

**THE IRON ISOTOPIC COMPOSITION OF 3.7-3.8 Ga CHEMICAL SEDIMENTS: COMPARISON BETWEEN ISUA (GREENLAND) AND NUVVUAGITTUQ (NORTHERN QUÉBEC).** N. Dauphas<sup>1,2,3</sup>, N.L. Cates<sup>4</sup>, S.J. Mojzsis<sup>4</sup>, M. van Zuilen<sup>5</sup>, M. Wadhwa<sup>2,3</sup>, P.E. Janney<sup>2,3</sup>, V. Busigny<sup>1,2,3</sup>, A.M. Davis<sup>1,3</sup>, <sup>1</sup>Origins Laboratory, Department of the Geophysical Sciences, and Enrico Fermi Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago IL 60637, USA ([dauphas@uchicago.edu](mailto:dauphas@uchicago.edu)), <sup>2</sup>Department of Geology, The Field Museum, 1400 South Lake Shore Drive, Chicago IL 60605, USA, <sup>3</sup>Chicago Center for Cosmochemistry, <sup>4</sup>Department of Geological Sciences, Center for Astrobiology, University of Colorado, Boulder, Colorado 80309-0399, USA, <sup>5</sup>Institut de Physique du Globe de Paris, 4 Place Jussieu, 75252 Paris Cedex 05, France.

**Introduction:** Studies of the surface chemistry of the Early Archean Earth over the past several decades have been limited to 3.7-3.8 Ga metasediments found in southern West Greenland (Isua Supracrustal Belt and Akilia Association [*e.g.*, 1,2]) as these are, by far, the oldest recognized chemical sediments on Earth. A major difficulty with these rocks is that they only sample a limited portion of the Earth's surface from that time, yet conclusions derived from them have planetary-scale implications (*e.g.*, habitability of the Earth, presence of life, extraterrestrial bombardment history and atmospheric chemistry). Recently, David *et al.* [3,4] discovered a 3.7-3.8 Ga volcano-sedimentary sequence (Nuvvuagittuq Belt) located within the Inukjuak terrane of the Superior Province, Northern Québec (Canada). This sequence is comprised of mafic extrusives (layered and massive amphibolites), chemical sediments (banded iron formations; BIFs) and a polymict conglomerate [5]. As is observed in southern West Greenland, the rocks have been metamorphosed to amphibolite-granulite facies. Nadeau [5] obtained a minimum age of 3825±16 Ma for the emplacement of the Nuvvuagittuq supracrustals based on U-Pb bulk zircon dating. More recently, Cates and Mojzsis [6] obtained a slightly lower age of 3760 Ma, from detailed ion microprobe U-Th-Pb zircon geochronology. The rocks from Northern Québec are as old as those in West Greenland and provide a valuable comparison point for tracing the development of a habitable environment on Earth.

The isotopic composition of iron is sensitive to biotic (*e.g.*, dissimilatory iron reduction, anoxygenic photosynthesis) and abiotic (*e.g.*, photo-oxidation, precipitation of ferrihydrite from ferrous iron) redox changes (see recent reviews [7-10]). BIFs are chemical sediments formed by oxidation of Fe(II)<sub>aq</sub> and subsequent precipitation of hydrous ferric oxides (HFO). Iron isotopes address central issues to the evolution of the Earth's past surface environments, such as (i) what processes permitted the oxidation and precipitation of iron in an atmosphere that was globally anoxic [11,12]; (ii) can we distinguish between metamorphosed BIFs

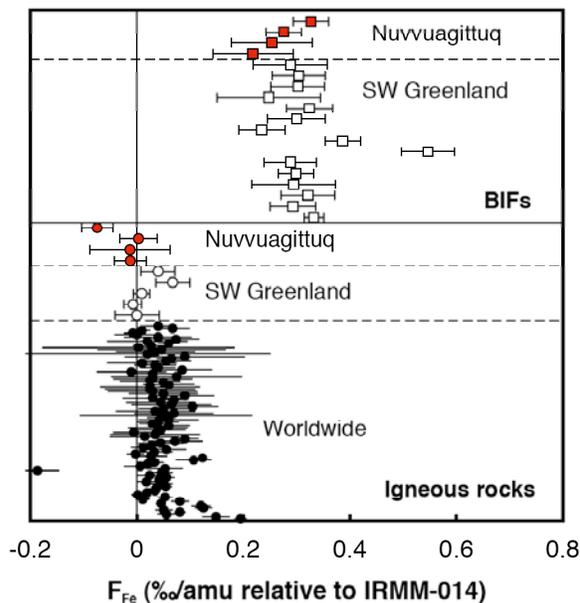
and metasomatized igneous rocks [12]; and (iii) when did the atmosphere become oxic [13].

**Isotope fractionation during iron oxidation-precipitation:** Johnson *et al.* [11] analyzed the iron isotopic compositions of 2.5 Ga BIFs from the Kaapvaal Craton (South Africa). These samples are fairly well preserved and provide a useful framework for interpreting metamorphic rocks from Isua [12]. The Kaapvaal BIFs show variable iron isotopic compositions with a strong mineralogical control. Pyrite and iron-carbonates tend to have light iron isotopic compositions relative to igneous rocks while hematite and magnetite tend to have heavy iron isotopic compositions. This is reasonably well explained by oxidation and subsequent precipitation of Fe(II)<sub>aq</sub> deriving from mid-ocean ridge hydrothermal vents.

Iron-oxidation is associated with an equilibrium isotopic fractionation that tends to enrich Fe(III)<sub>aq</sub> in the heavy isotopes relative to Fe(II)<sub>aq</sub>. The experimentally determined fractionation between Fe(III)<sub>aq</sub> and Fe(II)<sub>aq</sub> is approximately 1.4 ‰/amu, regardless of whether the oxidation is biologically mediated or not [7-11, and references therein]. Precipitation of hematite is associated with a kinetic isotope effect that tends to enrich the precipitate in the light isotopes relative to Fe(III)<sub>aq</sub>. The isotopic fractionation associated with iron-precipitation increases as the rate of precipitation increases. Overall, iron oxidation/precipitation can be described in a 2-stage model, which is amenable to quantification [7,8,10]. In most cases, the net isotopic effect corresponds to an enrichment in the heavy isotopes of iron in Fe(III)<sub>s</sub> relative to Fe(II)<sub>aq</sub>.

**Isua (southern West Greenland):** Dauphas *et al.* [12] showed that BIFs from the Isua Supracrustal Belt and the Akilia Association have heavy iron isotopic compositions, up to 0.5 ‰/amu relative to the reference material IRMM-014 (which has iron isotopic composition close to worldwide igneous rocks). Here, we report new bulk rock measurements of BIFs from Isua. Most measurements were replicated, including sample dissolution. Iron was purified by ion exchange chromatography and analyzed by MC-ICPMS (Micromass Isoprobe, Isotope Geochemistry Laboratory of the Field Museum) following the protocol described in

[10,14]. All BIF samples show positive iron isotopic compositions relative to IRMM-014, confirming previous results. One sample (IS-04-06) is a well-preserved, finely laminated BIF with alternate layers of magnetite and quartz (carbonates and amphiboles are also present). As discussed in [12], the enrichment in heavy iron isotopes could result from partial oxidation of  $\text{Fe(II)}_{\text{aq}}$  by  $\text{O}_2$  or microbes doing anoxygenic photosynthesis. The data may also bear on the composition of the fluid from which the BIF precipitated if the oxidation was complete.



**Fig.1.** Iron isotopic compositions (in permil per atomic mass unit variation relative to the IRMM-014 reference material) in worldwide igneous rocks (filled circles), SW Greenland igneous rocks (empty circles [12]), amphibolites from the 3.7-3.8 Ga Nuvvuagittuq Supracrustal Belt (this study), BIFs from Isua (empty squares [12, this study]) and BIFs from Nuvvuagittuq (red squares).

**Nuvvuagittuq (Northern Québec, Canada):** We have analyzed the iron isotopic compositions of BIFs and associated amphibolites (meta-igneous rocks) from the *ca.* 3760 Ma [6] Nuvvuagittuq Belt to establish the nature of the protolith of these rocks and trace iron oxidation in the early Archean ocean (Fig. 1). The massive and banded amphibolites from Nuvvuagittuq (samples IN05019, IN05047, IN05013, and IN05045) have iron isotopic compositions similar to IRMM-014 and igneous rocks. These data demonstrate that the iron isotopic composition of the terrestrial mantle has not changed with time, which is in agreement with the results obtained in Isua. A quartz-pyroxene unit of uncertain origin (IN05048) has iron isotopic composition indistinguishable from the igneous value, which

suggests that iron in this rock derives from an igneous source or that the oxidation was total, so that no fractionation occurred between iron dissolved in the oceans and iron precipitated. Two BIF samples (IN05007 and IN05009) have heavy iron isotopic compositions of around 0.2-0.3 ‰/amu relative to IRMM-014, supporting the interpretation based on mineralogy and field relations that they have a chemical sedimentary origin. The enrichments in heavy iron isotopes observed in Nuvvuagittuq are similar to those observed in Isua (0.3-0.6 ‰/amu). This may reflect the fact that the degree of partial oxidation at the two localities was similar because otherwise, one would expect to find different isotopic compositions for BIFs from these separate localities. It could also reflect the composition of the fluid from which the BIFs precipitated if the oxidation was total.

**Conclusions:** The BIFs in the 3.7-3.8 Ga Nuvvuagittuq Belt have heavy Fe isotopic compositions, similar to those measured in the better-characterized Isua Supracrustal Belt. This result demonstrates that the BIFs from Nuvvuagittuq have a chemical sedimentary origin. The similarities in iron isotopic compositions between the two localities can be explained by similar degrees of partial oxidation or by total oxidation and precipitation from a fluid already enriched in heavy iron isotopes. This is the first time in 40 years that an early Archean supracrustal belt has been opened up for study.

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