



Limited Zn and Ni mobility during simulated iron formation diagenesis



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ARTICLE INFO

Article history:

Received 24 July 2014

Received in revised form 21 February 2015

Accepted 27 February 2015

Available online 9 March 2015

Editor: Michael E. Böttcher

Keywords:

Iron formations

Zinc

Nickel

Diagenesis

Iron oxyhydroxides

Trace metal mobility

ABSTRACT

Iron formations (IF) are iron- and silica-rich chemical precipitates that were deposited during the Precambrian. Several recent studies have demonstrated how the trace metal abundances in IF can be used as proxies for the bioavailability of trace metals in ancient seawater; with the ultimate goal being to understand first-order controls on the composition of the ancient biosphere. However, the utility of IF as proxies depends on the immobilization of trace metals during diagenesis. Here, we assess the mobility of Zn and Ni from ferric oxyhydroxides (ferrihydrite) in the absence and presence of organic matter (glucose) during simulated diagenesis (170 °C, 1.2 kbar); similar to what some Precambrian IF experienced. Quantitative concentration data, coupled with X-ray diffraction analysis and electron microprobe element mapping, demonstrate that both metals are relatively immobile during simulated diagenesis. Additionally, the mechanism for initial Ni sorption is examined using X-ray adsorption spectroscopy. For the initial sorption of trace elements in abiotic ferrihydrite experiments, 93.38% Zn and 65.95% Ni were initially sorbed. In experiments utilizing biogenic ferrihydrite, 97.03% of Zn and 93.38% of Ni were initially sorbed. Following the diagenetic capsule treatments, more than 99% of Zn and more than 91.9% of Ni were retained under the varied conditions considered here. Capsule experiments suggest the strong retention of Zn and Ni following the diagenesis of either abiotic or biogenic ferrihydrite. Overall, our results indicate that paleomarine Zn and Ni concentrations are likely to be faithfully recorded in well-preserved IF deposits.

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1. Introduction

Iron formations (IF) are a key sedimentary proxy record for tracking the chemical history of seawater and reconstructing trace metal abundances in the Precambrian oceans. Many trace metals, such as zinc (Zn) and nickel (Ni), are critical components of a variety of eukaryotic and prokaryotic metalloenzymes, respectively (Williams and da Silva, 1996). As a result, reconstructing their concentrations in ancient seawater may provide crucial information about the constraints imposed on the evolving early biosphere (e.g., Dupont et al., 2010).

Iron formations contain iron (Fe) minerals with various oxidation states, such as hematite (Fe₂O₃), magnetite (Fe₃O₄) and siderite (FeCO₃), often in a cherty matrix. Additionally, some IF may contain significant Fe(II)- and/or Fe(III)-silicates, such as greenalite, stilpnomelane, minnesotaite, chamosite, riebeckite, and ferri-annite (Klein, 2005). It is important to note, however, that these are all secondary minerals,

and that the primary iron precipitates probably comprised ferric oxyhydroxides, such as ferrihydrite (Fe(OH)₃) (see Bekker et al., 2010 for review). Although the actual mechanisms of Fe(II) oxidation remain uncertain, they appear to have been biologically mediated (e.g., Posth et al., 2013a, 2014; Pecoits et al., 2015). The organic biomass deposited with Fe(OH)₃ would subsequently serve as a reductant during diagenesis and metamorphism (e.g., Perry et al., 1973; Konhauser et al., 2005; Johnson et al., 2008; Craddock and Dauphas, 2011). Fe(III) reduction by organic matter is indicated by (i) the presence of ferrous iron-containing minerals, such as magnetite (Fe₃O₄) and siderite (FeCO₃), (ii) the low organic carbon content of IF today (<0.5%; Gole and Klein, 1981), and (iii) Fe, C and O isotope compositions in Fe-carbonates associated with IF (Johnson et al., 2008; Heimann et al., 2010; Craddock and Dauphas, 2011). In addition to Fe(III) reduction coupled to organic carbon oxidation (i.e., anaerobic chemoheterotrophy), when a solution containing ferrous iron (Fe(II)) is present, redox-driven recrystallization of the primary Fe(OH)₃ minerals may cause loss of Ni to solution (Friedrich et al., 2011). Therefore, constraining the mobility of elements, such as Zn and Ni, under realistic diagenetic scenarios is critical for our interpretation of the IF record, and the implications for paleomarine systems which are drawn from it.

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There are indications from Archean IF that Ni and Zn may be relatively enriched, and therefore, available as key nutrients on the early Earth. These include relatively high Ni and Zn concentrations found in the 3.75 Ga Nuvvuagittiq IF, Canada (Mloszewska et al., 2012) and Ni enrichments considered to be primary in origin in the IF of the Mesoarchean Witwatersrand Supergroup in South Africa (Smith et al., 2013). Furthermore, compilations of both Ni and Zn in the IF record have recently been presented (Konhauser et al., 2009; Robbins et al., 2013), as well as for Zn in the shale record (Scott et al., 2013). Distribution coefficients (K_D) between seawater and $\text{Fe}(\text{OH})_3$ have been applied to the IF record to extrapolate paleomarine Ni and Zn concentrations (Konhauser et al., 2009; Robbins et al., 2013). These studies have shown dissimilar temporal trends throughout the Precambrian, with seawater Ni concentrations appearing to have decreased rapidly from ~400 to 100 nM between 2.7 and 2.5 Ga (Konhauser et al., 2009). The IF record for Ni indicates a sudden, dramatic decrease in marine Ni levels immediately prior to the Great Oxidation Event (GOE) (Konhauser et al., 2009). This crash in Ni may have been a contributing factor leading to the GOE and had significant implications for the biosphere ~2.7 Ga. However, the marine Zn reservoir appears to have remained constant with an estimated seawater concentration of ~10 nM (Robbins et al., 2013). When taken together, the IF and shale records for Zn through time effectively and independently point to near modern levels of marine Zn from the Archean through to the modern (Robbins et al., 2013; Scott et al., 2013). This is in contradiction to previous estimates based on thermodynamic models (e.g., Saito et al., 2003) and the idea that Zn would have been biolimiting to early eukaryotes and delayed their diversification (Dupont et al., 2010). Accordingly, studying the IF record provides a key window into evaluating paleomarine conditions, especially with regard to trace metal abundances. As such, understanding the potential diagenetic impacts is critical to such evaluations.

However, the extent to which Zn and Ni are mobilized when the precursor ferrihydrite underwent reduction and dehydration during diagenesis remains unclear. Our work builds on methodologies of previous simulated IF diagenesis experiments that focused on Fe-mineral transformations (Köhler et al., 2013; Posth et al., 2013b), in order to evaluate trace element mobilization during diagenesis and the robustness of previous paleomarine Zn and Ni estimates. Additionally, due to the role of organic matter as a diagenetic reductant, we consider reactions between organic carbon and Fe(III) in our diagenetic experiments; with Zn or Ni sorbed to either synthetic 2-line ferrihydrite with added glucose in the capsule or sorbed directly to biogenic ferrihydrite. We couple these results with micro X-ray diffraction (μXRD) analysis of the post-diagenetic mineralogy for selected samples and electron microprobe mapping (EMPA) of Zn and Ni to examine diagenetic trace element redistribution.

2. Methods

2.1. Simulated diagenesis experiments

Diagenetic capsule experiments on synthetic Fe oxyhydroxide precipitates (Posth et al., 2013b) demonstrate that the Fe mineralogy observed in IF today can be reproduced after incubation of synthetic 2-line ferrihydrite in the presence or absence of glucose (as a proxy for biomass). Capsules were subjected for 14 days at 170 °C and 1.2 kbar, approximately the diagenetic pressure and temperature (P–T) conditions of one of the largest and most studied iron formations on Earth, the Transvaal Supergroup BIF (Miyano and Klein, 1984; Miyano, 1987). Furthermore, these conditions mimic previous diagenetic capsule experiments (Köhler et al., 2013; Posth et al., 2013b), and therefore, facilitate a ready comparison between experimental conditions. Our experimental duration and P–T parameters are obviously much abbreviated compared to natural burial diagenesis and metamorphism that take thousands to millions of years; and are less than experienced by some IF which were subjected to amphibolite facies. However, we still

effectively capture the crucial step of the transformation of $\text{Fe}(\text{OH})_3$ to the minerals typically observed in IF, i.e., hematite (Fe_2O_3), some of which is thought to have occurred during early diagenesis at temperatures below 140 °C (Becker and Clayton, 1976).

Diagenetic experiments and analysis were performed at the University of Tübingen using similar procedures and apparatuses as per Posth et al. (2013b). Our experiments consider diagenetic mobilization of Zn and Ni from (1) 2-line ferrihydrite (Fh), as a proxy for primary Fe-oxyhydroxides formed from the chemical oxidation of Fe(II) with O_2 , and (2) biogenic ferrihydrite (BF) precipitated by a marine, Fe(II)-oxidizing phototrophic bacterial culture (*Rhodovulum iodolum*, see Wu et al., 2014; Eickhoff et al., 2014). We utilize the BF as a proxy for primary Fe-oxyhydroxides formed by Fe(II)-oxidizing bacteria. Our experiments consisted of three general steps: (i) the synthesis of Fh, either as abiotic or cell–mineral aggregates, and sorption of Ni and Zn, (ii) treatment of the trace element sorbed minerals, with or without organic material, under simulated diagenetic P–T conditions, and (iii) quantification of the concentration of Ni and Zn mobilized.

Capsules were named according to a consistent scheme, i.e., ZnFh-1, where Zn or Ni refers to the trace element sorbed, and Fh or BF indicates abiotic 2-line ferrihydrite or the biogenic cell–mineral aggregates, respectively. The numbers refer to the experimental replicates, where for the abiotic Fh experiments, replicates 1 and 2 contained glucose added as an organic carbon source, and replicates 3 and 4 lacked glucose. In experiments with BF, no glucose was added because cell material served as a source of organic carbon. In these samples, the numbers only serve to identify the respective capsule among replicates. For example, NiFh-1 indicates a capsule containing Ni sorbed to Fh with glucose, while ZnBF3 indicates Zn sorbed to BF. Capsules ZnFh-1, NiFh-3 and ZnBF1 were excluded from further analysis as the integrity of the seals were compromised during diagenetic treatments. Finally, the prefix C- denotes a control capsule (e.g., C-ZnFh1). Control capsules were set up to mirror experimental capsules but were stored in the dark in Eppendorf tubes and subjected to room temperature and pressure for the same period of time as experimental capsules.

2.1.1. Synthesis of ferrihydrite and sorption of Zn or Ni

Synthetic Fh used in abiotic experiments was prepared via methods previously described (cf. Cornell and Schwertmann, 2003) and freeze-dried prior to sorption of Ni or Zn. The marine photoferrotroph, *R. iodolum*, was cultivated in artificial seawater medium as described by Wu et al. (2014); the phosphate content was reduced to 1 mM to minimize FePO_4 precipitation, with additional NaCl added to maintain the same ionic strength as per Eickhoff (2013). FeCl_2 was added to a concentration of 10 mM, but the medium was not filtered to remove initial Fe carbonate and Fe phosphate that precipitated. The strain was then inoculated and grown at 12.82 $\mu\text{mol photons/m}^2/\text{s}^2$ until all Fe^{2+} was oxidized, as determined by the ferrozine assay (Stookey, 1970). The cell–mineral aggregates were then collected by centrifugation and washed four times with the growth medium lacking bicarbonate buffer and harvested by centrifugation at 4000 rpm for 10 min before freeze-drying.

Sorption of Zn and Ni to both Fh and BF was accomplished by introducing ~50 μM of Zn or Ni (from Merck ICP-MS standards) in the presence of 1 g/L Fh or BF in solution prepared to seawater ionic strength with 0.5 M NaNO_3 and buffered by 0.1 M H_3BO_3 to a pH value of 8. Sorption occurred over a 24-hour period, before the solution was passed through a 0.2 μm Millipore filter, and the solid particles were recovered. Filtrates were analyzed for Zn and Ni by inductively coupled plasma optical emission spectroscopy (ICP-OES), on a Perkin Elmer Optima 5300 at the University of Tübingen, to determine the amount of Zn or Ni lost due to sorption. For ICP-OES measurements, the percent relative standard deviation (%RSD) was better than $\pm 8\%$ and $\pm 5\%$ for Zn and Ni, respectively. Calculations of the amount of Zn and Ni added normalized to the weight of solid particles, as well as the percentage of Zn or Ni sorbed, are provided in Table 1. In all cases the majority of Zn and Ni

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