

## Iron and oxygen isotope fractionation during photo-oxidation

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Banded iron formations (BIFs) provide a unique archive of Earth's ocean chemistry and biology in the Archaean and Paleoproterozoic. It is still under debate, however, whether their precipitation involved photosynthesis or was due to chemical UV photo-oxidation. The two biologically mediated scenarios of, anoxygenic photosynthesis in which bacteria use Fe(II) as an electron donor and, O<sub>2</sub>-mediated oxidation in which gaseous O<sub>2</sub> is produced during photosynthesis, have been investigated previously using isotope methods and both were found to fractionate Fe isotopes to a similar extent as that of BIFs [1, 2]. However, Fe isotope fractionation during photo-oxidation is not well constrained. To compare the abiological photo-oxidation and the two biogenic alternatives, we performed lab photo-oxidation experiments and measured Fe and oxygen isotope fractionation during the process.

The experiments were conducted at 45 °C. Initial Fe(II) solution (Fe(II)<sub>aq</sub>) was prepared by dissolving salt of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and buffering to pH=7.3 with borate. Iron isotopic compositions of the solution and precipitate during photo-oxidation follow a Rayleigh distillation model associated with a fractionation between Fe(III) precipitate (Fe(III)<sub>ppt</sub>) and Fe(II)<sub>aq</sub> of +1.2±0.1‰ for <sup>56</sup>Fe/<sup>54</sup>Fe ratio, close to the two bio-related oxidation processes (+1.5‰ for anoxygenic photosynthesis [1] and +1.0‰ for O<sub>2</sub>-mediated oxidation [2]). Further high-precision Fe isotope measurements suggest that photo-oxidation follows the equilibrium mass fractionation law. The oxygen isotopic composition of Fe(III)<sub>ppt</sub> is about +0.8±0.2‰ heavier than the water used here in terms of δ<sup>18</sup>O, consistent with previous studies finding little equilibrium oxygen isotope fractionation between Fe(III) oxide-hydroxide minerals and water at room temperature [3, 4]. No mass-independent fractionation was observed in our experiments, despite such behaviour being seen in present day atmospheric oxygen due to photochemical processes. Our results therefore support photo-oxidation as a possible mechanism for BIF precipitation.

[1] Croal et al. (2004) *GCA* **68**, 1227–1242. [2] Bullen et al. (2001) *Geology* **29**, 699–702. [3] Bao and Koch (1999) *GCA* **63**, 599–613. [4] Frierdich et al. (2015) *GCA* **160**, 38–54.