



# Manganese mineralogy and diagenesis in the sedimentary rock record

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## Abstract

Oxidation of manganese (II) to manganese (III,IV) demands oxidants with very high redox potentials; consequently, manganese oxides are both excellent proxies for molecular oxygen and highly favorable electron acceptors when oxygen is absent. The first of these features results in manganese-enriched sedimentary rocks (manganese deposits, commonly Mn ore deposits), which generally correspond to the availability of molecular oxygen in Earth surface environments. And yet because manganese reduction is promoted by a variety of chemical species, these ancient manganese deposits are often significantly more reduced than modern environmental manganese-rich sediments. We document the impacts of manganese reduction and the mineral phases that form stable manganese deposits from seven sedimentary examples spanning from modern surface environments to rocks over 2 billion years old. Integrating redox and coordination information from synchrotron X-ray absorption spectroscopy and X-ray microprobe imaging with scanning electron microscopy and energy and wavelength-dispersive spectroscopy, we find that unlike the Mn(IV)-dominated modern manganese deposits, three manganese minerals dominate these representative ancient deposits: kutnohorite ( $\text{CaMn}(\text{CO}_3)_2$ ), rhodochrosite ( $\text{MnCO}_3$ ), and braunite ( $\text{Mn}(\text{III})_6\text{Mn}(\text{II})\text{O}_8\text{SiO}_4$ ). Pairing these mineral and textural observations with previous studies of manganese geochemistry, we develop a paragenetic model of post-depositional manganese mineralization with kutnohorite and calcian rhodochrosite as the earliest diagenetic mineral phases, rhodochrosite and braunite forming secondarily, and later alteration forming Mn-silicates.

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## 1. INTRODUCTION

Manganese oxides are critical environmental materials as powerful oxidants, as scavengers of important trace elements and reactive oxygen species, and as electron acceptors for anaerobic respiration (Myers and Nealson, 1988a; Tebo et al., 2005). Manganese is both the third most abundant transition metal in Earth's crust and has the largest number of oxidation states of 3d row elements (Armstrong, 2008), and so consequently the manganese cycle—both modern and ancient—involves multiple redox conversions.

Manganese is present exclusively in divalent form in a wide range of igneous minerals where it substitutes for iron (Post, 1999). Ultrabasic, basaltic, granitic and syenitic igneous rocks average at about 0.1% Mn(II) (Turekian and Wedepohl, 1961). Thus silicate weathering provides a substantial source of  $\text{Mn}^{2+}$  to surface and ground waters, especially since Mn(II) is highly soluble—even more so than iron (Gross, 1965; Post, 1999).  $\text{Mn}^{2+}$  is also sourced from seafloor hydrothermal vent fluids, at high but variable concentrations ranging from hundreds to thousands of micromoles per kilogram (Von Damm, 1990).

To concentrate Mn into significant sedimentary deposits, manganese needs to be oxidized to Mn(III) or Mn(IV) (Calvert and Pedersen, 1996). These ions form oxyhydroxide minerals that are deposited in sediments (Calvert and

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Pedersen, 1996; Armstrong, 2008). Unlike iron, manganese does not readily form sulfides, but is only insoluble in its oxidized forms (Van Cappellen et al., 1998; Maynard, 2010). Thus, the presence of significant manganese deposition in the sedimentary record should reflect the history of manganese oxidation.

However, there are a couple exceptions to this general relationship that manganese enrichment in the sediments signifies manganese oxidation. When there are high levels of soluble  $Mn^{2+}$ , this divalent ion can substitute for  $Ca^{2+}$  in authigenic carbonate phases. In Phanerozoic carbonates, Mn concentration is often used as a characteristic marker for secondary alteration (Brand and Veizer, 1980); this is due to sedimentary pore waters becoming enriched in  $Mn^{2+}$  due to the reduction and dissolution of Mn(IV) oxides (Calvert and Pedersen, 1996; Van Cappellen et al., 1998) and the elevated Mn concentrations in hydrothermal fluids (Von Damm, 1990). While elevated Mn in carbonates usually relates to alteration, primary well-preserved carbonates from the Archean Eon (4 billion years ago (Ga) to 2.5 Ga) have elevated Mn levels-up to 1% Mn rather than typical Phanerozoic carbonates of 10–50 ppm in well-preserved carbonates (Veizer, 1978; Brand and Veizer, 1980; Holland, 1984; Beukes, 1987; Komiya et al., 2008; Fischer and Knoll, 2009). These anomalous Mn-enriched carbonate platforms occur because the oceans during this time were anoxic and able to concentrate soluble  $Mn^{2+}$  to relatively high levels (estimated to be as much as 3–7  $\mu m$ , (Holland, 1984)). Karst weathering, the near-surface dissolution of carbonates from interaction with meteoritic waters, of Archean (Mn-bearing) carbonates can lead to further supergene concentration of Mn as the carbonate is dissolved and  $Mn^{2+}$  is oxidized. This process can produce small but economically meaningful Mn ores after the rise of oxygen such

as the Postmasburg and Woodie Woodie Mn deposits (Gutzmer and Beukes, 1996a; Jones et al., 2013).

The high  $Mn^{2+}$  concentration in Archean seawater was directly related to the lack of Mn oxidation before the rise of oxygen, approximately 2.3 billion years ago. There is a very limited set of processes and oxidants able to oxidize manganese due to its high redox potential (Tebo et al., 2004). Low levels of manganese oxidation is possible from reactions with UV light, but this is suppressed in the presence of  $Fe^{2+}$  or other reductants (Anbar and Holland, 1992). Manganese is oxidized phototrophically during the biosynthesis of the water-oxidizing complex of Photosystem II in Cyanobacteria, plants and algae (Tamura and Cheniae, 1987; Büchel et al., 1999). However, this phototrophic Mn oxidation is not thought to produce environmentally-significant manganese oxides (Madison et al., 2013) and no solely manganese-oxidizing photosystem has been documented in modern phototrophs (White, 2007). With a possible evolutionary exception (Johnson et al., 2013), Mn(II) is only oxidized at meaningful rates by molecular oxygen or  $O_2$ -derived species like superoxide (Calvert and Pedersen, 1996; Post, 1999; Tebo et al., 2004; Morgan, 2005; Dick et al., 2009; Hansel et al., 2012), so the presence of manganese (III,IV) oxides in sedimentary rocks can indicate free oxygen was once present in the environment.

Due to the high-potential redox chemistry of Mn, the geologic record of manganese deposits should reflect ancient oxygen availability and the paleo-environmental chemistry (Maynard, 2010). In Fig. 1, we present an updated compilation of Mn deposits through geologic time, and also plot size estimates of each terrestrial deposit (Fig. 1, Table 1). The lack of significant Archean Mn deposits is striking, as is the massive Hotazel deposit at around 2.22 Ga. Several

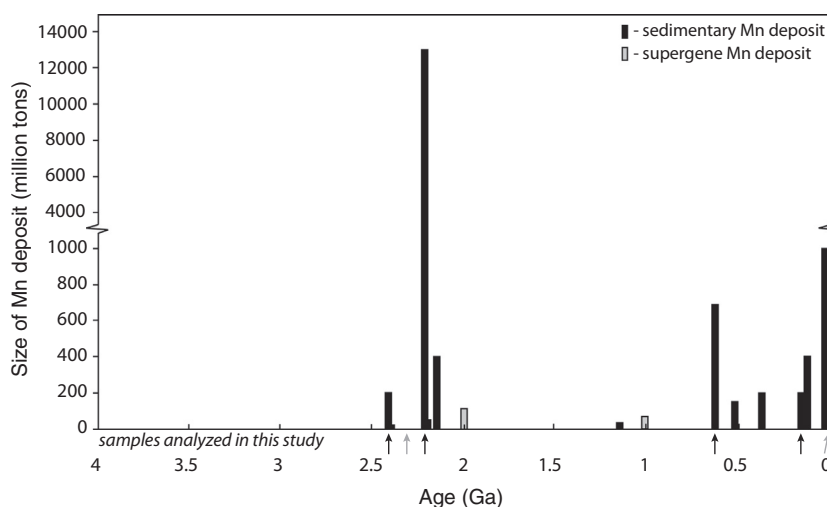


Fig. 1. Manganese ore deposits through time. Estimated volumes of major sedimentary manganese deposits plotted as a function of their best-constrained geologic age. Arrows mark deposits analyzed in this study, with black signifying large manganese deposits plotted and grey indicating timing of smaller deposits. Supergene deposits are shown in grey for cases where the age of mineralization is known; deposits from Archean proto-ore, primarily in India, occur but the age of mineralization is not known. References: (Maxwell, 1972; Varentsov and Grasselly, 1976; National Materials Advisory Board, 1981; Taljaardt, 1982; Martino, 1986; Dasgupta et al., 1991; Pracejus and Bolton, 1992; Urban et al., 1992; Davis et al., 1994; Babinski et al., 1995; Gutzmer and Beukes, 1996b; Fan and Yang, 1999; Rodionov et al., 2004; Cairncross and Beukes, 2013; Jones et al., 2013).

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