A flash of magnesium

Magnesium is commonly found in rocks and sea water as well as living organisms. **Paul Knochel** relates how this element has also sparked a great deal of interest among chemists.

ne of the most abundant elements on Earth (the sixth in order of weight abundance), magnesium occurs naturally in crustal rocks, mainly in the form of insoluble carbonates, sulfates and silicates. Its name derives from the Magnesia district of Thessaly, where the soft white mineral steatite talc — a hydrated magnesium silicate - was found in ancient Greece. Magnesium was first isolated in pure form in 1808 by Sir Humphry Davy, who used an electrolytic method that had been previously developed by the Swedish chemists Jöns Jakob Berzelius and Magnus Martin Pontin to isolate sodium, barium, potassium, strontium and calcium, between 1807–1808. Elemental magnesium is a fairly strong, silvery white, light-weight metal. It tarnishes slightly in air, and is thus protected against further oxidation by a thin impermeable layer of oxide.

Magnesium reacts exothermically with most acids, and with water at room temperature to give magnesium hydroxide and hydrogen. It is a very flammable metal, able to burn in both nitrogen and carbon dioxide, and famously creates a brilliant white light on burning in air. This resulted in its use as a source of illumination in early photography. It is still employed in flash bulbs, and in fireworks to produce brighter sparks. Its very low density (1.74 g cm⁻³) makes it an attractive component for alloys - for example, the best magnesium alloy weighs only a quarter as much as steel — and because its metallurgy is simpler than that of other metals, it is also popular in the construction and the aircraft industries, and for optical and electronic devices.

In China, the large-scale production of magnesium metal is achieved by 'silicothermal reduction' of dolomite (MgO·CaO), but the process used in the USA is the electrolysis of hydrated MgCl₂, abundant in sea water. Magnesium

Si



ions are also widely present in the basic nucleic acid chemistry of life. It is vital to the cells or enzymes of living organisms for synthesizing adenosine triphosphate, DNA and RNA, as well as to green plants — chlorophylls, which are responsible for photosynthesis, are magnesium-centred porphyrins. This also means that it is a common additive in fertilizers, and is used in medicine. For example 'milk of magnesia,' a white aqueous solution of magnesium hydroxide, is commonly used as a laxative and an antacid.

Magnesium also has a central position in organic and organometallic chemistry. Although organomagnesium compounds have been known since the last decades of the nineteenth century, their insolubility initially precluded general applications. In 1900, the young French PhD student Victor Grignard (1871-1935) had the idea to prepare these elusive reagents in solution; this was a new concept. The reaction of various organic halides with magnesium ribbons (often called turnings) in ether led to stable solutions of organomagnesium reagents that bear Grignard's name. In fact, his first publication in 1900 was so successful that many organic chemists around the

world immediately applied his procedure — Grignard subsequently had problems finding enough examples of applications of his reagents that were still unpublished to complete his PhD thesis. This key discovery, for which he was awarded a Nobel Prize in 1912, revolutionized organic chemistry.

Organometallic compounds bearing a carbon-magnesium bond are now among the most popular nucleophilic reagents. More than 100,000 publications dealing with the reactivity of these intermediates have now appeared in the chemical literature. Why such popularity? The reactivity of a carbon-magnesium bond can be readily tuned by appropriate transmetallations with many metallic salts, increasing its use in synthesis dramatically.

Furthermore, the carbon-magnesium bond possesses an intrinsic reactivity that is compatible with the presence of many important organic functional groups in the same molecule. Now, methods for preparing polyfunctional aryl and heteroaryl magnesium compounds bearing an ester, a nitrile or an aromatic ketone are also available, which further increases the scope of Grignard reagents in organic synthesis. Moreover, the low price and low toxicity of magnesium makes these compounds suitable intermediates for large-scale applications in industry. Important drugs such as tamoxifen citrate, a non-steroidal oestrogen antagonist used in the treatment of advanced breast cancer, are prepared industrially using Grignard reagents.

Although magnesium captured the attention of chemists more than a century ago in the form of Grignard reagents, it will certainly continue to have a key role in many research fields, including materials science, biochemistry and synthetic organic chemistry.

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