

Recognizing rhenium

Rhenium and technetium not only share the same group in the periodic table, but also have some common history relating to how they were — or indeed weren't — discovered. Eric Scerri explains.

Rhenium lies two places below manganese in group 7 of the periodic table and its existence was predicted by Mendeleev in 1869. In fact, when his periodic system was first published, group 7 was rather unique because it contained only one element known at the time — manganese — and had at least two gaps below it. The first gap was eventually filled by element 43, technetium¹, with the second gap being filled by element 75, rhenium.

Rhenium was the first of these two new group-7-elements to be discovered — in 1925 — and accepted by the scientific community. In the course of an arduously long extraction, Walter Noddack, Ida Tacke (later Noddack) and Otto Berg obtained just one gram of rhenium after they processed approximately 660 kg of the ore molybdenite in Germany². Today, rhenium is isolated far more efficiently as the byproduct of the purification of molybdenum and copper.

The German discoverers called their element rhenium, after Rhenus, the Latin name for the river Rhine (pictured) that flows close to the place where they were working. They also claimed to have isolated the other element missing from group 7 — element 43 — that eventually became known as technetium, but this claim was hotly disputed by several other groups. As recently as the early years of the twenty-first century, however, research teams from Belgium and the USA re-analysed the X-ray evidence from the Noddacks and argued that they had in fact isolated element 43 (ref. 3). But these further claims have also been fiercely debated by many radiochemists and physicists and now have been laid to rest, at least for the time being⁴.

And while we are on the subject of Ida Noddack in particular, it was she who first proposed in 1934 that nuclear fission might be possible as the result of the break up of a nucleus into fragments. Her speculation was generally ignored and it had to wait until



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1939 when Hahn, Strassmann and Meitner really discovered fission. The main reason Noddack's proposal fell on deaf ears seems to be that her reputation had been badly damaged by the controversy surrounding the announcement of the discovery of element 43 back in 1925.

By a further odd twist of fate, the Japanese chemist Masataka Ogawa believed that he had isolated element 43 even earlier in 1908, and called it nipponium. His claim too was discredited at the time, but in 2004 it emerged that he had in fact isolated rhenium, rather than element 43, and well before the Noddacks and Berg⁵.

Until quite recently, no mineral containing just rhenium as the only type of cation (in combination with a non-metallic element) had ever been found. As reported in 1994, however, a team of Russian scientists discovered rhenium sulfide at the mouth of a volcano on a remote island off the east coast of Russia⁶. Based on its appearance in the field, the substance was initially thought to be molybdenite (the mineral from which Re was first extracted), but after analysis back in the laboratory it was found to contain no Mo and was shown to contain approximately 75% Re and 25% S by weight.

The chemistry of rhenium is rather diverse. Among other things, it shows the largest range of oxidation states of any

known element, namely $-1, 0, +1, +2$ and so on all the way up to $+7$ — the last of which is its most common oxidation state. It is also the metal that led to the discovery of the first metal-metal quadruple bond. In 1964, Albert Cotton and co-workers in the USA discovered the existence of such a Re-Re quadruple bond in the form of the rhenium ion, $[\text{Re}_2\text{Cl}_8]^{2-}$ (ref. 7).

A large quantity of rhenium is made into super-alloys to be used for parts in jet engines. Typically for a transition metal, rhenium also acts a catalyst for many reactions. For example, a combination of rhenium and platinum comprise the catalyst of choice in the very important process of making lead-free and high-octane petrol. Rhenium catalysts are especially resistant to chemical attack from nitrogen, phosphorus and sulfur, which makes them useful in hydrogenation reactions in various industrial processes.

More recently a rather simple compound of the element, rhenium diboride, has attracted some attention because it is one of the hardest of all known substances. Unlike other super-hard materials, such as diamond, it does not have to be manufactured under high pressure⁸.

So, although rhenium was the last stable element to be discovered, it is certainly not the least when it comes to its properties and applications. □

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