

Appendix A – Supplemental Information

METHODS

Using Electron Paramagnetic Resonance spectroscopy

One approach to assess the redox properties of manganese in a sample has focused on electron paramagnetic resonance (EPR) spectroscopy. EPR is an extremely sensitive technique to measure molecules with unpaired electrons (including Mn(II) and Mn(IV) species), and it has been useful for understanding the electronic structure and redox states of Mn in biochemical systems (see More et al., 1999; McEvoy and Brudvig, 2006). However, when this technique is applied to geological samples, results can become more complicated and nonunique. From observations of particularly narrow EPR line widths, it was suggested that EPR could be useful for distinguishing the biogenicity of the oxides (Kim et al., 2011). Yet in concentrated geological samples, dipole-dipole interactions between closely packed Mn atoms affect the EPR signals (Pingitore et al., 1988). Thus, when Mn is concentrated in samples, it is difficult to distinguish Mn(II) minerals like rhodochrosite (MnCO_3) from Mn(III) or Mn(IV) minerals (Pingitore et al., 1988). Furthermore, EPR of samples is effectively a bulk measurement that requires sample homogenization and thus does not pair redox data to mineral textures.

Distinguishing Kutnohorite vs. Rhodochrosite by X-rays

After initial observations that we had two end-members in the Mn-carbonate family, we measured XANES spectra of standards of kutnohorite and rhodochrosite. Our rhodochrosite standard from the Pachapaqui District, Peru has a relatively uniform composition averaging $\text{Mn}_{0.97}\text{Ca}_{0.02}\text{Mg}_{0.01}\text{CO}_3$. We had two kutnohorite samples, one from a 5cm crystalline cluster from South Africa and one microdrilled from carbonate nodules with a composition $\text{CaMn}_{0.7}\text{Mg}_{0.3}(\text{CO}_3)_2$ in the South African Hotazel formation. The kutnohorite crystal cluster had a variable Mn:Ca ratio with some pure calcite but we use a homogenized powder which we approximate at $\text{Ca}_{0.63}\text{Mn}_{0.36}\text{Mg}_{0.01}\text{CO}_3$ from an average of EDS spectra (chosen from spectra which had measurable Mn since XANES of only Mn will not measure pure calcite). Previous compilations had determined that rhodochrosite was an abundant mineral in many Mn deposits (Maynard, 2010) and kutnohorite also appeared to be an important phase in several ancient deposits of manganese, including the giant Hotazel formation and the Koegas Subgroup in South Africa (Gutzmer, 1996; Tsikos et al., 2003; Johnson et al., 2013). Our standard spectra and sample measurements highlight the subtle XAS differences between rhodochrosite and a kutnohorite or Mn-bearing calcite. These differences arise from the expansion of the hexagonal unit cell of kutnohorite and calcite (kutnohorite ideally $a = b = 4.850$, $c = 16.340$; calcite ideally $a=b=4.989$, $c=17.061$, crystal cluster standard measured $a=b=4.949$, $c=17.062$) as compared to rhodochrosite (ideally $a = b = 4.7680$, $c = 15.6350$; measured $a=b=4.779$, $c=17.062$), resulting in slightly larger distances from the central Mn to the carbonate groups and tertiary Ca and Mn shell distances. We harnessed these slight XAS differences to map the spatial distribution of these two carbonate types were located in carbonate-dominated Mn deposits, which enabled us to better understand the primary vs. secondary nature of rhodochrosite and kutnohorite in these formations.

GEOLOGICAL BACKGROUNDS ON SAMPLE SET

Sources of samples

The deep-sea manganese nodule was collected from the seafloor surface of the South Pacific Gyre as part of Expedition Knox-02RR in Dec 2006-January 2007 and donated by V. Orphan. Four samples from the IODP Leg 128 cores held at the Kochi Core Center in Kochi, Japan were acquired by a sample request application. J.B. Maynard, from the University of Cincinnati, graciously donated a variety of his samples from the Molango manganese deposit in Mexico. T. Piacentini, then at University of Queensland-Brisbane, kindly donated one thin section and two powdered samples from the Urucum mine in Brazil for this project. Hotazel samples examined were collected from a well-preserved open mine by T. Raub and J. Kirschvink (Caltech). Koegas samples are derived from the Agouron drilling project and a trip funded by the Lewis and Clark Astrobiology Fund. Kungarra samples were collected by J. Johnson from the Bolgeeda-Turee Creek 'Boundary section' described in Williford et al (2011) during the course of an Agouron-sponsored field research excursion. The geological contexts for each Mn deposit is described below.

ODP drill core from Japan Sea

We studied materials from an ODP Site 799 core drilled in the Japan Sea which had reported high manganese levels from intervals > 50 meters below sea floor (Matsumoto, 1992). This ODP core was drilled into the Kito-Yamato trough, an organic carbon-rich deep trench formed as a failed rift basin in the center of the Japan Sea (Matsumoto, 1992). The sediments contain a suite of unusual diagenetic carbonates, including lansfordite (a hydrated magnesium carbonate), magnesite, rhodochrosite, as well as calcite and dolomite. Rhodochrosite was reported in Quaternary to Miocene-aged rocks, especially abundant in Pliocene and upper Miocene sediments and interpreted as diagenetic. Calcian (22.5-38.5% Ca) rhodochrosite microspherules, about 2 to 12 μm in diameter, were described as filling interstices of the matrix (Matsumoto, 1992). This sedimentological description and the depleted carbon isotopes (-4 to -15 per mill, reflecting incorporation of organic carbon-derived CO_2) implies the rhodochrosite was secondary (Matsumoto, 1992). Matsumoto (1992) observed several micrometer-sized bright spots in the rhodochrosite that he was unable to identify as either iron sulfides, or manganese or iron oxides (Matsumoto, 1992).

Molango Deposit in Mexico

The largest manganese deposit in North America is the Upper Jurassic-age (~155 Ma) Molango deposit in Mexico. During this time, Mexico's large rift basins had become open to marine waters and had developed a carbonate platform-shelf, lying behind a trough-island arc system (Scott, 1984). The manganese enrichments are hosted by marine limestone and have been determined to be primarily in rhodochrosite and kutnohorite, with the Mn ore zone directly overlying a black calcareous shale (Okita et al., 1988; Okita, 1992). Okita et al (1988) proposed that the stratiform, laminated manganese-bearing carbonates formed from the diagenetic reduction of manganese oxides by organic carbon—a hypothesis supported by ^{13}C -depleted carbon isotopic data from the Mn-

enriched carbonates. Dispersed organic matter occurs throughout the manganese ore bed, suggesting that manganese oxide reduction had occurred in pore waters (Okita et al., 1988). The isotopic composition of the Mn-carbonates reflects a mixture of seawater and dissolved inorganic carbon (DIC) produced from the respiration of organic carbon; measured rhodochrosite carbon isotopes average at -13 per mill and kutnohorite carbon isotopes covary systematically from -7 to 1.7 per mill with decreasing Mn content (Okita et al., 1988).

Neoproterozoic Iron-Manganese Santa Cruz Formation

During the extreme Neoproterozoic glaciations, significant iron-and-manganese formations were deposited on several cratons (Hoffman and Schrag, 2002; Klein, 2005). One iron-manganese deposit from Brazil was described early on as the “youngest” banded iron formation remarkably enriched in manganese, from 27% to 45% Mn by weight (Urban et al., 1992). This deposit, in the Santa Cruz Formation, has age constraints between 889 ± 44 Ma and 587 ± 7 Ma (Hasui and Almeida, 1970; Piacentini et al., 2013) and is associated with diamictites. It is located in the Jacadigo Basin, an ancient continental rift basin which records the transition from clastic basin fill to lacustrine or marine gulf deposits that include iron and manganese formation and carbonate deposits (Freitas et al., 2011). While most authors consider the outsized clasts in the manganese and iron deposits as dropstones from glacial retreat (e.g., Urban et al., 1992; Klein and Ladeira, 2004), these have also been interpreted as rift-related mass flow deposits (Freitas et al., 2011).

Despite the still-contentious regional tectonics of the Jacadigo Basin, the Santa Cruz formation has been better studied in terms of manganese and iron mineralogy. There are four separate Mn-rich intervals throughout the formation, with manganese occurring as nodules, as cements around clastic detritus, and as massive sedimentary horizons, separated by ferruginous sandstones and hematite jaspelites (Urban et al., 1992). Urban et al. identified cryptomelane, a K-bearing manganese oxide $[\text{KMn(IV)}_6\text{Mn(II)}_2\text{O}_{16}]$, as the dominant manganese mineral but also found braunite $[\text{Mn(III)}_6\text{Mn(II)}\text{O}_8\text{SiO}_4]$ and noted that braunite was replaced by cryptomelane and pyrolusite, another Mn(IV) oxide mineral $[\text{Mn(IV)}\text{O}_2]$. They found other accessory manganese minerals like lithiophorite $[\text{Mn(IV)}(\text{Al,Li})\text{O}_2(\text{OH})_2]$, manganite $[\text{Mn(III)}\text{OOH}]$, and fissure-associated metamorphic minerals such as Mn-rich amphiboles and nambulite $[\text{LiMn(II)}_4\text{Si}_5\text{O}_{14}(\text{OH})]$ (Urban et al., 1992). Later, Klein and Ladeira (2004) also described another manganese-bearing mineral from this deposit as manganoan dolomite, which they found in both the iron and manganese layers.

Hotazel Formation in South Africa

The enormous *circa* 2.2 billion-year-old manganese deposit within the Hotazel Formation in the ancient Kaapvaal Craton of South Africa is a marine sedimentary deposit consisting of interbedded manganese-rich and iron-rich rock strata (Gutzmer and Beukes, 1996). The timing of its deposition—soon after the first ‘great’ rise of oxygen—has invoked the hypothesis that the deposit might be recording interactions between the newly sourced O_2 and the iron- and manganese-rich ocean (Kirschvink et al., 2000). The Hotazel Formation was deposited in a marine setting, either in a back-arc setting with a

distant volcanic source (Beukes, 1983) or a proximal mid-ocean ridge environment (Cornell and Schütte, 1995). Jaspilitic iron formation and manganese intervals overlie the subaqueous Ongeluk basalts and then transition into the Mooidrai Formation carbonate platform, which progrades across the basin from east to west (Gutzmer and Beukes, 1996; Kirschvink et al., 2000). The three manganese ore units have been well-characterized as mineralogically braunite and kutnohorite (Gutzmer and Beukes, 1996; Tsikos et al., 2003), but highly altered and hydrothermal regions of the Hotazel Formation have exotic minerals and spectacular gemstones (Cairncross and Beukes, 2013).

Koegas Subgroup in South Africa

Also on the western side of the Kaapvaal Craton, there are older manganese deposits in the Koegas Subgroup of the Transvaal Supergroup. The Koegas strata are composed of mainly deltaic and near-shore marine siliciclastics intermixed with banded and granular iron formation, with a paleoenvironmental gradient from proximal to distal (broadly east to west). Manganese enrichments occur in clastic-starved intervals of iron formation deposition (Schröder et al., 2011; Johnson et al., 2013; Johnson et al., 2014). This Koegas Subgroup manganese deposit has been shown to pre-date the rise of oxygen and thus the manganese oxidation mechanism was inferred to be a manganese-oxidizing photosystem prior water-oxidizing photosynthesis (Johnson et al., 2013). From examining two drill cores (GEC and GTF) drilled as part of the Agouron Drilling project, the manganese in the Koegas Subgroup was determined to be hosted entirely by Mn-bearing carbonates (Johnson et al., 2013).

Kungarra Formation in Australia

A sample from the Paleoproterozoic-age Kungarra Formation in Australia represents the third highly weathered manganese location. This sample comes from a thin sedimentary bed with 7% Mn just above the lower contact with the Bolgeeda Iron Formation (Williford et al., 2011). The original mineralogy is unknown, and the age constraints on the Proterozoic deposit are similarly uncertain. The Kungarra Mn horizon appears to be younger than 2449 +/- 3 Ma (Barley et al., 1997) and older than overlying 2209 +/- 15 Ma Cheela Springs Basalt (Martin et al., 1998) and older than intruding mafic sills dated at 2208 Ma +/- 15 Ma (Müller et al., 2005). Detrital zircons in the Kungarra Formation restrict the depositional age to younger than 2420 Ma (Takehara et al., 2010). Thus, the Kungarra deposit may be a contemporary deposit to the Koegas strata, or it may be better correlated to the 2.2 Ga South African Hotazel manganese deposit. We note that the Hotazel deposit does lie above glacial deposits similar to the Kungarra Formation (Williford et al., 2011), but the Hotazel is significantly more Mn-enriched (up to 38% in well-preserved examples) than the Kungarra deposit, which only has 7.4% Mn (Williford et al., 2011), more similar to the Koegas manganese levels.

SUPPORTING FIGURES

Fig. A1: Full standard reference set for X-ray absorption spectra
X-ray absorption spectra of geologically relevant Mn mineral standards.

Fig. A2: EBSD patterns and identifications
Electron backscatter diffraction patterns measured on microscale phases within various samples to help assess mineralogy. These confirm phase identifications made from XANES, electron microscopy, and electron microprobe. These results also highlight that Mn(IV) oxides do not typically produce good diffraction patterns, in both ancient and modern samples.

Fig. A3: Molango deposit: additional examples
A. Aco section at 0m (see Okita and Shanks, 1992) with Mn concentration mapped by X-ray fluorescence (jet colors, from 0 to 2066 $\mu\text{g}/\text{cm}^2$) and Mn and Ca measured in counts per second of a subsection. B. Tetzintla mine section at 26.5m (see Okita and Shanks, 1992) with Mn concentration in jet colors from a large section and Mn and Ca concentration in a subsection (jet colors, cps). C and D. Mn redox map (Mn(II) in blue, Mn(III) in red, Mn(IV) in green) and carbonate speciation map (rhodochrosite in pink, kutnohorite in green) of Aco 0m and Tet 26.5m respectively. All Mn is Mn(II) in carbonates, but Aco 0m at ore zone is essentially all rhodochrosite while Tet 26.5m is above the ore zone and mostly comprised of kutnohorite. Point spectra (bottom right) confirm the carbonate speciation mapping. Additional bulk spectra are shown as well.

Fig. A4: Additional SEM photos of Santa Cruz Formation thin section
SEM photo of entire region mapped by X-ray spectroscopic mapping shown on left, with subsections of area highlighted in right panels showing context of small-scale SEM photos in Fig. 6. Identifications were made using electron dispersive spectrometry on the SEM.

Fig. A5 (above): Raman identification of caryopilite
Raman spectra helped constrain the identity of an unknown but common Mn-silicate observed in the Santa Cruz Formation. Two possible options from other data for this mineral were caryopilite and kellyite from electron microprobe measurements, but Raman shifts indicate only caryopilite has same peaks as the sample while kellyite is a poor match for the sample.

Fig. A6: Hotazel SEM contextual photographs
Left images show two of the regions mapped by X-ray spectroscopic imaging; the third region is shown on top right. Center top photo is of broader environment surrounding potentially intact Mn(IV) inclusion: note braunite cross-cutting CaMn carbonate nodule. Bottom center shows vein that runs through Mn carbonate with wavy lamination (on bottom left). Vein is also made of mixed CaMn carbonate. A second fibrous Mn(IV) oxide is shown on bottom right, with zoom as inset.

Fig. A7: Koegas Subgroup Supplemental Microscopy

Two more nodules from the Koegas Subgroup section are shown in addition to the one highlighted in Fig. 8. Points where wavelength-dispersive spectrometry measurements were made are shown in red and blue, with red being the points used to average the grey carbonate (manganiferous ferrous calcite) and blue points being used to average the bright-white carbonate (rhodochrosite/siderite solid solution).

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