Green rust formation controls nutrient availability in a ferruginous water column

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ABSTRACT
Iron-rich (ferruginous) conditions were a prevalent feature of the ocean throughout much of Earth’s history. The nature of elemental cycling in such settings is poorly understood, however, thus hampering reconstruction of paleoenvironmental conditions during key periods in Earth evolution. This is particularly true regarding controls on nutrient bioavailability, which is intimately linked to Earth’s oxygenation history. Elemental scavenging during precipitation of iron minerals exerts a major control on nutrient cycling in ferruginous basins, and the predictable nature of removal processes provides a mechanism for reconstructing ancient ocean chemistry. Such reconstructions depend, however, on precise knowledge of the iron minerals formed in the water column. Here, we combine mineralogical and geochemical analyses to demonstrate formation of the mixed-valence iron mineral, green rust, in ferruginous Lake Matano, Indonesia. Carbonated green rust (GR1), along with significant amounts of magnetite, forms below the chemocline via the reduction of ferrihydrite. Further, we show that uptake of dissolved nickel, a key micronutrient required for methanogenesis, is significantly enhanced during green rust formation, suggesting a major control on methane production in ancient ferruginous settings.

INTRODUCTION
The chemistry of the ocean has varied greatly through Earth’s history. In contrast to the dominantly well-oxygenated condition of the modern ocean, anoxic deep ocean conditions likely prevailed throughout much of the Precambrian (Holland, 1984; Canfield et al., 2008) and at various times in the Phanerozoic (Jenkyns, 2010). During most of the Precambrian, anoxic deep ocean waters were likely ferruginous, as indicated both by the extensive deposition of banded iron formations up until ca. 1.8 b.y. ago, and by the chemical nature of Fe enrichments in marine sediments deposited throughout much of the subsequent Proterozoic (Canfield et al., 2008; Poulton et al., 2010; Planavsky et al., 2011). For Phanerozoic oceanic anoxic events (OAEs), widespread euxinic conditions are commonly envisaged (Jenkyns, 2010). However, emerging insight suggests that redox conditions may have fluctuated between euxinic and ferruginous during Phanerozoic OAEs, leading to fundamental differences in nutrient cycling (März et al., 2008).

Freshly precipitated Fe minerals such as ferrihydrite are believed to exert a strong influence on nutrient availability under ferruginous conditions, and thus ferrihydrite has been the model mineral for reconstructing P and N bioavailability in the ancient ocean (Konhauser et al., 2009; Planavsky et al., 2010). However, while ferrihydrite commonly precipitates during dissolved Fe2+ oxidation under oxic oceanic conditions, other Fe minerals could form during anaerobic oxidation pathways (e.g., Kappler and Newman, 2004). Here, we investigate the geochemistry and mineralogy of Fe in ferruginous Lake Matano, Indonesia. Within the chemocline, Fe2+ is oxidized, generating authigenic mineral particles (Crowe et al., 2008a). Lake Matano thus represents an ideal location to explore mineralization processes and nutrient cycling under ferruginous conditions.

METHODS
Full details of sampling protocols and methods are provided in the GSA Data Repository1. Water column particulates were collected by filtering water pumped from depth through an in-line filtration device under N2. Filters were transferred to airtight vials and stored in the dark at 4 °C until analysis. Particulate Fe speciation was determined via a modified sequential extraction procedure (Poulton and Canfield, 2005). This technique operationally defines the proportion of Fe that is considered highly reactive (Feoxy) toward reductive dissolution, consisting of hydrous ferric oxides (e.g., ferrihydrite: Fe(III)HFO), reduced particulate Fe (e.g., adsorbed Fe2+, FeCO3; Fe(II)red), crystalline ferric (oxyhydr)oxides (e.g., goethite: Feo), and magnetite (Femag).

Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) were conducted on filters that were stub-mounted and gold-sputter-coated. For transmission electron microscopy (TEM), particles were deposited onto a carbon Cu TEM grid and dried at room temperature under anoxic conditions. Samples were transported in an anoxic transfer chamber and loaded onto the TEM (within a few seconds of opening the transfer chamber). For synchrotron X-ray spectroscopic analyses (µX-ray fluorescence [µXRF] and µX-ray diffraction [µXRD]), particles were mounted on Kapton™ film and sealed in Kapton™ tape under N2.

WATER COLUMN CHEMISTRY
Water column profiles are presented in Figure 1. Oxygen was undetectable (<1 µmol L−1) below 120.1 m, and dissolved Fe2+ was first detected at 120.5 m, reaching stable concentrations of ~60 µmol L−1 at 135 m over the three sampling days. Ferrihydrite (Fe(III)HFO) is formed from the oxidation of Fe2+ at the oxycline, and this accounts for the presence of Fe(III)HFO above the depth where Fe2+ first accumulates (Fig. 1B). This Fe(III) pool is reduced below the oxycline, resulting in an increase in Fe(II)red with depth and complete reduction of the Fe(III)HFO pool in the...
underlying sediments. The extractions also indicate significant concentrations of magnetite (Fe$_{magnet}$), increasing to ~15% of Fe$_{sed}$ content in deposited sediments, consistent with the saturated state of waters below 125 m with respect to magnetite (Fig. 1D). This observation is supported by magnetic studies of deposited sediments, which confirm the presence of high concentrations of nanoparticulate magnetite or titanomagnetite (Crowe et al., 2004). Crystalline ferric (oxyhydr)oxide minerals (dominantly goethite: Fe$_{ox}$) remain essentially constant with depth (Fe$_{ox}$/Fe$_{HR}$ = 0.33 ± 0.06), demonstrating that ferrihydrite (Fe(III)HFO) is the dominant precursor mineral from which the Fe(II)$_{red}$ and Fe$_{magnet}$ fractions ultimately form.

**PARTICLE MINERALOGY**

Examination of water column particulates by SEM reveals the presence of hexagonal plates of up to ~400 nm width in the upper chemocline at 118 m (Fig. 2A). Abundant nanoparticulate clusters are also observed at this depth (Fig. 2B), which, based on the chemical extraction data, likely represent ferricydrate or nanogoethite (Fig. 2B). TEM analysis shows similar hexagonal plates at 131 m (Fig. 2C) and 132.5 m (Fig. 2D). Selected area electron diffraction patterns generated from particles at 132.5 m reveal several crystalline minerals with dhkl (interplanar spacing) values (spots 1–7; Fig. 2E; Table 1) corresponding to the mixed

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**Figure 1.** Water column geochemical and saturation index (SI) profiles. A: Dissolved O$_2$ and Fe(II). B: Particulate Fe partitioning. Highly reactive Fe (Fe$_{HR}$) = Fe(II)$_{red}$ + Fe(III)$_{HFO}$ + Fe$_{ox}$ + Fe$_{magnet}$. Fe$_{sed}$ refers to each Fe fraction. Data at 135 m refer to sediment 0–0.5 cm below the sediment-water interface (214 m water depth), and Fe(II)$_{red}$ includes Fe present as sulfides (~21% of Fe$_{sed}$). C: Total dissolved inorganic carbon (ΣCO$_2$) and pH values used to calculate SI profiles. D: SI profiles for carbonated green rust (GR1), siderite, Fe$_{SAm}$ (amorphous FeS), and magnetite. Note separate scale for magnetite. Values above zero indicate saturation.

**Figure 2.** A: Scanning electron microscopy (SEM) image of hexagonal green rust (GR) from 118 m depth (upper limit of the chemocline). B: SEM image showing poorly crystalline mineral aggregates (probably ferricydrate or nanoparticulate goethite) at 118 m depth. C: Transmission electron microscopy (TEM) image of hexagonal GR from 131 m depth. D: TEM image showing hexagonal GR and nanoparticulates (possibly magnetite) at 132.5 m depth. E: Selected area electron diffraction pattern of the GR mineral from D. Numbers correspond to representative spots of different diffraction rings used to calculate the d$_{min}$ (interplanar spacing) parameters reported in Table 1. F: High-resolution TEM image of a GR particle at 132.5 m, including a schematic representation of the lattice fringes with a d-spacing of 2.793 Å characteristic of the (100) plane of a GR1 crystal. Dashed lines represent lattice fringes, while black dots correspond to Fe cations with a = 3.175 Å. G: Energy-dispersive spectrometry trace for the GR mineral at 132.5 m. The Cu signal arises from the sample grid. H: Two-dimensional μX-ray diffraction (μXRD) on charge-coupled device (CCD) image of particles at 123.5 m depth. I: One-dimensional diffraction pattern for the image shown in H. The peak at 3.82 Å is characteristic of the (hkl 006) plane of GR1. The more intense (003) plane could not be observed due to the large beam stop blocking any diffraction spots at low angles. The broad peak at ~3.4 Å is from the Kapton™ sample cover.
Fe(II)/Fe(III) hydroxide, carbonated green rust (GR1). This is confirmed by the hexagonal morphology of the crystals (Ahmed et al., 2010) and the high-resolution TEM image of the crystal viewed parallel to the (001) plane, which shows a lattice spacing of 2.793 ± 0.05 Å (Fig. 2F), characteristic of the (100) plane of GR1. The elemental composition of the same particle determined by EDS (Fig. 2G) is also consistent with GR1. Further evidence comes from the synchrotron-based µX-ray diffraction (µXRD) shown in Figure 2F. d_{hkl} values from the high-resolution TEM image of the crystal viewed parallel to the c-axis are also consistent with synthetic GR. References: 1—Drissi et al., 1995; 2—Génin et al., 2006.

NUTRIENT UPTAKE

Green rust has a strong adsorptive capacity for anions (Randall et al., 2001) and trace metals (Parmar et al., 2001), implying that formation of GR would likely exert a major control on macro- and micronutrient cycling under ferruginous conditions. We explore this by considering the role of GR in Ni cycling in Lake Matano. Nickel is a key metal cofactor in hydrogenases and methyl-coenzyme M reductase, which is used by methanogens to generate methane. Reconstructions based on Ni uptake by ferrihydrite suggest stepwise decreases in oceanic Ni concentrations through time (Konhauser et al., 2009). This may have limited rates of methanogenesis, thus depleting a major atmospheric sink for O2, and driving the oxygenation of Earth’s atmosphere (Konhauser et al., 2009). However, the scavenging efficiency of Ni by GR is particularly high, and dissolved Ni2+ is largely immobilized in response to GR formation during bacterial reduction of ferrihydrite (Parmar et al., 2001). Abiotic GR formation also effectively scavenges Ni2+ from solution through both substitution into the mineral structure and adsorption (Chaves et al., 2007). Thus, reconstruction of Ni concentrations through time requires detailed understanding of the relative roles of ferrihydrite and GR in Ni uptake under ferruginous conditions.

Nickel uptake by the most reactive Fe fraction in our extractions (i.e., ferrihydrite and GR) increases significantly with depth below the chemocline (Fig. 3A), suggesting Ni uptake as ferrihydrite is transformed to GR. This observation is supported by synchrotron µXRF analyses. Particles at 118 m (Fig. 3B) show a strong linear relationship between Ni and Fe, which likely relates to Ni associated with ferrihydrite and goethite, the dominant Fe phases at this depth (goethite is introduced to the basin as a weathering product and is a major particulate source of Ni; Crowe et al., 2008b). At 129 m, Ni-Fe associations suggest two distinct particle populations (Fig. 3C). In the dominant population, Ni correlates strongly with Fe, but with a steeper slope than the particles at 118 m, demonstrating more effective Ni uptake, consistent with the chemical extraction results (Fig. 3A). Because most of the ferrihydrite has been reduced at this depth (Fig. 1) and because magnetite is not an effective scavenger of Ni (Parmar et al., 2001), this population likely represents Ni associated with GR and goethite. The more minor population shows highly variable Ni, but no relationship with Fe. We suggest that this represents water column formation of a non-Fe-associated Ni phase, which is likely to be Ni sulfide (Crowe et al., 2008b) or possibly Ni associated with organic matter, but this is negligible relative to the Fe-associated phase.

Since the µXRF analyses include Ni associated with goethite, we use the Ni and Fe extraction data to examine the relative efficiency of dissolved Ni uptake as ferrihydrite is converted to GR, via comparison of the distribution coefficients (Kd) obtained at 118 m and 129 m (this

![Figure 3. A: Particulate Ni concentration (open circles) in the most reactive Fe fraction (comprising Fe(II)red plus Fe(III)HFO) and the ratio relative to Fe(II)red plus Fe(III)HFO (open diamonds). B: Synchrotron µXRF of particles at 118 m depth. C: Synchrotron µXRF of particles at 129 m depth. Filled circles represent particles attributed to NiS or organic matter; open circles represent Ni attributed to Fe minerals.](https://www.geoscienceworld.org/gsa/geology/article-pdf/40/7/599/3542421/599.pdf)
comparison is valid because particulate Fe concentrations are similar at these two depths:

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\frac{\text{Ni}_{\text{part}}}{\text{Fe}_{\text{part}}} = K_i \left[\text{Ni}^2+\right].
\]  

(1)

Nickel concentrations are 31 nM at 118 m and 50 nM at 129 m, suggesting that the GR-rich particles at 129 m are approximately three times more efficient at scavenging Ni than the ferrhydrite-rich particles at 118 m (see the Data Repository). It should be noted that a corresponding threefold decrease in dissolved Ni does not occur over this interval, because Ni is largely sourced from reductive dissolution of goethite at depth and the water column is not well mixed above and below the chemocline. However, this does not affect the validity of our Ni uptake comparison of the two minerals based on the calculated distribution coefficients.

**IMPLICATIONS**

The elemental control that GR exerts in ferruginous settings clearly has important implications for reconstructions of both macro- and micro-nutrients in the ancient oceans. Unlike the early Precambrian, however, dissolved silica in Lake Matano (300–420 µM; Crowe et al., 2008a) is below saturation with respect to cristobalite (0.67 mM) and amorphous silica (2.20 mM). Although the impact of higher silica concentrations on the uptake of Ni by GR is not known, silica has been shown to have a significant influence on Ni uptake by ferrhydrite (Konhauser et al., 2009), and thus our results are not currently directly applicable to reconstructions of dissolved Ni in the early Precambrian (although they are more comparable to later time periods). Our findings do, however, indicate that paleoreconstructions of dissolved nutrient concentrations based on the adsorption characteristics of ferrhydrite require re-evaluation.

Green rust is also an important precursor during magnetite formation (Sumoondur et al., 2008). Our observation that magnetite begins to form in the water column, probably via transformation from GR, suggests that some of the magnetite found in sediments deposited under ferruginous conditions is likely syngenetic in origin. Overall, we assert that the role of GR in a variety of elemental cycles is significant, and thus requires careful consideration, in studies of both modern and ancient ferruginous environments.

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