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## The nature of Mesoarchaean seawater and continental weathering in 2.85 Ga banded iron formation, Slave craton, NW Canada

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## Abstract

Banded iron formations (BIF) have been extensively used as proxies to infer the chemical composition of ancient bulk seawater. However, their proximity to ancient crust suggests that they might also be used to reveal the composition of emergent continental landmass at the time of their deposition. Here we use the combination of geochemistry and Sm-Nd isotopes on a layer-by-layer basis to interpret the relative contributions of hydrothermal, hydrogenous and terrestrial input to one of the oldest documented Superior-type BIF in the world. The ~2.85 Ga Central Slave Cover Group BIF is deposited within a rift basin related to a continental margin and is found associated with basement gneisses, as well as shoreline and shallow-shelf type facies, such as fuchsitic quartizte and pebble-to-cobble conglomerate, that confirm a near-shore depositional setting for the BIF. The BIF ranges from a pure chemical oxide (magnetite)-silicate (grunerite + actinolite) sediment with low Al<sub>2</sub>O<sub>3</sub> (<1 wt.%) into a mixture of chemical and clastic sediment characterized by higher Al<sub>2</sub>O<sub>3</sub> ( $\leq$ 10 wt.%) and the occurrence of ferro-hornblende, biotite and garnet. The silica bands have low trace metal content (e.g., Ni), low  $\sum REE$  (average of 6 ppm) and a shale-normalized rare earth and yttrium (REY) pattern that is HREE-to-LREE enriched with (Pr/Yb)<sub>SN</sub> values reaching < 0.2. The iron bands are more enriched, with average  $\sum \text{REE}$  of 26 and with a more uniform and less fractionated REY pattern (average  $(Pr/Yb)_{SN}$  of 0.5). During active rifting of the basement, excess of Eu<sup>2+</sup> impacted the basin yielding seawater with Eu anomalies [(Eu/Eu<sup>\*</sup>)<sub>SN</sub>] as high as 3.85 (average 2.75), larger than similarly-aged BIF. High-resolution geochemistry shows that there is more silica (19.4 wt.% SiO<sub>2</sub>) in the iron bands than iron (8.7 wt.% Fe<sub>2</sub>O<sub>3</sub>) in the silica bands, implying that dissolved Fe<sup>2+</sup> came to the BIF site in pulses and that silica likely represents background deposition. Consistently radiogenic  $\varepsilon_{Nd}(t)$  values for the iron bands (average +1.7) show that the dissolved REY in the source water during ferric iron precipitation was provided by submarine hydrothermal fluids with relatively uniform <sup>143</sup>Nd/<sup>144</sup>Nd. The silica bands, by contrast, reveal high variation in seawater  ${}^{143}$ Nd/ ${}^{144}$ Nd as evident from the bimodal  $\varepsilon_{Nd}(t)$  distribution with one segment exhibiting negative  $\varepsilon_{Nd}(t)$  values averaging -1.1 and another with positive  $\varepsilon_{Nd}(t)$  values averaging +2.5. This suggests input of dissolved REY into the upper seawater from weathering of isotopically different crustal components in the source region. Collectively, we speculate that the low REY in the upper seawater and the overall low Ni content implies a highly weathered crustal surface that was unable to contribute a significant dissolved load to the shelf environment. © 2016 Elsevier Ltd. All rights reserved.

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## **1. INTRODUCTION**

Banded iron formations (BIF) are iron-rich (15-40 wt. %) and siliceous (40-60 wt.%) sedimentary deposits that precipitated from seawater throughout much of the Archaean. The mineralogy of Archaean BIF from the best-preserved successions is remarkably uniform, comprising mostly microcrystalline quartz (chert), magnetite, hematite, and Fe-rich silicate minerals (etc., actinolite, grunerite, hornblende). They typically contain low concentrations of  $Al_2O_3$  (<1 wt.%) and incompatible elements (Ti  $\leq$  50 ppm, Zr, Th, Nb, Hf and Sc  $\leq$  20 ppm), which indicates low input of epiclastic material (e.g., Trendall, 2002; Pickard et al., 2004). Based on their shalenormalized rare earth element and yttrium (REY) patterns, it is also now generally accepted that BIF captured the composition of bulk seawater. This observation has allowed for the chemical composition of BIF to be used as a proxy not only for the source of solutes to the Precambrian oceans (e.g., Jacobsen and Pimentel-Klose, 1988; Derry and Jacobsen, 1990; Danielson et al., 1992; Alibert and McCulloch, 1993; Bau and Möller, 1993; Bau and Dulski, 1999; Hamade et al., 2003; Sreenivas and Murakami, 2005; Frei and Polat, 2007; Haugaard et al., 2016), but also as a means to estimate the bulk composition and redoxstructure of ancient seawater (e.g., Bjerrum and Canfield, 2002; Ohmoto et al., 2006; Konhauser et al., 2009).

Some of the most compelling research into the environmental conditions of BIF deposition comes from the measurement of samarium (Sm) and neodymium (Nd) because: (1) they share similar chemical affinities which makes the Sm/Nd ratio highly resistance towards disturbances by different geological processes (e.g., metamorsubmarine hydrothermal alteration phism, and continental weathering), and (2) Nd is a non-conservative element with a residence time in the oceans of 300-1000 years (much shorter than the mixing time for the oceans) making it useful to track small timescale variations (e.g., Piepgras and Wasserburg, 1987; Elderfield et al., 1990; Andersson et al., 1992). BIF older than ca. 2.7 Ga generally have relatively homogenous  $\varepsilon_{Nd}(t)$  of +1 to +2 that are typical of deep-waters dominated by hydrothermal fluids (Alexander et al., 2009). Deviation towards more negative values down to  $\varepsilon_{Nd}(t)$  of -3 indicate the influence of older terrestrial sources in BIF deposition (e.g., Miller and O'Nions, 1985; Alexander et al., 2008).

Recent studies, however, have shown that some BIF do not conform to the canonical view of chemical sediments reflecting bulk ocean water conditions. For instance, Alexander et al. (2008) demonstrated that the 2.9 Ga Pongola BIF in South Africa was deposited in a near-shore environment with interbedded and intermixed epiclastic detritus sourced from emergent continental crustal sources. Similarly, Haugaard et al. (2013) showed the existence of shaley-BIF with mixed chemical and siliciclastic components within the 2.9 Ga Itilliarsuk BIF in West Greenland. Collectively, the  $\varepsilon_{Nd}(t)$  values in both BIF units were partly inherited by local-to-regional crustal sources. Some BIF, therefore, reflect local seawater variations as a function of the specific tectonic and depositional environment. In this regard, one of the main issues pertaining to using BIF as palaeo-proxies is that much of the existing dataset is based on bulk rock analyses, meaning that short-term trends in the chemical fabric of the sedimentary rock record are not fully captured.

In this work, we present new field, petrologic, and geochemical data from the ca. 2.85 Ga BIF from the Central Slave Cover Group (CSCG), Slave craton, northwestern Canada that was initially described by Bleeker et al. (1999a). The BIF are deposited alongside shelf- and shoreline-type deposits, such as quartz pebbleconglomerate and fuchsitic quartzite (Padgham and Fyson, 1992), and indicate that the BIF was deposited in a continental margin setting during attenuation and drowning of the basement (Mueller et al., 2005; Bleeker and Hall, 2007). This novelty allows for a determination of the relative importance of hydrothermal versus continental sourcing of the elemental constituents during the time span of deposition. On a layer-by-layer basis, we demonstrate that these BIF are complex sedimentary units that provide important clues about internal seawater variations and the nature of local-to-regional landmasses.

## 2. THE SLAVE CRATON: ANCIENT BASEMENT AND AUTOCHTHONOUS COVER

The Slave craton constitutes ~200,000 km<sup>2</sup> of the northwestern part of the Canadian Shield (Fig. 1A) and has a preserved Archaean rock record that extends deep in time from the earliest Eoarchaean to the very late Neoarchaean. In the south and central Slave craton, the Central Slave Basement Complex (CSBC; Bleeker et al., 1999a) is composed of a variety of polymetamorphic gneiss assemblages ranging from tonalitic, dioritic to granodioritic in composition, some of which are migmatized and mylonitized (Isachsen and Bowring, 1994, 1997; Bleeker et al., 1999a, b; Ketchum et al., 2004; Reimink et al., 2014). Apart from the minor and ancient Eoarchaean tonalitic to gabbroic Acasta gneisses, the majority of the CSBC ranges between 3.3 and 2.9 Ga (Bleeker et al., 1999b; Ketchum et al., 2004).

The basement gneisses are truncated by a ca. 2.9-2.8 Ga regional unconformity that marks the depositional onset of an autochtonous supracrustal package, the Central Slave Cover Group (CSCG; Bleeker et al., 1999a; Fig. 1B). The CSCG is not continuously preserved but individual exposures can be stratigraphically correlated over distances of hundreds to a thousand kilometers throughout the central and western part of the Slave craton (Fig. 1A; Roscoe, 1990; Bleeker et al., 1999a; Mueller and Pickett, 2005; Mueller et al., 2005). Each stratigraphic section is slightly different than the next, but common components are fuchsitic quartzite  $\pm$  quartz-pebble conglomerate  $\pm$  semi-pelite  $\pm$  BIF  $\pm$  rare ultramatic sills (Fig. 1B). The fuchsitic quartzites are the most common and identifiable rock-type, and generally it is only 2-200 m thick (Roscoe, 1990; Bleeker et al., 1999a; Mueller et al., 2005) The term quartzite is used to represent a mixture of mostly clean, white to white-green weathered, metamorphosed and recrystallized quartz arenite (as used in Mueller and Pickett, 2005; Mueller et al., 2005) and arenite that locally contains detrital chromite.

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