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Master of Missing Elements

Henry Moseley's discoveries sorted out the periodic table and transformed how scientists look for new forms of the most basic substances.

Eric R. Scerri

ust over 100 years ago, a young English physicist named Henry Moseley gave new life to the periodic table of the elements, and helped resolve a number of problems in chemistry and physics. There is a good chance you have never heard of him. Soon after Moseley published this work, World War I broke out, and the 27-year-old patriot felt compelled to volunteer for service on the war front, where he was killed by a sniper's bullet. Despite his abbreviated life, Moseley's work continues to influence the world of chemistry. In fact, his research is more influential than ever today, as new elements are being synthesized and added to the periodic table, such as the yet-tobe-named elements 115 and 118.

Moseley discovered a way to use x-rays in a vacuum to identify the atomic charge of elements (a critical measurement of their chemical properties, now known to correspond to the number of electrons in each element). His work allowed for the definitive identification of substances, and revealed that several elements were missing from the periodic table of the time, setting up subsequent researchers to make groundbreaking discoveries about the composition of the world. His methods also showed the logic of the now standard ordering of the periodic table. Moseley worked with some giants in physics, including the legendary Ernest Rutherford, who discovered the structure of the atom. It is likely that Moseley would have won the Nobel Prize himself, if not for his untimely death.

Henry Moseley seemed destined to leave his mark on science. He was born in the county of Dorset in England in 1887, into a family with an extraordinary scientific pedigree. Both of his grandfathers as well as his father, who died when he was just four years old, were fellows of the Royal Society. One grandfather was a mathematician; the other and Moseley's father were zoologists. In 1901 the young Moseley earned a scholarship to study at Eton, one of England's most prestigious schools. There he excelled at academic work as well as sports; he also became infused with a patriotic spirit that eventually cost him his life.

In 1906 Moseley gained another scholarship, this time to Trinity College at the University of Oxford. He was disappointed with the lack of interest in academic work in general and physics in particular at the college, however. He noticed that pursuits such as fox hunting were regarded as more important than academic excellence. After failing to gain a first-class honors degree in physics-probably because he was too interested in the subject matter rather than techniques for passing exams-Moseley transferred his studies to the University of Manchester to work with Rutherford.

Rutherford immediately set Moseley to work on experiments with radioactive isotopes, apparently recognizing his talents. But what really excited Moseley was another new area of physics, one that had begun slightly before the discovery of radioactivity. In 1897 the German physicist Wilhelm Röntgen had discovered some mysterious rays that he named x-rays, which found immediate applications in medicine as well as basic scientific research. In 1912 another German physicist, Max von Laue, proposed that crystals of inorganic compounds (substances that are not based on carbon-hydrogen bonded molecules) might be capable of diffracting x-rays. This prediction was almost immediately confirmed by independent researchers, who found that the diffracted rays produced discrete lines on photographic film.

The diffraction of x-rays differed based on the type of crystal used; the pattern of lines could be precisely measured to obtain detailed information about the distance between the planes of atoms that make up the crystals, unveiling their structure. Furthermore, a British physicist, Charles Barkla, found that each element scattered x-rays to a different extent, producing distinctive lines and thereby indicating the scatterer's composition. Two other British physicists, Henry Bragg and his son William, found that even reflection from crystals could be used to obtain useful information on the distances between planes of atoms.

At the same time, there was a great deal of debate as to whether x-rays were waves or particles. The study of x-rays was one of the first areas of physics in which *wave-particle duality* the view that some phenomena might be neither one nor the other but both together—began to take shape. That same realization was eventually made of electrons, thus opening up the possibility of treating the electron as a wave, as Erwin Schrödinger went on to do. Modern ideas about quantum physics emerged from there.

Henry Moseley followed all these developments closely and asked Rutherford if he too could initiate a program of research on x-rays. Initially Rutherford was reluctant to allow Moseley to discontinue his work on isotopes, but he relented after Bragg the elder invited Moseley in October 1912 to the University of Leeds to train him in working with x-rays. On his return to Manchester a month later, Moseley teamed up with the math-

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ematician Charles Darwin (the grandson of the "right Darwin," as the Danish physicist Niels Bohr later described him). Together Moseley and Darwin repeated the work of the Braggs and tried to extend it into new directions.

After publishing a couple of articles together, Moseley rather mysteriously decided to return to Oxford, where he would work as an independent scholar, possibly awaiting an appointment at the university. Whatever the reason, the move to Oxford proved enormously fruitful. It was after returning that Moseley conducted his epoch-making work, which resolved a puzzle about the ordering of the periodic table and which continues to be felt up to the present day.

Dawn of the Nuclear Era

Moseley began his crucial experiment in the early 1900s, at a time A young Henry Moseley, shown during his student days at Trinity College, holds laboratory equipment similar to pieces he later used to make breakthrough discoveries about the ordering of the periodic table. Moseley's career was cut short by his death during the Battle of Gallipoli in 1915, but his work continues to influence elemental studies today.

when physics was undergoing great discoveries about the atom. Several lines of research were beginning to illuminate the relationship between the electrical charge of the nucleus and the atomic weight of any particular element. Barkla's experiments, on the degree to which x-rays were scattered by samples of different elements, suggested that nuclear charge was approximately equal to half of the atomic weight of any element. Rutherford and his colleagues came to exactly the same conclusion from their work bombarding elements with highly energetic, radioactive alpha particles (now understood as the

nucleus of a helium atom, consisting of two protons and two neutrons), which also scatter in patterns dependent on the element.

The next piece in this puzzle to understand the elements came from a most unlikely source, but proved highly influential for Moseley and other researchers. A Dutch economist and amateur scientist, Anton van den Broek, had a long-standing interest in the periodic table, and attempted to improve on Dmitri Mendeleev's classic system of listing the chemical elements. Van den Broek attempted various improvements by drawing on the results of Barkla and Rutherford. He

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A figure from one of Moseley's publications shows how he ordered his x-ray spectra data by wavelength to indicate where additional elemental spectra should be inserted, demonstrating the presence of elements yet to be discovered at the time. When he made this figure, Moseley had not yet examined scandium, which should lie between calcium (Ca) and titanium (Ti) at the top of the spectra. Brass showed a mixture of lines from copper and zinc.

suggested the existence of a new fundamental particle that he called the *alphon*, which was to have a charge of +1 and a mass of two units, or twice the mass of the hydrogen atom. (At this point, the separate positive protons and neutral neutrons in the atomic nucleus had not been discovered, hence van den Broek's use of the alphon particle in their stead.)

Most periodic tables at the time ordered the elements by their atomic weights. Van den Broek proceeded to publish a version of the periodic table that included all the known elements, up to uranium, which he took to have an atomic weight of 240. In this table each element differed from the following one by two units of atomic weight or by one alphon particle. Moreover, because the alphon bore a charge of +1, each element differed from the following one by one unit of positive charge. Here is the origin of the idea that the elements can be ordered by means of increasing nuclear charge, or units of +1 charge, instead of by weight, which Moseley proceeded to confirm experimentally.

Atomic weights had also created three places in the periodic table where a mysteriouslooking anomaly had long bothered chemists. In the cases of argon and potassium, cobalt and nickel, and tellurium and iodine, something strange was evident. The first element in each of the pairs had an atomic weight that was higher than the subsequent element. But the chemical properties of these elements, in keeping with the properties of their surrounding elements, made it necessary to invert their order and violate the principle of atomic weight ordering. Such pair reversals, as they became known, implied that all was not well and that there might be a more fundamental way of ordering the elements.

It was a view that also had begun to fer-

ment in the minds of physicists such as Rutherford and Bohr, but it was not until the complete outsider van den Broek stepped into the picture that it became stated explicitly. Perhaps physicists were focusing more

on individual elements, whereas van den Broek took a wider chemical perspective involving all the elements in the periodic table. Whatever the precise sequence of events, Moseley used the skills in handling x-ray experiments that he had learned from Bragg and in Rutherford's lab and set out to test van den Broek's hypothesis.

One of Moseley's vacuum chambers, along with the small train in the attached tube that brought different samples into the path of an x-ray beam, is on display at the Museum of the History of Science at the University of Oxford. Moseley's results were his great breakthrough. He found that van den Broek had been correct in assuming that the elements are more properly ordered using atomic charge, or *atomic number* as it became known, than by using atomic weight.

In the case of atomic weight, the variation between successive elements is rather irregular, making it unclear whether new elements might be lurking undiscovered between the already known elements. A good example is provided by the two first elements hydrogen and helium, which have approximate atomic weights of one and four units, respectively, a gap of three units. In other parts of the periodic table, the gap in atomic weight values between successive elements is usually closer to two units, leading many chemists and physicists to suppose that one or even two elements might lie between hydrogen and helium. The result of Moseley's research helped to settle many debates about precisely how many elements remained to be discovered in the periodic table.

In July 1913, Moseley and Bohr, who was visiting Rutherford's lab in Manchester, had at least one conversation about pair reversals. Bohr suggested to Moseley that in the case of cobalt and nickel, the degree of scattering of x-rays might be proportional to the atomic charge of each of these two elements rather than to their atomic weights. The thought linked the ideas of the periodic table, atomic number, and x-rays. Moseley's response was: "We shall see."



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Moseley's Experiment

Moseley made good on his comment to Bohr and set up equipment to conduct the appropriate experiments. His apparatus consisted of an evacuated glass bulb, which allowed the passage of a beam of x-rays to strike a target sample, and a photographic plate to record the resulting position of the reflected x-ray beam when it arrived at the detector screen. From knowledge of the position of the beam, Moseley was able to calculate the frequency of the rays. He also devised a method of varying the sample without opening the bulb, because he wanted to examine the effect of x-rays on a range of elements under precisely the same pressure. At this time reducing pressure was not a well-developed technology and starting again each time for separate element samples would have complicated the experiments too much. Moseley's experimental setup contained a small train onto which the various samples were mounted, and a simple device allowed the movement of the train to bring successive samples into the line of fire of the x-ray beam.

After conducting his experiments, Moseley found an unexpectedly simple relationship between the reflected x-rays and the elements, which is now known as Moseley's law. The square

Moseley's experimental apparatus consisted of an evacuated glass bulb, which allowed the

passage of a beam of x-rays to strike a sample, connected to a spectrometer. Inside the spec-

trometer was a crystal that deflected the x-rays onto a photographic plate, which recorded the

resulting spectrum. Moseley did not want to reestablish a vacuum in the bulb each time he

switched samples, so he devised a small train onto which he mounted the various samples,

root of the frequency of the x-rays reflected from an element was proportional to Z-1, where Z is a whole number representing the charge on the nucleus of the atoms of any particular element. The symbol Z (from the German Zahl, meaning number) became known as the atomic number for an element and is of fundamental importance in chemistry and physics. (See the figure on page 362 for more on what happens

provided with a physical foundation (and as it was later discovered, atomic number relates to the number of electrons in an element, therefore providing the basis for placing the elements in ascending order of charge, which affects the element's chemical properties). Moseley had confirmed van den Broek's hypothesis that atomic number is a better ordering principle for the elements in the periodic table than is atomic weight.

Bohr suggested the degree of scattering of x-rays might be proportionate to the atomic charge of each of these elements. Moseley's response was "We shall see."

within an atom when it is struck by x-rays.) This result solved the long-standing issue of pair reversals. It now became clear that the reversal of elements such as iodine and tellurium was perfectly

justified on the basis of tellurium having a lower atomic number than iodine. The reversals like this one that chemists had made on chemical grounds was now

But Moseley's method went far beyond merely confirming van den Broek's idea and providing a physical foundation. It also provided a simple experimental method to identify any element by measuring the wavelength of the x-ray lines that it produced, and checking whether the observed value corresponded with the value calculated using Moseley's law. For example, Moseley was able to put his new method to good use in showing that certain reported new elements did not in fact exist. Such was the case with an element that the French chemist Georges Urbain had claimed to find.





As Moseley discovered, the pattern, or spectrum, of wavelengths produced when an x-ray beam strikes an atom is unique to each element, so it can be used to identify the composition of samples. Electrons in an atom fall into shells, the innermost denoted K and subsequent ones labeled with the next alphabetical letter. An x-ray beam knocks out certain electrons in each shell. Electrons from the next higher shell move down to fill the vacancy. But inhabiting a lower shell takes less energy, so the electrons emit the extra energy as x-rays, each of a characteristic wavelength that depend on the shell it now inhabits.

Mendeleev, a main early creator of comprehensive periodic tables, had predicted an element would lie directly below zirconium in the periodic table. Urbain called it celtium and gave it the symbol Ct. This symbol even appeared on published periodic tables in several parts of the world. But not everybody accepted the claim by Urbain, which is why he seized the opportunity after hearing that Moseley had developed a unique method for identifying and validating new elements. Urbain traveled to Oxford and brought with him some samples that he believed contained some celtium. It took Moseley just a few hours to conclude that it did not give any spectral lines expected of an element that had not previously been observed but was instead a mix of already known rare earth metals. Fortunately Urbain reacted with grace despite his undoubted disappointment.

In addition, Moseley recognized that at least three undiscovered elements existed between hydrogen with atomic number 1 and gold whose atomic number is 79. (He could not extrapolate beyond gold because that was the last element for which he had made measurements, and so there was no guarantee that his law would hold for higher atomic numbers. In addition, he lacked samples of some of the elements, so he missed a few gaps.) The three missing elements that he identified had atomic numbers of 43, 61, and 75. Some time later, other scientists used Moseley's method to determine that there were in fact four more elements yet remaining to be discovered between the old boundaries of the periodic table, which spanned atomic numbers between 1 (hydrogen) and 92 (uranium). The additional missing elements, beyond the three that Moseley himself identified, were elements 72, 85, 87, and 91. That meant a total of seven gaps in the list of the constituent atoms that make up all of the natural world.

Moreover, Moseley was able to categorically rule out the possible existence of any elements lying between hydrogen and helium. In spite of the large atomic weight gap that exists between these two elements, there is no gap between their atomic numbers. At a stroke, Moseley was able to refute predictions for the existence of such intermediate elements that had been made by the likes of Mendeleev, influential Swiss inorganic chemist Alfred Werner, the Swedish spectroscopist Johannes Rydberg, and several others.

It is a tragedy that Moseley's death ended his work just as it was about to have huge scientific repercussions.

Fights for First

Knowledge of the complete periodic table was a necessary precursor for full understanding of the natural world, and the discovery of an element would guarantee the finder a place in history. One might think that the knowledge that precisely seven elements remained to be discovered, as well as Moseley's x-ray method that allowed their experimental identification, would have made the race to discover these elements a relatively straightforward matter. But this was not the case, and in fact the attempts to discover the missing elements were fraught with difficulties and led to many bitter priority disputes among the participating scientists. However, in each discovery, Moseley's x-ray methods were the key for proving or disproving the finding.

The first to be identified was the element with the highest atomic number among the missing seven, element 91, which was eventually given the name protactinium (Pa). It was discovered by several physicists and chemists and it is rather difficult to state categorically who the first discoverers might have been. First the Polish-born chemist Kasimir Fajans discovered a short-lived radioactive isotope (which has the same atomic number but a different number of neutrons, thus a changed atomic weight) of the element. Fajans named it brevium on account of its short half-life (the time it takes for half of its radioactive atoms to decay, or transform, into something more stable) of just 1.2 minutes.

A little later, a far longer-lived isotope of element 91 was discovered at about the same time by two independent teams. In 1917 in Berlin, Lise Meitner and Otto Hahn, who later discovered nuclear fission, discovered an isotope of element 91 with a half-life of 32,500 years. The same isotope was observed by John Cranston and Frederick Soddy in Glasgow, but they failed to characterize it chemically. To their credit, both Fajans and the team from Glasgow ceded priority to Hahn and Meitner. Fajans followed a rule that if isotopes of any new



A modern periodic table is ordered by atomic number (related to the charge of an atom), rather than atomic weight, in part because of Moseley's discoveries. All of the elements above uranium (atomic number 92) were unknown in Moseley's time. Moseley's work proved that three elements were missing from the periodic table at the time (atomic numbers 43, 61, and 75). Others soon used his methods to show additional gaps (atomic numbers 72, 85, 87, and 91), bringing the total number of missing elements to seven. The race to discover these seven elements proved to be contentious and dramatic, with protracted priority disputes arising among the participating scientists. (Image of the periodic table of the elements adapted from Brian D'Alessandro, www.briandalessandro.com.)



The most recently confirmed element on the periodic table has atomic number 115 and is unofficially known as Unupentium (Uup). It was first synthesized in 2003 but was not officially confirmed until 2013.

element were discovered, the priority should be accorded to the discoverer of the longest-lived isotope. Clearly this case presented no contest in view of the vast difference in the half-lives of the two isotopes in question.

As for the British team, they accepted that they had failed to provide the chemical support for the claim of an element one place before uranium. Incidentally, the name protactinium comes from the fact that element 91 is a precursor to the formation of element 89 or actinium. If protactinium loses an alpha particle it undergoes a decrease in atomic number of two units, resulting in the formation of actinium. The next element among the seven to be found was element 72, which was discovered by Dirk Coster and George Hevesy, working at the Niels Bohr Institute for Physics in Copenhagen in 1923. It was given the name hafnium (Hf) after the Latin name for that city, which is Hafnia. But before the discovery of this element was settled, a rather acrimonious priority dispute broke out among several participants and their followers. Urbain, whose sample of celtium had been dismissed by Moseley in 1914, was now claiming his discovery was the missing element 72.

The dispute over element 72 took on almost comical nationalistic overtones when the British newspapers sided with Urbain on the basis that France had been an ally of England during the recently completed World War I. Meanwhile the French press declared in one headline "Ça pue le Boche" or "It stinks of the Hun" to describe the discovery in Copenhagen. Ironically, Denmark had been neutral during the war, and neither Coster nor Hevesy were either German or Danish. Nevertheless the men from Copenhagen had the last word, because they observed several x-ray spectral lines at precisely the frequencies predicted by Moseley's law for an element of atomic number 72.

Element 75, rhenium (Re), was next. It is a metal discovered in 1925 by the husband-and-wife team of Walter and Ida Noddack, as well as Otto Berg, all German chemists, after a great deal of painstaking extraction work. Although the discovery of this element did not cause any controversy, the Noddacks and Berg also claimed to have discovered element 43, which they named masurium. This second claim failed to stand up to the experimental evidence obtained in other labs, yet the Noddacks refused to withdraw their claim.

Unlike those others, element 43 was not discovered in nature due to its very short half-life, but was artificially synthesized in 1937, and was eventually given the name technetium (Tc) because of its artificial or "technical" origins. The Italian physicist Emilio Segrè had spent a period of time working at the University of California at Berkeley. After returning to his home institution in Palermo, Sicily, he received a plate made of molybdenum that had been irradiated. On analyzing this substance with the help of a chemist, Carlo Perrier, they discovered that a completely new element had been created. It was to be the first of what now amounts to almost 30 elements that have been artificially produced and have taken their places in the periodic table.

Element 87 was falsely claimed by several people who believed that they had isolated it. It was finally discovered

Several prominent women scientists featured highly in the discovery of new elements. Ida Noddack (*left*) helped identify rhenium, element 75, in 1925. Marguerite Perey (*middle*) discovered francium, element 87, in 1939. And Lise Meiner (*right*) helped definitively find protinactium, element 91, in 1917.







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in 1939 by a French laboratory technician, Marguerite Perey, who had been trained by Marie Curie, one of the early pioneers of the study of radioactivity who was also responsible for coining the name for this field. Eventually Perey earned a Ph.D. and rose to the rank of professor of nuclear chemistry. Her work involved carrying out the careful and rapid handling of radioactive isotopes. As it turns out, element 87, element beyond uranium, and so began the extension of the periodic table from atomic numbers 93 to, so far, 118. Although many of these elements are too unstable to be of commercial importance, their synthesis provides new understanding of nuclear stability and radioactivity, especially under extreme conditions of very high charge, and also can be used to test relativistic quantum theories of atoms. (However, several of

American and Russian facilities that competed to find elements during the Cold War now collaborate on synthesis.

which she named francium (Fr), was the last natural element to be discovered. Estimates of the abundance of francium suggest that there is only about 30 grams of it in the whole of the Earth's crust, and its longest-lived isotope has a half-life of just 21 minutes.

The last two of the seven elements were also claimed by several chemists and physicists but were only definitely identified after they had been artificially synthesized. Element 85 was synthesized in 1940 by Dale Corson, Kenneth Ross MacKenzie, and Segrè in the United States. They called it astatine (At) after *astatos*, the Greek word for unstable. Indeed the element has no stable isotopes, but a few years later, other researchers discovered that it was a natural product of several radioactive decay processes.

The final element of the seven was atomic number 61, promethium (Pm), which was synthesized in 1945 by Americans Jacob A. Marinsky, Lawrence Glendenin, and Charles D. Coryell. Like astatine and technetium, promethium has no stable isotopes. But promethium has found some specialized applications, notably the manufacture of atomic batteries that have life times of five years or more and thus lend themselves to powering devices where battery changes are dangerous to impossible, such as in pacemakers and spacecraft.

Going Beyond Uranium

Even before the last of these elements was discovered, in 1940 Edwin McMillan at the University of California at Berkeley succeeded in synthesizing an these elements have found industrial use. For instance, californium is used in medical imaging and americium is used in home smoke detectors.)

This work too has had its share of controversy and priority disputes. For example, during the height of the Cold War, two of the few facilities that are capable of creating such elementsone at Berkeley and the other at Dubna in Russia-began a long-running dispute as to which site had first produced a sequence of transuranium elements. Even more controversial perhaps was the case of the yet unnamed element 118 that was first claimed by the American team but later retracted, before finally being genuinely discovered in 2006 in Dubna. It is unofficially known as Ununoctium (Uuo).

However, in 2003, Russian scientists from Dubna worked together with Americans at Lawrence Livermore National Laboratory to put forth a claim of discovery for element 115, unofficially known at Ununpentium (Uup). The claim was ruled to be unsupported until two other groups confirmed synthesis in 2013. The element's longest measured half-life is about 200 milliseconds.

In the current age where high-tech synthesis seems to be the only means to discover new elements, it is appropriate to remember that Henry Moseley's atomic number criterion still serves to identify any element. His unfortunate death, so soon after his crucial discovery, was lamented by scientists on both sides in World War I. Among other things, it led to the implementation of regulations to prevent scientists from being sent into front-line combat in a time of war.

Would it not be a fitting tribute to Moseley's legacy if a new element were to be named after him? Unfortunately there is currently a regulation by the International Union of Pure and Applied Chemistry that requires that any name given to an element, which later turns out to be spurious, can never be used again. In 1924 two chemists, C. H. Bosanquet and T. C. Keeley, believed they had extracted element 43 and proposed to name it mosleyum. It was soon shown that their element did not in fact exist.

Nevertheless regulations can be changed. For example when it was first suggested that element 106 should be named seaborgium (Sg) after American chemist Glenn Seaborg, there was a good deal of resistance because this too would mean breaking an official rule concerning how elements are named. This rule was that an element cannot be named after a person who was still living, and Seaborg was still very much alive at the time. However he had been involved in the discovery of ten transuranium elements, and that may have contributed to the international naming commission's finally relenting and officially naming one of these elements after Seaborg.

The periodic table was given a new lease of life by Moseley's work, which enabled it to become a far more exact and complete system than it had been when it was based solely on macroscopic chemical and physical properties. It would be only appropriate that his name be used for one of the elements that has still not been officially named, including 113, 115, 117, or 118—or even one that has yet to be synthesized.

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