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MANGANESE: A MINERAL SYSTEMS ANALYSIS

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**Geological Survey of
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Manganese: a mineral systems analysis

T Brown*, P Duuring, S Morin-Ka and CA Strong

Abstract

Manganese is an important raw ingredient in several expanding industries, including in the manufacture of renewable/dry cell batteries, wind turbines and aluminium/steel alloys. Demand for this critical metal is forecast to grow, with expansion of these industries placing pressure on the discovery of new manganese (Mn) resources. An assessment of globally occurring Mn deposit classes has led to the grouping of stratiform, supergene, hypogene and iron-formation deposit classes into a Mn mineral systems model. A mineral systems analysis has been undertaken to identify critical and constituent processes that control their genesis, as well as determine mappable proxies for these processes. Critical processes include: (i) the addition and concentration of dissolved Mn^{2+} in ancient anoxic seawater, (ii) the subsequent addition of oxygen from biological outputs to anoxic seawater, triggering precipitation of Mn oxides, (iii) post-depositional modification of stratiform Mn ores that result in enrichment of Mn in rocks to economic ore grades, and (iv) the exhumation and preservation of these Mn oxide ores.

KEYWORDS: basin, hydrothermal, hypogene, iron formation, manganese, pyrolusite, supergene

Introduction

The Mineral Systems Atlas (MSA) is an interactive geological information system (GIS)-based platform that collates and delivers map-based geoscience data layers filtered to be specifically relevant to understanding and exploring for mineral deposits in Western Australia (www.dmirs.wa.gov.au/mineralsystems atlas). Atlas content is systematically defined by applying the mineral systems concept advocated by Wyborn et al. (1994) and McCuaig et al. (2010). The premise of this concept is that mineral deposits will only form and remain preserved where there has been a spatial and temporal coincidence of critical earth processes (geodynamic setting; lithosphere architecture; fluid, ligand and ore component reservoir/s; fluid flow drivers and pathways; depositional mechanisms; post-depositional processes), and that the occurrence of these critical processes might be recognized from mappable geological features expected to result from them. It is these geological features ('targeting elements' or 'geological proxies') that can be extracted as digital map layers from geoscience datasets, and may be used in GIS-based prospectivity studies.

Mineral systems, as defined by Fraser et al. (2007), are analysed to define the mappable geological proxies for critical mineralizing processes. Such analyses draw on in-house knowledge, existing literature and collaborations with subject-matter experts. Structured queries are then used to extract relevant data from one or more statewide Geological Survey of Western Australia (GSWA) geoscience databases, for those proxies that can be practicably produced. These queries operate directly on, and are dynamically linked to, primary GSWA geoscience data sources. No new data are

acquired or created, although some information may be reformatted to meet the internal requirements of particular map layers. Furthermore, the queries are scheduled to automatically update the derived proxy map layers whenever new data are added to the primary databases. Users may therefore be confident that the data layers portrayed in the MSA are always current.

Manganese is a useful addition to the MSA because of its importance to Australia's critical minerals strategy, with manganese being specifically mentioned in the Federal Government's policy for advancing the critical minerals industry through investment, innovation and infrastructure (Commonwealth of Australia, 2019). Manganese is used in a variety of industries, including in manufacture of renewable/dry cell batteries, wind turbines and aluminium steel alloys. Western Australia has produced about 14.8 Mt of Mn ore since 1948 (GSWA, 2021) and is fortunate to host several large Mn projects at various stages of development, including Butcherbird (26.13 Mt of contained Mn, calculated with an average ore grade of 10%), Woodie Woodie (15.00 Mt, 31% Mn), Oakover (6.42 Mt, 10% Mn), Nicholas Downs (2.09 Mt, 24% Mn), Balfour South (4.19 Mt, 19% Mn), South Woodie Woodie (1.90 Mt, 13% Mn), Flanagan Bore (1.70 Mt, 11% Mn) and Ant Hill – Sunday Hill (1.67 Mt, 21% Mn) (GSWA, 2021). Although Australia has a projected remaining Mn resource life expectancy of about 35 years (Senior et al., 2019), additional discoveries are essential to ensure a long-term, undisrupted and local supply of this metal to Australia's battery and steel-making industries.

Published reviews of Mn deposits typically describe their physical-chemical characteristics, spatial and temporal distribution, and ore-formation processes (see reviews by National Materials Advisory Board, 1981; Roy, 1997; Kuleshov, 2011; Cannon et al., 2017). Recently, Xiang et al. (2020) applied a mineral systems approach to understanding

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Mn mineralization – identifying critical processes, including: (i) the source of Mn, (ii) pathways for the transport of fluids and metal, (iii) triggers for the precipitation of Mn from fluids, as well as (iv) diagenetic, enrichment and preservation processes, which not only modify the primary characteristics of manganese-bearing host rocks, but also result in the secondary enrichment of Mn to produce higher-grade ores. These authors briefly describe the link between the critical processes and their respective mappable proxies and recommended GIS layers.

This Record presents a mineral system analysis for the “Sedimentary Mn” mineral system with the objective of developing a list of mappable proxies that will direct construction of GIS map layers in the MSA. In this Record, a brief description of the different Mn deposit classes is mentioned before an evaluation of the mineral systems analysis is presented in graphic form as a Mineral System Tree. Additional information about the Mn mineral system, specifically how the GIS map layers are created, is provided in the online Guide to the MSA. The information in the Guide and Atlas will be updated based on improvements in our understanding about this mineral system and additions of related geoscience data to the GSWA databases.

Classification of manganese deposits

Existing classification schemes of global Mn mineralization occurrences (e.g. National Materials Advisory Board, 1981; Roy, 1997; Kuleshov and Maynard, 2017; Cannon et al., 2017) divide Mn deposits into three main classes: Sedimentary (also called Sedimentary/Diagenetic or Stratiform), Supergene and Hydrothermal. The MINEDEX database employs these three major divisions, although with different descriptive titles (Table 1): (i) ‘Mn in sedimentary or carbonate rock’ is analogous to the Sedimentary class, (ii) ‘supergene and residual Mn’ corresponds to the Supergene class, while (iii) ‘vein and hydrothermal’ is equivalent to the Hydrothermal class. The MINEDEX database also includes three less common Mn ore types: (iv) Fe–Mn associated with iron formations, (v) nickeliferous laterite with Mn, and (vi) Mn associated with base metals (Fig. 1).

This present study proposes the Mn mineral system that includes the three main deposit classes: Stratiform, Supergene and Hydrothermal (here called Hypogene).

These deposit classes display strong spatial correlation and similar genetic controls. Figure 2 shows the parent–child relationships between the deposit classes and their potential ore types.

Stratiform deposits

Stratiform deposits are the most common and the best understood of the Mn deposit classes. Global examples of stratiform deposits include the Datangpo deposit in China (Li et al., 2012), Molango in Mexico (Okita and Shanks III, 1992) and Groote Eylandt in the Northern Territory (Frakes and Bolton, 1984). Stratiform deposits formed after about 3 Ga (Roy, 1997; Kuleshov and Maynard, 2017) and are in basinal settings: including marginal basins, subduction-related trenches, back-arc basins, island arcs, small inter-arc basins and subduction-related shallow marginal basins (‘basin’ refers to a depressed area of the Earth’s crust in which sediments accumulate in substantial thickness; Bates and Jackson, 1987). Western Australian basin examples containing stratiform Mn deposits include the Bryah Basin (Paleoproterozoic, 2.0 – 1.9 Ga), Earahedy Basin (Paleoproterozoic, ~1.8 – 1.6 Ga), Edmund Basin, (Early Mesoproterozoic, ~1.6 – 1.45 Ga) and the Collier and ‘Oakover’ Basins (Late Mesoproterozoic, ~1.1 Ga).

The primary source of Mn in stratiform deposits is most likely the addition of manganese-bearing terrestrial sediments, undersea hydrothermal vents and volcanic ash to ancient seawater (Fig. 3). The redox-sensitivity of Mn, reduced seawater conditions and the reluctance of Mn to precipitate as sulfide minerals resulted in an increased concentration of dissolved Mn^{2+} (with Fe^{2+}) in seawater. This process continued without disruption until significant oxygen was added to the atmosphere and hydrosphere due to biological outputs. Oxygen addition took place mainly after 3 Ga, and particularly during the Great Oxidation Event from ~2.45 to 2.1 Ga (Lyon et al., 2014); this led to the oxidation of dissolved Mn^{2+} and Fe^{2+} in seawater to precipitate Mn and Fe oxides. Stratification of oxygen concentrations in oceans during the Great Oxidation Event, and probably persisting until the Neoproterozoic Oxidation Event at c. 800–600 Ma, resulted in Mn oxide precipitation mainly occurring at the interface between (deeper) reduced seawater and (shallower) oxidized seawater. Consequently, basin margins were key sites for Mn oxide precipitation because of the rapid change in the slope of the sea floor and the greater likelihood for mixing between deeper and shallower waters.

Table 1. Nomenclature for classifying manganese deposits

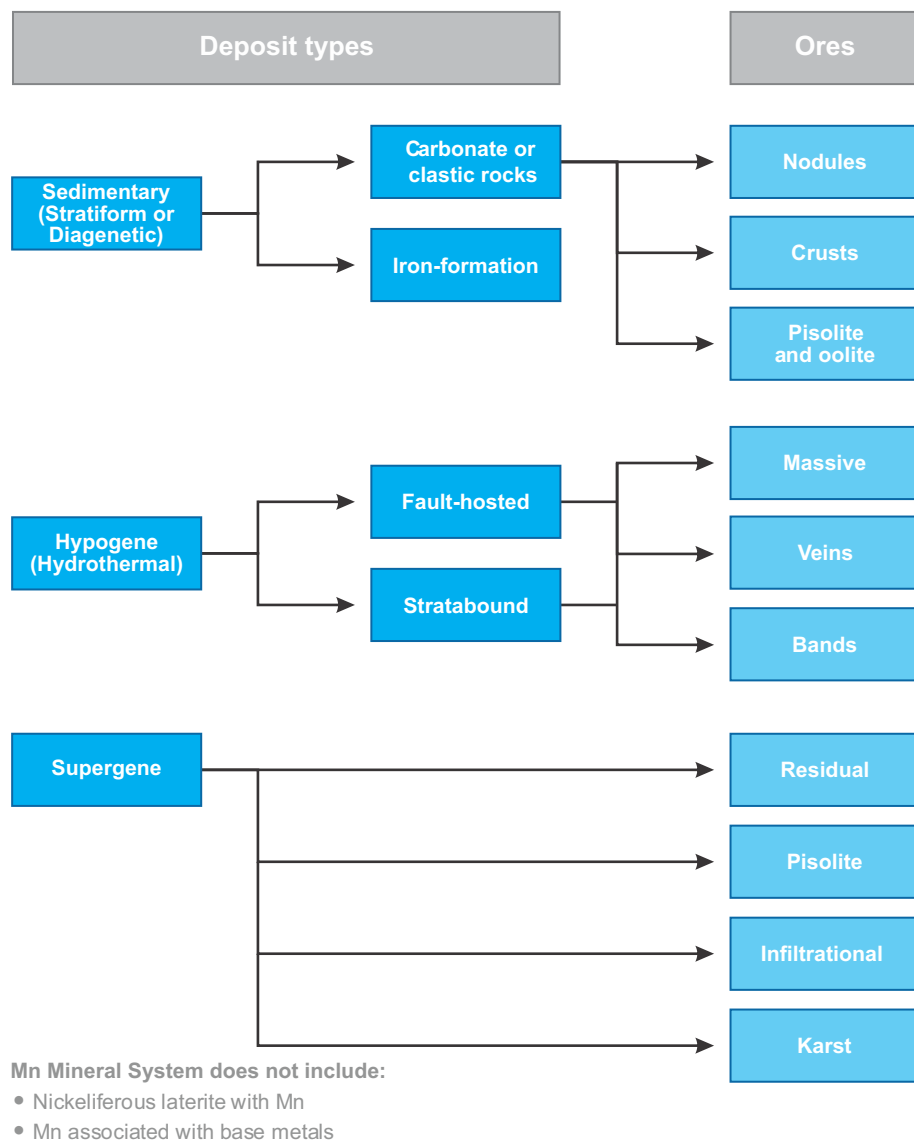
<i>Existing classification scheme categories</i>	<i>Equivalent GSWA MINEDEX category</i>	<i>Used in this Record for the Mn mineral system</i>
Sedimentary/ diagenetic/ stratiform	Mn in sedimentary or carbonate rock	Stratiform
Supergene	Supergene and residual Mn	Supergene
Hydrothermal	Vein and hydrothermal	Hypogene
–	Fe–Mn associated with iron formations	Fe–Mn associated with iron formations
–	Nickeliferous laterite with Mn	–
–	Mn associated with base metals	–



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Figure 1. Location of Mn mines, deposits and prospects in Western Australia overlying a solid geology map of the state (GSWA, 2021)



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Figure 2. The Mineral Systems Atlas 'Mn mineral system' incorporates several of the globally recognized Mn deposit classes plus their possible Mn ore types

Marine transgressions increased the accommodation space and facilitated the development of large stratiform deposits on the edges of the continental shelves.

Local sea floor environmental conditions were probably important for controlling Mn mineral speciation and textures, and influencing the precipitation of Mn oxides vs Mn carbonates, and Mn nodules vs crusts (Exon, 1997; Roy, 1997) (Fig. 3). *Nodules and ferromanganese crust ores* are limited to deep anoxic water environment conditions. Nodules are restricted to low sedimentation areas of the deep oceans, such as abyssal plains and plateaus; whereas, ferromanganese crusts may be on the flanks of seamounts and plateaus (Hein et al., 1990; Usui et al., 2020). In contrast, *Mn oxide and Mn carbonate ores* are restricted to shallow basins, where manganese-rich anoxic waters mixed with oxygenated surface waters. Oxide deposits typically contain pisolites and oolites that formed from high-energy wave agitation in the shallow, mostly oxic seawater conditions.

Manganese carbonate ores are typically laminated or layered within shale units, and represent lower energy deposition in mostly anoxic conditions (Cannon et al., 2017).

Post-deposition, burial and diagenesis processes modified the composition and textures of stratiform deposits through the reduction of Mn^{4+} to Mn^{2+} , and led to the redistribution of Mn in basinal sediments. Dissolved Mn reacted with sedimentary carbonates to form Mn carbonates and resulted in manganese-carbonate layers that are interlayered with clastic beds, such as black shales (Spinks et al., 2018).

The *Fe–Mn associated with iron-formations* style of Mn mineralization mentioned above is here regarded as a subclass of the stratiform deposit class, based on their precipitation from reduced seawater that is enriched in Mn and Fe. Furthermore, they are both hosted in basin settings (e.g. Lake Superior-type iron formations; see details about iron-formation deposition processes in Bekker et al., 2010).

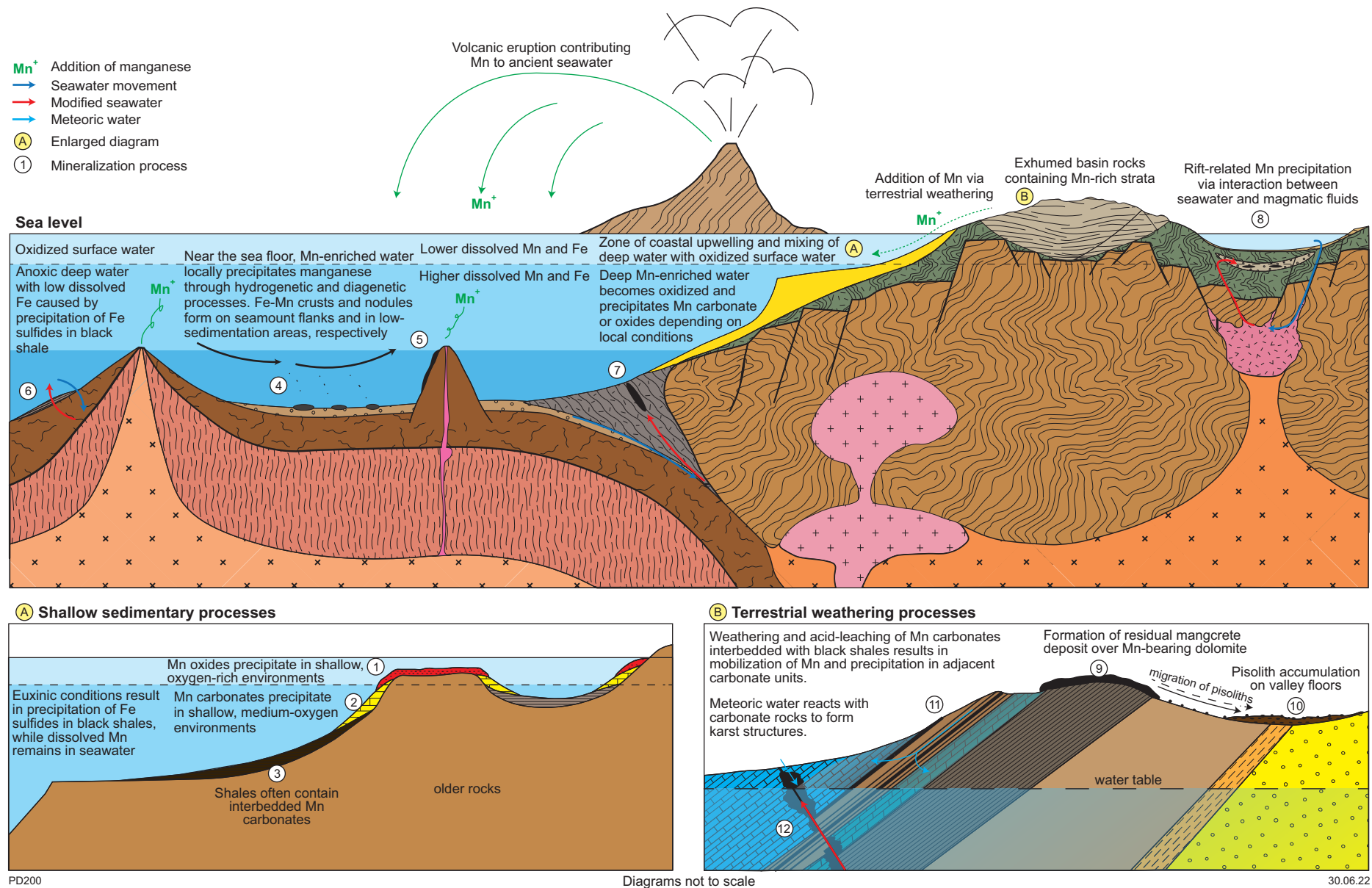


Figure 3. The schematic cross-sections summarize the main physical and chemical processes controlling Mn enrichment in rocks (modified after Kuleshov, 2011). Dissolved Mn in deep, anoxic ancient seawater is sourced from a variety of processes, including from volcanism, deepwater hydrothermal venting or continental weathering and erosion. Cross-sections (A) and (B) are enlarged portions of the main sketch, demonstrating local environment influences on the precipitation of Mn. Details of specific processes are labelled numerically, with notes provided on the figure.

For example, notable Mn ore zones are documented in the Urucum BIF-hosted deposit in Brazil (Biondi and Lopez, 2017), the Mamatwan and Wessels deposits in South Africa (Tsikos et al., 2003) and the Roy Hill deposit in Western Australia (Clout and Fitzgerald, 2011).

Supergene deposits

Supergene Mn deposits commonly overlie stratiform occurrences. They form from the interaction of lower-grade stratiform Mn ores with near-surface, oxidized meteoric fluids. Higher-grade supergene ores result from dissolution of silicate minerals by meteoric fluids and concentration of less soluble Mn oxides. Supergene deposits display massive-texture and vein ores. The best geological environments for supergene mineralization are those that have well-developed lateritic weathering crusts, such as those preserved in parts of Africa, South America, Australia, India and China (Kuleshov and Maynard, 2017). Global examples include deposits in the Serra do Navio, Amapá, Brazil (Scarpelli and Horikawa, 2017), Molango in Mexico (Okita and Shanks III, 1992), Groote Eylandt in the Northern Territory of Australia (Frakes and Bolton, 1984) and near-surface ores in the Woodie Woodie deposit in Western Australia (Jones et al., 2013, 2017).

Supergene Mn deposits can be divided into four subtypes: (i) residual, (ii) pisolite, (iii) infiltrational, and (iv) karst (Kuleshov and Maynard, 2017) (Fig. 2). *Residual* deposits have thick caps expressed as local topographic highs resulting from the removal of more chemically and physically susceptible materials during weathering (Spinks et al., 2018). *Pisolite* deposits formed from the transport of pisoliths across pediments by sheetwash and accumulated as thick deposits on valley floors (Lascelles, 2016). *Infiltrational* deposits form due to the migration of manganese-rich meteoric fluids from manganese-bearing source rocks that also contain sulfide minerals. Fluid reactions with the sulfides produce acidic solutions that dissolve and transport manganese-bearing minerals (Tu et al., 1996). *Karst* deposits formed via the migration of low-temperature (100–200 °C) hydrothermal fluids from artesian basins or infiltrating meteoric water that travels via fractures and pore spaces within carbonate-rich rocks, or both, and created secondary porosity in these rocks where Mn from nearby rocks can accumulate (Varentsov, 2013).

Hypogene deposits

Hypogene Mn deposits, also known as ‘hydrothermal’ or more specifically as ‘vein and hydrothermal’ in the MINEDEX database, occur as narrow, steeply dipping, fault-hosted or veined Mn ores in unweathered rocks and as stratabound

zones adjacent to or above the fault-hosted Mn ores. Higher-temperature Mn oxide species, such as braunite, are more common in hypogene ores. Supergene overprint may increase ore reserves and ore grades (e.g. the ~50 m-thick, near-surface ore zones overlying the deeper extensions of the Woodie Woodie deposit in Western Australia; Jones et al., 2013, 2017), although notable standalone exceptions include the Orthris deposit in Greece (Robertson and Varnavas, 1993) and Burmister in Arizona (Hewett et al., 1963). The hypogene Mn deposits display similar controls to volcanic-related hydrothermal vent systems, such as volcanic-hosted massive sulfides (VMS). Hypogene Mn deposits occur in mid-ocean ridge and subduction zone settings, including back-arc basins, small inter-arc basins, fore-arc terraces, as well as their shallow marginal basins and trenches adjacent to continental plate margins (Bonatti et al., 1976; Glasby, 1988; Roy, 1997; Maghfouri et al., 2017). In these areas, shallow magmatism most likely drives convection of seawater through the crust. Manganese is scavenged from rocks and transported in solution by hot, reduced, modified seawater. Fluids released at vent sites interact with surrounding cooler seawater and trigger the precipitation of Mn oxides and precious metals (Hein et al., 2000).

Manganese deposit classes not included in the manganese mineral system

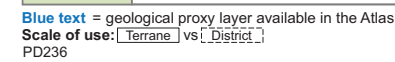
Nickeliferous Mn laterite and Mn associated with base metals are excluded from the Mn mineral system because they do not share strong genetic links with sedimentary depositional processes.

Critical processes in the manganese mineral system

The Mn mineral systems model proposed here incorporates the stratiform, supergene and hypogene deposit classes (Fig. 2). These Mn deposit classes share the same critical processes (Table 2): (i) the source of Mn is the addition and concentration of dissolved Mn²⁺ in ancient anoxic seawater, (ii) the subsequent addition of oxygen from biological outputs to anoxic seawater that triggers precipitation of Mn oxides, (iii) post-depositional modification of stratiform Mn ores that result in enrichment of Mn in rocks to economic ore grades, and lastly (iv) the exhumation and preservation of these Mn oxide ores. Relationships between the critical and constituent processes, and their mappable proxies, are best portrayed graphically – here summarized in a Mineral System Tree (Fig. 4).

Table 2. Critical processes of the manganese mineral system

Critical process	Description
Source	Addition and concentration of dissolved Mn to anoxic seawater
Trap	Addition of oxygen to anoxic seawater and precipitation of Mn oxides
Modification	Post-depositional modification of stratiform Mn in rocks
Preservation	Exhumation and preservation of Mn oxide ores



Conclusions

This study provides a mineral systems model for Mn, which includes stratiform, supergene and hypogene deposit classes. The aim is to determine links between critical geological processes for mineralization and GIS map layers, which will be useful for Mn exploration. The critical processes are: (i) the source of Mn being the addition and concentration of dissolved Mn^{2+} in ancient anoxic seawater, (ii) the subsequent addition of oxygen from biological outputs to anoxic seawater that triggers precipitation of Mn oxides, (iii) post-depositional modification of stratiform Mn ores that results in enrichment of Mn in rocks to economic ore grades, and lastly (iv) the exhumation and preservation of these Mn oxide ores. The resultant Mineral Systems Tree for the mineral systems model shows the reasoning behind GIS map layers recommended for Mn exploration.

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