in your element

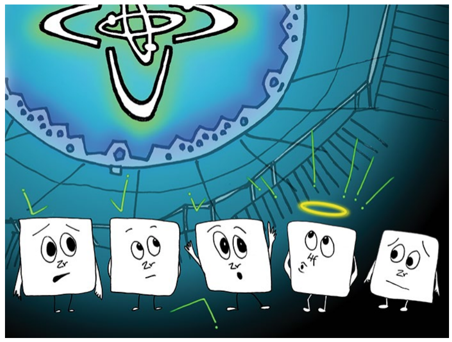
Hafnium the lutécium I used to be

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. ❐

Shawn C. Burdette[1]* and Brett F. Thornton[2]*
[1]*Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, MA, USA.*
[2]*Department of Geological Sciences and Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden. Twitter: @WPIBurdette; @geochembrett*
**e-mail: scburdette@wpi.edu; brett.thornton@geo.su.se*

Published online: 20 September 2018
https://doi.org/10.1038/s41557-018-0140-6

References

1. Marshall, J. L. & Marshall, V. R. in *The Hexagon* 36–41 (2011).
2. Scerri, E. R. *Ann. Sci.* **51**, 137–150 (1994).
3. Urbain, G. *C. R. Acad. Sci* **152**, 141–143 (1911).
4. Heimann, P. *Ann. Sci.* **23**, 249–260 (1967).
5. Coster, D. & Hevesy, G. *Nature* **111**, 79 (1923).
6. Fahrenholtz, W. G., Hilmas, G. E., Talmy, I. G. & Zaykoski, J. A. *J. Am. Ceram. Soc.* **90**, 1347–1364 (2007).
7. Frazier, K. A. et al. *Organometallics* **30**, 3318–3329 (2011).
8. Scherer, E., Münker, C. & Mezger, K. *Science* **293**, 683–687 (2001).

Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra Ac