Rediscovery of the Elements

Element 72—Hafnium

Urbain's Search for Element 72. In a previous HEXAGON we witnessed the 1914 visit of Georges Urbain (1872-1938) to Oxford, England, to enlist the aid of Henry Gwyn Jeffreys Moseley (1887-1915), who, with his new x-ray method had been able to determine the atomic numbers of 38 elements ranging from aluminum (13) to gold (79). Urbain wished to study some of his rare earth samples which he had been investigating for two decades. The preparations he brought from his laboratory in Paris had been separated from ytterbium, originally discovered in 1878 by Jean-Charles Galissard de Marignac (1817-1894) in Geneva, Switzerland. Urbain had previously announced the discovery of lutetium in these ytterbium mixtures, but he also wanted to confirm "celtium," a new element which he had proposed on the basis of its different optical spectrum and magnetic properties.

In the matter of a few hours, Moseley was able to establish that indeed ytterbium and lutetium were present in the mixtures; their respective atomic numbers were determined to be 70 and 71. However, none of the putative celtium was detected. Urbain returned to Paris disappointed, but determined to continue the search. With Moseley's previous respective identifications of tantalum and tungsten as 73 and 74, a vacancy existed at 72 and Urbain assigned this atomic number to his celtium.

After the hiatus of World War I, Urbain resumed his research on rare earths. He persuaded Alexandre Dauvillier (1892-1979), assistant to Louis-Victor-Pierre-Raymond de Broglie (1892-1987; Nobel Laureate in physics, 1929), to reinvestigate his rare earth mixtures. In 1919 Dauvillier set up an x-ray laboratory in de Broglie's Parisian mansion, and three years later he and Urbain published papers identifying two faint lines as element 72 which "demonstrated the existence of a trace of celtium." Urbain explained the earlier negative results in 1914: Moseley's crude instrumentation "had not been sensitive enough." Even though Urbain was never able to gather any further evidence beyond these "two faint lines," for years he maintained his claim to the discovery of element 72.

The Niels Bohr Institute and Hevesy. Niels Bohr (1885-1962; Nobel Laureate in physics, 1922) worked with Ernest Rutherford in Manchester and had adopted Rutherford's model of the nuclear atom in his future researches. Returning to his home in Copenhagen (Figure 1), Bohr became professor of physics at the University of Copenhagen in 1916 and was made director of the newly founded Institute of Theoretical Physics two years later (Figure 2). Whereas Urbain had assumed that the element 72 would be a rare earth, Bohr's work suggested that the undiscovered element would belong with the main transition metals and would lie directly below zirconium in the Periodic Table. Thus, element 72 should be sought not in rare earth mixtures, but instead in zirconium minerals.

Bohr invited the Hungarian György de Hevesy (1885-1966), who also had worked in Rutherford's laboratory, to join the Bohr Institute in an attempt to isolate element 72. Joining Hevesy was Dirk Coster (1889-1950), who had worked with Karl Manne Georg Siegbahn (1886-1978), whose sophisticated instrumentation had extended Moseley's x-ray work to establish atomic numbers through uranium. Hevesy and Coster procured samples of zircon (zirconium silicate, ZrSiO4) from the Geological Museum (Figures 3, 4) in

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Figure 2. The Bohr Institute (Niels Bohr Institutet, Københavns Universitet), built in 1920 for Niels Bohr, and originally financially sponsored by the Carlsberg brewing company. Niels Bohr studied under Ernest Rutherford at Manchester 1912–1916 and then returned to Denmark to work in this building.

Figure 3. The Geological Museum in Copenhagen houses samples of alvite (hafnium-rich zircon specimens) and cryolite (aluminum minerals) described earlier by the authors.

Copenhagen and rapidly established that indeed element number 72 existed in Norwegian minerals. In their paper "On the missing element of atomic number 72," they proclaimed that they were the first to observe the element, and they named it hafnium (Latin for Copenhagen). By the use of potassium and ammonium tetrafluoro salts (Figure 8), they were able to concentrate hafnium and differentiate zirconium and hafnium x-ray lines cleanly.

Hevesy and Coster proceeded with a complete chemical and physical characterization of hafnium. Recognizing that hafnium might have unusual electric properties, Philips Laboratories of the Netherlands became interested and contracted to own exclusive rights to scientific knowledge gained during Coster and Hevesy's researches. At Philips NatLabs in Eindhoven, Netherlands (Figure 9), ultrapure hafnium was prepared and investigated in electronic devices.

Why was hafnium so chemically similar to zirconium? Hevesy in his review discussed the almost identical chemistry of zirconium and hafnium, pointing out that they were "more closely related than any other two elements belonging to different periods of the Periodic Table." He reminded us that columbium [niobium] and tantalum were also "very closely related chemically," and to a lesser extent other family pairs such as molybdenum and tungsten. (A century earlier Wollaston had concluded columbium and tantalum were the same element, but he was puzzled over their different densities).

Explanation of this behavior was furnished by Victor M. Goldschmidt (1888–1947), professor at the Royal Frederick University (became University of Oslo in 1939) (he actually submitted a report, a scant 29 days after Coster and Hevesy's announcement, that he had also detected hafnium in Norwegian mineral samples). One of Goldschmidt's major contributions was his recognition of the "lanthanide contraction," a gradual decrease in the atomic radii as one progresses through the lanthanides (because of poor shielding by the 4f electrons) with the result that hafnium and zirconium have virtually identical ionic radii. Hence, even...
though hafnium is denser than zirconium, it behaves crystallographically and chemically the same, even if its electronic and nuclear properties may be different (as an example, hafnium is an efficient neutron-adsorber used in nuclear reactors, but zirconium is relatively transparent).

The Response of the French. In the initial announcement by Coster and Hevesy appearing eight months after the x-ray work of Dauvillier and Urbain, the Bohr Institute scientists did not neglect to mention that the conclusions of Dauvillier’s and Urbain were “not justified.” The response was swift. The attack on celtium was an assault on French science itself—the words of Charles Adolphe Wurtz (1817-1884) echoed from 56 years earlier: “La chimie est une science française. Elle fut constituée par Lavoisier d’immortelle mémoire.”

It was still fresh in the minds of Europeans, and excessive patriotism could dominate the national scene. The French press excoriated the Copenhagen announcement of hafnium with its opinion: “Ça pue le boche” (“This reeks of the Hun”). Urban and Dauvillier grudgingly admitted that Coster and Hevesy’s work was a “very important result” but denounced the conclusions as “regrettable” which “cast discredit” on their results. If Coster and Hevesy’s element was 72, Urbain maintained, then the Copenhagen team was merely lucky to have stumbled on a richer source of the element, and that in any case the original discovery belonged with the Parisian research group.

The British claim to “Oceanium.” Hostility to the Copenhagen group extended across the English Channel—the British press protested, “We do not accept the name which was given to it by the Danes who only pocketed the spoil after the war.” Not wanting to lose out on the action, British scientists were exhorted to claim elements from the dwindling list of the undiscovered “before it is too late.” Promptly a declaration was made by Alexander Scott (1853-1947; FRS, Head of Laboratory, British Museum) that he should be given credit for element 72, having discovered “oceanium” in “black sand from New Zealand.” Congratulations were extended by the Chemical Society for the element which was “identical with that announced by Coster and Hevesy,” but a subsequent careful analysis indicated nothing but titanium and silicon dioxide.

The Slow Demise of Celtium. In response to the objections of Urbain and Dauvillier, Coster and Hevesy carefully laid out their case; both the optical and x-ray properties of hafnium and “celtium” were not the same; the paramagnetic data which Urbain originally used to argue for celtium was actually due to an ever-increasing concentration of lutetium in his original crude preparations. They argued that Urbain’s
Figure 8. The “shoeshine box” full of “Hevesy’s Chemical Collection” includes samples of $K_2ZrF_6$, $K_2HfF_6$, $HfOCl_2$, and other compounds prepared by Hevesy. Hevesy discovered that potassium hexafluorohafnate ($K_2HfF_6$) is more soluble than potassium hexafluorozirconate ($K_2ZrF_6$). Repeated recrystallizations slowly led to an enrichment of the hafnium compound in the soluble portion.

Figure 9. Pure metallic hafnium was first prepared by Anton Eduard van Arkel (1893–1976) and Jan Hendrik de Boer (1899–1971) at Philips NatLab (Natuurkundig Laboratorium = Physics Laboratory) in 1925 in the Strijp district of Eindhoven, Netherlands (Kastanjelaan - N51° 26.75 E05° 27.25). Philips had drawn up a contract with Coster and Hevesy and was using hafnium in its electronic equipment. In this building immediately after its construction in 1923, both Lise Meitner and Albert Einstein gave lectures on the atomic nucleus and quantum mechanics, respectively. Today the area is being renovated into a historical park, as Philips NatLab moved in 1968 to its High Tech Campus 4 km south of Eindhoven.

trivalent rare earths could not contain tetravalent hafnium ($Hf^{4+}$). In fact, it was impossible for Urbain’s rare earth mixtures to contain any hafnium, even as an accidental impurity, because Urbain had carefully purified his rare earth mixtures by oxalic acid treatment which would have removed any traces of zirconium and hafnium. The Danish group went further and suggested that Welsbach, who had cleaner preparations of lutetium (71), should be credited with the discovery of element 71 which should be named “cassiopeium” as he had suggested.

Urbain should have been suspicious from the very beginning: the faintness of the two lines did not portend an element which exhibited an intense optical spectrum and measurable magnetic properties which he had reported as being characteristic of celtium. However, he was bitterly disappointed that years of painstaking work might be preempted by a younger group of theoretical physicists, and his zeal to prevent “Teutonic priority claims” overwhelmed his judgment. With no new evidence supporting celtium, he resorted to “distortions of historical facts.” He called upon the expertise of Moseley, affirming that the now-deceased scientist “himself set forward the hypothesis that celtium is identified with element number 72.” In fact, Moseley had originally accepted celtium only upon the word of Urbain; and after his rare earth x-ray analysis, Moseley declared that clearly Urbain’s “lutetium” was merely crude ytterbium contaminated with lutetium, and his “celtium” was simply more highly purified lutetium (this pronouncement was later shown to be correct). Next, Dauvillier claimed he and Urbain had actually anticipated hafnium being a tetravalent homologue to zirconium—when all along the French scientists had been searching in the trivalent rare earths. Finally, Urbain contended that even though he may have been mistaken about the optical and magnetic spectral data, nevertheless his claim was validated by his x-ray spectrum of celtium, which was the same as Coster and Hevesy’s. Careful inspection of Dauvillier’s spectrum shows this was embarrassing nonsense (Figure 10).

Hevesy and Coster fully characterized hafnium by 1925, including its atomic weight. Nevertheless, that year the Committee on Chemical Elements, which was chaired by Urbain (Note 1), omitted element 72 in its “International Table of Atomic Weights of the Chemical Elements.” Bohr was frustrated: “[Urbain pays] no regard to the important scientific discussion of the properties of the element 72, but tries only to claim a priority for announcing a detection of such an element.” Rutherford quietly told him not to fret, that they “need pay no attention to such irresponsible utterances.” Fortunately, during this post-war period of “national prejudices and professional jealousy,” cooler heads eventually prevailed, notably Ernest Rutherford, Niels Bohr, Marie Curie, and Charles James, whose professionalism reined in extrascientific propaganda. Finally, in 1927 the Committee officially recognized “hafnium,” which finally
The Belated Recognition of the Co-discoverers of Lutetium. In the early 1900s three scientists were working to separate out the suspected companion in Marignac's ytterbium—not only Georges Urbain in France, but also Carl Auer von Welsbach and Charles James (1880-1928) of the University of New Hampshire (AXE, Mu, '11). The first to report evidence of this element was Welsbach (30 March 1905), obtaining convincing spectral data by 1906. Nevertheless, the International Committee on Atomic Weights stated that, in 1909, Urbain had "clear priority"—because he named it "one month before the more cautious and meticulous Welsbach ("cassiopeium")—even though the Committee admitted that Urbain's atomic weight values were inferior to Welsbach's values. The course of the Committee proceedings is puzzling until it is remembered that the four-man committee included Urbain (Note 1). Countries of Eastern Europe, recognizing the injustice of the Committee's action, used the name "cassiopeium" for years. (In their travels the authors themselves have seen several archived Periodic Tables with "Cp" under element 72).

In reality, the source sample is merely a crude mixture of lutetium and ytterbium. The lines attributed to celtium are identified by "Ct," the chemical symbol for the putative "celtium." However, the overall arrangement and the position of the lines do not correspond with the six hafnium lines observed by Coster and Hevesy, and crucially an even stronger line is missing; hence, the "Ct" lines cannot be due to element 72. In 1922, Charles James had delayed publication of his research posing a parody of chemical history: "[Urbain] recognized the presence of still another element—let alone for the illusory celtium. Meanwhile, the cautious Charles James had delayed publication of his research to prepare perhaps the purest samples of lutetia (Lu₂O₃)." Today the injustice of the lutetium episode has been moderated by a generation attending the "Rediscovery" articles and who has always made many insightful suggestions.

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Notes.

Note 1. Urbain was appointed to the International Committee on Atomic Weights in 1907 upon the death of Henri Moissan (1852–1907; Nobel Laureate in chemistry, 1906). Moissan had been appointed in 1903 to fill out the three-man committee elected from the USA, England, and Germany two years earlier (Moissan was the only Frenchman to receive a vote out of a slate of 12). It is easy to understand how the ardent Urbain wished to rectify what he considered to be undue German influence on international chemical committees at the turn of the century. After World War I, the Committee on Atomic Weights was reorganized (1921) and renamed the Committee on Chemical Elements, presided over by Urbain.

Note 2. Upon Urbain's death in 1938, authors of his obituary lauded the late-Renaissance man by extolling his skills as a painter, sculptor, and scientist, but unfortunately they elected to promote la gloire while composing a parody of chemical history: "$[Urbain] recognized the presence of still another element, celtium, not of the rare earth family. This element was thought by Moseley to be the missing element number 72...[Dauvillier's examination] indicated the presence of element number 72...[Moissan's examination]..." [the] International Committee on Atomic Weights has accepted two names, celtium and hafnium, and two symbols Ct and Hf." Even today the fable persists in French Wikipedia, where Urbain is given credit as "the discoverer of celtium later called hafnium" [http://fr.wikipedia.org/wiki/Georges_Urbain].
References.


2. H. G. J. Moseley, *Phil. Mag.*, (a) 1913, 26, 1025–1034; (b) 1914, 27, 703–713.

3. G. Urbain, *Compt. rend.*, (a) 1907, 145, 759–762; (b) 1911, 152, 141–143; (c) 1922, 174, 1349–1351; (d) 1923, 176, 469–470.

Urbain originally announced “lutecium,” whose spelling was changed to “lutetium” in 1949.


8. (a). D. Coster and G. von Hevesy, 1923, *Nature*, 111, 79; (b) 182; (c) 252; (d). 462–263.


