New constraints on ferrous Fe concentrations in the Archean ocean

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Ferrous Fe (Fe^{2+}) was an important reductant in the Archean ocean, and steady accumulation of atmospheric O_2 eventually required complete titration of Fe^{2+} through reactions with O_2 produced by photosynthesis. Estimates of Fe^{2+} concentrations in the early oceans, therefore, pose significant constraints on oxygen production in the Archean. Previous estimates of seawater Fe^{2+} based on the size of banded iron formation (BIF) deposits or the stability of siderite ($FeCO_3$) suffer from a variety of uncertainties.

Here we propose a novel approach to constrain Fe^{2+} concentrations in the Archean ocean based on an improved understanding of stable Si isotope systematics in Precambrian BIFs and cherts, which indicates that Fe-Si gels were important precursors to BIFs [1, 2, 3]. Our results corroborate studies from other groups [4, 5], showing that the Fe and Si cycles were intimately coupled in the Archean ocean. Because Si was likely to be always saturated with respect to Fe-Si gels in the absence of a biological Si cycle in the Archean, its concentrations can be estimated using Fe-Si gel solubilities [1]. Seawater Fe^{2+} concentrations, which were not bounded to solubility due to Fe redox cycling, can be then estimated in two steps: (1) estimation of minimum Fe^{2+} concentrations required to form Fe-Si gels at the Fe:Si ratio obtained from BIFs; (2) estimation of total Fe^{2+} concentrations considering that only part of Fe^{2+} was oxided to form Fe-Si gels. Percent Fe^{2+} oxidation can be constrained by Fe isotope analyses. Applying this new method to the data reported for ~3.2 Ga BIFs from the Barberton region of South Africa [6], Fe^{2+} concentrations were estimated to be ~80 μM in shallow waters and ~640 μM in deep waters in the same basin, translating to a O_2 level ~3-times higher in the shallow waters based on a dispersion-reactive model. Refinement of this approach calls for further studies on Fe-Si gel nucleation under various conditions pertinent to the Archean ocean.

[1] Zheng et al., 2016; [2] Reddy et al., 2016; [3] Konhauser et al., 2017; [4] Rasmussen et al., 2015; [5] Tosca et al., 2016; [6] Satkoski et al., 2015