

Praseodymium unpaired

Adrian Dingle relates how one 'element' that fell off the periodic table was eventually replaced by two.

If there's a single thread that runs through the history of the lanthanoids, it's the manner in which they persistently resisted easy distinction from one another. The similarity in the chemistry of the 4f elements confounded nineteenth-century chemists for decades, and it took a new analytical technique to finally tease praseodymium from its hiding place.

The story of element 59 starts with Carl Gustav Mosander in 1841, and his discovery of what he thought was a new element in cerite. He named it didymium¹, Greek for 'twin element', because it so closely resembled lanthanum. As it turned out, his choice of name could hardly have been a better one, although for an entirely different reason.

In addition to didymium (which turned out to be fictional), by 1843, the actual elements cerium, lanthanum, erbium and terbium of the modern 4f series had all been discovered. There then came a pause in the discovery of the remainder of the lanthanoids. The traditional analytical method of the time — the extraordinarily tedious fractional precipitation and crystallization — had reached the end of its useful life as a technique able to, on its own, distinguish between elements so similar to each other: they looked the same and behaved in similar ways. Further discoveries would only come with a new impetus, which came from both practice and theory.

The advent, and subsequent perfection, of Bunsen and Kirchhoff's spectroscopy² throughout the early 1860s coincided with an increased understanding of patterns in the properties of elements, which culminated with Mendeleev's first periodic table of 1869. At the time didymium was sufficiently well established as an 'element' to appear on Mendeleev's table with the symbol Di — it is the only one from the original table that does not appear on the contemporary version.

The advances in spectroscopy enabled chemists to finally distinguish lanthanides from each other thanks to their unique



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spectral fingerprints. Taken together with the fractional precipitation and crystallization method and the development of the periodic system, they led to a new surge of rare-earth discovery between 1878 and 1886, yielding holmium, ytterbium, samarium, thulium, gadolinium, praseodymium, neodymium and dysprosium.

It is Carl Auer von Welsbach who is credited with the separation of didymium into neodymium and praseodymium. Long before his successful fractional crystallization of the double ammonium nitrates³, though, the potential for didymium to be something other than the singular substance Mosander proposed was recognized by several chemists. Jean-Charles Galissard de Marignac, Paul-Émile Lecoq de Boisbaudran, and Per Teodor Cleve were among the prominent names of the time to believe didymium was not pure. Two others went further and embarked on spectroscopic studies: Marc Delafontaine in 1878, and in 1882 Bohuslav Brauner, who like Auer von Welsbach was a student of Bunsen's in Heidelberg.

But despite apparently having written a note to the Austrian newspaper *Wiener Anzeiger*⁴, it seems that Brauner never formally published his work. In 1885, Auer von Welsbach announced to the Vienna Academy of Sciences his successful separation of didymium into two 'earths' (as oxides were then known): neodymia and praseodymia, from which the

elements neodymium (the new twin) and praseodymium (the green twin) would ultimately be isolated.

Despite the death of didymium as an element, the name lives on in the specialized glass used in the lenses of goggles worn by welders and glassblowers. The combination of praseodymium and neodymium allows the filtering out of both yellow light and infrared wavelengths, thus protecting the wearer's eyes from potentially harmful radiation without affecting their vision.

As is the same for all of the lanthanoids, the chemistry of praseodymium is dominated by the +3 oxidation state — but its electronic configuration of [Xe]4f⁶6s² makes it a good candidate for creating higher oxidation states, including that of +5. In 2016, a Pr(v) centre was reported⁵ in PrO₂⁺. One year later, NPr(v)O was described, together with NPr(IV)O⁻ — both featuring a Pr≡N triple bond and a Pr=O double bond⁶.

Another oxide of praseodymium has found use as a spacer layer in a potentially super-conducting material⁷. The compound Pr₄Ni₅O₈, whose structure can be described as three layers of a nickel oxide separated by two layers of praseodymium oxide, represents a chance for high-temperature superconductors to become a reality — and one where praseodymium is literally at the centre of things. □

Adrian Dingle

Author of 'The Elements: An Encyclopedic Tour of the Periodic Table', teaches at Westminster, Atlanta, GA, USA.

e-mail: adrian@adriandingleschemistrypages.com

Twitter: @adchempages

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