

Peculiar protactinium

Richard Wilson relates how the rare, highly radioactive, highly toxic element protactinium puzzled chemists for a long time, and was discovered and named twice from two different isotopes before finding its place in fundamental research.

The first glimpse of element 91 came in 1900, thirty years after Dmitri Mendeleev predicted its existence, when William Crookes, the discoverer of thallium, put down his studies with cathode rays and spectroscopy to investigate Becquerel's newly reported phenomenon — radioactivity.

Crookes separated a highly radioactive material from his uranium salts that was able to expose a photographic plate, yet could not be detected by a spectroscope¹, leaving him unable to identify the material as a new element. It was in 1913, based on the work of Rutherford and Soddy on the nature of radioactive decay and isotopes, that Fajans and Göhring identified element 91. They named it brevium because the isotope they had encountered (^{234m}Pa) had a brief half-life of only one minute².

Meanwhile, a hunt was on for the element whose decay would generate actinium, which Fajans's isotope was not. Soddy hypothesized that this element must be an alpha particle (⁴He) emitter of the group v elements positioned under tantalum in the periodic table, and thus named eka-tantalum in those days. In March of 1918, Lise Meitner and the conscripted Otto Hahn beat Soddy in the hunt for eka-tantalum and discovered the isotope ²³¹Pa, code-named “abrakadabra” in their correspondence, which indeed converted into actinium through alpha decay. Their suggested name protoactinium — meaning ‘parent of actinium’ — superseded Fajans's brevium because of the longer half-life (roughly 32,000 years) of their isotope ²³¹Pa (refs 3,4). In 1949, IUPAC would simplify it to protactinium, Pa.

Little chemical research would be conducted with protactinium for the following forty years — a consequence of its rarity, difficulty of isolation, radiotoxicity and lack of commercial application. In the 1950s, the development of nuclear power, along with the



recognition of uranium as a strategic resource for weapons, inspired the investigation of a thorium-based nuclear fuel cycle, which involves protactinium as a major player. This newly identified use for protactinium resulted in the separation of approximately 100 grams of it from 60 tonnes of uranium-refining sludges. The availability of this stock for research in the 1950s led H. W. Kirby, an American pioneer in protactinium research, to speculate that the 1960s would see much of the “mystery and witchcraft” fade from the chemistry of this element⁵.

The mystery and witchcraft mostly came from protactinium's confusing chemical properties, not quite truly actinide yet not quite transition metal. This confusion persisted until the actinide elements were identified as a discrete periodic series. Element 91 shares a pentavalent oxidation state with the transition metals niobium and tantalum, and possesses a tetravalent oxidation state accessible under reducing conditions, in a similar manner to the other tetravalent actinides. However, unlike the other pentavalent actinides, protactinium exists as a mono-oxo ion rather than the di-oxo ones archetypical of uranium, neptunium, plutonium and americium, which makes it a truly unique actinide. But Pa(v)'s most lamented property is perhaps its insolubility, which causes protactinium to adsorb to glass surfaces. It proved fortunate for Meitner and Hahn, however, because it was the silica fraction of their pitchblende

residues that contained the protactinium they succeeded in isolating.

The 1960s and 70s saw our knowledge of protactinium's chemistry expand vastly to include its oxides, halides, coordination complexes and organometallic complexes such as protactinocene. A declining interest in a thorium fuel cycle, however, and the abandonment of research on its chemistry by all but a few by the mid-1980s, sent protactinium back into relative obscurity despite its importance in the actinide series.

Protactinium's significance stems from the fact that it is the first actinide to possess a 5f electron, with intermediate properties between those of thorium and uranium. Its ground-state electron configuration [Rn]5f²6d7s² is only marginally more stable than the [Rn]5f6d²7s² configuration, a result of its nearly degenerate 5f and 6d orbitals. Its unique electronic structure makes protactinium a critical stepping stone for understanding the electronic structure and bonding of the 5f elements.

This becomes increasingly evident as computational chemists continue to demonstrate the important interplay of the 5f, 6d and even the core 6p electrons, when describing the electronic structure and bonding behaviour of the actinides, suggesting that protactinium still has more contributions to make to chemistry. Although laboratory work with protactinium has been largely abandoned, its future contributions to chemistry may well come from where Meitner and Hahn first found it, *in silico*. □

RICHARD E. WILSON is in the Heavy Elements Group, Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439, USA. e-mail: rewilson@anl.gov

References

1. Crookes, W. *Proc. R. Soc. London* **66**, 409–423 (1900)
2. Fajans, K. & Göhring, O. *Naturwissenschaften* **14**, 339 (1913).
3. Hahn, O. & Meitner, L. *Phys. Z.* **19**, 208 (1918).
4. Fajans, K. & Morris, D. F. K. *Nature*. **244**, 137–138 (1973).
5. Kirby, H. W. *The Radiochemistry of Protactinium* (National Academy of Sciences – National Research Council, 1959).

