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Fe isotope and trace element geochemistry of the Neoproterozoic syn-glacial Rapitan iron formation

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ABSTRACT

We have measured the iron isotope compositions and trace element concentrations of a suite of iron formation (IF) samples from the Neoproterozoic Rapitan Group, which was deposited during the older of two glacial episodes recorded in the Windermere Supergroup of the northern Canadian Cordillera. Like most other Neoproterozoic examples, iron in the Rapitan IF resides almost exclusively as hematite. This mineralogical simplicity compared to Archean and Paleoproterozoic banded iron formations is attributed to a limited supply of organic carbon to the Rapitan glacial ocean that inhibited diagenetic production of reduced iron phases. Sedimentological considerations indicate that the Rapitan IF was deposited during a rise in relative sea level related to a period of glacial advance and isostatic subsidence. Trace element data, including rare earth element plus yttrium (REE + Y) patterns, suggest an anoxic deep ocean dominated by low-temperature hydrothermal input and capped by a weakly oxic surface ocean. The iron isotope data show a trend of increasing δ^{57}Fe (versus IRMM-14) up-section from ~−0.7‰ to 1.2‰, corresponding to a shift from a muddy IF facies to a dominantly jaspilitic IF facies. This distinct isotopic pattern likely records a steep isotopic gradient across the iron chemocline in Rapitan seawater.

1. Introduction

The cycling of iron is of major interest in the study of the Earth system because of its abundance in rock-forming minerals, sensitivity to redox, role in microbial metabolism, and function as a micronutrient (Anbar, 2004; Beard et al., 2003a; Johnson et al., 2008a). Iron isotopes have become a mainstream tool in studying iron cycling due to the large isotopic fractionations attending redox transformations in the near surface environment. A natural application of iron isotope geochemistry is to ancient sedimentary banded-iron formation (BIF). A common theme among studies of Archean and Paleoproterozoic BIFs is the extraordinary variability in iron isotope compositions, from the stratigraphic (e.g. Beard et al., 2003a; Czaja et al., 2010; Heimann et al., 2010; Johnson et al., 2008b; Tsikos et al., 2010) to the mineral (2008b; Frost et al., 2007, Johnson et al., 2003) and micro scale (Steinhoefel et al., 2009, 2010). Although these variations are ultimately attributable to the large fractionation resulting from reduction and oxidation of iron and the isotopic differences between mineral phases, the models to account for the iron isotope patterns in ancient BIFs are diverse and controversial (Anbar and Rouxel, 2007; Johnson et al., 2008a).

Neoproterozoic iron formations (IF) present a unique opportunity to understand processes responsible for iron isotopic variations during deposition of iron-rich chemical precipitates. In contrast to some Archean–Paleoproterozoic BIFs in which iron occurs as both Fe^{2+} and Fe^{3+} in a range of different minerals, iron occurs almost exclusively in hematite in little-metamorphosed Neoproterozoic IFs (Klein and Beukes, 1993). Therefore, primary isotope signatures are easier to obtain and their interpretation is unhindered by complex mineralogy and diagenesis. Furthermore, the Neoproterozoic IFs are associated with episodes of global glaciation, and hence models to account for their iron isotope composition have implications for the chemistry of the glacial ocean. Here we report new iron isotope and trace element data from a section of the Rapitan IF in the Mackenzie Mountains, northwest Canada, and present a new model to account for large iron isotope variations in IFs.

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2. Background

2.1. Neoproterozoic iron formations

Whereas the precise mechanisms involved in the precipitation of iron minerals in BIFs are still debated (e.g. Konhauser et al., 2002), it is widely accepted that oxide facies BIFs record precipitation of precursor, poorly crystalline ferric oxyhydroxide (Fe-OH) minerals across a redoxcline, followed by deposition, diagenetic dewatering, and conversion to hematite (Beukes et al., 1990; Krapez et al., 2003). In turn, mixed valence and reduced iron phases in unmetamorphosed BIFs are dominantly diagenetic in origin and coupled to the organic carbon flux, whereby dissimilatory iron reduction (DIR) produces reactive ferrous iron and alkalinity (Beukes and Gutzmer, 2008; Johnson et al., 2008b). The widespread deposition of BIFs in the late Archean and Paleoproterozoic has been cited as evidence for the progressive oxidation of the earth surface environment (Cloud, 1973; Holland, 1984; Kasting, 1993), but an alternative explanation is that their disappearance around 1.8 Ga represents the spread of deep ocean euxinia rather than total oxidation of the oceans (Canfield, 1998).

Iron formation returns as a minor but important part of the Neoproterozoic (1000–542 Ma) stratigraphic record. Neoproterozoic IF is distinct from Archean–Paleoproterozoic BIFs insofar as it typically lacks their characteristic mesoscale chert banding. Nevertheless, it implies a reprise of anoxic, ferrous deep-oceans. An association between the Neoproterozoic IFs and glaciation is a central component of the snowball Earth model (Hoffman et al., 1998; Kirschvink, 1992; Klein and Beukes, 1993), with an ice-covered ocean allowing hydrothermal iron to accumulate in isolation from major sources of oxidants. Iron accumulation may have been enhanced by increased iron concentrations in hydrothermal fluids due to low seawater sulfate concentrations and glacioeustatic depressurization of mid-ocean ridges (Kump and Seyfried, 2005). Glacial erosion of thick paleosols may have increased iron delivery to the ocean during and after glaciation (Swanson-Hysell et al., 2010). Sulfate delivery in runoff had also been declining through the loss of pyrite being subducted into the mantle during the previous billion years of chronic sulfidic deepwater (Canfield, 2004). All of these factors likely contributed to late Neoproterozoic iron-rich deepwater anoxia (Canfield et al., 2008). In the classic model, these IFs were precipitated during upwelling of cold, deep waters and mixing with surface waters at the onset of ice melting (Klein and Beukes, 1993). Alternatively, IF could have been deposited during a global glaciation wherever oxic subglacial meltwater plumes entered ferrous waters (Hoffman, 2005).

2.2. The Rapitan Group iron formation

The Rapitan Group (Eisbacher, 1978) is the older of two discrete glacial units in the lower Windermere Supergroup of the northern Canadian Cordillera (Aitken, 1982, 1991; Eisbacher, 1985; Young, 1976) (Fig. 1). Its age is constrained by a U–Pb zircon date of 716.5 ± 0.2 on an ash bed in the basal Rapitan-equivalent glacial member of the upper Mount Harper Group in the western Yukon Territory (Macdonald et al., 2010). Reliable paleomagnetic data from dated dikes, sills and lavas of the Franklin large igneous province, coeval with the upper Mount Harper Group (Denyszyn et al., 2009), place our sample site at 18° ± 3° north paleolatitude at the onset of Rapitan glaciation. The Rapitan Group is widely regarded to be coeval with iron formation-hosting glacial deposits in southern Africa and South Australia (e.g. Bell and Jefferson, 1987; Eisbacher, 1985; Young, 1992), and was likely deposited during the first of two global glacial epochs in the Neoproterozoic Era.

Rapitan Group sediments outcrop in a fold-and-thrust belt in the Mackenzie Mountains in northwest Canada (Fig. 1a). They fill a complex of north to northeast-trending grabens that deepen toward the central part of the Mackenzie Mountains (Eisbacher, 1985; Yeo, 1986). Rifting followed the eruption of flood basalt at ca. 780 Ma (Harlan, et al., 2003) onto the Little Dal Group carbonate platform (Aitken and Long, 1978) and accompanied deposition of mixed clastics, carbonates and evaporites of the Coates Lake Group (Aitken, 1982; Jefferson and Ruelle, 1986). Basal Rapitan strata unconformably overlie the Coates Lake Group (Aitken, 1982; Eisbacher, 1985; Jefferson and Ruelle, 1986).

The Rapitan Group consists of three formations (Fig. 1c), all displaying evidence of glacial processes (Eisbacher, 1981; Klein and Beukes, 1993; Yeo, 1981). The Mount Berg Formation at the base is best developed in the southeastern part of the belt where it exceeds 300 m in thickness and consists predominantly of massive diamictite with intrabasinal carbonate clasts (Eisbacher, 1981; Yeo, 1981). The 300–600 m-thick Sayunei Formation interfingers with the Mount Berg Formation (where it is present) and comprises mostly ferruginous, maroon- to brick-colored turbiditic siltstone, with lesser amounts of sandstone and conglomerate (Yeo, 1981). Lonestones of carbonate, basalt and rare extrabasinal granitoid 'till pellets' and resedimented diamictite increase in abundance upsection. The Shezal Formation is 400–600 m thick and consists of decameter-scale units of massive or foliated, mud- or wacke-supported, boulder diamictite, separated by thinner layers of clay, silt, and sand (Fig. 1).

In most sections, the uppermost Sayunei Formation is marked by a decrease in grain size and turbidite bed-thickness and abundance, interpreted to correspond to a relative rise in sea level (Fig. 3; Klein and Beukes, 1993), an expected consequence of isostatic loading by advancing ice sheets. Iron-formation of variable thickness is concentrated in this transition (Figs. 1–3). Locally, it contains dropstones, prominent among which are extrabasinal quartz-monzonite (Fig. 2b). Where thickest, the IF occurs as multiple iron-rich zones over an interval of up to 150 m in the upper Sayunei and lower Shezal formations (Yeo, 1981). Regionally, the IF consists of a variety of facies that include hematitic siltstone and mudstone and finely banded, nodular, or peloidal hematite–jaspilite (Klein and Beukes, 1993; Yeo, 1986). In the section sampled for this study, near Hayhook Lake (Fig. 1c), the BIF is restricted to a single 16.4 m-thick horizon that can be separated into a lower zone consisting of fine hematitic mudstone and siltstone turbidites (hematitic mud/silt facies; Fig. 2c) and an upper zone comprising predominantly fine hematite and jaspilite laminae (hematite–jaspilite facies; Fig. 2d) that are commonly convoluted and interbedded with subordinate hematitic mudstone (Fig. 3). The iron formation is truncated disconformably by the basal massive diamictite of the Shezal Formation (Fig. 2a), which contains Sayunei-derived debris including rounded clasts of iron formation (Fig. 3).

The Rapitan IF is composed primarily of hematite and quartz, with minor abundances of authigenic calcite, dolomite and detrital minerals in the hematitic silt/mudstone facies (Table 1), and chlorite. Organic matter is sparse to absent. Laminations in the hematitic mud/silt facies are defined by the relative concentration or grain size of hematite (Klein and Beukes, 1993); subtle grading in coarser laminae is apparent. In the hematite–jaspilite facies, laminations are defined by alternating layers of almost pure hematite and jasper. Nodular IF, which is a prominent facies in other sections of the Rapitan IF (Klein and Beukes, 1993) is absent at Hayhook Lake. Minor occurrence of iron silicates within the IF attests to the low grade of metamorphism these rocks have experienced (Yeo, 1986).

3. Methods

Twelve hand specimens spanning the 16.4 m-thick IF interval were collected from a stratigraphic section of the Sayunei and Shezal formations near Hayhook Lake in the central Rapitan basin (Fig. 1). All samples were slabbed for petrographic analysis, and ~50 g portions of unweathered bulk rock spanning multiple laminations were ground in an agate mortar to a fine powder, aliquots of which were used for X-ray