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# Precambrian to modern manganese mineralization: changes in ore type and depositional environment

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Manganese mineralization is diverse in occurrence, origin, mineralogy and geochemistry. These variations reflect differences in the processes of formation and depositional environments, which in turn are a response to changes in the land-ocean-atmosphere system over geological time. As such, manganese deposits can act as markers of major events in the dynamic evolution of the Earth's surface. Modern manganese accumulations provide insights into key factors controlling manganese deposition that cannot readily be determined from examination of ancient ores. A knowledge of oceanic currents, ocean chemistry or small-scale variations in physicochemical patterns of recent basins, for example, may extend our understanding of depositional processes in the past. Equally, the study of Precambrian deposits not only elucidates ancient mechanisms of manganese metallogenesis, but also helps to unravel the impact of comprehensive environmental changes on metal deposition on a scale not realized in younger geological times.

The papers collected in this volume provide insights into this changing nature of manganese mineralization from Precambrian sedimentary ores to crusts and nodules on the Cenozoic sea bed. The volume is introduced by **Supriya Roy** with a review of the range of terrestrial manganese deposits and their relative abundance through geological time.

## **Precambrian deposits**

The manner in which manganese mineralization reflects changes in planetary environmental chemistry that was noted above and mentioned by Roy is further developed by papers in this section. **Glasby** illustrates the concomitant changes in iron-manganese aqueous geochemistry and fractionation with the evolution of seawater chemistry. Low concentrations of sulphate ions in the early oceans prevented deposition of iron as a sulphide with a consequent reduction in iron-manganese fractionation in contrast to Phanerozoic deposits where fractionation can be significant. As a consequence, Precambrian banded iron formations commonly show high levels of manganese. This observation is taken further by **Kulik & Korzhnev** who developed a model for Ukrainian **BIF** deposition in which the manganese content is an indicator of the proportion of the original iron that precipitated as a carbonate.

Returning to the chemical evolution of the environment, **Bühn & Stanistreet** show that periods of manganese formation development are related to continental rifting periods. Precambrian glacial episodes may be causally related to such tectonic events, increasing ocean salinity and enhancing metal solubility to promote marine manganese and iron accumulation. The importance of seawater chemistry as a depositional control on manganese ores is further discussed by **Manikyamba & Naqvi** in considering deposits of the Dharwar Craton, India, which they suggest show evidence of enhanced biological activity in the local proto-ocean.

The palaeodepositional environment of Proterozoic sedimentary manganese ores is commonly cited as a shelf or basin margin setting. However, **Mukhopadhyay** et al., by applying facies analysis to carbonaceous host sediments of the Pengana Group manganese deposits were able to recognize a deep-water, base-of-slope depositional setting which adds a previously unknown depositional regime for Precambrian manganese formations.

The sources of manganese in Precambrian deposits have been discussed by both Roy and Glasby, who recognize the greater importance of a hydrothermal contribution of manganese into early oceans relative to modern environments.

From Nicholson, K., Hein, J. R., Bühn, B. & Dasgupta, S. (eds), 1997, Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, Geological Society Special Publication No. 119, pp. 1–3.

Lateral transport of hydrothermal manganese permitted it to be a principal source for the manganiferous shelf sediments common in the Proterozoic. **Nicholson** *et al.* used geochemical evidence to suggest a mixed manganese source for deposits in Orissa, India. There, episodic hydrothermal-source manganese precipitation is characterized by arsenic enrichments. These deposits are intermixed with arsenic-poor ores, with manganese contributed by a second, nonhydrothermal source.

#### **Cenozoic deposits**

Younger manganese deposits show a wide diversity of genetic types, from nodules, crusts and stratabound layers in ocean basins, to deposits precipitated from terrestrial and marine hydrothermal fluids. The papers in this section reflect this diversity in reviewing and describing representative deposits.

Hein et al. review the depositional processes, setting, morphology and chemistry of manganese-iron oxide mineralization in the Pacific Ocean. These include examples of oxides formed by hydrogenetic precipitation from ambient seawater, deposition from hydrothermal fluids and sediment pore waters, and replacement deposits. They also discuss the chemical mechanisms related to oxide formation. Biogeochemical controls on oxide chemistry are considered by Cronan. He highlights the importance of organic matter and therefore biological activity as a factor in manganese deposition in the South Pacific. As bioproductivity increases northwards towards the equator, there is a concomitant increase in the amount of manganese and trace metals that reach the sea bed, a trend reflected in the nickel and copper enrichments in manganese nodules. The importance of high biological activity to nodule development is discussed in relation to the Peru Basin by von Stackelberg. Like Cronan, he emphasizes the correlation between nodule abundance, growth rate and the CCD, the latter of which is controlled by bioproductivity. Large nodules show increased diagenetic accumulations as they sink in soft sediment to the redox boundary. Movement of the nodules by organisms between diagenetic and hydrogenetic growth regimes produces layering in the nodule. Variations in nodule abundance and chemistry with geological setting are recognised in the northwest Pacific Ocean by Usui & Someya. They produced a database of deposits in the area, through which they identify nodule-setting associations. Nodules and crusts on Cretaceous seamounts, for example, are enriched in cobalt relative to other deposits.

Hydrothermal iron-manganese crusts from the Indian Ocean described by Nath *et al.* show depositional periods where a hydrogenetic input is dominant. The composition of the crusts reflect an episodic hydrothermal discharge and manganese contribution to the crusts – a modern analogue to the depositional process proposed by Nicholson *et al.* for a Precambrian ore.

As manganese ores can reflect changes in the natural chemical evolution of the environment, so they may also record zones of metal pollution. **Glasby** *et al.* describe the distribution, morphology and chemistry of rapidly growing concretions from the Baltic Sea and show how these are influenced by anthropogenic metal inputs, raising their potential as a sampling medium in environmental monitoring.

Hydrothermal fluids from both marine and terrestrial geothermal systems can deposit manganese minerals in sub-surface vein systems and stratabound layers as well as surface discharge precipitates. Both modern and ancient examples of these types of mineralization are described in the following papers. In the Antarctic, Rey et al. identified an area of redundant hot springs and fumaroles. Enrichments in the marine sediments of Deception Island show the area as an exploration target for iron-manganese mineralization. Crespo & Lunar describe a sequence in Spain where terrestrial hot-spring manganese mineralization grades into distal sedimentary, stratabound ores. These Cenozoic deposits are related to failed-rift volcanism and show high cobalt enrichments. Cenozoic manganese mineralization in Greece is described by Michailidis et al. who elucidate the controls on the formation of an oxide mineral assemblage formed by the weathering of vein carbonates and sulphide minerals. Modern manganese-depositing terrestrial hot-springs are rare. Those in Hokkaido, Japan are described by Miura & Hariya, who recognise a biogenic influence in some of the oxides deposited by these geothermal systems. Geochemical enrichments in the oxides are related to the manganese minerals present, and high arsenic values in some of the deposits are notable.

### Geochemistry and mineralogy

Any investigation into the genesis of manganese mineralization needs to consider the geochemistry and mineralogy of the deposit. Experimental and modelling approaches to manganese geochemistry and mineralogy can further aid our understanding of the formational and depositional processes involved and thereby our interpretation of deposit metallogenesis.

Gramm-Osipov examines the chemical thermodynamics of manganese oxide deposition in aqueous environments, with emphasis on seawater. He suggests that formation of the oxides is a two-stage process commencing with an oxyhydroxide compound that is subsequently transformed into more complex oxides. The processes behind the development of the distinctive genetic geochemical signatures of many deposits is investigated by Nicholson & Eley, who model and compare the adsorption of trace metals onto manganese oxides in simulated freshwater and seawater environments. They show that relative metal enrichments are less in seawater deposits due to multi-ion competition. and for the level of enrichments commonly observed in deep-sea nodules to be achieved, the active surface laver of the oxides must be replenished by regular oxide precipitation.

Metamorphosed sedimentary ores represent a major deposit type, but by their nature are demanding to model. Dasgupta critically reviews the mineralogical and geochemical changes that occur on metamorphism of manganiferous sedimentary rocks, and evaluates experimental data and the use of petrogenic grids. He additionally suggests areas for future research.

An unusually zinc-rich rancieite from Greece is described by **Nimfopoulous** *et al.* The mineral is formed in the later stages of the weathering profile of a carbonate-sulphide hydrothermal vein deposit. A novel, rapid method for the determination of manganese oxidation state in oxide minerals has been developed by **Gamblin & Urch**. They use variations in the form of the K $\beta$  X-ray emission spectrum related to the manganese oxidation state that can be easily recognized.

Overall the collection of papers in this volume illustrates the breadth of study necessary to understand the formation of manganese deposits – ores that provide markers to changes in palaeo-environmental conditions and which may find future applications in environmental monitoring and technology.

This volume is the outcome of three IGCP 318 (Genesis and correlation of marine polymetallic oxides) meetings in Germany, the UK and India. The IGCP 318 session in Germany was held in Freiberg in conjunction with the seventy-second Annual Meeting of the German Mineralogical Association. The field workshop in India was to the Madhya Pradesh-Maharashtra manganese ore belt in central India. The UK meeting was part of a Lecture Series of The Geological Society of London that commemorates L. L. Fermor - an outstanding manganese researcher from the early part of this century. IGCP 318 ended in 1995 after a five-year tenure. This book is a fitting conclusion to the diversity and interdisciplinary nature of the IGCP 318.

As the work of L. L. Fermor was commemorated so, as this century draws to a close, we should also like to honour the contributions to the understanding of manganese mineralization made by D. A. Crerar, Roger Burns and J. Hem, their guidance and insights will be deeply missed.

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