

## The Fe homeostasis of the pre-GOE ocean

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Banded iron formations (BIF) are a remarkable feature of the Archean and Early Proterozoic sedimentary record. Whether they reflect a specific inorganic geochemical configuration of the ocean-atmosphere system or herald the rise of biological processes is still a matter of dispute [1-3]. In the modern ocean, iron solubility is limited to about 0.6 nmol L<sup>-1</sup> [4] by Fe(III) oxyhydroxide precipitation. In contrast, prior to the Great Oxygenation Event (GOE) ~2.4 Gy ago, oceanic iron was in its Fe(II) form and its solubility, in the presence of magnetite and carbonates, estimated at 50 μmol L<sup>-1</sup> for the Proterozoic [5] and 100 μmol L<sup>-1</sup> for the Archean [6]. Here, we report on Fe isotope compositions in BIF from three cores from the pre-GOE Transvaal Supergroup, South Africa, and one core from the pre-GOE Joffre Member of the Hamersley Group, Australia. Cobalt accumulation rates are used to establish a high-resolution time scale and deduce chemical fluxes. The inferred sedimentation rates are consistent with U-Pb chronological evidence. The e-folding time of δ<sup>56</sup>Fe variations up the stratigraphy is used to determine Fe oceanic residence times and Fe concentrations as well as the dissolved carbonate content of Early Proterozoic seas. Iron oceanic residence times increased from 0.3 to 5 Ma from 2521 to 2394 Ma, which translates into ocean Fe concentrations increasing from 6.4 to 37 mmol kg<sup>-1</sup> and a [CO<sub>3</sub><sup>2-</sup>] decrease from 3.1 to 0.5 mmol kg<sup>-1</sup>. Massive BIF precipitation was triggered by release of CO<sub>2</sub> into the atmosphere and subsequent surges of alkalinity into the ocean due to the weathering of large subaerial volcanic systems. It is argued that magnetite precipitation from seawater Fe(II) was allowed by two electron acceptors, manganese dioxide and dissolved inorganic carbonate ions. Although methanotrophs may have assisted carbonate reduction, biological processes are not a requisite for magnetite deposition.

[1] Bekker et al. (2010) *Econ. Geol.* **105**, 467-508. [2] Dauphas et al. (2017) *Rev. Mineral. Geochem.* **82**, 415-510. [3] Konhauser et al. (2017) *Earth. Sci. Rev.* **172**, 140-177. [4] Conway et al. (2016) *Mar. Chem.* **183**, 50-61. [5] Holland (1984) Princeton University Press 598 [6] Sumner (1997) *Am. J. Sci.* **297**, 455-487.