

Critical-metal mineralogy and ore genesis: contributions from the European Mineralogical Conference held in Rimini, September 2016

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CRITICAL raw materials (CRM), often also known collectively as critical metals and minerals, are those that are deemed essential to industry and economic development, but are at risk of supply interruption. The markets and industry of the European Union are dependent on the import of most of the 27 critical raw materials (European Commission, 2017). Although such contrasting materials as baryte, borates, coking coal, natural rubber, fluorspar, graphite, helium and phosphorous/phosphate rock are included in these 27 most critical raw materials, the remaining majority are metals and metalloids, including antimony (Sb), beryllium (Be), bismuth (Bi), cobalt (Co), gallium (Ga), germanium (Ge), hafnium (Hf), indium (In), magnesium (Mg), niobium (Nb), scandium (Sc), tantalum (Ta), tungsten (W), vanadium (V), platinum-group metals (PGM) and the rare-earth elements (REE), the latter which are further subdivided into heavy (HREE) and light (LREE). Of these, the metals deemed to have the highest supply-risk classifications are the REE, Sb, Bi, Mg and W.

In addition to their wide applications throughout high-technology, industry, research and military applications, CRM are now used extensively in the development of green technologies essential to a low-carbon energy future (e.g. high-performance

neodymium magnets in wind turbines), in innovative technologies such as electric vehicles (cobalt, graphite and lithium as components in batteries), energy-saving lighting technologies (gallium in LEDs), and in technologies that have become everyday items such as smartphones, tablets and HD televisions (e.g. indium in flat screens and REE compounds in colour screens). The quantity of CRM in an individual item is often small, but with a large number of items in production, the total demand and consumption is significant. Where CRM are wholly supplied from one region, country or even a single mine, there is a significant potential for problems with supply control, interruption or even cessation due to political or economic pressures. In addition, demands for the sustainable production of raw materials such as cobalt, the REE, tellurium and lithium are predicted to grow beyond current supply rates (Gunn, 2014; Olivetti *et al.*, 2017; Vidal *et al.*, 2017; Rabe *et al.*, 2017; Roskill, 2017).

These concerns have been addressed by the development of numerous industrial and academic collaborations (many of which are reflected in papers in this special issue of *Mineralogical Magazine*) and these offer a more secure future through innovative exploration methodologies, a deeper understanding of ore genesis or new knowledge about specific deposit types and the potential for extraction of the ore minerals they contain.

The first European Mineralogical Conference (EMC), held in Frankfurt in 2012, was well

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attended and very successful. Participants were struck by the enthusiasm and ‘buzz’ of the meeting so that we saw the proposal for EMC 2016 in Rimini as an opportunity to discuss topics relevant to the future supply of CRM for Europe. We convened Session 23: ‘The future of critical metals: mineralogy, metallogenesis and geometallurgy’ and Session 20: ‘High-tech metal minerals in Europe’ and contributed to Session 22: ‘Platinum-group minerals and accessory minerals: development in their characterisation’. These sessions were well attended and attracted >70 oral presentations and posters. There was a deliberate policy to encourage younger workers to contribute. The success of these sessions led to a proposal that this issue of *Mineralogical Magazine* should be devoted to papers from the meeting and the convenors promptly morphed into guest editors. The next EMC will be held in Kraków in 2020.

This special issue begins with ‘Indium and selenium distribution in the Neves-Corvo deposit, Iberian Pyrite Belt, Portugal’ (Carvalho *et al.*, 2018) which was the keynote lecture for Session 23. Indium and Se are most abundant in the Cu-rich ores at Neves-Corvo which is an enigma because In is more abundant in sphalerite than in chalcopyrite. Indium minerals such as roquesite (CuInS_2) are rare, and Se occurs preferentially in galena. The ore-forming processes and later metamorphism explain the distribution. Overall there is a significant In and Se resource which may be available for future exploitation. The study of In continues with ‘Deposition conditions for the indium-bearing polymetallic quartz veins at Sarvlaxviken, south-eastern Finland’ (Broman *et al.*, 2018). Fluid inclusion studies of the In-rich (up to 1500 ppm) polymetallic quartz veins show that the metals were derived from an adjacent F-rich granite and associated dykes. Metal deposition occurred at 100 to 500°C, regardless of vein generation with a chaotic zonation pattern with respect to where in the vein system each metal precipitated.

Emphasizing that CRM are of global interest, the following two papers provide accounts of key ore deposits in South America and Africa. In ‘Enrichment in critical metals (In-Ge) and Te-Se in epithermal deposits of the “La Carolina” District, San Luis (Argentina)’ (Gallard-Esquivel *et al.*, 2018), epithermal Au-Ag deposits are shown to contain In-rich sphalerite (up to 5490 ppm In) and the Cu, Ag, Ga, Ge content of the sphalerite suggests a coupled substitution. The paper by Mondillo *et al.* (2018) looks at ‘Critical elements in non-sulfide Zn deposits: A reanalysis of the Kabwe

Zn-Pb ores (central Zambia)’ where there are both mixed sulfide and non-sulfide ore bodies. The paper focuses on the non-sulfide mineralization in which a few ppm of Ga occurs in willemite, sphalerite, goethite and hematite, Ge is found mainly in willemite and In occurs in goethite and hematite. This partitioning is probably due to the initial Ga, In and Ge abundances, their different solubilities and their contrasting affinities with the host minerals.

The next sequence of papers addresses deposits containing REE in Scandinavia, Hungary and Australia starting with ‘The hydrothermal alteration of carbonatite in the Fen Complex, Norway: mineralogy, geochemistry and implications for rare-earth element resource formation’ (Marien *et al.*, 2018). In the Fen carbonatite Complex up to 1.6 wt.% total REE occurs in hydrothermally altered, so-called rødbergite (hematite-rich carbonatite) due to the breakdown of primary REE fluorocarbonates and apatite in carbonatite, leading to precipitation of monazite-(Ce) with a ten-fold increase in REE concentration. The highest HREE and Th concentrations occur in the rødbergite whilst the highest LREE concentrations are in cross-cutting rødbergite-rich veins indicating partitioning caused by oxidation of the hydrothermal fluid. Another famous group of REE deposits in Scandinavia is described by: ‘Gadolinite-(Nd), a new member of the gadolinite supergroup from Fe-REE deposits of Bastnäs-type, Sweden’ (Škoda *et al.*, 2018). New studies of REE-rich magnetite skarns from the Bergslagen ore province, south central Sweden, have resulted in the discovery of a new Nd-dominant species in the gadolinite group of minerals, gadolinite-(Nd) with an ideal formula of $\text{Nd}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$. It is monoclinic, $P21/c$, with $a = 4.8216(3) \text{ \AA}$, $b = 7.6985(4) \text{ \AA}$, $c = 10.1362(6) \text{ \AA}$, with $\beta = 90.234(4)^\circ$, $V = 376.24(6) \text{ \AA}^3$ and $Z = 2$. It is biaxial and weakly pleochroic in shades of green and may originally have been mistaken for törnebohmit-(Ce). The type material is from the Malmkärna mine, but it also occurs in the Johanna and Nya Bastnäs mines and could represent a significant sink for Nd.

Molnár *et al.* (2018) examine the ‘Geochemical characteristics of Triassic and Cretaceous phosphorite horizons from the Transdanubian Mountain Range (western Hungary): genetic implications’. Uranium and REE enrichment in Triassic phosphorite horizons is hosted by carbonate-bearing fluorapatite containing 137–612 ppm U and 113–261 ppm total REE+Y. In Cretaceous REE-enriched nodular phosphorite, carbonate-bearing

fluorapatite is again the main host for the *REE* (748–2953 ppm total *REE*+Y). The Triassic phosphorite was formed by inorganic precipitation in a reducing environment close to sea mounts whilst the Cretaceous occurrence resulted from a concentric growth in cold, ascending seawater at the continental margin under anoxic conditions.

Although not currently exploited, *REE* are a conspicuous component of the Olympic Dam iron-oxide copper gold system, one of the largest ore deposits on Earth. In ‘Feldspar mineralogy and rare earth element (re)mobilization in iron-oxide copper gold systems from South Australia: a nanoscale study’, Kontonikas-Charos *et al.* (2018) describe perthitic feldspar textures in granites that host the Olympic Dam deposit and in skarns elsewhere in the same ore province that are anomalously rich in *REE*, Ba and Fe and are sometimes pseudomorphed by assemblages of *REE*-fluorocarbonates+molybdenite. Concentration of *REE* occurred during intense metasomatism associated with the transition from a magmatic to hydrothermal fluid regime.

A Sn-Ta deposit in NW Spain is described in ‘Textural and mineral-chemistry constraints regarding the columbite-group minerals in the Penouta deposit: evidence of magmatic and fluid-related processes’ (Alfonso *et al.*, 2018). This deposit is in a greisenized granitic cupola where Ta minerals occur as disseminations in a leucogranite. Zoned columbite-group minerals (CGM) are the most common Ta-bearing phases, but microlite, wodginitite, tapiolite and Ta-rich cassiterite (up to 9 wt.% Ta₂O₅) occur also. Dissolution and Ta enrichment of the columbite is probably related to a late-stage granitic fluid.

Papers on platinum-group minerals (PGM) in this special issue include ‘The mineralogy, geochemistry and genesis of the alluvial platinum-group minerals of the Freetown Layered Complex, Sierra Leone’ (Bowles *et al.*, 2018). Large alluvial PGM-containing Pt-Fe-Cu alloys, laurite–erlichmanite and Os-Ir-Ru alloys differ from the mineral assemblage in the source rocks and the oxidized PGM found in weathered rocks. Features such as dendritic growths and an organic coating support belief in a secondary origin. A second PGM paper examines the mertieite-II structure in ‘Mertieite-II, Pd₈Sb_{2.5}As_{0.5}, crystal-structure refinement and formula revision’ (Karimova *et al.*, 2018). The crystal structure of the mertieite-II from Finland is trigonal, space group is *R*3̄*c*. The unit-cell parameters for two crystals are: *a* = 7.5172(3) Å, *c* = 43.037(2) Å, *V* = 2106.1(2) Å³ and *a* = 7.5135(4) Å, *c* = 43.003(3) Å, *V* = 2102.4(3) Å³ with *Z* = 12. The

structure consists of Sb and (Sb,As) triangular 3⁶, Pd triangular 3⁶ and Pd pentagon-triangular 5.3³ layers. These are stacked along the *z* axis to produce an extension of the unit cell that contains 36 layers.

Two papers address molybdenum resources. In the first: ‘Fe-, Fe,Mn- and Fe,Mg-chlorite: A genetic linkage to W,(Cu,Mo) mineralization in the magmatic-hydrothermal system of Borralha, northern Portugal’, Bobos *et al.* (2018) show how chlorite compositions and mineral associations can be linked to the fluids present during mineralization. Fe,Mn-chlorite crystallized from a magmatic-hydrothermal fluid, whereas Fe- and Fe,Mg-chlorite, quartz and adularia owe their origin to a mix of meteoric and magmatic-hydrothermal fluids. Molybdenite from porphyry copper ores occurs at Kalinovskoe and Birgilda (Plotinskaya *et al.*, 2018). In ‘Trace-element geochemistry of molybdenite from porphyry Cu deposits of the Birgilda-Tomino ore cluster (South Urals, Russia)’ these authors show that Si, Fe, Co, Cu, Zn, Ag, Sb, Te, Pb, Bi, Au, As and Se form mineral inclusions within molybdenite with very variable Re contents. A temperature decrease favours the formation of Re-rich molybdenite which, with compositional heterogeneity, suggests a mantle source for the molybdenum.

Although gold is not among the critical raw materials of today, largely due to the diverse sources of supply, the global economic impact of changing gold prices is significant so a fundamental understanding of genesis of gold deposits is vital. ‘Supergene gold enrichment in the Castromil-Serra da Quinta gold deposit, NW Portugal’ (Cruz *et al.*, 2018) shows that gold deposits hosted by Variscan granites and Precambrian to Palaeozoic metasediments are marked by gossans that were exploited by early miners. Early-formed gold in primary sulfides (arsenopyrite and pyrite) contains 15–40 wt.% Ag whilst later gold occurring along grain boundaries and in microfractures in the sulfides or in associated quartz veins contains more Ag (37–52 wt.%). Supergene gold in the gossan contains <16 wt.% Ag as a result of gold enrichment during weathering.

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