The composition of Earth's oldest iron formations: The Nuvvuagittuq Supracrustal Belt (Québec, Canada)

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A B S T R A C T

The composition of iron formations in the ≥3.75 Ga yr old Nuvvuagittuq Supracrustal Belt in northern Québec provides a proxy for seawater composition of the Eoarchean, and perhaps Hadean oceans, as well as constraints on the types of nutrients available to Earth's earliest life forms. Integrated petrologic and geochemical relationships, mapped between mineral phases in thin section and whole-rock chemistry, provide a framework for interpreting bulk and micro-scale variations in these chemical sedimentary precipitates. Results show that there are two distinct chemical sedimentary units in the Nuvvuagittuq belt: i) a banded iron formation (BIF) consisting of alternating micro-bands of magnetite, Ca–Mg–Fe-silicates and quartz, and ii) a more silicate-rich (Fe-poor) unit, the banded silicate-formation (BSF), of alternating micro-bands of quartz and Ca–Mg–Fe silicates. Precursor BIF and BSF deposits were likely layered amorphous silica and ferric-oxyhydroxides, fine-grained carbonate oozes and/or Ca–Mg–Fe rich silicate gels deposited in a marine setting. Low Al₂O₃, TiO₂, and HFSE concentrations show that they are relatively detritus-free, with distinctively seawater-like REE + Y profiles and consistently positive Eu anomalies. These features suggest that the rocks preserved their seawater-like compositions despite metamorphic overprinting. The most significant trace elements in the sediments are Ni and Zn. Experimentally-derived partitioning coefficients show that Ni was enriched in Eoarchean seawater as compared to today (up to 300 nM), while Zn was fairly similar (up to 20 nM). Compositional resemblances between the Nuvvuagittuq sediments and those documented in the ca. 3.8 Ga Isua supracrustals (West Greenland) provide a plausible case that global ocean processes – in terms of trace metal abundances – had reached steady-state by the Eoarchean.

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1. Introduction

Banded iron formations (BIF) are iron- and silica-rich marine, chemical sedimentary precipitates that were deposited with some hiatuses throughout the Archean and much of the Proterozoic. Because the precursor minerals of these rocks precipitated directly out of seawater, the primary ferric-oxyhydroxide minerals that comprised the initial sediments retained chemical signatures of the seawater. In this regard, BIF compositions have long been used as proxies for the compositional evolution of seawater over time (e.g. Bau and Dulski, 1996; Bolhar et al., 2004; Jacobsen and Pimentel-Klose, 1988), and ultimately for the types of nutrients that were available to ancient planktonic life (e.g. Bjerrum and Canfield, 2002; Konhauser et al., 2009). For instance, based on documented P:Fe ratios in 3.2 to 1.9 Ga BIF, Bjerrum and Canfield (2002) proposed that the Archean–Paleoproterozoic oceans may have been phosphate limited. This condition could have hindered initial cyanobacterial phytoplanktonic growth, and consequently delayed the rise of oxygen until the demise of Fe(II)-rich marine waters that accompanied the decline of BIF deposition in the Paleoproterozoic. Konhauser et al. (2009) used Ni/Fe ratios to infer a trace metal crisis starting at around 2.7 Ga for methanogenic bacteria, and proposed that the subsequent decline of methanogens aided in the rise of atmospheric oxygen. It is noteworthy that the metabolic trace metal requirements of ancient microbes could have been established by their bioavailability in the ancient oceans, and that a record of this is preserved in the genomes of their modern descendants (daSilva and Williams, 1991; Saito et al., 2003).

Although banded iron formations formed throughout much of the Precambrian, the paucity of pre-3.5 Ga supracrustal rocks severely hampers the use of BIFs for discerning compositional changes in Earth's earliest oceans and hence of the nature of habitats for putative early life forms. By far the most intensely studied Eoarchean BIFs are

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from the Isua Supracrustal Belt (ISB), as well as various BIF enclaves (termed the Akilia association) scattered throughout the ca. 3000 km² Itsaq Gneiss Complex in West Greenland (Nutman et al., 1996). Much of the published work from these complex BSFs has focused on describing (and debating) their origins (e.g., Cates and Mojzsis, 2006; Dauphas et al., 2004; Dauphas et al., 2007b; Dynek and Klein, 1988; Frei and Polat, 2007; Manning et al., 2006; Polat and Frei, 2005; Whitehouse and Fedo, 2007). The recent discovery of well-preserved, banded quartz–magnetite units of BIF protolith, and another composed of banded quartz and Fe-silicate minerals (hereafter termed BSF), in the Nuvvuagittuq Supracrustal Belt in Northern Québec provides an excellent opportunity to study the early oceans especially in the context of global environmental conditions which led to BIF sedimentation. The belt is at least 3.75 Ga in age, and perhaps as old as 4.28 Ga (cf. Cates and Mojzsis, 2007, 2009; O'Neil et al. 2008, 2011—see Section 2).

While research on the Nuvvuagittuq rocks is still in its infancy, preliminary chemical and isotopic work has conclusively shown that the BIF, and a representative portion of the BSF, possess many distinguishing characteristics of rocks of chemical sedimentary protolith (Cates and Mojzsis, 2007; Dauphas et al., 2007a, 2007b; O'Neil et al., 2007). Bulk chemical analyses further indicate that these rocks retain seawater-like rare earth element and yttrium (REE + Y) signatures such as concave-upward profiles, positive La and Eu anomalies and superchondritic Y/Ho ratios (Bolhar et al. 2004; Cates and Mojzsis, 2007; Dauphas et al. 2007a; O'Neil et al. 2007).

A currently acknowledged possibility for the origins of the Fe-oxide layers in BIF is that they were a by-product of microbial metabolism (Konhauser et al., 2002). Dauphas et al. (2007a) pointed out that the relatively heavy Fe-isotope compositions of Nuvvuagittuq ferruginous quartz–amphibole rocks of chemical sedimentary protolith can be most simply explained by a microbial oxygenic or anoxygenic photosynthetic origin. If correct, this underscores the notion that microbial life was already established at the beginning of anoxygenic photosynthetic origin. If correct, this underscores the notion that microbial life was already established at the beginning of pre-3.5 Ga seawater could not develop the heavy Fe-isotope compositions of Nuvvuagittuq ferruginous quartz–amphibole rocks of chemical sedimentary protolith, including banded iron formation (Fig. 1). The amphibolite unit is the most voluminous of the three main rock types. It has a generally basaltic to andesitic composition and locally preserves millimeter- to meter-scale compositional layering, and has been interpreted to be an altered mafic volcanic pyroclastic deposit (O'Neil et al., 2011). The progression from chlorite–epidote-bearing rocks and garnet-free cummingtonite amphibolites in the western portion of the belt, to garnet-bearing cummingtonite amphibolites in the east suggests a map-scale metamorphic gradient from upper-greenschist-facies in the west to upper-amphibolite facies in the east (O'Neil et al., 2007).

The amphibolite unit can be divided into three stratigraphically superimposed, geochemically distinct groups (O'Neil et al., 2011) with the iron formation units positioned between two of these groups. The group stratigraphically below these units has high Ti content, low Al/Ti ratios and relatively flat REE profiles, whereas the two groups above are characterized by low Ti contents and higher Al/Ti ratios. The group directly above has the highest Al/Ti ratios and displays distinct U-shape REE profiles with low Ta and Nb. The group at top of the sequence also has large negative Ta and Nb anomalies, but is characterized by enriched LREE profiles. The transition between low Al/high Ti amphibolites to the high Al/low Ti amphibolites is interpreted by O'Neil et al. (2011) to represent a transition from rocks resembling those of oceanic tholeiites to rocks sharing chemical features typically observed in a volcanic island arc setting. Regardless of tectonic setting, the iron formation units occur stratigraphically at the transition between the geochemically distinct amphibolites.

The 5–30 meter wide BIF is composed of alternating bands of magnetite and greunerite with variable amounts of, locally, finely layered quartz (0.1–0.3 cm), which outcrops continuously along the western limb of the synform and discontinuously along the eastern limb (Fig. 1). Positioned ~50 m up section from this unit is a fine-to-coarsely-banded unit (0.1–1 cm) of alternating Fe–Ca–Mg silicate (greunerite, actinolite and pyroxene) and quartz bands (Fig. 1). It can be traced continuously down the western limb of the fold and discontinuously around to the southern tip of the belt. This unit grades...
into a 100 m-wide cherty unit composed of recrystallized quartz with minor amounts of disseminated pyrite, on the western limb of the fold (O’Neil et al., 2007). The repetitive sequence of these units on either limb of the fold suggests that some of the original volcano-sedimentary succession of the belt has been preserved despite numerous post-depositional disturbances.

3. Methods

Polished thin sections of samples were prepared and used for reflected and transmitted light microscopy in order to establish the mineralogy and petrology. Nine representative samples of the BIF and BSF were selected for bulk trace element analysis; rocks were broken and sub-sampled to avoid secondary veining and strongly recrystallized areas. Samples were crushed in a tungsten-carbide mill and the rock powder submitted for bulk XRF and ICP-MS analysis on a PerkinElmer Elan6000 quadrupole inductively coupled plasma mass spectrometer (Quad-ICP-MS) at the University of Alberta (Edmonton, Canada). Mineral-phase chemistry of major (K, Na, Si, Fe, P, Mg, Al, Mn) elements was determined and backscattered-electron images as well as elemental maps produced on the University of Alberta’s JEOL 900 electron microprobe. Analytical conditions used on the electron microprobe were: beam diameter (3 μm); voltage (20 kV); current (20 nA); and concentrations were calculated using ZAF matrix correction. Mineral-phase trace element chemistry was analyzed using a Quad-ICP-MS coupled to a laser ablation system with the following analytical conditions: PR power (1200 W); peak hopping acquisition (50 ms dwell time); spot diameter (between 60 μm and 100 μm depending on grain size); repetition rate (5 Hz); and energy density (~13 J/cm²). The international glass standard NIST SRM 610 was used to calibrate the instrument and Fe concentrations from the electron microprobe were used as an internal standard for each analysis. GLITTER© (XP version, New Wave Research) software was used for data reduction. Bulk XRF analyses were carried out at Activation Laboratories Ltd. (Ancaster, Ontario).

4. Results

4.1. Petrography and mineral chemistry

Rocks of chemical sedimentary protolith in the Nuvvuagittuq belt preserve an upper amphibolite (locally to lower granulite facies) metamorphic assemblages, are coarsely crystalline and are well-banded where silica mobility did not result in complete recrystallization. The BSF consists of fine to coarse (>0.1 mm-wide) bands of quartz which alternate with bands consisting of grunerite [(Fe,Mg)7(Si,Al)8O22], augite [Ca(Fe,Mg)(Si,Al)2O6], and actinolite[(Ca,Na,Mn)2(Fe,Mg)5(Si,Al)8O22] (Fig. 2A). Actinolite, which was only observed in the BSF, typically occurs as lamellae within a grunerite host. Magnetite (Fe3O4) is scattered throughout these Fe-bearing silicate layers, while calcite, pyrite and anorthite (in one sample only, 090709–3) occur as accessory phases (together making up ~2 modal % of the rock). The BIF ranges from fine (~300 μm to 0.3 cm-thick) alternating bands of quartz, magnetite and grunerite (~70 μm-wide), to the more common assemblage of fine, alternating bands of grunerite and magnetite with quartz and augite scattered throughout (Fig. 2B,C). The occurrence of pyroxene in these samples corroborates with observations in previously published work on the Nuvvuagittuq chemical sediments (Cates and Mojzsis, 2007; Dauphas et al., 2007a; David et al., 2009). A summary of mineral geochemical analyses are presented in Table 1, and full analyses are available in the Supplementary Data.

4.1.1. Magnetite

Magnetite is the main Fe-oxide mineral component of the Nuvvuagittuq chemical sediments, occurring as a dominant constituent of the BIF (~40 modal %) and as a minor constituent of the BSF (<10 modal %). In both units, magnetite occurs as anhedral to subhedral grains typically between 50 and 200 μm in size. Magnetite in the BSF occurs as individual grains typically associated with the grunerite, and are found both in grain-boundary contact with and as inclusions in grains of magnetite, quartz and augite (Fig. 2A,D). In contrast, magnetite in the BIF comprises defined Fe-oxide bands that range in size from 250 μm to...
0.3 cm thick, occurring both as individual grains and as large aggregates. Smaller individual magnetite grains are typically found as inclusions within grains of grunerite, quartz and clinopyroxene (Fig. 2).

Chemical analyses of magnetite in both BIF and BSF show that they are overwhelmingly iron-rich (FeO_total 93–94 wt.%) with BIF magnetite slightly more Al₂O₃ and SiO₂-rich (~0.5 and 0.2 wt.% vs. ~0.1 wt.%). In BSF magnetite, Cr, Ni and V occur in the highest concentrations of all the trace elements while in BIF magnetite Ni and Zn occur in the highest concentrations, and average concentrations of all other trace elements are below 35 ppm. For most trace metals BIF magnetite is also enriched compared to BSF magnetite (Table 1, Fig. 3A,B).

### 4.1.2. Quartz

Quartz makes up to 60 modal% of the BSF and 20–60 modal% of the BIF (Fig. 2A–C). Quartz in the BSF occurs as bands and as individual grains within grunerite bands, and is often found as inclusions within grains of grunerite and clinopyroxene. Much of the quartz has a granoblastic-texture, suggestive of static recrystallization. In some BSF samples the quartz is large and has an anhedral habit, extending to over 0.5 cm in size. This larger quartz component shows signs of deformation such as the presence of subgrains, undulose extinction and sutured grain margins. In most of the BSF samples, quartz occurs as individual, 50 to 300 µm-large anhedral to euhedral grains as well as granoblastic-textured aggregates within the grunerite and magnetite bands; aggregates commonly grade into individual grains along a particular band, and some aggregates cross-cut the banding. In one BSF sample (090709–5), quartz makes up regular, 0.5 mm to 2 mm wide, granoblastic-textured bands alternating with the magnetite bands.

Major element composition for quartz is ~100 wt.% SiO₂. The average trace element composition of BSF quartz is below 35 ppm. In BIF
quartz, only Zn occurs at concentrations >36 ppm. Similar to the magnetite, BIF quartz is higher in most trace elements than the BSF quartz (Table 1; Fig. 3C,D).

4.1.3. Grunerite

Grunerite in the BSF is composed of <0.3 cm-wide bands that alternate with quartz bands, and occurs as anhedral to subhedral grains. Grunerite grains are hosts to lamellae of actinolite, a feature not observed in the BIF (Fig. 2F). In the BIF, grunerite tends to be noticeably larger in size, varying from 50 μm to at least 2 cm in length, often making up the whole grunerite band along the length of the thin section. Magnetite, quartz and augite grains can be found as inclusions within the grunerite (Fig. 2E). In BIF sample 090709–5, bands of magnetite and quartz alternate with thin (~70 μm-wide) bands of grunerite, however the inconsistent distribution of these bands between the magnetite and quartz banding might suggest that this is a primary texture (Fig. 2B).

Major element analyses for grunerite show SiO₂ of 50–52 wt.%. BIF grunerite has higher average FeO<sub>total</sub> than BSF grunerite (47 wt.% compared to 30 wt.%), while average MgO is lower in the BIF grunerite (5 wt.% compared to 13 wt.%). Of all the trace elements, grunerite has the highest Zn and Ni concentrations while all other trace elements have concentrations below 35 ppm. In contrast to magnetite and quartz, BSF grunerite has higher average trace element concentrations than BIF grunerite (Table 1; Fig. 3E,F).

4.1.4. Augite

Augite in the BSF is associated with the grunerite bands, while in the BIF, it is associated with both grunerite and magnetite bands. In both units, it occurs as individual, 20 to 150 μm large, anhedral to subhedral grains, commonly with inclusions of quartz and magnetite, and can also be found as an inclusion in grunerite (Fig. 2C). Within a single crystal, bands of different interference colors under polarized light points to compositional zoning; exolved lamellae of orthopyroxene are reportedly common in calcic clinopyroxenes (Deer et al., 1992).

Major element analyses for augite show SiO₂ around 51 wt.% and CaO between 21 and 23 wt.% FeO<sub>total</sub> for BIF augite if higher than for BSF augite (21 wt.% compared to 12 wt.%), while MgO is slightly lower in the BIF augite (7 wt.% compared to 11 wt.%). Trace element analyses show that BSF augite is significantly more enriched in Sc, V, Ni, Co and Zn than in the BIF augite where Sr and Y occur in higher concentrations (Table 1; Fig. 3G,H). The augite in sample 090709–3 is especially high in Cr compared to augite in the other BSF samples (500 ppm compared to below detection limit).

4.1.5. Actinolite

Actinolite was only observed in the BSF, but is also mentioned in previous publications on the Nuvvuagittuq chemical sediments as a minor component of the BIF unit (e.g. O'Neil et al., 2007). Actinolite is associated with the grunerite bands of the BSF, and occurs most commonly as lamellae within a grunerite host. They can also be found as anhedral to subhedral, >50 μm-large grains (Fig. 2F).

Major element analyses of actinolite show average compositions of SiO₂ at ~53 wt.%; FeO<sub>total</sub> at ~20 wt.%; CaO at ~13 wt.%, and MgO at 12 wt.% in terms of the trace elements, actinolite contains high Zn (198 ppm), Ni (66 ppm) and Cr (47 ppm), while the average composition of most other trace elements is below 37 ppm (Fig. 3I).

4.2. BSF bulk geochemistry

The BSF is characterized by high, but variable, concentrations of SiO₂ (28–90 wt.%), Fe₂O₃<sub>total</sub> (2–55 wt.%), MgO (2–12 wt.%) and CaO (3–16 wt.%) while all other oxides occur in concentrations below 2 wt.% (Fig. 4A, Supplementary Data). The concentrations tend to vary from sample to sample depending on the relative percentage of each mineral phase; sample 090709–3 has the highest Si, Al, and Ti concentrations and the lowest Fe concentrations. Ni, Cu

Table 1

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Fig. 3. Plots showing selected trace element chemistry of the main mineral phases (magnetite, quartz, grunerite, augite and actinolite) in the BSF units on the right, and BIF units on the left.
and Zn vary greatly from sample to sample, sometimes by up to three orders of magnitude (Fig. 5A). All the BSF samples are highest in Ni and Zn compared to the other trace elements. Sample 090710-13 is significantly higher in Cu and S compared to the other samples suggesting the presence of sulfide grains, and has the highest concentrations of incompatible elements. The other samples have concentrations of Hf and Th $<0.5$ ppm, Zr $<3$ ppm, and Y $<5$ ppm. The remainder of the trace elements generally have concentrations $<35$ ppm. Bulk Post Archean Average Shale composite (PAAS – Taylor and McLennan, 1985) normalized REE + Y profiles for the BSF show: (i) positive La/La* anomalies ($2.31 \pm 1$) (Fig. 7A); (ii) strong positive Eu/Eu* anomalies ($1.84 \pm 0.16$) (Fig. 7B); (iii) superchondritic Y/Ho ratios ($37.40 \pm 6.83$); (iv) depleted LREE relative to HREE ($\text{Pr/Yb}_{	ext{sn}}: 0.30 \pm 0.19$), and (v) MREE relative to HREE ($\text{La}_{	ext{sn}}/\text{Yb}_{	ext{sn}}: 0.70 \pm 0.23$). With the exception to Eu and Ce anomalies, the overall REE + Y profile is similar to that of modern-day seawater (Fig. 6A; e.g., Bolhar et al., 2004). Sample 090710–13 has the highest REE + Y concentrations of all the samples and the attest overall profile.

4.3. BIF bulk geochemistry

The BIF is characterized by high, variable concentrations of SiO$_2$ (33–63 wt.%) and Fe$_2$O$_3$$_{total}$ (32–66 wt.%), while the other major element oxides occur in concentrations $<3$ wt.% (Fig. 4B, Supplementary Data). Only P is slightly higher in the BIF (0.01–0.09 wt.%) when compared to the BSF. Sample 090710–12 has the highest SiO$_2$ and lowest Fe$_2$O$_3$ concentrations of all the BSF samples; the simultaneously high Cu and S concentrations suggest a contribution by sulfide minerals to the composition of this sample (Supplementary Data). Similar to the BSF, Ni and Zn have the highest concentrations for transition metals in the BIF, while all others are $<15$ ppm (Fig. 5B). In terms of incompatible elements, Hf and Th have average concentrations of 0.3 ppm; Zr has slightly higher average concentrations of 2 ppm, while Y is even higher at 9 ppm. The shaled-normalized REE + Y profile is similar to that of modern-day seawater (Fig. 6A; e.g., Bolhar et al., 2004). Sample 090710–13 has the highest REE + Y concentrations of all the samples and the flattest overall profile.
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similar to that of modern-day seawater (Fig. 6B), with the exception of Eu and Ce anomalies (e.g. Bolhar et al., 2004). Sample 090710–12 has the highest REE+Y abundances of all the samples, and the flattest overall profile.

5. Discussion

5.1. Paragenesis

In order to infer the initial mineralogy of the Nuvvuagittuq BSF and BIF units, it is necessary to assess the metamorphic modifications that took place and establish the different stages of mineral genesis. The mineral assemblages in both units (i.e. magnetite, grunerite, actinolite, augite and quartz) are typical of an upper amphibolite/lower granulite facies assemblage for banded iron formation (e.g. Klein, 2005); these minerals are similarly well-represented in the quartz–magnetite BIFs of the Isua Supracrustal Belt (Dymek and Klein, 1988). Despite the multiphase metamorphic history of the Nuvvuagittuq belt (Cates and Mojzsis, 2009), petrographic evidence leads us to infer that the precursors of the BSF and BIF units consisted of ferric-oxyhydroxides, amorphous carbonate and silicate phases rich in Ca–Mg–Fe and amorphous silica. There was an insignificant clastic component.

Magnetite in BIF is generally thought to be a secondary product of diagenetic/metamorphic alteration of certain pre-existing Fe-rich mineral phases (Ayres, 1972). In the Nuvvuagittuq BSF and BIF, magnetite is the main Fe-oxide mineral present in either unit. It can commonly be found as inclusions within all the other mineral phase types suggesting that, of the current mineral phases, it was formed first. Magnetite can be the metamorphic by-product of hematite and siderite, at temperatures ranging from 480 °C to 650 °C and pressures of 5–12 kbar according to the following equation (Koziol, 2004):

\[ 3\text{FeCO}_3\text{(siderite)} + \text{Fe}_2\text{O}_3\text{(hematite)} \rightarrow \text{Fe}_3\text{O}_4\text{(magnetite)} + \text{CO}_2 \]

The metamorphic grade of the Nuvvuagittuq belt would have been sufficient for this reaction to take place (Cates and Mojzsis, 2009). Ohmoto (2003) suggested that magnetite can also be formed through the reaction between pre-existing hematite and Fe(II)-rich hydrothermal fluids at <200 °C, resulting in the massive transformation of hematite to magnetite. However this scenario seems unlikely in this case, due to the lack of evidence for the supergene enrichment which would likely accompany such a flux of hydrothermal fluids. The production of biogenic magnetite via the reduction of ferric-oxyhydroxides through dissimilatory iron reduction (DIR; Lovley, 1993) is also an unlikely source for the magnetite in the Nuvvuagittuq chemical sediments. Whereas DIR typically produces magnetite with \( \delta^{56}\text{Fe} < 0 \)‰ (Johnson et al., 2008), the heavy Fe isotope composition (up to 0.97‰ – Dauphas et al., 2007a; O’Neil et al., 2007) of these sediments led Dauphas et al. (2007a) to suggest that this signature was a product of the binary mixing between more primary Fe-oxides and carbonate deposits. It seems likely therefore, that the magnetite in these chemical sediments formed as a metamorphic by-product of hematite and siderite.

Quartz in iron formations is generally thought to be the stable end product of an initially amorphous silica precipitate that was recrystallized to chert and then to quartz at greenschist-facies conditions, as

Fig. 7. (A) Positive La anomalies and negative Ce anomalies persist in all sample. (B) Eu anomalies persist in all BSF and BIF samples. Calculations for La, Eu and Ce anomaly verifications from Bolhar et al. (2004). (C) Plot comparing Zr over Th, and (D) plot comparing Zr over Y/Ho.
denoted by the 120° triple junctions that characterize the granoblastic texture of the quartz (Klein, 2005; Trendall and Morris, 1983; Young, 1976). In the BSF and BIF units of the Nuvvuagittuq belt, quartz can be found as inclusions within grunerite and actinolite, while magnetite can be found as inclusions within the quartz, suggesting that the latter was the second phase, after magnetite, to crystallize.

Metamorphic Fe-bearing silicate minerals are commonly thought of as the products of metamorphic dehydration of pre-existing silicate and carbonate phases (Mel'nik, 1982). Grunerite can be produced in the reaction between quartz and siderite or the conversion from minnesotaite (Klein, 2005; Trendall and Morris, 1983):

\[
8(\text{Fe, Mg})\text{CO}_3(\text{minnesotaite}) + 8\text{SiO}_2(\text{quartz}) + H_2O \rightarrow (\text{Fe, Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_{2}(\text{grunerite}) + 7\text{CO}_2
\]

or

\[
7\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{minnesotaite}) \rightarrow 3\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{grunerite}) + 4\text{SiO}_2(\text{quartz}) + 4\text{SiO}_2 + 4\text{H}_2\text{O}
\]

The occurrence of actinolite as exsolution lamellae in grunerite is thought to be a result of selective crystallization from a homogeneous amphibole as a consequence of slow-cooling from amphibolite-facies peak metamorphic temperature (Ross et al., 1969). Clinopyroxene is a characteristic granulite-facies mineral, and occurs in BIF due to the decarbonation reaction between ankerite and quartz according to the following reaction (Klein, 2005):

\[
\text{Ca}(\text{Fe, Mg})\text{CO}_3(\text{ankerite}) + \text{SiO}_2(\text{quartz}) \rightarrow \text{Ca}(\text{Fe, Mg})\text{Si}_2\text{O}_6(\text{clino.pyroxene}) + 2\text{CO}_2
\]

That augite as well as actinolite is present in Nuvvuagittuq chemical sediments suggests that some of the primary precipitates were Ca-bearing. Indeed, Dauphas et al. (2007a) concluded that in order to produce the range of Fe isotope compositions in the Nuvvuagittuq chemical sediments, binary mixing between Fe-oxides and some type of carbonate precursor was necessary. The precursors to the Fe-carbonates in most BIF are considered to have been very fine-grained carbonate oozes (Klein, 2005), however, the possibility that the source of Ca and Mg in the Nuvvuagittuq chemical sediments came from a Ca–Mg–Fe-bearing silicate precursor cannot be ruled out.

5.2. Geochemistry

The composition of Archean chemical sediments ought to reflect input of solutes from both crustal weathering and hydrothermal emissions. Detrital input can also occur in shallow water facies iron formations, and such clastic particles tend to obscure the seawater signal.

Identification of a detrital component in BIF was done mainly through elevated concentrations of Al₂O₃, TiO₂ and high field strength elements — HFSE (e.g., Zr, Hf, Ta, Th) as well as through co-variations between HFSE and REE + Y ratios (La/La*, Y/Ho, Pr/Yb, Ce/Ce* — Bau, 1993; Bolhar et al. 2004; Ewers and Morris, 1981; McLennan et al., 1993). Despite being sandwiched in between high-Ti amphibolites below, and high-Al amphibolites above, both BIF and BSF units have low absolute concentrations of Al₂O₃ and TiO₂ concentrations (Al₂O₃; generally <0.5 wt.%; TiO₂; <0.03 wt.%). Concentrations of both REE + Y and HFSE are low in iron formations because dissolved REE + Y in the water column are normally scavenged by particulate matter before being adsorbed by Fe and Si gels on the seafloor, and input from a detrital source would commonly generate co-variations between HFSE and REE + Y in BIF (Bau, 1993). With the exception of samples 090710–13 (BSF) and 090710–12 (BIF), low concentrations of Zr, Hf, Ta and Th (<2.5 ppm) in the Nuvvuagittuq chemical sediments suggest little to no detrital input (Fig. 7C,D; Supplementary Data). The two aforementioned samples have slightly higher Zr, Hf, Ta and Th concentrations, low Y/Ho ratios and flatter REE + Y profiles (Fig. 6). However, even these concentrations are relatively low when compared to BIF with a recognized detrital component (e.g., Dales Gorge BIF).

The REE + Y profile of modern seawater is distinctive; the purest BIF and marine carbonates share certain seawater-like characteristics including (i) positive La and Eu anomalies; (ii) negative Ce anomalies (except for Archean BIFs); (iii) a relative depletion of LREE and MREE compared to HREE, and (iv) superchondritic Y/Ho ratios (i.e., >26) (Bau and Dulska, 1996; Bolhar et al., 2004). The reasons why these chemical sediments retain seawater-like REE + Y patterns are poorly understood, but the similarity of REE + Y profiles in BIF units spanning the Mesoarchean (Alexander et al., 2008) through the Proterozoic (e.g. Derry and Jacobsen, 1990 and references therein) demonstrates that they seem to reflect the seawater from which they precipitated. Apart from the negative Ce anomaly, all the aforementioned seawater-like anomalies are observed in the REE + Y profiles for both the Nuvvuagittuq BSF and BIF. In oxic seawater, soluble Ce(III) is converted to insoluble Ce(IV) and thus, the lack of Ce anomalies in Archean BIF has been used in order to confirm anoxic conditions (e.g. Derry and Jacobsen, 1990; Kato et al., 1998). Although superchondritic Y/Ho ratios are a characteristic shared by both Archean BIF and modern ferromanganese crusts, shale-normalized Y anomalies are positive in the former and negative in the latter; it has been suggested that this could be related to the rate of deposition of ferric-oxyhydroxide particles (e.g., Bau and Dulska, 1996). The REE + Y in BIF are fairly immobile even at amphibolite facies metamorphism, and their mobility depends on high water/rock ratios (w/r > 100) which are seldom achieved (Bau, 1991; Grauch, 1989). Of all the REE + Y, Eu is especially mobile due to the larger difference between its ionic radius and that of Fe²⁺. Negative Eu anomalies, or inconsistent positive and negative Eu anomalies between samples, occur (Bau, 1993). The consistently positive Eu in all Nuvvuagittuq bulk samples suggests that there has been little REE + Y mobility.

It is possible to put a few constraints on the sources of REE + Y in the Nuvvuagittuq BSF and BIF. First, the strong positive Eu anomalies are distinctive of high-temperature (>350 °C) hydrothermal fluids. A conservative, two component mixing model between modern seawater and high-temperature hydrothermal fluids using Sm/Yb as a function of Eu/Sm implies that, like in the Isua BIF, a surprisingly small proportion of high-temperature hydrothermal fluids (~0.1%) were enough to cause such high Eu anomalies in the Nuvvuagittuq BSF and BIF (Fig. 8). Second, the Sm/Yb ratios of samples 0907010–13...
(BSF), 090709–3 (BSF) and 090710–12 (BIF) are higher than the others and also display a subsequent decrease in Eu/Sm (Fig. 8), a signature which can be produced upon the addition of clastic material (e.g. Bau, 1993). No BIF is completely devoid of some detrital component, and although these samples also have the highest Zr, Hf, Ta, Th and REE + Y concentrations of all the samples, they still have seawater-like La/La’ and Eu/Eu’ anomalies, and no Ce/Ce’ anomalies (Fig. 7A,B) which indicates that detrital inputs were minimal during chemical precipitation and the BSF and BIF units of the Nuvvuagittuq belt are relatively pure chemical sediments.

5.3. Comparing the Nuvvuagittuq chemical sediments with the Isua iron formations

Few Archean-aged BIFs are known, and the recent discovery of the Nuvvuagittuq chemical sediments permits comparisons to be made with BIF from the Isua Gneiss Complex in West Greenland. Previous studies established that the chemical sediments from the Isua and Nuvvuagittuq belts are relatively pure chemical sediments.

From the perspective of mineralogy and metamorphic histories the amphibolite-facies Isua BIF and the upper-amphibolite/ lower granulite facies Nuvvuagittuq chemical sediments show similarities in terms of relative trace element abundances, where Zn and Ni occur in the highest concentrations. Regarding absolute abundances however, Ni (Nuvvuagittuq median: 57 ppm; Isua median: 24 ppm) and Zn (Nuvvuagittuq median: 50 ppm; Isua median: 21 ppm) occur in slightly higher concentrations in the former (Appel, 1979; Bolhar et al. 2004; Dymek and Klein, 1988; Frei and Polat, 2007, Polat and Frei, 2005; Shimizu et al., 1990). Detrital indicators (Al2O3, TiO2, HFSE) at both locations are low, which suggests that both locations are relatively detritus free. Their REE + Y profiles show seawater-like anomalies with a relative depletion in LREE compared to MREE and HREE, consistently positive La and Eu anomalies, negative Y/Ho ratios, and overall, similar REE + Y concentrations (e.g. Bolhar et al., 2004; Dymek and Klein, 1988). Moreover, ratios of Sm/Yb and Eu/Sm suggest that both the Isua and Nuvvuagittuq chemical sediments had similar contributions (~0.1%) by high-temperature hydrothermal sources (Fig. 8; Alexander et al., 2008). The similarities in the characteristics of the iron formations at Isua and Nuvvuagittuq would suggest that they were deposited under comparable environmental conditions, input sources and via the similar processes. This is the expected result for rocks of similar age and overall depositional setting.

5.4. Implications for the composition of the Eoarchean/Hadean oceans

It is widely held, though unsubstantiated due to the scarcity of an Eoarchean rock record, that metal requirements in microbes co-evolved with seawater metal availability through time (daSilva and Williams, 1991). As such, a key step in understanding the early evolution of life on Earth is to better understand the evolution of seawater composition. Studies that have sought to place quantitative constraints on the composition of the earliest oceans point to ferruginous waters (Holland, 1984) that were siliceous (Maliva et al., 2005), possibly mildly sulfidic (Saito et al., 2003), and likely contained an abundance of mafic–volcanic associated trace transition elements, such as Ni (Konhauser et al., 2009). Most BIFs older than ~2.0 Ga yr also possess chemical characteristics which suggest significant hydrothermal input into the oceans during their deposition, including positive Eu anomalies, a relative depletion of LREE in REE + Y profiles, and mantle-like Nd signatures (Beukes and Klein, 1990; Derry and Jacobsen, 1990; Jacobsen and Pimentel-Klose, 1988). Moreover, Isley (1995) estimated that, due to larger mantle heat flow during the Archean, rates of hydrothermal cycling were up to three times greater than at present, which provides an intimate link between the composition of seawater and the composition of oceanic crust, and by extension, mantle activity. Indeed, Isley and Abbott (1999) show a strong correlation between mantle plume activity and BIF occurrence through time.

With experimentally derived partitioning coefficients (Kp), it is possible to derive the concentration of a specific metal ion in the seawater from which chemical sediments precipitated. Kp values for Ni and Zn to ferric-oxhydroxides were calculated in the laboratory using the methodology of Konhauser et al. (2007, 2009), and were then applied to bulk (i.e., XRF and ICP-MS) values of Ni, Zn and Fe in BIF; BSF rocks were not used as they contain sulfide grains that may imply secondary Zn enrichment (see Supplementary Data). Our calculations indicate that Ni values in the ocean at the time of the deposition of the Nuvvuagittuq BIF reached up to ~300 nM as compared to ~12 nM of modern seawater, while Zn concentrations appeared to have only reached up to ~20 nM as compared to ~9 nM in today’s oceans (Bruland and Lohan, 2004).

It was recently proposed that the enhanced mantle partial-melting regime for peridotites in the Eo- and Mesoarchean and the related extrusion of Ni-rich ultra(mafic) volcanic rocks on the seafloor promoted high dissolved Ni concentrations in seawater; Archean-aged komatiite, tholeiites and basalts contained preferentially higher abundances of siderophile elements (e.g., Ni, Co, Cr, Fe) than their younger Proterozoic counterparts (e.g. Arndt, 1991; Taylor and McLennan, 1985) which could then become incorporated into BIF (Konhauser et al., 2009). Therefore, Ni-enrichment in the Nuvvuagittuq BIF is to be expected. Crucially, Ni is a key component in several enzymes of methane-producing bacteria (methanogens), and thus, its abundance would have facilitated increased methane production on the early Earth (Kida et al., 2001).

Zinc is also ultimately sourced from (ultra)mafic volcanics (Le Roux et al., 2010), and accordingly, one would predict high Zn concentrations in the Nuvvuagittuq BIF. However, translating Zn concentrations in BIF to seawater concentrations is complicated by the fact that a number of dissolved species and mineral phases have high sorptive capacities for Zn, and therefore Zn may not have accumulated in seawater. For instance, experimental data has shown that both ferric-oxhydroxides and amorphous silica (Balisatrier et al., 2008; Pivovarov, 2008) can also sequester Zn, and thereby reduce its dissolved concentrations. In this regard, our application of Kp values for both Fe-only and silica-rich oceans both yield relatively low dissolved Zn concentrations. Planavsky et al. (2010) found that, based on the Zn concentration of black shales through time, dissolved Zn concentrations in the Archean did not change significantly contrary to some suggestions (e.g., Dupont et al., 2010). Correspondingly, Zn concentrations in the Nuvvuagittuq BIF are comparable to Zn compositions in the Neorarchean (e.g., 2.75 Ga yr old Carájas Formation; Dymek and Klein, 1988), Paleoproterozoic (e.g., 2.3 Ga yr old Hotazel Formation BIF; Tsikos and Moore, 1997), and Neoproterozoic (590 Ma yr old Yerbal formation; Pecois et al., in press).

Our results provide additional support for high Archean seawater Ni concentrations, and have important implications on Zn availability for early microbial metalloenzymes. Eukaryotes have a much more significant Zn requirement than prokaryotes, and previous studies have attributed the small number of ancient zinc enzymes (e.g., Dupont et al., 2006, 2010) to the non-bioavailability of Zn sulfide complexes, which dissociate slowly in seawater (Saito et al., 2003). Geochemical modeling results by Saito et al. (2003) suggest that even at dissolved sulfide levels on the order of 0.05 mM, enough sulfide exists in solution, following the formation of FeH5S4, to completely complex trace metals such as Cu, Cd and Zn. However, results from
3. Low Al
2. The primary precipitates to these units were Fe\(^{3+}\) ferric-oxyhydroxide particles in the form of Zn sul-
some of the Zn present in the Nuvvuagittuq BIFs likely sorbed onto
mentsary Data for full modeling results and parameters). Although
Saito et al., 2003
Holland, 1984
side other trace metals; 50

4. The most significant trace elements in the Nuvvuagittuq chemical
sediments are Ni and Zn, with relative depletions (~15 ppm) in
all other trace elements. In the BSF, Ni and Zn are particularly
abundant in grunerite and actinolite. In the BIF, Ni is particularly
abundant in magnete, while Zn is abundant in grunerite and
actinolite. The application of experimentally-derived partitioning
coefficients to absolute concentrations in the BIF show that, com-
pared to modern seawater, Earth’s earliest oceans had relatively
high dissolved Ni concentrations (up to ~300 nM), but somewhat
similar Zn concentrations (up to ~20 nM). A biologically significant
portion of the zinc was likely to have occurred as Zn\(^{2+}\) and able to
form bioavailable complexes.

5. The petrographic and compositional similarities between the
chemical sediments in the Nuvvuagittuq and Isua Supracrustal
Belts suggest very similar depositional environments in terms of
seawater composition, as well as relative input sources.

6. Conclusions

Petrographic and geochemical analyses of chemical sediments in
the Nuvvuagittuq Supracrustal Belt in northern Québec (Canada)
lead us to conclude that:

1. There are two distinct chemical sedimentary units in the Nuvvu-
gittuq belt, a BIF unit consisting of alternating microbands of mag-
netite, Fe–Mg–Ca silicates and quartz, and a more silicate rich
unit consisting of alternating microbands of quartz and Fe–Mg–Ca si-
licates (BSF).

2. The primary precipitates to these units were Fe–Mg–Ca-bearing
silicate and/or carbonate minerals, chert, siderite and hematite.
The precursor deposits were made up of layered amorphous silica
and ferric-oxyhydroxides, fine grained carbonate oozes and/or Fe–
Mg–Ca rich silicate gels.

3. Low Al\(^{3+}\), TiO\(_2\), Zr, Hf, Ta and Th concentrations in most of the BSF
and BIF samples suggest detritus-free chemical sediments; REE + Y
profiles with distinctive seawater-like signatures. Furthermore,
consistently positive Eu anomalies suggest that these units have
preserved much of their seawater-like composition despite
metamorphic overprinting, with an ~0.1% contribution by high-
temperature hydrothermal fluids, similar to the Isua BIF.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.

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Table 2
Model output results examining the effect of sulfide and increasing iron on Zn and Ni spe-
ciation in Archean seawater. Models are for speciation, and do not assume precipitation.

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<th>Component</th>
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<th>1.8 mM Fe(^{3+})</th>
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<td>Ni(<em>{eq})(</em>{2})(OH)(<em>{eq})(</em>{2})Cl(_{eq})</td>
<td>2.456</td>
<td>10.681</td>
</tr>
</tbody>
</table>