

Al led to considerable confusion concerning the valency and atomic weight of Be (2×4.7 or 3×4.7); this was not resolved until Mendeleev 70 y later stated that there was no room for a trivalent element of atomic weight 14 near nitrogen in his periodic table, but that a divalent element of atomic weight 9 would fit snugly between Li and B. Beryllium metal was first prepared by F. Wöhler in 1828 (the year he carried out his celebrated synthesis of urea from NH_4CNO); he suggested the name by allusion to the mineral (Latin *beryllus* from Greek $\beta\eta\rho\upsilon\lambda\lambda\omicron\varsigma$). The metal was independently isolated in the same year by A.-B. Bussy using the same method — reduction of BeCl_2 with metallic K. The first electrolytic preparation was by P. Lebeau in 1898 and the first commercial process (electrolysis of a fused mixture of BeF_2 and BaF_2) was devised by A. Stock and H. Goldschmidt in 1932. The close parallel with the development of Li technology (pp. 68–70) is notable.

Compounds of Mg and Ca, like those of their Group 1 neighbours Na and K, have been known from ancient times though nothing was known of their chemical nature until the seventeenth century. Magnesian stone (Greek Μαγνησία λιθος) was the name given to the soft white mineral steatite (otherwise called soapstone or talc) which was found in the Magnesia district of Thessaly, whereas calcium derives from the Latin *calx*, *calcis* — lime. The Romans used a mortar prepared from sand and lime (obtained by heating limestone, CaCO_3) because these lime mortars withstood the moist climate of Italy better than the Egyptian mortars based on partly dehydrated gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); these had been used, for example, in the Great Pyramid of Gizeh, and all the plaster in Tutankhamun's tomb was based on gypsum. The names of the elements themselves were coined by H. Davy in 1808 when he isolated Mg and Ca, along with Sr and Ba by an electrolytic method following work by J. J. Berzelius and M. M. Pontin: the moist earth (oxide) was mixed with one-third its weight of HgO on a Pt plate which served as anode; the cathode was a Pt wire dipping into a pool of Hg and electrolysis

gave an amalgam from which the desired metal could be isolated by distilling off the Hg.

A mineral found in a lead mine near Strontian, Scotland, in 1787 was shown to be a compound of a new element by A. Crawford in 1790. This was confirmed by T. C. Hope the following year and he clearly distinguished the compounds of Ba, Sr and Ca, using amongst other things their characteristic flame colorations: Ba yellow-green, Sr bright red, Ca orange-red. Barium-containing minerals had been known since the seventeenth century but the complex process of unravelling the relation between them was not accomplished until the independent work of C. W. Scheele and J. G. Gahn between 1774 and 1779: heavy spar was found to be BaSO_4 and called barite or barytes (Greek $\beta\alpha\rho\acute{\upsilon}\varsigma$, heavy), whence Scheele's new base baryta (BaO) from which Davy isolated barium in 1808.

Radium, the last element in the group, was isolated in trace amounts as the chloride by P. and M. Curie in 1898 after their historic processing of tonnes of pitchblende. It was named by Mme Curie in allusion to its radioactivity, a word also coined by her (Latin *radius*, a ray); the element itself was isolated electrolytically via an amalgam by M. Curie and A. Debierne in 1910 and its compounds give a carmine-red flame test.

5.2 The Elements

5.2.1 Terrestrial abundance and distribution

Beryllium, like its neighbours Li and B, is relatively unabundant in the earth's crust; it occurs to the extent of about 2 ppm and is thus similar to Sn (2.1 ppm), Eu (2.1 ppm) and As (1.8 ppm). However, its occurrence as surface deposits of beryl in pegmatite rocks (which are the last portions of granite domes to crystallize) makes it readily accessible. Crystals as large as 1 m on edge and weighing up to 60 tonnes have been reported. World reserves in commercial deposits are about 4 million tonnes of contained Be and mined production in 1985–86 was USA

223, USSR 76 and Brazil 37 tonnes of contained Be, which together accounted for 98% of world production. The cost of Be metal was \$690/kg in 1987. By contrast, world supplies of magnesium are virtually limitless: it occurs to the extent of 0.13% in sea water, and electrolytic extraction at the present annual rate, if continued for a million years, would only reduce this to 0.12%.

Magnesium, like its heavier congeners Ca, Sr and Ba, occurs in crustal rocks mainly as the insoluble carbonates and sulfates, and (less accessibly) as silicates. Estimates of its total abundance depend sensitively on the geochemical model used, particularly on the relative weightings given to the various igneous and sedimentary rock types, and values ranging from 20 000 to 133 000 ppm are current.⁽³⁾ Perhaps the most acceptable value is 27 640 ppm (2.76%), which places Mg sixth in order of abundance by weight immediately following Ca (4.66%) and preceding Na (2.27%) and K (1.84%). Large land masses such as the Dolomites in Italy consist predominantly of the magnesian limestone mineral dolomite [$\text{MgCa}(\text{CO}_3)_2$], and there are substantial deposits of magnesite (MgCO_3), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and other evaporites such as carnallite ($\text{K}_2\text{MgCl}_4 \cdot 6\text{H}_2\text{O}$) and langbeinite [$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$]. Silicates are represented by the common basaltic mineral olivine [$(\text{Mg,Fe})_2\text{SiO}_4$] and by soapstone (talc) [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], asbestos (chrysotile) [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$] and micas. Spinel (MgAl_2O_4) is a metamorphic mineral and gemstone. It should also be remembered that the green leaves of plants, though not a commercial source of Mg, contain chlorophylls which are the Mg-porphine complexes primarily involved in photosynthesis.

Calcium, as noted above, is the fifth most abundant element in the earth's crust and hence the third most abundant metal after Al and Fe. Vast sedimentary deposits of CaCO_3 , which represent the fossilized remains of earlier marine life, occur over large parts of the earth's surface. The deposits are of two main

types — rhombohedral calcite, which is the more common, and orthorhombic aragonite, which sometimes forms in more temperate seas. Representative minerals of the first type are limestone itself, dolomite, marble, chalk and iceland spar. Extensive beds of the aragonite form of CaCO_3 make up the Bahamas, the Florida Keys and the Red Sea basin. Corals, sea shells and pearls are also mainly CaCO_3 . Other important minerals are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), fluorite (CaF_2 ; also blue john and fluorspar) and apatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$].

Strontium (384 ppm) and barium (390 ppm) are respectively the fifteenth and fourteenth elements in order of abundance, being bracketed by S (340 ppm) and F (544 ppm). The most important mineral of Sr is celestite (SrSO_4), and strontianite (SrCO_3) is also mined. The largest producers are Mexico, Spain, Turkey and the UK, and the world production of these two minerals in 1985 was 10^5 tonnes. The main uses of Sr compounds, especially SrCO_3 , are in the manufacture of special glasses for colour television and computer monitors (53%), for pyrotechnic displays (14%) and magnetic materials (11%). Strontium carbonate and sulfate are critical raw materials for the USA which is totally dependent on imports for supplies. The sulfate (barite) is also the most important mineral of Ba: it is mined commercially in over 40 countries throughout the world. Production in 1985 was 6.0 million tonnes, of which 44% was mined in the USA. The major use of BaSO_4 (92%) is as a heavy mud slurry in well drilling; production of Ba chemicals accounts for only 7%.

Radium occurs only in association with uranium (Chapter 31); the observed ratio $^{226}\text{Ra}/\text{U}$ is ~ 1 mg per 3 kg, leading to a terrestrial abundance for Ra of $\sim 10^{-6}$ ppm. As uranium ores normally contain only a few hundred ppm of U, it follows that about 10 tonnes of ore must be processed for 1 mg Ra. The total amount of Ra available worldwide is of the order of a few kilograms, but its use in cancer therapy has been superseded by the use of other isotopes, and the

³ K. K. TUREKIAN, Elements, geochemical distribution of, *McGraw Hill Encyclopedia of Science and Technology*, Vol. 4, pp. 627–30, 1977.

annual production of separated Ra compounds is probably now only about 100 g. Chief suppliers are Belgium, Canada, Czechoslovakia, the UK, and the former Soviet Union. ^{226}Ra decays by α -emission with a half-life of 1600 y, although 3 in every 10^{11} decays occur by ^{14}C emission ($^{226}_{88}\text{Ra} \longrightarrow ^{212}_{82}\text{Pb} + ^{14}_6\text{C}$). This exceedingly rare form of radioactivity was discovered in 1984 in the rare naturally occurring radium isotope ^{223}Ra where about 1 in 10^9 of the atoms decays by ^{14}C rather than α -emission.⁽⁴⁾

5.2.2 Production and uses of the metals⁽⁵⁾

Beryllium is extracted from beryl by roasting the mineral with Na_2SiF_6 at 700–750°C, leaching the soluble fluoride with water and then precipitating $\text{Be}(\text{OH})_2$ at about pH 12. The metal is usually prepared by reduction of BeF_2 (p. 116) with Mg at about 1300°C or by electrolysis of fused mixtures of BeCl_2 and alkali metal chlorides. It is one of the lightest metals known and has one of the highest mps of the light metals. Its modulus of elasticity is one-third greater than that of steel. The largest use of Be is in high-strength alloys of Cu and Ni (see Panel below).

Magnesium is produced on a large scale (400 000 tonnes in 1985) either by electrolysis or

silicothermal reduction. The major producers are the USA (43%), the former Soviet Union (26%), and Norway (17%). The electrolytic process uses either fused anhydrous MgCl_2 at 750°C or partly hydrated MgCl_2 from sea water at a slightly lower temperature. The silicothermal process uses calcined dolomite and ferrosilicon alloy under reduced pressure at 1150°C:



Magnesium is industry's lightest constructional metal, having a density less than two-thirds that of Al (see Panel on the next page). The price of the metal (99.8% purity) was \$3.4/kg in 1994.

The other alkaline earth metals Ca, Sr and Ba are produced on a much smaller scale than Mg. Calcium is produced by electrolysis of fused CaCl_2 (obtained either as a byproduct of the Solvay process (p. 71) or by the action of HCl or CaCO_3). It is less reactive than Sr or Ba, forming a protective oxide-nitride coating in air which enables it to be machined in a lathe or handled by other standard metallurgical techniques. Calcium metal is used mainly as an alloying agent to strengthen Al bearings, to control graphitic C in cast-iron and to remove Bi from Pb. Chemically it is used as a scavenger in the steel industry (O, S and P), as a getter for oxygen and nitrogen, to remove N_2 from argon and as a reducing agent in the production of other metals such as Cr, Zr, Th and U. Calcium also reacts directly with H_2 to give CaH_2 , which is a useful source of H_2 . World production of

⁴ H. J. ROSE and G. A. JONES, *Nature* **307**, 245–7 (1984).

⁵ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, New York, 1989, pp. 231–46.

Uses of Beryllium Metal and Alloys

The ability of Be to age-harden Cu was discovered by M. G. Corson in 1926 and it is now known that ~2% of Be increases the strength of Cu sixfold. In addition, the alloys (which also usually contain 0.25% Co) have good electrical conductivity, high strength, unusual wear resistance, and resistance to anelastic behaviour (hysteresis, damping, etc.): they are non-magnetic and corrosion resistant, and find numerous applications in critical moving parts of aero-engines, key components in precision instruments, control relays and electronics. They are also non-sparking and are thus of great use for hand tools in the petroleum industry. A nickel alloy containing 2% Be is used for high-temperature springs, clips, bellows and electrical connections. Another major use for Be is in nuclear reactors since it is one of the most effective neutron moderators and reflectors known. A small, but important, use of Be is as a window material in X-ray tubes: it transmits X-rays 17 times better than Al and 8 times better than Lindemann glass. A mixture of compounds of radium and beryllium has long been used as a convenient laboratory source of neutrons and, indeed, led to the discovery of the neutron by J. Chadwick in 1932: $^9\text{Be}(\alpha, n)^{12}\text{C}$.

Magnesium Metal and Alloys

The principal advantage of Mg as a structural metal is its low density (1.7 g cm^{-3} compared with 2.70 for Al and 7.80 for steel). For equal strength, the best Mg alloy weighs only a quarter as much as steel, and the best Al alloy weighs about one-third as much as steel. In addition, Mg has excellent machinability and it can be cast or fabricated by any of the standard metallurgical methods (rolling, extruding, drawing, forging, welding, brazing or riveting). Its major use therefore is as a light-weight construction metal, not only in aircraft but also in luggage, photographic and optical equipment, etc. It is also used for cathodic protection of other metals from corrosion, as an oxygen scavenger, and as a reducing agent in the production of Be, Ti, Zr, Hf and U. World production approaches 400 000 tonnes pa.

Magnesium alloys typically contain >90% Mg together with 2–9% Al, 1–3% Zn and 0.2–1% Mn. Greatly improved retention of strength at high temperature (up to 450°C) is achieved by alloying with rare-earth metals (e.g. Pr/Nd) or Th. These alloys can be used for automobile engine casings and for aeroplane fuselages and landing wheels. Other uses are in light-weight tread-plates, dock-boards, loading platforms, gravity conveyors and shovels.

Up to 5% Mg is added to most commercial Al to improve its mechanical properties, weldability and resistance to corrosion.

For further details see *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., 1995, Vol. 15, pp. 622–74.

the metal is about 2500 tonnes pa of which >50% was in the USA (price \$5.00–8.00/kg in 1991).

Metallic Sr and Ba are best prepared by high-temperature reduction of their oxides with Al in an evacuated retort or by small-scale electrolysis of fused chloride baths. They have limited use as getters, and a Ni–Ba alloy is used for spark-plug wire because of its high emissivity. Annual production of Ba metal is about 20–30 tonnes worldwide and the 1991 price about \$80–140/kg depending on quality.

5.2.3 Properties of the elements

Table 5.1 lists some of the atomic properties of the Group 2 elements. Comparison with the data for Group 1 elements (p. 75) shows the substantial increase in the ionization energies; this is related to their smaller size and higher nuclear charge, and is particularly notable for Be. Indeed, the “ionic radius” of Be is purely a notional figure since no compounds are known in which uncoordinated Be has a 2+ charge. In aqueous solutions the reduction potential of

Table 5.1 Atomic properties of the alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Number of naturally occurring isotopes	1	3	6	4	7	4 ^a
Atomic weight	9.012 182(3)	24.3050(6)	40.078(4)	87.62(1)	137.327(7)	(226.0254) ^b
Electronic configuration	[He]2s ²	[Ne]3s ²	[Ar]4s ²	[Kr]5s ²	[Xe]6s ²	[Rn]7s ²
Ionization energies/ kJ mol ⁻¹	899.4 1757.1	737.7 1450.7	589.8 1145.4	549.5 1064.2	502.9 965.2	509.3 979.0
Metal radius/pm	112	160	197	215	222	—
Ionic radius (6 coord)/pm	(27) ^c	72	100	118	135	148
E°/V for $M^{2+}(\text{aq}) + 2e^- \rightarrow M(\text{s})$	-1.97	-2.356	-2.84	-2.89	-2.92	-2.916

(^a) All isotopes are radioactive: longest $t_{1/2}$ 1600 y for Ra(226).

(^b) Value refers to isotope with longest half-life.

(^c) Four-coordinate.

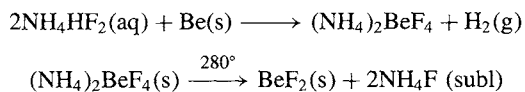
Be is much less than that of its congeners, again indicating its lower electropositivity. By contrast, Ca, Sr, Ba and Ra have reduction potentials which are almost identical with those of the heavier alkali metals; Mg occupies an intermediate position.

Be and Mg are silvery white metals whereas Ca, Sr and Ba are pale yellow (as are the divalent rare earth metals Eu and Yb) although the colour is less intense than for Cs (p. 74). All the alkaline earth metals are lustrous and relatively soft, and their physical properties (Table 5.2), when compared with those of Group 1 metals, show that they have a substantially higher mp, bp, density and enthalpies of fusion and vaporization. This can be understood in terms of the size factor mentioned in the preceding paragraph and the fact that 2 valency electrons per atom are now available for bonding. Again, Be is notable in melting more than 1100° above Li and being nearly 3.5 times as dense; its enthalpy of fusion is more than 5 times that of Li. Beryllium resembles Al in being stable in moist air due to the formation of a protective oxide layer, and highly polished specimens retain their shine indefinitely. Magnesium also resists oxidation but the heavier metals tarnish readily. Beryllium, like Mg and the high-temperature form of Ca (>450°C), crystallizes in the hcp arrangement, and this confers a marked anisotropy on its properties; Sr is fcc, Ba and Ra are bcc like the alkali metals.

5.2.4 Chemical reactivity and trends

Beryllium metal is relatively unreactive at room temperature, particularly in its massive form. It does not react with water or steam even

at red heat and does not oxidize in air below 600°C, though powdered Be burns brilliantly on ignition to give BeO and Be₃N₂. The halogens (X₂) react above about 600°C to give BeX₂ but the chalcogens (S, Se, Te) require even higher temperatures to form BeS, etc. Ammonia reacts above 1200°C to give Be₃N₂ and carbon forms Be₂C at 1700°C. In contrast with the other Group 2 metals, Be does not react directly with hydrogen, and BeH₂ must be prepared indirectly (p. 115). Cold, concentrated HNO₃ passivates Be but the metal dissolves readily in dilute aqueous acids (HCl, H₂SO₄, HNO₃) with evolution of hydrogen. Beryllium is sharply distinguished from the other alkaline earth metals in reacting with aqueous alkalis (NaOH, KOH) with evolution of hydrogen. It also dissolves rapidly in aqueous NH₄HF₂ (as does Be(OH)₂), a reaction of some technological importance in the preparation of anhydrous BeF₂ and purified Be:



Magnesium is more electropositive than the amphoteric Be and reacts more readily with most of the non-metals. It ignites with the halogens, particularly when they are moist, to give MgX₂, and burns with dazzling brilliance in air to give MgO and Mg₃N₂. It also reacts directly with the other elements in Groups 15 and 16 (and Group 14) when heated and even forms MgH₂ with hydrogen at 570° and 200 atm. Steam produces MgO (or Mg(OH)₂) plus H₂, and ammonia reacts at elevated temperature to give Mg₃N₂. Methanol reacts at 200° to give Mg(OMe)₂ and ethanol (when activated

Table 5.2 Physical properties of the alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
MP/°C	1289	650	842	769	729	700
BP/°C	2472	1090	1494	1382	1805	(1700)
Density (20°C)/g cm ⁻³	1.848	1.738	1.55	2.63	3.59	5.5
ΔH _{fus} /kJ mol ⁻¹	15	8.9	8.6	8.2	7.8	(8.5)
ΔH _{vap} /kJ mol ⁻¹	309	127.4	155	158	136	(113)
ΔH _f (monatomic gas)/kJ mol ⁻¹	324	146	178	164	178	—
Electrical resistivity (25°C)/μohm cm	3.70	4.48	3.42	13.4	34.0	(100)