

## Triple iron isotope variations in Archean ocean sediments

A HEARD<sup>1</sup>, N. DAUPHAS<sup>1</sup>, O. ROUXEL<sup>2</sup>, N. NIE<sup>1</sup>

<sup>1</sup>Origins Laboratory, University of Chicago, USA.

<sup>2</sup>Department of Oceanography, University of Hawaii, USA.

The Archean saw the deposition of sediments with a huge range in iron isotopic compositions [1]. This, along with the occurrence of ferric-iron rich banded iron formation (BIF), provide evidence that redox cycling of iron occurred in the Archean oceans despite the anoxic state of the atmosphere at that time [2]. In a pre-oxygenated world, iron may have been a key electron donor and acceptor to microbial metabolisms, such as in photoferrotrophy, and dissimilatory iron respiration (DIR). Iron isotope variations measured in BIF and shale may indeed reflect the imprint of microbial activity, along with that of abiotic oxidants such as UV photons and localized O<sub>2</sub>.

The prevalence of extremely isotopically light pyrites in Archean black shales, with  $\delta^{56}\text{Fe}$  extending below -3 ‰, has been taken separately as: evidence for a strongly depleted oceanic ferrous iron reservoir, formed complimentary to the deposition of isotopically heavy BIF [1]; an imprint of DIR in sediments following its early evolution in Earth history [3,4]; or a kinetic isotope effect occurring in an iron-rich Archean diagenetic environment [5]. These pathways either create an isotopically depleted ferrous iron pool for pyrite formation, or directly form isotopically light pyrite; but traditional iron isotope analyses cannot distinguish isotopically light pyrite signatures stemming from reservoir effects, DIR, or kinetics.

We previously showed that UV photo-oxidation followed a specific mass dependent fractionation law for iron isotopes [6]. We now explore the slope of the mass dependent fractionation law for iron isotopes in Archean BIF, pyrite and black shales to assess whether the processes which led to the formation of these strongly fractionated sedimentary components are distinguishable in three isotope (<sup>54</sup>Fe, <sup>56</sup>Fe, <sup>57</sup>Fe) space. Crucially, the depleted reservoir model for light pyrite of [1] can be directly tested, as this model predicts a cogenetic relationship for BIF and pyrites which implies they would follow a single mass fractionation law. The results of these exploratory studies will be reported at the meeting.

References: [1] Rouxel, O. J. *et al.* (2005) *Science*, 307, 1088-1091. [2] Holland (1984) *The Chemical Evolution of the Atmosphere and Oceans*. [3] Archer, C. & Vance, D. (2006) *Geology*, 34, 3, 153-156. [4] Czaja, A. D. *et al.* (2010) *EPSL*, 292, 1, 170-180. [5] Guilbaud, R. *et al.* (2011) *Science*, 332, 1548-1551. [6] Nie N. X. *et al.* (2017) *EPSL*, 458, 179-191.