

## Early Archean Fe oxidation revealed by meso- and micron-scale Fe isotope analyses of the 3.7–3.8 Ga Isua BIFs

ANDREW D. CZAJA<sup>1,2\*</sup>, CLARK M. JOHNSON<sup>1,2</sup>, BRIAN L. BEARD<sup>1,2</sup>, STEPHEN MOORBATH<sup>3</sup>

<sup>1</sup>Department of Geoscience, University of Wisconsin, Madison, WI, USA, aczaja@geology.wisc.edu (\* presenting author)

<sup>2</sup>NASA Astrobiology Institute

<sup>3</sup>Department of Earth Sciences, University of Oxford, Oxford, GBR

Iron isotopes are increasingly used to constrain the conditions of Earth's paleoenvironments and even suggest the influence of biological activity. Interpretations of Fe isotope fractionations in Archean and Paleoproterozoic banded iron formations (BIFs), shales, and carbonates suggest a role for biological processes (bacterial dissimilatory iron reduction (DIR) and anoxygenic photosynthetic iron oxidation (APIO)) and abiological processes (oxidation by free O<sub>2</sub>). Measurements of rock powders micromilled from individual magnetite layers and of individual magnetite grains analyzed by femtosecond laser ablation ICP-MS (fs-LA-ICP-MS) from BIFs of the 3.7–3.8 Ga Isua Greenstone Belt reveal a consistently narrow range of non-zero  $\delta^{56}\text{Fe}$  values. Analyses by fs-LA-ICP-MS allow for precise and accurate micron-scale analyses without the orientation effects associated with secondary ion mass spectrometry analyses of magnetite [1]. Magnetite  $\delta^{56}\text{Fe}$  values range from +0.4‰ to +1.1‰ among different bands, but within individual layers magnetites are homogenous. In bulk samples,  $\delta^{56}\text{Fe}$  and SiO<sub>2</sub> concentration are negatively correlated, whereas  $\delta^{56}\text{Fe}$  and total Fe concentrations are positively correlated, reflecting mixtures between magnetite and Fe silicate. A simple mixing model between a low- $\delta^{56}\text{Fe}$  component (Fe silicate) and a high- $\delta^{56}\text{Fe}$  component (magnetite) can explain the range in Fe isotope compositions of the micromilled rock powders. Although these BIFs have been metamorphosed to greenschist- to amphibolite-facies, the isotopic heterogeneity observed on both scales suggests that the Fe isotope compositions reflect primary, low-temperature sedimentary values.

The positive  $\delta^{56}\text{Fe}$  values measured from the Isua magnetites are best explained by deposition of Fe-oxides produced by partial oxidation of Fe(II)-rich ocean water either by free O<sub>2</sub> or APIO. Comparison of the Fe isotope data from the Isua BIFs with those from the 2.5 Ga BIFs from the Hamersley and Transvaal basins suggests a striking difference in Fe sources and pathways. The Neoproterozoic magnetite facies BIFs of Australia and South Africa have  $\delta^{56}\text{Fe}$  values that range from -1.2 to +1.2 ‰ [2] and are on average significantly lower than those reported here from the Isua BIFs. Such a range suggests a role for DIR, the most likely means by which to produce large masses of negatively fractionated Fe. The absence of low  $\delta^{56}\text{Fe}$  values in the Isua BIFs may indicate formation prior to the evolution of DIR or in an environment that excluded this metabolism.

### Acknowledgements

We thank Morgan Herrick, Robert Dymek, Cornelius Klein for provision of samples, assistance with analyses, and discussions.

[1] Kita (2010) *Surf. Interface Anal.* **43**, 427-431. [2] Johnson (2008) *Annu. Rev. Earth Planet. Sci.* **36**, 457-493.