



NSW DEPARTMENT OF
PRIMARY INDUSTRIES

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Potential and Outlook

New South Wales has many small manganese deposits that were extensively worked in the past for secondary oxide ore. Primary silicate ore was mined on a small scale in a few deposits in the New England Orogen and significant resources potentially remain, but have little commercial value other than as a source of rhodonite for use as a semiprecious gem and ornamental stone.

There is considerable potential for additional deposits, particularly in the New England Orogen, but they are likely to be small or lack surface oxide caps.

Nature and Occurrence

Manganese is a hard, brittle, silvery metal with variable valency (2^+ to 4^+ in nature, up to 7^+ artificially). It reacts readily with oxygen and water and dissolves in weak acids.

Manganese occurs in about 300 minerals, but few are economically significant — mainly oxides such as pyrolusite, psilomelane, braunite and manganite (Table 21). Pyrolusite commonly replaces other manganese minerals as a result of oxidation. Psilomelane is common in secondary deposits and is typically colloidal, with adsorbed water and sodium, potassium or barium oxides. Braunite is an oxysilicate and is usually secondary. Manganite forms by reduction of pyrolusite. Hausmannite forms in contact metamorphism of manganese oxides and forms a reaction relationship with silica (hausmannite–tephroite–rhodonite–quartz).

In 2004, estimated world manganese production was 10.9 Mt (Table 22) (Corathers 2004). Major producers were China, South Africa, Ukraine, Australia and Brazil. Major suppliers of non-metallurgical ore include Gabon, Mexico, Morocco and Australia (Harben 1999). South Africa holds about 80% of world reserves.

Table 21. Main manganese minerals

Mineral	Formula	% Mn	Colour	Hardness	SG
Braunite	$2\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$	64.3	Brownish black	6.0–6.5	4.75–4.82
Cryptomelane	$\text{KMn}_8\text{O}_{16}$	59.8	Black to steel grey to bluish black	6.0–6.5	4.4
Hausmannite	Mn_3O_4	72	Brown to black	5.5	4.8
Manganite	$\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$	62.5	Iron-black to dark steel-grey	4	4.2–4.4
Pyrolusite	MnO_2	60–63	Iron-black to dark steel-grey	2.0–2.5	4.8
Psilomelane	$\text{BaMn}_9\text{O}_{18} \cdot 2\text{H}_2\text{O}$	45–60	Iron-black to dark steel-grey	5.0–6.0	3.7–4.7
Rhodochrosite	MnCO_3	48	Red–rose to brown	3.5–4.5	3.3–3.6
Rhodonite	MnSiO_3	41.9	Pink to rose–red, brownish red, yellow to grey	5.5–6.5	3.6–3.8

Source: Harben and Kužvart (1996)

Table 22. World manganese ore production 2004

Country	Production (000 tonnes)
Australia	3 300
South Africa	1 800
Gabon	1 300
Brazil	1 000
China	800
Ukraine	800
India	600
Mexico	120
Other	1 200
Total	10 920

Source: Modified from Corathers (2004)

Deposit Types

Manganese deposits are widely distributed, geologically and geographically. A number of deposit types have been recognised, as follows (Roy 1969, 1976; Harben & Kuřvart 1996).

Non-volcanogenic sedimentary deposits

Sedimentary manganese deposits are the largest and most important (commercially). They occur in diverse settings but are most common in Cainozoic platform sequences. The depositional environment determines the mineralogy of manganese deposits. Manganese precipitates as carbonates in deep water or in closed basins under reducing conditions, and as oxides in freely circulating, strongly oxidising nearshore waters.

Volcanogenic sedimentary deposits

Manganese deposits of volcanic origin are formed by either the weathering of volcanic rocks or as a direct result of volcanic activity, particularly submarine volcanism. Deposits of this type are generally relatively small, rarely containing more than 1 Mt of ore (Roy 1976).

Nodule deposits

Consist of ocean-floor manganese nodules that precipitate directly from seawater on nuclei, such as shark teeth, whale earbones, rock fragments or other nodules. Other metals in the nodules include iron, nickel, cobalt, molybdenum and copper. Three trillion tonnes of potato-sized nodules are estimated to litter the world's deep ocean floors. Nodules form in irregular, single-layer fields in the Pacific Ocean at

the rate of 10 Mt per annum. These nodules occur at or within a metre of the interface between the water and ocean floor, which contains up to 65% clay (illite, kaolinite or smectite) and siliceous ooze. The highest-grade nodules develop farthest from land.

Hypogene and exhalative deposits

These deposits form from rising thermal waters derived from crystallising igneous rocks or from heated groundwaters. Pressure decreases and chemical changes associated with reactions with the country rocks cause precipitation of manganese carbonates and oxides, along with barite, fluorite and sulphides. Subaqueous exhalations are associated with seabed manganese.

Surface-residual deposits

Manganese deposits associated with the regolith form above the water table under tropical weathering conditions by intense leaching of silica and other components from low-grade deposits. Enrichment occurs by replacement by mobilised manganese.

Main Australian Deposits

The major Australian deposits are at Groote Eylandt in the Gulf of Carpentaria (Northern Territory), and in the eastern Pilbara Craton in Western Australia.

At Groote Eylandt, manganese occurs in the upper 15 m of the Early to Middle Cretaceous Mullaman beds (sandstone, claystone, pebble gravel and manganese marl), which are unconformably overlain by lateritic Tertiary conglomerate (MacIntosh et al. 1975). Mineralisation occurs over about 150 km², mainly on the western side of the island. Ore horizons average about 3 m in thickness, under an overburden of 3–12 m. The ore consists mainly of pyrolusite, cryptomelane and minor manganite, with minor to trace amounts of several other manganese minerals. The deposit is believed to have formed as a non-volcanogenic shallow-water marine sedimentary deposit on Proterozoic basement. It was subsequently enriched by diagenesis, supergene alteration and late-stage pedogenic processes (Bolton et al. 1990).

Significant quantities of manganese have been produced from the eastern Pilbara Craton in Western Australia (Fetherston 2002a,b). Deposits appear to have formed by supergene enrichment of manganese-bearing sedimentary rocks and also by filling of cavities and fissures in dolomite and fault zones. At Woodie Woodie, manganese is mined from deposits in Archaean to Proterozoic rocks of the Carawine Dolomite and Pinjian Chert Breccia formations.

A number of other prospects in the area have also been explored (Consolidated Minerals Limited 2002; Corathers 2004).

New South Wales Occurrences

Most manganese occurrences in New South Wales are metamorphosed stratiform deposits of manganese silicates that are generally capped by zones of supergene manganese oxides. The deposits, which are typically small and lenticular, occur in metasedimentary terranes associated with chert/jasper sequences and lesser metabasalt (Hall 1959; Fitzpatrick 1975a,b; Bowman 1975; Ashley 1986; Gilligan & Brownlow 1987; Brown et al. 1992). The deposits have been interpreted as the ancient metamorphosed analogues of nodular manganese occurrences currently forming on the deep ocean floor (Fitzpatrick 1975a,b; Ashley 1986).

In the Gundagai–Cootamundra–Thuddungra–Grenfell–Parkes areas of the central Lachlan Orogen, manganese deposits are principally associated with the Brawlin Formation, Jindalee Group and Kirribilli Formation (Fitzpatrick 1975a,b; Bowman 1975; Downes et al. 2004).

Secondary manganese oxides were worked in many localities, mainly between World War I and 1960, as sources of high-grade manganese oxides, for use in making dry-cell batteries and in steel manufacture (Hall 1959; Fitzpatrick 1975b). The Hoskins mine, near Grenfell, was the largest producer and produced 25 700 tonnes of ore between 1915 and 1941. Secondary mineralisation at the Hoskins Mine extends intermittently over a distance of about 400 m laterally and to a depth of 45 m (Ashley 1986).

Deposits are common in the southern Central Block of the New England Orogen, principally hosted by the Woolomin Group and Myra beds. Manganese oxide deposits in the New England region are typically up to 10 m wide, 40 m long, and 25 m deep (Fitzpatrick 1975b). They probably have similar dimensions to the underlying primary deposits.

Rhodonite is the dominant primary manganese mineral in New South Wales and some, particularly from deposits in the New England region, is suitable for use as a semiprecious gem and ornamental stone. Deposits that have been affected by contact metamorphism contain a greater range of primary manganese minerals than regionally metamorphosed deposits. Tephroite (Mn_2SiO_4) and hausmannite (Mn_3O_4) are common in such deposits and a variety of other manganese minerals has also been recorded (Segnit 1962; Fitzpatrick 1975b; Ashley 1986).

Rhodonite also occurs as a common gangue mineral in the Broken Hill lead–zinc–silver lodes.

A few deposits in the New England Orogen produced significant amounts of primary manganese silicates. During the late 1950s, the BHP steelworks at Newcastle obtained several thousand tonnes of manganese silicates (tephroite and rhodonite), probably from the Black and White mine, near Bendemeer, for use in making silico-manganese (W.S. Chesnut [Geological Survey of New South Wales] pers. comm. 1989).

Until 1961, production statistics collected by the (then) Department of Mineral Resources did not differentiate between rhodonite produced for industrial use, and rhodonite used as a gemstone. Since 1961, production of about 180 tonnes of industrial rhodonite and 600 tonnes to 700 tonnes of rhodonite for gemstones has been recorded.

Most of the rhodonite has been won from contact-metamorphosed occurrences, which typically contain higher-quality, brighter-coloured rhodonite than regionally metamorphosed deposits (Fitzpatrick 1975b; Goodwin 1998). Seven tonnes of rhodonite (including what is known as ‘Imperial Red’) were produced from the Black and White mine (northeast of Tamworth) in 1960 and shipped to the USA for use in dress jewellery. This material, and material produced more recently from Woods mine (north of Tamworth), represents some of the finest ornamental rhodonite produced in the world (Goodwin 1998).

Applications

Manganese is the most widely consumed metal after iron, aluminium and copper. It is mainly used in metallurgical applications (95% of production), primarily in steelmaking, for removing sulphur and oxygen from molten steel, and as an alloying element to increase toughness and hardness of metals.

Manganese is also used, in relatively small amounts, in non-ferrous alloys, principally with aluminium, to improve such properties as hot and cold strength, corrosion resistance and formability (Harben 1999).

Industrial uses of ground manganese ore are numerous, and mainly employ manganese dioxide. Manganese carbonate is also used, despite its lower grade (maximum 45% Mn compared to maximum 62.3% Mn in dioxide), because its susceptibility to acid attack simplifies the production of electrolytic MnO_2 .

The principal, non-metallurgical use of manganese is in dry-cell batteries, in which natural, activated or synthetic manganese dioxide is used as an oxidising agent or depolariser. Battery grade manganese dioxide should contain 70–85% MnO_2 (44–54% Mn) and less than 0.05% metals which are more electronegative than

zinc (e.g. copper, nickel, cobalt and arsenic). A number of other properties are also important in determining whether a particular manganese dioxide is suitable for dry-cell manufacture ('battery active') (Harben 1999). These properties include crystal structure, surface area, porosity, particle shape and size, and electrical conductivity. Relatively few natural manganese oxide ores have the properties required for use in dry cells (i.e. are 'battery active'). The principal sources of natural battery grade manganese dioxide are Gabon, Ghana, Brazil, China, Mexico and India.

Activated MnO_2 is produced by heating ground manganese ore to 600–800°C and adding sulphuric acid to form a porous, hydrated and chemically active ('battery active') product.

Synthetic manganese is used in higher performance dry cells (e.g. alkaline cells). Synthetic manganese dioxide is manufactured from manganese ores or manganese chemicals by electrolysis (EMD or electrochemical manganese dioxide) or chemical processes (CMD or chemical manganese dioxide). High-purity electrolytic manganese oxide (EMD) is produced by Delta EMD Australia Pty Ltd at a plant in Newcastle, using ore from Groote Eylandt. An EMD plant is also proposed to be constructed in Western Australia by HiTec Energy. This plant will initially use waste tailings from the Woodie Woodie Mine. Construction of the plant, however, has yet to commence.

Ground manganese ore may be used directly as a micronutrient in certain animal feeds and fertilisers. Manganese is used as a colourant (brown to purple colour) in bricks and ceramics; as a pigment in paint; and as a colouriser, decolouriser or chemical 'scavenger' in some glasses. Other uses include: as an oxidiser in chemical production (e.g. manufacture of hydroquinone, colouring agents, and certain medicines); a slag former (welding rod coating and flux); and for enhancing the adherence of frits in ceramic manufacturing (Harben 1999). In addition, it is used as a feedstock for the production of manganese ferrite, which is widely used in electronics (e.g. television circuit boards) (Anon 2005).

Ground manganese ore is also the starting point for the manufacture of a range of manganese chemicals, such as manganese sulphate (animal feed and fertiliser, fungicide and feedstock for electrolytic manganese metal production). Manganese carbonate is used as a catalyst in polymerising olefins, and as a feedstock to produce manganese acetate, linoleate, naphthenate, octoate, tallate, resinate and stearate, battery-grade manganese oxide and manganese ethylene bithiocarbonate. Reacting manganese

ore with potassium hydroxide produces potassium permanganate ($KMnO_4$), a widely used catalyst, bleach and disinfectant, circuit board cleaner — and which is also used in gas purification and water treatment (Harben 1999; Anon 2005).

Rhodonite with stronger red colours is attractive and sold for cutting as a semiprecious stone. Its major use is in costume jewellery.

Alternative Materials

There are no satisfactory substitutes for manganese in its major applications.

Health Issues

Manganese is an essential trace element in all living organisms but is toxic in excessive doses (Anon 2005). Inhalation is the most common form of exposure, the level of risk varying according to the form in which the manganese occurs and the particle size. Many countries have imposed restrictions on permissible levels of airborne manganese in dust and fumes.

Economic Factors

Demand for manganese is driven by the requirements of the iron and steel industry.

Annual global production of EMD (currently over 250 000 tpa) is growing rapidly due to increasing demand for high-performance batteries. Because of the small size of this market relative to metallurgical markets, this growth will have little impact on overall demand for manganese in the foreseeable future.

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