Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada

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Abstract

An Eoarchean supracrustal belt dated at ca. 3750 Ma was recently identified in the Innusuaq Complex, northern Québec (Canada). Rocks from the Nuvvuagittuq locality include mafic and ultramafic amphibolites, quartz–biotite and pelitic schists, orthogneisses, and banded quartz–magnetite–amphibole/pyroxene rocks of probable chemical sedimentary origin. The purported metasediments are enriched in the heavy isotopes of Fe by approximately 0.3‰/amu relative to IRMM-014. They also have high Fe/Ti ratios, up to 100× that of associated amphibolite units. These signatures demonstrate that quartz–magnetite–amphibole/pyroxene rocks from Nuvvuagittuq are chemical sediments (e.g. banded iron-formations, BIFs) formed by precipitation of dissolved ferrous iron in a marine setting. All units were metamorphosed to upper amphibolite facies, which partly homogenized Fe isotopes. Variable Fe isotope compositions of bulk quartz–magnetite rocks are interpreted to reflect binary mixing between primary oxides and carbonates. Mixing relationships with major element chemistry (Ca/Fe, Mg/Fe, and Mn/Fe) are used to estimate the Fe isotope composition of the primary Fe-oxide phase (0.3 to 0.4‰/amu) and the chemistry of the carbonate (siderite and ankerite). Iron isotopes can thus be used to constrain the primary mineralogy of Fe-rich chemical sedimentary precipitates before metamorphism. The possible presence of siderite in the primary mineral assemblage supports deposition under high PCO2. We developed an isotope distillation model that includes two possible abiotic oxidation paths, homogeneous and heterogeneous. The isotopic composition of Fe in the precursor phase of magnetite in BIFs can be explained by partial oxidation through oxygenic or anoxygenic photosynthesis of Fe from a hydrothermal source.© 2006 Elsevier B.V. All rights reserved.

Keywords: Archean; Sediment; BIF; Iron; Isotopes; Metamorphism

1. Introduction

No terrestrial rocks formed before ca. 4.03 Ga are known to have survived subsequent crustal recycling processes [1]. The only direct witnesses of the earliest times are tiny zircon grains accumulated in younger detrital sediments [2]. In this respect, the large exposures...
of Eoarchean (3.6–3.8 Ga) supracrustal rocks preserved in the North Atlantic province of the North American craton (Isua supracrustal belt, ISB; and Akilia association, AA of southern West Greenland; Nulliak assemblage of northeast Labrador, Canada) are important [3–9]. The protoliths of some of these formed as marine sediments and convey crucial information on the early history of our planet. Was the Earth habitable by 3.8 Ga? Had life already emerged? If so, what was the nature of the biosphere? How was the chemistry of the atmosphere–ocean system different? What was the flux of extraterrestrial matter to the Earth? A principal issue with these samples is that until recently, they were thought to be exclusive to West Greenland and parts of Labrador, and it was unclear whether they offered an unbiased perspective of the Earth at that time.

In 2002, David et al. reported the discovery of a new Eoarchean volcano–sedimentary (supracrustal) sequence in northern Québec along the eastern shore of Hudson Bay (Ungava Peninsula, Canada) [10]. The Nuvvuagittuq supracrustal belt (NSB) is located in the Inukjuak lithotectonic domain of the Northeastern Superior Province (Minto block, Canadian Shield, Fig. 1). Other supracrustals in the area comprise the Innuksuac Complex. David and coworkers [10,11] determined the age of a felsic unit from the NSB as 3825±16 Ma based on U–Pb TIMS geochronology of zircons, after rejection of an outlier (3805±77 Ma if it is included [12]). Zircon morphologies and trace element geochemistry were used to suggest the host rock was a volcanic tuff and that the zircons were not xenocrystic [13]. More recently, Cates and Mojzsis [12] reported an

Fig. 1. Map of the Ungava Peninsula, Northern Québec. The Nuvvuagittuq supracrustal belt (NSB, marked with a white star) is located in the Inukjuak lithotectonic domain of the Northeastern Superior Province (Canadian Shield). The inset map also shows (marked with black stars) other exposures of Eoarchean supracrustal rocks in SW Greenland (Isua supracrustal belt ISB and Akilia Association AA) and NE Labrador (Nulliak assemblage). Map modified from [73,74].
The best preserved examples that escaped silica mobility and strain retain bands of magnetite alternating with bands of quartz and amphibole which resemble banded iron-formation. In more metamorphosed samples (IN05048), pyroxenes rather than amphiboles are present. REE patterns, including positive Eu anomalies, are consistent with an origin from hydrothermal sediments for this unit [12,26]. Because sample IN05007 is the best-preserved quartz–magnetite rock analyzed in this study, it was selected for detailed petrographic and Fe isotope characterizations (Figs. 2 and 3). The hand-specimen (approximately 2.8 × 3.7 × 1.8 cm in size), consists of parallel, partly anastomosing, bands of

by tonalite–trondhjemite–granodiorite (TTG) composition orthogneisses, including 3.76 Ga trondhjemitic gneisses, some with clear cross-cutting relationships to the paragneisses (see [12] for detailed descriptions of these units).

Mafic amphibolites have tholeiitic compositions with flat chondrite-normalized rare earth element (REE) patterns [12] and radiogenic initial Nd isotope compositions indicative of a depleted mantle source [25]. Major mineral phases are amphibole, plagioclase, garnet, and quartz. Textures range from massive to banded. Ultramafic lenses of basaltic komatiite composition are intercalated with the amphibolite units (IN05047).

Rocks that contain highly-strained polycrystalline quartz embedded in a biotite–clinozoisite matrix have trace element geochemistry consistent with a detrital origin. Due to the high strain, protolith assignment to this unit is uncertain.

A pelitic–psammitic quartzite unit preserves fine laminations a few millimetres to a few centimetres thick. Pelitic layers are dominantly biotite, with minor clinozoisite, carbonate and disseminated quartz, whereas quartzite layers are dominantly fine-grained quartz in aggregates of grains with (annealed) triple-junctions + minor biotite, clinozoisite and carbonate.

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magnetite (1–4 mm in thickness) alternating with bands of quartz and amphibole. Although the rock has been strongly deformed, these layers may represent relict sedimentary banding. Carbonates are also present and crosscut in some places the layering. Image analysis of a 0.5 mm² area reveals that these carbonates consist of 20% ankerite (Ca_{0.495}Mg_{0.239}Fe_{0.191}Mn_{0.075}) and 80% calcite (Ca_{0.910}Mg_{0.015}Fe_{0.030}Mn_{0.045}). The width of the solvus between these two phases can be used as a thermometer [27] and generates a temperature of 380 °C, much lower than inferred peak metamorphic conditions of >550 °C. This can be explained by equilibration on the retrograde path or mobilization by fluids. The amphiboles consist predominantly (>99%) of cummingtonite (Na_{2.04}Mg_{11.28}Al_{2.03}Si_{53.77}O_{22.30}Fe_{0.78}wt.%) with minor actinolite (Na_{2.05}Mg_{12.02}Al_{2.03}Si_{54.50}O_{22.30}Fe_{0.78}wt.%). Disseminated pyrite is also present in IN05007. Overall, the petrography and chemistry of this sample (also see [12]) is very similar to what has been described for banded iron-formations from the ISB [28].

3. Analytical methods

Large specimens were cut or broken to offer fresh surfaces and minimize the influence of alteration. After cleaning with acetone, the bulk samples (typically ~1 g) were reduced to powder in an agate mortar. Sampling of individual magnetite bands in IN05007 was done using a micromill apparatus (MicroMill, New Wave Research) equipped with a tungsten carbide mill bit (Brasseler, scriber H1621.11). The section was extensively characterized before microsampling using X-ray and BSE imaging on a JEOL JSM-5800LV SEM (Figs. 2 and 3). At each of the 25 sample points, the following sequence was followed. A drop of MilliQ water was deposited at the surface of the polished sample. The computer-controlled bit was moved within the water droplet to mill an array of holes (~18), each approximately 100 μm in
diameter and 500 μm in depth (assuming a cylindrical geometry, this corresponds to a total of ~270 μg Fe milled in magnetite). The sample slurry containing 100–500 μg of Fe was transferred in a Teflon beaker using a micropipette. It was then digested following the same protocol as for bulk samples described hereafter.

The protocol for sample dissolution, purification, and isotope analysis of Fe has been described elsewhere [29,30], and is only briefly reviewed here. Powder aliquots weighing less than 10 mg were dissolved in Teflon beakers in 1 mL HF, 0.5 mL HNO₃, and a few drops of HClO₄ at ~100 °C for 5–10 h (unless otherwise noted, all acids listed are concentrated solutions). The solutions were then evaporated to dryness on hot plates under heat lamps and the salts were dissolved in 0.25 mL HNO₃, 0.75 mL HCl, and a few drops of HClO₄, evaporated, dissolved in 0.5 mL HNO₃, 1 mL HCl, and a few drops of HClO₄, evaporated again, and finally dissolved in 0.5 mL HCl 6 M. At this stage, the samples were ready for loading on anion exchange resin (typically 50–500 μg Fe).

Iron was separated from matrix elements and direct isobars (¹⁴Cr and ⁵⁸Ni can interfere on ⁵⁴Fe and ⁵⁸Fe, respectively) by anion exchange chromatography. After loading of sample solutions onto Bio-Rad Poly-Prep columns filled with 1 mL of AG1-X8 200–400 mesh resin, matrix elements were eluted with 8 mL of HCl 6 M, and Fe was recovered using 9 mL of HCl 0.4 M. This sequence was repeated. The yield is close to 100% and no isotope fractionation is introduced by the chemistry [29]. The blank of the whole procedure is <40 ng Fe (<0.1% of the amount of Fe loaded on the column).

Iron isotopic compositions were measured on an Isoprobe (Micromass) multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) installed at the Field Museum. The samples (2 ppm Fe in HNO₃ 0.45 M) were introduced into the mass spectrometer using a Cetac Aridus desolvating system. Instrumental
The δ⁰⁰⁰/amu was calculated for the reference materials IRMM-014 (5.845% ⁵⁵Fe, 91.754% ⁵⁶Fe, 2.1191% ⁵⁷Fe, and 0.2819% ⁵⁸Fe) [31]. Isotopic compositions are calculated using the δ notation, averaged over 2–8 replicate analyses of the same solution,

\[ \delta^{i/j}{\text{Fe}} = \left[ \left( \frac{{^{i/Fe}}}{{^{j/Fe}}} \right)_{\text{Sample}} / \left( \frac{{^{i/Fe}}}{{^{j/Fe}}} \right)_{\text{IRMM–014}} - 1 \right] \times 10^3. \]  

Because different laboratories measure different isotope ratios, we prefer to use the \( F_{\text{Fe}} \) notation [30], which is expressed in permil per atomic mass unit (%/amu) deviation relative to the composition of the standard,

\[ F_{\text{Fe}} = \delta^{i/j}{\text{Fe}} / (i-j). \]

If isotope ratios do not depart significantly from linear mass fractionation over the range of variations investigated, then the \( F_{\text{Fe}} \) notation should give identical values for any pair of isotopes considered (in this study ⁵⁴Fe and ⁵⁶Fe). Error bars are calculated based on multiple standard analyses and are reported as 95% confidence intervals.

At the beginning of each session of analyses, several geostandards and igneous rocks were measured to test the stability of the instrumental mass bias and confirm that there had been no problem during sample digestion and chromatography (Table 1). The samples T4D2#1 (basalt from Loihi, Hawaii), Payun (pseudomorph of hematite after magnetite from Payun Matra volcano, Argentina), and Naoned#1 (Eclogite from St-Philibert-de-Bouaine, France) have Fe isotope compositions (0.041 ± 0.041, −0.027 ± 0.032, and 0.045 ± 0.088%/amu, respectively) identical to earlier results reported for these samples (0.072 ± 0.051%/amu for T4D2#1 [17] and 0.004 ± 0.03%/amu for Payun [32]) or for igneous rocks (0.039 ± 0.008%/amu [20,30]). Eight replicate analyses (including dissolution and chromatography) of the geostandard IF-G (a 3.7–3.8 Ga BIF from the ISB [33]), give a weighted average of 0.288 ± 0.019%/amu, indistinguishable from the recommended value of 0.316 ± 0.010%/amu [30]. The external reproducibility of these 8 replicate measurements is 0.09%/amu (2σ), which is in good agreement with internal precisions obtained for individual analyses (from 0.04 to 0.10%/amu).

4. Results

Mafic and ultramafic samples from the Nuvvuagittuq supracrustal belt \((n=4)\) have Fe isotopic compositions very close to IRMM-014 (1/σ² weighted average −0.030 ± 0.018%/amu or −0.006 ± 0.022%/amu if IN05045, a banded amphibolite with a low Fe isotopic composition, is excluded, Table 1). This is similar to values reported for ≥3.83 Ga amphibolite rocks [7] from the Akilia association (+0.011 ± 0.010%/amu) [17] and carbonaceous chondrites (−0.012 ± 0.010%/amu, Table 1) [30]. Beard et al. [20] showed that modern (<0.1 Ga) igneous rocks sampled in a variety of tectonic settings have almost homogeneous Fe isotopic compositions, around +0.04%/amu. This is slightly heavier than the values found for Eoarchean samples. Variations of −0.15 to +0.20%/amu have been documented in carbonatites (Dauphas et al., in prep) and granitoids [34]. The values measured in mafic and ultramafic rocks from NSB fall well within this range. There are few measurements published in the literature with which 3.8 Ga mafic and ultramafic rocks from the NSB can be compared. Poitrasson et al. [35] reported a value of +0.019 ± 0.008%/amu for a 3.5 Ga komatiite from Barberton (South Africa), which is close to the values reported here.

All quartz–biotite schists of possible conglomeratic (detrital) origin \((n=4)\) have indistinguishable Fe isotopic compositions, averaging −0.026 ± 0.025%/amu. This is identical to the signature of igneous rocks from the NSB.

The pelitic schists have light Fe isotopic compositions \((n=2, −0.118 ± 0.070\) and −0.240 ± 0.070%/amu) relative to IRMM-014 and igneous rocks. Similar signatures have been documented for other Archean pelitic rocks. Yamaguchi et al. [16] measured the Fe isotope compositions of well-preserved shales and greywackes from drill cores ranging in age from 2.20 to 3.25 Ga. Samples with small amounts of organic carbon, carbonates, and sulfides, have Fe isotopic compositions close to the signature measured in igneous rocks and suspended river loads. In contrast, most of the samples that contain significant siderite, organic carbon, and magnetite have negative isotopic compositions, down to −1%/amu. Negative \( F_{\text{Fe}} \) values are also found in well-preserved BIFs from the Kaapvaal craton, especially in pyrite and Fe-carbonate rich layers (down to −1.20%/amu [15]).

The banded quartz–magnetite rocks of likely BIF protolith \((n=5)\) are, for the majority, enriched in the heavy isotope of Fe (around +0.3%/amu). The only exception is IN05048, a highly deformed quartz–pyroxene rock within the finely banded quartz–magnetite unit, with a \( F_{\text{Fe}} \) of +0.038 ± 0.023%/amu. These heavy Fe values are close to those reported for bulk ferruginous quartzites from supracrustals rocks of the Akilia association and Isua (from +0.1 to +0.5%/amu [17]). The Mean Square Weighted Deviate (MSWD, also
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<td>Basalt (Loihi, HI)</td>
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<td>0.059±0.158</td>
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<td>Naoned#1</td>
<td>Eclogite (St-Philbert-de-Bouaine, France)</td>
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<td>0.089±0.175</td>
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<td>Hmt, pseudomorph after mgt (Argentina)</td>
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<td>−0.039±0.080</td>
<td>−0.045±0.167</td>
<td>−0.020±0.040</td>
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<td>Average Payun CV3 chondrite</td>
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<td>0.034±0.110</td>
<td>−0.140±0.074</td>
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<td>CO₃ chondrite</td>
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<td>−0.094±0.082</td>
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<td>CO₃ chondrite</td>
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<td>0.030±0.157</td>
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<td>Basalt (Columbia River, OR)</td>
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<td>0.001730</td>
<td>0.022±0.080</td>
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<td>Average IF-G</td>
<td>BIF geostandard (Isua, Greenland)</td>
<td>0.469±0.087</td>
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<td>IN05019</td>
<td>Massive amphibolite</td>
<td>0.006995</td>
<td>0.576±0.037</td>
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<td>IN05048</td>
<td>Coarse Qtz–Px rock</td>
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<td>Average IN05048 Relatively well preserved BIF</td>
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<td>0.634±0.243</td>
<td>0.218±0.076</td>
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<td>IN05009</td>
<td>Intermediate between IN05007 and IN05048</td>
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<td>IN1S1</td>
<td>Microsampling IN05007 (0.17 cm)</td>
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<td>Microsampling IN05007 (0.17 cm)</td>
<td>0.436±0.088</td>
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<td>Microsampling IN05007 (0.21 cm)</td>
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Table 1 (continued)

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<td>1.082±0.268</td>
<td>0.314±0.080</td>
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<td>IN05007 (0.39 cm)</td>
<td>0.566±0.088</td>
<td>0.934±0.182</td>
<td>0.283±0.044</td>
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<td>0.606±0.222</td>
<td>0.187±0.054</td>
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<td>IN05007 (0.83 cm)</td>
<td>0.614±0.113</td>
<td>0.890±0.160</td>
<td>0.307±0.056</td>
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<tr>
<td>Microsampling</td>
<td>IN6S2</td>
<td>IN05007 (0.79 cm)</td>
<td>0.510±0.173</td>
<td>0.790±0.245</td>
<td>0.255±0.087</td>
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<tr>
<td>Microsampling</td>
<td>IN6S3</td>
<td>IN05007 (0.77 cm)</td>
<td>0.524±0.173</td>
<td>0.787±0.245</td>
<td>0.262±0.087</td>
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<tr>
<td>Microsampling</td>
<td>IN7S1</td>
<td>IN05007 (1.03 cm)</td>
<td>0.757±0.159</td>
<td>1.037±0.268</td>
<td>0.379±0.080</td>
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<td>Microsampling</td>
<td>IN7S2</td>
<td>IN05007 (1.03 cm)</td>
<td>0.511±0.091</td>
<td>0.669±0.097</td>
<td>0.256±0.045</td>
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<tr>
<td>Microsampling</td>
<td>IN7S3</td>
<td>IN05007 (1.00 cm)</td>
<td>0.510±0.091</td>
<td>0.797±0.097</td>
<td>0.255±0.045</td>
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<td>IN05007 (0.96 cm)</td>
<td>0.509±0.193</td>
<td>0.830±0.256</td>
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<td>0.597±0.193</td>
<td>0.787±0.256</td>
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<td>0.741±0.256</td>
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<td>IN05007 (1.50 cm)</td>
<td>0.638±0.091</td>
<td>0.940±0.097</td>
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<td>0.758±0.125</td>
<td>1.123±0.174</td>
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<tr>
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<td>0.716±0.125</td>
<td>1.073±0.174</td>
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<td>IN05007 (1.52 cm)</td>
<td>0.703±0.125</td>
<td>0.993±0.174</td>
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<td>0.976±0.097</td>
<td>0.319±0.045</td>
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<td>0.570±0.179</td>
<td>0.883±0.291</td>
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<tr>
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<td>0.917±0.264</td>
<td>0.296±0.083</td>
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<th>N Québec conglomerate</th>
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<table>
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<th>N Québec schists</th>
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Isotopic compositions are expressed relative to IRMM-014 (Eqs. (1) and (2)). The chemical compositions of geostandards are from [17] for Ti in IF-G and [33] for others. The chemical compositions of supracrustal rocks from the NSB are from [12]. Uncertainties are 95% confidence intervals. They correspond to 2–8 replicate analyses of the same solution and were calculated using student’s t-distribution. For the samples that have been micromilled from the section of IN05007, the numbers in parentheses are the distances from the bottom (Fig. 3).
known as the $\chi^2$ per degree of freedom or reduced $\chi^2$) for the microdrill analyses of individual magnetite bands in sample IN05007 is 2.64. This is outside the 95% confidence interval of 0.52 to 1.64 given by $\chi^2$ statistics. At the scale of the section studied (10 cm$^2$), the Fe isotopic composition appears to vary more than predicted from analytical uncertainty (Table 1). This may be a relict depositional feature [19] or may indicate the presence of inter-mineral equilibrium fractionation in BIF’s at $>550$ °C [36] if the micro-drilled magnetite was mixed with other phases. The average of the 25 microsample analyses (+0.284±0.012‰/amu) is identical within error to the average of the 2 bulk measurements performed on the same sample (+0.236±0.054‰/amu).

The Fe/Ti ratio has proven to be useful for tracing Fe mobilization in altered basalts [37] and distinguishing between metasomatized igneous rocks and rocks of chemical sedimentary origin such as BIFs [17]. The mafic and ultramafic rocks, quartz–biotite (polymict conglomerate?) schists, and pelitic schists from the NSB have identical Fe/Ti ratios (18–42) as metagneous rocks from the Akilia association. The only exception is IN05045, a banded amphibolite with a low Fe/Ti ratio of 8.50 and low Fe isotopic composition (−0.15‰/amu). For comparison, the bulk silicate Earth (BSE) Fe/Ti ratio is 44.5. All candidate rocks of BIF origin investigated in this study have extremely high Fe/Ti ratios compared to surrounding igneous rocks (Fig. 4). For some, Ti was below detection level and only a lower limit could be derived for the Fe/Ti ratio. In those cases, the Fe/Ti ratio is at least 3 orders of magnitude higher than the ratio measured in mafic and ultramafic units. This is similar to what has been observed for the metamorphosed chemical sedimentary precipitates documented from the ISB and Akilia association [6,7,17,38,39]. IN05048, a quartz–pyroxene rock with Fe isotopic composition indistinguishable to igneous rocks has high Fe/Ti ratio (720.9).

5. Discussion

5.1. Protolith identification

Quartz–biotite schists of possible conglomeratic origin have Fe isotopic compositions that resemble mafic and ultramafic rocks from the NSB, but are distinct from modern basalts (Fig. 4). Cates and Mojzsis [12] showed that bulk element compositions normalized to NASC (North American Shale Composite) are consistent with a detrital origin for this unit. Modern clastic sediments formed in a variety of environments (aerosols, loess, soils, marine sediments, suspended river loads) have Fe isotopic compositions similar to igneous rocks [20]. Thus, Fe isotopes are not useful to distinguish between different sources of clastic sediments.

Two interpretations on the possible origin of the pelitic schist unit have been proposed in the literature. Nadeau suggested that they might derive from metasomatic alteration of a massive amphibolite unit [13] while Stevenson and David described them as “metapelites” [25]. We find that the $F_{Fe}$ value of this unit (−0.2‰/amu) is significantly lower than that of amphibolites (−0‰/amu) while the Fe/Ti ratio is close to that of surrounding igneous rocks. The later observation suggests that Fe was not extensively mobilized and that the low $F_{Fe}$ values measured in these rocks are likely primary depositional features. Such low values have been interpreted in Archean shales and greywackes to represent the imprint of authigenic phases (carbonates, oxides, and sulfides) carrying isotopically fractionated Fe [16]. Our results support a sedimentary rather than a metasomatic origin for this unit.

Iron isotopes have proven to be very useful to distinguish between rocks of true chemical sedimentary origin and metasomatized igneous rocks in SW Greenland [17]. This is an important step in early Earth studies because all known Eoarchean supracrustal rocks have been metamorphosed to at least amphibolite facies and recognition of their protoliths is rarely straightforward.

Fig. 4. Comparison between $F_{Fe}$ (%/amu relative to IRMM-014) and the atomic ratio of Fe to Ti in amphibolites, quartz–biotite conglomeratic (?) schists, psammitic schists, and quartz–magnetite ± amphibole/pyroxene rocks from the NSB. The Fe/Ti ratio of the bulk silicate Earth is 44.53 [40] and the $F_{Fe}$ of modern (<0.1 Ga) magmatic rocks (continental basalts, OIBs, and MORBs) is ∼0.05‰/amu [30,54]. The hatched field is the convex hull enclosing measurements of BIF’s and ferruginous quartz–amphibole/pyroxene rocks from the ISB and AA (SW Greenland) [17]. The heavy line is the trajectory for mixing between IF-G (BIF geostandard from the ISB) and igneous material.
Our results show that most banded quartz–magnetite rocks from the NSB have heavy Fe isotopic compositions and high Fe/Ti (Fig. 4). Many samples fall in the field covered by BIFs from the ISB and Fe-bearing quartz–pyroxene units from the Akilia association [17]. High Fe/Ti in these rocks probably reflects the low solubility of Ti in seawater, a feature that is transferred to the chemical sediment at precipitation. Furthermore, the high $F_{Fe}$ values of these rocks may be the imprint of partial Fe oxidation [15,17], which is known to enrich the precipitate in the heavy isotopes [21–24]. These results clearly establish the presence of rocks of BIF parentage in the NSB. Sample IN05048 (a quartz–pyroxene rock) has an Fe isotopic composition (+0.038±0.023‰/amu) similar to igneous rocks. This signature does not reflect simple admixture of igneous material because the Fe/Ti ratio of this rock is high (721). Fig. 4 shows a simple two-component mixing curve between IF-G, a BIF from Isua with the highest Fe/Ti ratio (721). The Fe isotopic compositions measured in BIFs from the NSB (from 0 to +0.4‰/amu) [17,18], and igneous material (Fe/Ti = 45 and $F_{Fe}$ = +0.04‰/amu) [20,40]. At an Fe/Ti ratio of 721, the $F_{Fe}$ value of the mixture would still be +0.300‰/amu. We conclude that the range of Fe isotopic compositions measured in BIFs from the NSB (from 0 to +0.4‰/amu) is a primary feature of the rock.

5.2. Metamorphic overprint

In this section, we examine the effect of upper amphibolite/lower granulite facies metamorphism on the Fe isotopic composition of BIFs in more detail. Comparison with the more extensively characterized ISB provides some insights on what may have been the metamorphic reactions involved. Magnetite-bearing quartzite units from the NSB contain amphiboles (and sometimes pyroxenes) that presumably formed by reaction between primary carbonates and quartz following the general reaction [41],

primary carbonates + quartz
+ water → secondary carbonates
+ amphiboles/pyroxenes + carbon dioxide. (3)

The primary carbonates may have had different origins. They could have been deposited as primary chemical sediments together with Fe-hydroxides, as is observed in younger, better preserved BIFs such as those of the Hamersley Range (Western Australia) or the Transvaal Supergroup (South Africa) [15,41]. They could have been introduced in the rock through carbonate metasomatism as has been extensively documented in the ISB [42–44]. It is also possible that they formed during diagenesis by microbial dissimilatory iron reduction of hydrous ferric oxide [19,45]. Carbonates were found and characterized in IN05007 (Figs. 2 and 3) but given the degree of metamorphism of the rock, it is impossible to distinguish between sedimentary, diagenetic, or metasomatic origins based solely on petrography or chemistry.

With amphiboles and pyroxenes derived from reaction between carbonates and quartz, magnetite (Fe₃O₄) is a major carrier of Fe in quartzitic supracrustals (including BIFs) from the NSB (Figs. 2 and 3). Magnetite is not an authigenic phase but was probably formed diagenetically shortly after deposition from the transformation of ferro–ferric hydroxide precursors [41,46]. After formation, magnetite is not involved in any metamorphic reaction [19,41]. There is little doubt that magnetite was ultimately derived from chemical precipitation in the water column and its Fe isotope composition may help us understand the mechanism that caused Fe oxidation and BIF precipitation in the Eoarchean oceans. The $F_{Fe}$ values of individual phases were presumably equilibrated at some scale and one cannot rely on single-phase measurements to infer their compositions before metamorphism.

Two approaches can be used to estimate the initial composition of magnetite. In the element map of IN05007 (Fig. 3, 10.00 cm²), the surface area of magnetite is 1.38 cm² and that of amphibole (mainly cummingtonite) is 2.15 cm² (quartz and other phases occupy 6.34 cm² and 0.14 cm², respectively). Assuming that the surface distribution is representative of the volume distribution, this analysis shows that approximately 74% of Fe is in magnetite and 26% is in cummingtonite (using densities of 5.1 and 3.4 g/cm³ and Fe concentrations of 0.724 and 0.246 g/g for magnetite and cummingtonite, respectively). Dideriksen et al. [47] and Markl et al. [48] analyzed the Fe isotopic compositions of natural carbonate minerals formed in a variety of geological settings (magmatic, metamorphic, hydrothermal, and sedimentary). All samples, without exception, have light Fe isotope compositions relative to IRMM-014, from −0.6 to 0‰/amu. This is similar to the range of $F_{Fe}$ values reported for carbonates in well-preserved BIFs from the Kaapvaal Craton (South Africa) and the Biwabik formation (Minnesota), from −0.5 to 0.1‰/amu [15,19]. One can reasonably assume that the carbonates that were involved in the formation of amphiboles had light Fe isotopic compositions. If the rock behaved as a closed system for Fe, it is straightforward to make the mass balance (0.26 * $F_{Fe}$ carbonate + 0.74 * $F_{Fe}$ magnetite = $F_{Fe}$ bulk) and calculate that the initial $F_{Fe}$ value of Fe-oxides in IN05007 must have been in the range 0.3 to 0.5‰/amu to explain the present value of 0.24‰/amu (for $F_{Fe}$ values of carbonates of 0 and −0.5‰/amu, respectively).
Another way to tackle this question is to recognize that carbonates should leave an imprint on the bulk chemistry of the rock if they were present at the time of formation. The possible cations present in appreciable quantities in the carbonates from rocks of the composition explored in this study are Fe, Mn, Ca, and Mg. In Fig. 5, the $F_{Fe}$ values of bulk ferruginous quartzites from the NSB are plotted as a function of Ca/Fe, Mg/Fe, and Mn/Fe ratios. Simple binary mixing is represented as straight lines in such diagrams. As discussed in Section 5.2, the low $F_{Fe}$ value of IN05048 (0.038±0.023‰/amu) cannot be attributed to admixture of an igneous component. Instead, this sample has high Ca/Fe, Mg/Fe, and Mn/Fe and its isotopic composition may reflect the contribution of carbonates with low $F_{Fe}$ values (Fig. 5). Note that similar relationships are obtained for ratios of transition metals with ionic radii similar to Fe (Ni/Fe, Cu/Fe, and Zn/Fe, see source data in [12]). If the mixing interpretation is correct, then one can extrapolate mixing lines shown in Fig. 5 to Ca/Fe or Mg/Fe equal to 0 (magnetite contains insignificant Ca or Mg) and estimate the $F_{Fe}$ value of an Fe-oxide end-member. The result of this analysis is that the initial $F_{Fe}$ value of the primary Fe-oxide phase must have been around 0.3–0.4‰/amu, in agreement with the value inferred previously (0.3 to 0.5‰/amu). The relationship between $F_{Fe}$ and Mn/Fe is less useful because the Mn/Fe ratio of the Fe-oxide end-member is not well defined. It is interesting to note that IF-G, a BIF geostandard from Isua [33] falls close to the mixing lines defined by quartz–magnetite rocks from the NSB on all diagrams [17,30,33]. This analysis also suggests that the carbonate end-member had light Fe isotopic composition, lower than 0‰/amu. Theoretically, it should be possible to follow the same approach using a trivalent ion that can partition into magnetite (Al, Cr, V) but not in carbonate to derive the isotopic composition of the carbonate end-member. However, no clear correlation was found between $F_{Fe}$ values and Al/Fe, Cr/Fe, and V/Fe ratios, possibly because these elements are present at trace levels and their concentrations in the source fluid may have been variable. If we assume that the primary carbonates had $F_{Fe}$ values between −0.5 and 0‰/amu, then it is possible to calculate the Ca/Fe, Mg/Fe, and Mn/Fe ratios of this end-member. The composition of the primary carbonate end-member is thus estimated to be between Ca$_{0.3}$Mg$_{0.7}$Fe$_{0.5}$ and Ca$_{0.7}$Mg$_{0.3}$Fe$_{0.2}$. It is a virtual component that must reflect mixing between Fe-oxide and carbonate phases (e.g., ankerite 0.5×Ca$_{0.4}$Mg$_{0.3}$Fe$_{0.2}$ + siderite 0.5×Mg$_{0.3}$Fe$_{0.7}$ = Ca$_{0.25}$Mg$_{0.36}$Fe$_{0.45}$). In a ternary diagram, this composition falls on a line that joins amphiboles and carbonates now present in IN05007, which is required by mass balance if these phases formed from reaction between primary carbonates and quartz (Fig. 6). The analysis presented here allows us to better define what may have been the metamorphic reactions involved in the formation of the mineral assemblage preserved in IN05007.
There are 7 free coefficients and 7 elements and this metamorphic reaction can be balanced (Fig. 6). The possible presence of siderite in the primary mineral assemblage supports deposition under high PCO$_2$ [49,50]. Whether this high PCO$_2$ translates into high PCO$_2$ in the Eoarchean atmosphere or reflects local conditions of precipitation is open to debate [51,52].

Because magnetite does not participate in these metamorphic reactions [41], its Fe isotopic composition may be less affected than other phases by metamorphism. This feature was documented during contact metamorphism in the Biwabik iron-formation (Minnesota), where primary Fe isotope heterogeneity of magnetite was preserved, up to temperatures in excess of 500 °C [19]. The self-diffusion coefficient of Fe in magnetite at 500 °C depends on the activity of O$_2$ but is greater than $\sim 10^{-16}$ cm$^2$/s [53]. The corresponding diffusion length for 1 My ($\sqrt{4Dt}$) is $\sim 0.1$ cm. Thus, over timescales relevant to regional metamorphism, the Fe isotope signature of magnetite in rocks of BIF parentage may have been homogenized at the scale of a hand specimen. The best-preserved quartz–magnetite rocks in the NSB have well-preserved bands of magnetite, quartz, and amphibole. Although deformed, these bands most likely reflect original sedimentary strata. Multiple measurements of IN05007 using a micromill apparatus (Fig. 3) show that magnetite has almost homogeneous Fe isotopic composition at the scale of the sample (small variations may be present but it is unclear whether they represent a depositional feature or a problem with sampling single phases, see Section 4). Overall, it seems that in the Nuvvuagittuq supracrustal samples we studied, precipitated Fe (hydr) oxides had almost constant Fe isotope compositions, around +0.3‰/amu.

5.3. Homogeneous/heterogeneous oxidation, source of Fe and mechanism of BIF precipitation

The aim of this section is to integrate the results obtained on the Fe isotopic composition of magnetite in
a feasible scenario for banded iron-formation deposition. As discussed previously, various chemical pathways may have led to the formation of magnetite [19,41]. Below, we shall make the simple assumption that Fe(II)aq was oxidized and precipitated as Fe(III)s. Upon diagenesis, part of Fe(III)s was reduced to form mixed valence magnetite. Beard and Johnson [54] and Dauphas and Rouxel [30] developed a two-stage distillation model to calculate Fe isotope fractionation during oxidation—precipitation of Fe(II)aq. This model may be relevant to Fe(II)aq oxidation at low pH, where significant Fe(III)aq can form. At circum-neutral pH, polymerization of ferric hydroxide occurs on a short time-scale so one would not expect large amounts of Fe(III)aq to be present at any time [55].

Walker [56] reviewed the possible conditions in the Archean ocean when BIFs formed. For PCO2 of ~0.1 atm, the pH would have been around 7 and the concentration of Fe(II)aq around 10^-3 mol/L (also see [46]). At these conditions of circum-neutral pH and high Fe concentrations, it is well documented that Fe oxidation can proceed along two paths [57–59] (Fig. 7). For low concentrations of solids (<3 mg/L), precipitation proceeds predominantly through oxidation of Fe(II)aq and subsequent polymerisation of ferric hydroxide to form colloids which eventually precipitate. In this case (homogeneous oxidation) the rate is,

\[
\frac{d[\text{Fe(II)aq}]}{dt} = -k_1[\text{O}_2][\text{OH}^-]^2[\text{Fe(II)aq}].
\]

(5)

This formula applies to most natural waters at present [60]. When the concentration of solids in suspension increases to above ~3 mg/L, Tamura et al. [57] showed that an autocatalytic effect occurs whereby the rate of oxidation increases with the concentration of Fe(III) hydroxide precipitate. In this case (heterogeneous oxidation) the rate is,

\[
\frac{d[\text{Fe(II)aq}]}{dt} = -k_2[\text{O}_2][\text{Fe(II)aq}][\text{Fe(III)s}]/[\text{H}^+].
\]

(6)

The two processes can happen concurrently. At constant pH and PO2 we can write,

\[
\frac{d[\text{Fe(II)aq}]}{dt} = -k[\text{Fe(II)aq}]-k'[\text{Fe(II)aq}][\text{Fe(III)s}].
\]

(7)

The ratio \(k'/k\) only depends on the nature of the phase precipitated and pH (\(\sim [\text{H}^+]\)). It is equal to \(5 \times 10^3\) mol\(^{-1}\) L at pH 7 for an amorphous ferric hydroxide formed by hydrolysis of Fe(III) perchlorate [57,58]. The dimensionless parameter (\(k\) is in s\(^{-1}\) and \(k'\) in mol\(^{-1}\) s\(^{-1}\)) that governs the evolution of the system is,

\[
c = \frac{k'[\text{Fe(II)aq}]}{k}
\]

(8)

where [Fe(II)aq] is the initial concentration of dissolved ferrous iron. For an initial concentration of 10^-3 mol L\(^{-1}\), \(c\) is equal to 5. This is higher than 1 and heterogeneous oxidation could clearly be relevant to BIF precipitation. In a closed system with only Fe(II)aq present at the beginning, the fraction of Fe precipitated is given by,

\[
\frac{\text{Fe(III)s}}{\text{Fe(II)aq}^0} = \frac{e^{(1+c)u-1}}{c + e^{(1+c)u}},
\]

(9)

where \(u\) is the dimensionless variable \(kt\) [57,59]. Iron isotopes could be fractionated to different extents along the two oxidation paths. Assuming that Fe oxidation results in Rayleigh-type transfer of isotopes (i.e., after precipitation there is no isotopic exchange between the precipitate and the fluid), then the composition of the precipitate can be calculated,

\[
F_{\text{Fe}}^{\text{III}s} = F_{\text{Fe}}^{\text{III}aq}(0) + \frac{1 + c}{1 - e^{(1+c)u}} \left[ \left( A_{\text{III}aq}^{\text{he}} - A_{\text{III}aq}^{\text{lo}} \right) u + A_{\text{III}aq}^{\text{he}} \ln \left( \frac{1 + c}{c + e^{(1+c)u}} \right) \right],
\]

(10)

where \(F_{\text{Fe}}^{\text{III}aq}(0)\) is the initial composition of ferrous iron, \(A_{\text{III}aq}^{\text{he}}\) and \(A_{\text{III}aq}^{\text{lo}}\) are the isotopic fractionations in \(^{\text{16}}\)O/amu between the instantaneous precipitate and the pool of Fe(II)aq for heterogeneous and homogeneous oxidations, respectively (see Appendix for details).

The three processes most commonly advocated for Fe oxidation in an anoxic atmosphere are, (i) oxidation from O\(_2\) generated by oxygenic photosynthesis, (ii) oxidation during anoxygenic photosynthesis where Fe (II)aq is used as an electron donor in place of H\(_2\)O, and (iii) photo-oxidation of Fe at the surface of oceans by energetic photons penetrating through an atmosphere transparent to UV radiation. As yet, the effect of photo-oxidation (iii) on the isotopic composition of Fe has not been documented. The other processes (i, ii) are known to enrich Fe(III)s in the heavy isotopes of Fe relative to Fe(II)aq. Welch et al. [22] and Balei et al. [24] studied Fe isotope fractionation during oxidation at low pH (<3), which may not be relevant to BIF formation. The isotopic fractionation between Fe(II)aq and Fe(III)aq at room temperature under sterile conditions is +1.4\(^{\text{16}}\)O/amu [22]. Bulk et al. [21] measured a
lower fractionation between Fe(II)aq and Fe(III)ₘ of around 0.5‰/amu during precipitation of ferrihydrite at pH around 6, which may partly reflect kinetic isotope fractionation during precipitation of Fe(III)ₘ into Fe (III)ₘ. These values would be relevant to oxidation from O₂ generated by oxygenic photosynthesis. Croal et al. [23] measured the Fe isotopic fractionation between Fe(II)ₙₐ and Fe(III)ₙ during anoxicogenic photosynthesis at pH ~7 and found values of around 0.7‰/amu. Again, this value may be the superposition of effects associated with Fe(II)ₙₐ–Fe(III)ₙₐ oxidation and Fe(III)ₙₐ–Fe(III)ₘ precipitation. Precipitation of Fe(III)ₙₐ into hematite is associated with little equilibrium fractionation but with a significant kinetic isotope effect that enriches the precipitate in the light isotopes [61]. This fractionation increases as the rate of precipitation increases and can reach values as low as ~0.5‰/amu. The isotopic fractionation associated with heterogeneous (O₂-mediated) oxidation is unknown. Adsorption may play a role in this process, which can potentially create isotopic fractionation, with Fe(II)₂ₐ being enriched in the heavy isotopes of Fe relative to the pool of Fe(II)ₙₐ. Icopini et al. [62] argued that the fractionation may be as large as 1.5‰/amu but values of around 0.2 to 0.4‰/amu may be more reasonable [63,64]. Multiple lines of evidence suggest that the primary source of Fe found in BIFs was hydrothermal [12,26,65]. Present hydrothermal fluids sampled at vents along ocean-ridges have negative Fₐ values, centred on ~0.15‰/amu [66–68]. The net isotopic fractionation between Fe-oxide precursors in banded quartz–magnetite rocks in the NSB (Fₐ = 0.35‰/amu) and the possible hydrothermal source of Fe (Fₐ = ~0.15‰/amu) is therefore ~0.5‰/amu.

For the purpose of illustration, we shall adopt the following set of parameters to model Fe isotope fractionation during BIF precipitation using Eqs. (9) and (10), (i) O₂-mediated abiotic oxidation: Fₐ(0)= −0.15‰/amu, c=5, Aₐ(0) = 0.5‰/amu, and Aₐ = 0.2‰/amu. (ii) Anoxogenic photosynthetic oxidation: standard Rayleigh distillation, equivalent to Fₐ(0)= −0.15‰/amu, c=0, Aₐ = 0.7‰/amu.

In Fig. 8, we report the calculated Fe isotopic composition of the precipitate as a function of the fraction of Fe precipitated. As shown, the Fe isotopic composition of the precursor of magnetite can be explained by both scenarios (i) and (ii). The fact that precipitated Fe(hydr) oxide in Isua and Nuvvuagittuq had almost constant Fe isotopic composition, around 0.3–0.4‰/amu, suggests that the fraction of Fe precipitated remained constant and probably represented a small fraction of the total inventory of dissolved Fe, presumably less than 10%. To summarize, the heavy Fe isotopic composition found in magnetite of quartz–magnetite rocks (banded iron-formations) from the Nuvvuagittuq supracrustal belt can be explained if Fe was derived from a hydrothermal source and was only partially oxidized in the water column.

5.4. The Fe isotopic composition of Eoarchean mafic and ultramafic magmas

Mantle-derived magmas and peridotites are the only samples available for estimating the Fe isotopic composition of the Bulk Silicate Earth (BSE). Beard et al. [20] showed that igneous rocks sampled in a variety of geological settings have almost uniform isotopic compositions. However, further detailed studies have revealed the presence of large-scale Fe isotope variations in mantle and magmatic rocks [34,69–72]. For instance, peridotites and granitoids have a large range of Fₐ values, from ~0.2 to ~0.4‰/amu [34,71]. Most mantle peridotites analyzed so far have light Fe isotopic compositions, down to ~0.2‰/amu [70–72]. In some cases, Fₐ values of bulk peridotites correlate with chemical indicators of depletion and oxidation [71]. A possible interpretation is that during partial melting, the melt does not have the same isotopic composition as the starting material because there is mineral/melt isotope fractionation and/or there is inter-mineral isotope fractionation and melting is non-modal. For degrees of melting between 0 and 40% of a spinel lherzolite composition, Williams et al. [71] showed that the
magmas produced could be fractionated by as much as 0.07‰/amu relative to the source and yet show little variation from one to another over a large melting interval. Thus, modern continental basalts, MORBs, and OIBs could be fractionated relative to the mantle but still show almost constant Fe isotopic compositions, around +0.05‰/amu (Fig. 9). Lherzolites may be a better proxy of the composition of the BSE [72]. The 7 bulk rock lherzolite measurements published so far range from 0 to +0.03‰/amu, with a weighted average of about +0.02 [17,71,72] (dominated by a very precise measurement of a single xenolith from Kilbourne Hole [71]). This is lower than the composition of modern basalts but even the most pristine peridotites have experienced melt depletion/metasomatism and it is crucial at this stage to extend the database of otherwise well-characterized fertile lherzolites.

Although this is at the limit of resolution with present analytical uncertainties, mafic and ultramafic magmatic rocks from the ca. 3.83 Ga Akilia island [7] and ca. 3.75 Ga NSB [12] localities may have light Fe isotopic compositions (+0.004±0.016 and −0.006±0.022‰/amu respectively, Table 1, Fig. 9) compared to modern basalts [17]. This could reflect modification of initial Fe isotopic compositions after emplacement of the rocks. Indeed, pervasive carbonate and alkali metasomatism has been documented in SW Greenland [42–44] and its effect on Fe isotopes has not been explored. However, it is unlikely that the diverse suite of samples analyzed in this study (Table 1) and in [17] would have experienced the same degree of metasomatic alteration and would all show the same shift in $F_{Fe}$ values. This suggests that the light Fe isotopic compositions measured in Akilia and the NSB may represent primary magmatic signatures. Poitrasson et al. [35] measured a 3.5 Ga komatiite from Barberton (geostandard WITS-1) and also found a low $F_{Fe}$ value of 0.019±0.008‰/amu. In contrast, Weyer et al. [72] measured a 2.7 Ga komatiite from Alexo (geostandard KAL-1, Ontario, Canada) and found a value that is indistinguishable from modern basalts (0.036±0.007‰/amu). The possible change in Fe isotopic composition of magmas formed by partial melting of the mantle (from ~0‰/amu in the early Archean to ~0.05‰/amu at present) could reflect changes in the thermal regime of the mantle and the conditions of magma generation (e.g., fraction of partial melting, temperature, buoyancy). Clearly, the database of Fe isotope analyses of Archean magmas must be extended to ascertain whether the secular variation discussed here is real and if it is, address its origin.

### 6. Conclusions

The recently discovered 3.75 Ga Nuvvuagittuq supracrustal belt provides us with a means to investigate the surface chemistry of the Eoarchean Earth from the perspective of a “new” terrane contemporaneous with the Isua locality. The best-preserved banded quartz–magnetite rocks (BIFs) contain alternating bands of magnetite and quartz/amphibole (actinolite and cummingtonite) with minor sulfide (pyrite) and carbonate (calcite and ankerite). The mineral paragenesis is best explained by amphibolite facies metamorphism of a BIF protolith consisting of magnetite, quartz, and carbonate as major constituents.

The heavy Fe isotopic compositions (around +0.3‰/amu relative to IRMM-014) and high Fe/Ti ratios (up to ~100× the ratio of surrounding igneous rocks) measured in some BIFs demonstrate that these rocks are true chemical sediments precipitated from seawater. These samples can therefore be used in future studies to document the chemistry of Eoarchean oceans.
We interpret the dispersion in Fe isotope compositions at a bulk sample scale in banded iron-formationations (from 0 to +0.3‰/amu) to reflect binary mixing between Fe-oxides and carbonates. By extrapolating mixing lines in Ca/Fe vs $F_{Fe}$ and Mg/Fe vs $F_{Fe}$ space to Ca/Fe=0 and Mg/Fe=0, one can estimate the Fe isotopic composition of the pure Fe-oxide end-member, which is between +0.3 to +0.4‰/amu. On the other hand, if it is assumed that the primary carbonates had Fe isotope compositions between −0.5 and 0‰/amu, which covers the range of values measured so far in carbonates from a variety of geological settings, one can derive the chemistry of the carbonate end-member. In a Fe–Mg–Ca ternary diagram, the calculated composition falls along a line connecting carbonates and amphiboles now present in the rock, which is consistent with derivation of these phases from reaction between quartz and primary carbonate. The composition of the primary carbonate does not correspond to a real phase but must reflect a mixture, possibly reaction between quartz and primary carbonate. The possible presence of siderite supports deposition under high PCO$_2$. Iron isotopes can thus be used as an independent means to infer the protolith mineralogy of heavily metamorphosed rocks that may otherwise be inaccessible, especially if the rocks did not behave as a perfect closed-systems.

A distillation model involving two possible oxidation paths (homogeneous and heterogeneous) was developed. It is used to demonstrate that the heavy Fe isotopic composition inferred for the precursor phase(s) of magnetite can be explained by partial oxidation of Fe(II)$_{aq}$ deriving from a hydrothermal source through oxygenic or anoxygenic photosynthesis.

Preliminary data suggest that mafic and ultramafic magmatic rocks from the NSB have lower Fe isotopic compositions than modern basalts. A more extensive characterization of magmas generated during the early history of the Earth is required to ascertain whether this effect is real or not, work that is currently in progress.

At neutral pH, ferrous iron in solution can be oxidized through the homogeneous and heterogeneous paths,

$$\frac{d\text{Fe}^{II}_{aq}}{dt} = -k\text{Fe}^{II}_{aq} F_{\text{Fe}^{II}_{aq}} - k\text{Fe}^{II}_{aq} F_{\text{Fe}^{III}}. \quad (A1)$$

For a system with all iron as $F_{\text{Fe}^{II}_{aq}}$ at time 0, we have,

$$\frac{d\text{Fe}^{II}_{aq}}{dt} = -kF_{\text{Fe}^{II}_{aq}} F_{\text{Fe}^{III}}\left(F_{0}^{\text{Fe}^{III}} F_{\text{Fe}^{II}_{aq}}\right). \quad (A2)$$

Using the dimensionless variables and parameters, $u=kt$, $f=F_{\text{Fe}^{II}_{aq}}/F_{0}^{\text{Fe}^{II}_{aq}}$, and $c=kF_{0}^{\text{Fe}^{II}_{aq}}/k$, one can write Eq. (A2) as,

$$\frac{df}{du} = -f-cf(1-f). \quad (A3)$$

Integration is straightforward (pose $h=f^{-1}$ and use the method of variation of the constant),

$$f = \frac{1 + c}{c + e^{(1+c)u}}. \quad (A4)$$

For the total amount of iron precipitated ($g=F_{\text{Fe}^{III}/F_{0}^{\text{Fe}^{II}_{aq}}}=1-f$) we have,

$$g = \frac{e^{(1+c)u} - 1}{c + e^{(1+c)u}}. \quad (A5)$$

The expressions had been derived in Tamura et al. [57]. We now turn to isotopes which is a new development of this work. Let us denote $a$ and $b$ two isotopes of Fe and $\phi_{i \rightarrow j}$ the flux of $a$ from reservoir $i$ to $j$. We have for the pool of ferrous iron in solution,

$$\frac{d\phi_{a}^{II}_{aq}}{dt} = -\phi_{a}^{II}_{aq} F_{\text{III he}} - \phi_{a}^{II}_{aq} F_{\text{III he}}. \quad (A6)$$
We note $R$ the ratio of the abundances of isotopes $a$ and $b$, with $R'$ the ratio in reservoir $i$ and $R''$ the ratio in the flux from $i$ to $j$. Eq. (A6) can be written,
\[
\frac{d\delta_{\text{IIaq}}^\text{IIaq}}{dR} = -\phi_b^{\text{IIaq}} - \phi_b^{\text{IIaq} \rightarrow \text{III he}} R^{\text{IIaq} \rightarrow \text{III he}} - \phi_b^{\text{IIaq} \rightarrow \text{IIaq} he} R^{\text{IIaq} \rightarrow \text{IIaq} he}.
\] (A7)

We impose Rayleigh conditions between $\text{Fe}^{\text{IIaq}}$ and $\text{Fe}^{\text{IIaq} \rightarrow \text{IIaq} he}$, Mathematically, this means that the ratios $\alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{III he}} = R^{\text{IIaq} \rightarrow \text{III he}}$ and $\alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} = R^{\text{IIaq} \rightarrow \text{IIaq} he}/R^{\text{IIaq}}$ must remain constant.

After some rearrangement of Eq. (A7), it can be shown that,
\[
\frac{d\text{Fe}^{\text{IIaq}}}{dR} + \text{Fe}^{\text{IIaq}} \frac{d\ln R^{\text{IIaq}}}{dR} = -\alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} \text{Fe}^{\text{IIaq}} \alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he}(\text{Fe}^{\text{IIaq}}_0 - \text{Fe}^{\text{IIaq}}). \tag{A8}
\]

In dimensionless coordinates, this takes the form,
\[
df + f \frac{d\ln R^{\text{IIaq}}}{du} = -\alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} f \alpha_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} c f (1-f). \tag{A9}
\]

Isotope variations are in most cases small and we use the following notation, $\delta = (R''/R'^{\text{IIaq}} - 1) \times 10^3$. The $\delta$ notation is used here to improve readability. We also write $A' = (\alpha'/1) \times 10^3$. Using these notations and the fact that $\delta/10^3 \approx 0$, Eq. (A9) can be rearranged,
\[
\frac{d\delta_{\text{IIaq}}^{\text{IIaq}}}{du} = -10^3 \frac{d\ln f}{du} - (A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} + 10^3) - c(A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} + 10^3)(1-f). \tag{A10}
\]

This equation can be integrated (inject the relationship between $d\ln f/du$ and $f$ from Eq. (A3) into Eq. (A10)),
\[
\delta_{\text{IIaq}} = \delta_{\text{IIaq}}^0 + (A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} - A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he})u + A_{\text{IIaq}}^{\text{IIaq} he} \ln \left(\frac{1 + c}{c + e^{(1+c)u}}\right). \tag{A11}
\]

The isotopic composition of the precipitate can easily be calculated from mass-balance considerations,
\[
\delta_{0}^{\text{IIaq}} = f \delta_{\text{IIaq}} + (1-f)\delta_{\text{III he}}. \tag{A12}
\]

It follows that,
\[
\delta_{\text{III he}} = \delta_{0}^{\text{IIaq}} + \frac{1 + c}{1 - e^{(1+c)u}} \left( (A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he} - A_{\text{IIaq}}^{\text{IIaq} \rightarrow \text{IIaq} he})u + A_{\text{IIaq}}^{\text{IIaq} he} \ln \left(\frac{1 + c}{c + e^{(1+c)u}}\right) \right). \tag{A13}
\]

References


