Seekers of the lost lanthanum

Lanthanum is the first lanthanide — or the last. Or it's not a lanthanide at all. In any case, Brett Thornton and Shawn Burdette are sure that it's an element that might or might not be in group three of the periodic table.

In the nineteenth century pantheon of Swedish chemists, Carl Gustaf Mosander was second only to his legendary mentor Jacob Berzelius. After completing his studies, Mosander worked as a chemistry lecturer under Berzelius at the Karolinska Institute in Stockholm. In 1826 he became convinced that Berzelius' cerium earth (oxide) was a mixture of several metal oxides. Unfortunately, his experiments depleted Berzelius' cerium oxide supplies, so he was forced to set aside his analysis for over 12 years.

Picking up in 1838, Mosander asked a student to produce several kilograms of KCeSO_4 from scrap cerite recovered during Mosander's efforts to organize the mineral collection at the Swedish Museum of Natural History. As before, Mosander sought to separate an unknown metal from his cerium compounds. Only after he had postulated that the unknown metal oxide might be more basic did he manage to extract it, in the form of chloride and nitrate salts. The new oxide was resistant to both oxidation and reduction.

By the end of 1838, Mosander knew he had found a new element in Berzelius' cerium oxide, but hesitated to tell his mentor in order to spare him any embarrassment from having failed to purify his element¹. Although initially reluctant to accept the new oxide, Berzelius eventually suggested the name 'lanthan', derived from the Greek word for hidden, because lanthanum was seemingly always concealed within cerium ores. Shortly after, Mosander reduced lanthanum chloride with potassium to the metal, and measured an atomic weight lower than that of cerium.

Despite having Berzelius' approval, Mosander was reluctant to publish because he now suspected that his lanthanum, like Berzelius' cerium, was also a mixture. Most troubling was a red-purple colour, which at times accompanied lanthanum in his experiments. By 1840, he had managed to separate Berzelius' original cerium oxide into yellow cerium oxide, white lanthanum oxide and a pinkish third substance, 'didymium oxide', which we now know as neodymium². In

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doing so, Mosander had initiated the process of deconvoluting the rare earth elements — which would prove a significant challenge for chemists in the second half of the nineteenth century.

February 2019 marks the 180th anniversary of Mosander's first use of the name lanthanum, yet the placement of this element on the periodic table remains unsettled. Element 57 lends its name to the lanthanides (or lanthanoids), but does it belong in this series with the 14 other elements? Linguistic purists would argue 'lanthanide' means lanthanum-like, which logically excludes lanthanum. Together with the other lanthanides and the lighter group three elements scandium and yttrium, element 57 is unambiguously designated as a rare earth — but is it a member of group 3 (ref. ³)?

With a $[\text{Xe}]6s^25d^1$ electron configuration, lanthanum could be the first *d*-block element in the 6th period, below yttrium, and between barium and cerium. However, lutetium has a similar configuration, $[\text{Xe}]6s^24f^{14}5d^1$ with a single *d*-electron, and could also plausibly sit below yttrium. Electron configurations provide only ambiguous answers in this part of the periodic table, and the correct placement of lanthanum remains controversial^{4,5}.

If lanthanum is a lanthanide, it is the third most abundant on Earth behind cerium and neodymium. In addition to relative abundance factors, other rare earth elements possess

valuable magnetic and luminescent properties, so element 57 is often the lanthanide of choice for non-magnetic applications. For example, modified bentonite clay, with lanthanum substituting for either sodium or calcium, has become popular with geoengineers for controlling lake eutrophication. The material traps phosphate in LaPO_4 hydrates, thereby reducing blue-green algae blooms⁶.

The rare earths have been long assumed to have no biological role. Recently, however, certain methanotrophic microbes were found that obtain energy by converting methane into methanol and subsequently formaldehyde, using a methanol dehydrogenase enzyme that features one of the chemically nearly identical light lanthanides (elements 57–60). It has even been suggested that the tiny abundance of lanthanum (35 pM) and the light lanthanides in the ocean could control rates of oceanic release of methane to the atmosphere — in extreme scenarios⁷. Presently, it appears the enzyme has no specific requirement for lanthanum — it simply utilizes whichever lanthanide is readily available, just like many anthropogenic users. □

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References

1. Tansjö, L. in *Episodes from the History of Rare Earth Elements* Vol. 15 (ed. Evans, C. H.) Ch. 3 (Springer Netherlands, 1996).
2. Thornton, B. F. & Burdette, S. C. *Nat. Chem.* **9**, 194 (2017).
3. Scerri, E. R. & Parsons, W. in *Mendeleev to Oganesson* (eds Scerri, E. & Restrepo, G.) Ch. 7 (Oxford Univ. Press, 2018).
4. Scerri, E. R. *Chem. Int.* **41**, 16–20 (2019).
5. Ball, P. The group 3 dilemma. *Chemistry World* <http://go.nature.com/2DDb1BV> (2017).
6. Spears, B. M. et al. *Water Res.* **97**, 111–121 (2016).
7. Shiller, A. M., Chan, E. W., Joung, D. J., Redmond, M. C. & Kessler, J. D. *Sci. Rep.* **7**, 10389 (2017).