Magically magnetic gadolinium

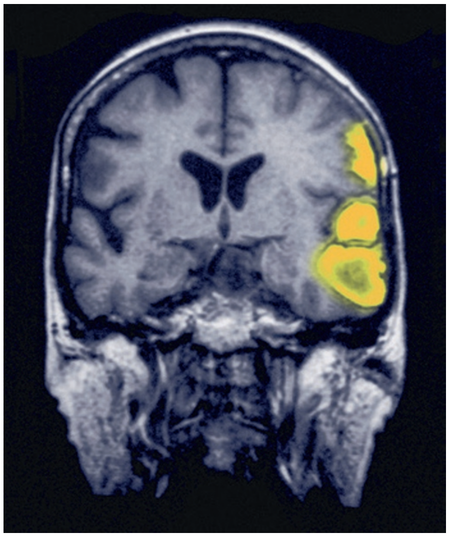
Pekka Pyykkö discusses the history and characteristics of gadolinium.

The lanthanides run from lanthanum to lutetium across the periodic table, and together with the chemically similar yttrium and scandium they form a family dubbed the rare-earth elements. An unspecified mixture of their oxides was isolated in 1794[1–3] by Johan Gadolin (1760–1852) from a mineral that had been discovered in Ytterby, near Stockholm, Sweden by Carl Axel Arrhenius, and described in 1788 by Geijer[4]. Gadolin cautiously stated that this oxide, or 'earth', could contain a new element. This would be a pity he said[1–3], because the elements were already "becoming far too numerous" — an interesting twist for an element that would be named after him. Gadolin's analysis was confirmed in 1797 by A. G. Ekeberg[5], and the original mineral was soon named gadolinite.

The oxide of gadolinium (symbol Gd) was discovered by repeated recrystallization by Marignac[6], who also determined its atomic weight, but it was Boisbaudran (with Marignac's approval) who suggested the name in 1880[7]. Although it is not known whether he was thinking of the mineral or the man, or both, gadolinium remains the only element with a name derived from Hebrew. Its root 'gadol' (pictured), meaning 'great', was chosen by Gadolin's grandfather as his surname and comes from a translation of Maunula, the name of the Finnish farm he lived on.

גדל

The chemical behaviour of most lanthanides is fairly similar, which explains why, in all, it took more than a century to split them into the individual elements. Despite their chemical similarities, their optical and magnetic properties are distinct. The magnetic properties of gadolinium in particular are unique, and underscore many of its applications. Element 64 is located half-way through the lanthanide 4*f* series and the trivalent Gd^{3+} ion can organize its seven 4*f* electrons in a half-filled shell with all spins parallel — a magic number, as it were. This gives Gd(III) the largest possible total spin $S = 7/2$, and a correspondingly very large spin magnetic moment. This characteristic can be used to improve permanent magnets. The 4*f* shell of lanthanides has electron binding energies in the valence range, making it possible to chemically vary the 4*f* occupation, but the compact 4*f* radial size is typical of the outermost core electrons and prevents most 4*f* electrons from directly participating in bond formation.



SCOTT CAMAZINE / ALAMY

Despite their name, the rare earths are not particularly rare; €111 per 10 g of metallic gadolinium (99.9% purity) is the going rate, though in metallurgy a much cheaper, unseparated *mischmetal* is normally used. An important current use is in medicine, as a 'contrast agent' in magnetic resonance imaging (MRI). The MRI signal comes from certain nuclear spins, such as the ubiquitous protons. That nuclear spin system, however, is heated by the radiofrequency field used for the magnetic resonance. This heating typically weakens the MRI signal. The large electronic magnetic moment of Gd(III) helps to couple the nuclear spin system to the 'lattice' and to keep it cool. This is called nuclear spin–lattice relaxation. To avoid health hazards, because Gd^{3+} is somewhat toxic, the gadolinium ion is surrounded by chelating ligands that prevent it from entering tissues. New ligands are under development to improve safety.

Both gadolinium and some of its alloys or salts play a prominent role in magnetic cooling. In this refrigeration process, a magnetic substance becomes hotter when placed under certain external magnetic field, owing to the orientation of its magnetic dipoles. Inversely when the field is removed, and the substance thermally isolated, it cools down. By varying the magnetic field, and the sample's insulation, one shuffles entropy between the material's electronic spin system and other degrees of freedom.

The conspicuous luminescence colours of certain other lanthanides are used in fluorescent lamps and in displays — both the old-style picture tubes, and the current flat screens. The compounds of element 64 itself are colourless, but they can be used to absorb UV radiation and to transfer its energy to other lanthanides that have emissions in the desired optical range. Moreover, the ^{155}Gd and ^{157}Gd nuclei have unusually large neutron absorption cross sections, which can be used in nuclear technology for reactor control rods.

Gadolin may have wished for fewer elements to exist, but gadolinium offers a rich history spanning over two centuries, intriguing characteristics, and a variety of practical applications. ❐

PEKKA PYYKKÖ is professor emeritus in the Department of Chemistry, University of Helsinki, POB 55, 00014 Helsinki, Finland. His former position as 'the parallel chair of chemistry' was split from Gadolin's chair of chemistry in 1908.
e-mail: pekka.pyykko@helsinki.fi

References

1. Gadolin, J. *Kungl. Svenska Vetenskapsak. Handl.* **15,** 137–155 (1794).
2. Gadolin, J. *Crells Ann.* 313–329 (1796).
3. Pyykkö, P. & Orama, O. in *Episodes from the History of the Rare Earth Elements* (ed. Evans, C. H.) 1–12 (Kluwer, 1996).
4. Geijer, B. R. *Crells Ann.* 229–230 (1788).
5. Ekeberg, A. G. *Kungl. Svenska Vetenskapsak. Handl.* **18,** 156–164 (1797).
6. de Marignac J.-C. G. *Arch. Sci. (Genève)* **3,** 413–418 (1880).
7. Lecoq de Boisbaudran, P.-E. *C. R. Acad. Sci.* **102,** 902 (1886).

m Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl