they never succeeded in reproducing its spectral lines or in isolating the material. In fact, using 'wet chemistry' techniques for this element was hopeless. In 1937, element 43 became the first to be artificially produced, named technetium.

Unlike Marie Curie, who was acknowledged in her own right and took up Pierre's chair at the University of Paris after his death, Ida Noddack worked as a guest in her husband's laboratory for most of her life. This was one reason why she was not taken seriously when, in 1934, she suggested that the nucleus could split, a process we now call fission.

The discoveries of the neutron in 1932 and of induced radioactivity in 1934 opened up a new line of research — manufacturing elements in the lab by bombarding atoms with particles. In 1934, physicist Enrico Fermi and his co-workers at the University of Rome announced that they had produced elements 93 and 94 by firing neutrons at uranium. Ida Noddack pointed out in an article in *Angewandte Chemie*[10] that Fermi had failed to show that no other chemical elements, including lighter ones, had been produced. "It is conceivable," she argued, "that the nucleus breaks up into several large fragments." The physicists ignored her.

Then, in 1938, Meitner and Hahn realized that one of the elements Fermi had made was barium, and that the uranium nucleus had indeed split. By that time, in the run-up to the Second World War, Meitner, being Jewish, had fled to Sweden. Although it was her calculations that had convinced Hahn the nucleus had split, he did not include Meitner's name on the 1939 publication of the result,

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nor did he set the record straight when he accepted the 1944 chemistry Nobel in 1945.

Most of these female pioneers worked with male collaborators, and it is hard to tease apart their contributions[11]. Marguerite Perey is an exception: the French physicist is considered the sole discoverer of element 87, francium, in 1939 (ref. 12). Perey joined Marie Curie's institute in Paris at the age of 19 as a lab technician, under the direction of Irène Joliot-Curie and André Debierne. Both independently asked her to provide a precise value for the half-life of the isotope actinium-227, a delicate technical procedure during which she identified the new element. Because neither could agree about whom Perey was working for at the time, each was unable to claim a role in the discovery. Perey went on to lead the department of nuclear chemistry at the University of Strasbourg, and in 1962 became the first woman to be elected to the French Academy of Sciences — as a corresponding member. (Although there was no rule against admitting women, the first female full member was not elected until 1979.)

Francium was the last element to be discovered in nature. Today, such discovery requires large teams with particle accelerators and big budgets. The meaning of a chemical element has changed, from Mendeleev's concept of a stable and untransmutable substance to isotopic species that exist for only milliseconds[13].

Using these techniques, US chemist Darleane Hoffman made a monumental leap in the early 1970s. She showed that the isotope fermium-257 could split spontaneously — not only after being bombarded with neutrons. The first woman to lead a scientific division at Los Alamos National Laboratory in New Mexico, Hoffman also uncovered plutonium-244 in nature. She trained generations of female scientists. One is Dawn Shaughnessy, now principal investigator of the heavy-element project (and several others) at Lawrence Livermore National Laboratory in California, which has helped to discover six new elements (numbers 113–118).

USING ELEMENTS

Many more women expanded our knowledge of elements. After French chemist Henri Moissan isolated fluorine in 1886, a team of women (notably, Carmen Brugger Romaní and Trinidad Salinas Ferrer) worked with José Casares Gil at the University of Madrid in the 1920s and early 1930s to study its health effects and presence in mineral waters. When they had to leave research after the Spanish civil war of 1936–39, their work fell into Casares' bibliography.

Chemist Reatha Clark King was the first African American female scientist to work at the National Bureau of Standards in Washington DC[14]. In the 1960s, she studied the combustion of gaseous mixtures of fluorine, oxygen and hydrogen: fluorine's high reactivity gave it a potential use in rocket propellants. Some mixtures were so explosive that they required special apparatus and techniques, which she devised and NASA adopted.

In the 1910s, US physician and researcher Alice Hamilton proved the toxicity of lead and its harm to the public and metal workers[15]. She forced insurance companies and manufacturers to take safety measures and to compensate those affected. She also organized social action to recognize work-related illnesses for people working with other heavy metals such as mercury. In 1919, she became the first woman appointed to the faculty of Harvard University in Cambridge, Massachusetts. She spoke against the introduction of lead in gasoline as early as 1925.

Japanese–American technician Toshiko 'Tosh' Mayeda mastered the measurement of oxygen radioisotopes in the 1950s. Appointed to wash glassware in Harold C. Urey's lab at the University of Chicago, Illinois, she was soon put in charge of the mass spectrometers[16]. She helped to measure the ratio of oxygen isotopes in fossilized shells to deduce the temperatures of prehistoric oceans, and expanded that method to meteorites.

Like all Americans of Japanese descent, Mayeda was sent to internment camps after Pearl Harbor was attacked on 7 December 1941, and faced discrimination. With only a bachelor's degree in chemistry, she could have been one of many female technicians who remained largely invisible while making crucial contributions. Happily, Mayeda was supported by her superiors, and her name appeared on publications on an equal footing with holders of PhDs and professorships.

WIDER PICTURE

As with the discoveries themselves, bringing these tales of female scientists to light has taken much teamwork, including by contributors Gisela Boeck, John Hudson, Claire Murray, Jessica Wade, Mary Mark Ockerbloom, Marelene Rayner-Canham, Geoffrey Rayner-Canham, Xavier Roqué, Matt Shindell and Ignacio Suay-Matallana.

Tracing women in the history of chemistry unveils a fuller picture of all the people working on scientific discoveries, from unpaid assistants and technicians to leaders of great labs. In this celebratory year of the periodic table, it is crucial to recognize how it has been built — and continues to be shaped — by these individual efforts and broad collaborations. ■


MUSÉE CURIE/ACJC

Marguerite Perey (left), discoverer of francium, and Sonia Cotelle at the Radium Institute in Paris in 1930.

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