

IDENTIFICATION OF A DISCRETE REDOXCLINE IN 3.2 GA SEAWATER A. M. Satkoski^{1,2}, C. M. Johnson^{1,2}, B. L. Beard^{1,2}, N. J. Beukes³ ¹University of Wisconsin-Madison, Department of Geoscience, 1215 West Dayton Street, Madison WI 53706, United States, ²NASA Astrobiology Institute, United States, ³Department of Geology, University of Johannesburg, PO BOX 524, Auckland Park, Johannesburg, South Africa

Introduction: Seawater before the 2.4-2.2 Ga Great Oxidation Event (GOE) is thought to be uniformly anoxic due primarily to the lack of oxygen producing microorganisms. Recent work, however, suggests that there were intervals (3.0, 2.8 and 2.5 Ga) when free oxygen was being produced, likely by cyanobacteria [1], [2], [3], [4]. Here, we present new Fe isotope and U concentration data on BIF from the 3.23 Ga Fig Tree Group, South Africa to assess if oxygen was being produced in shallow marine waters 200 millions years earlier than previously proposed.

BIF Samples: Samples for this work are from the BARB4 diamond drilled core, which was drilled in 2012. Specific samples are from fine-grained high-Fe cherts and granular low-Fe cherts of the Manzimnyama BIF. The textural evidence suggests that the high-Fe chert samples were deposited in deep waters, while the granular low-Fe samples were precipitated near shore in shallow waters and then transported to a deeper part of the basin. These samples give us a unique opportunity to compare both deep and shallow depositional settings, which can give insights into the chemistry of the entire water column during this interval of time. For this project both high-Fe and low-Fe chert samples were analyzed for Fe and Pb isotopes, and U-Th-Pb concentrations determined by isotope dilution.

Fe isotope data: On average, the Fe isotope values for the Fe-rich deep-water samples are more positive (+0.55‰) than those of the Fe-poor shallow water samples (+0.18‰). The ⁵⁶Fe/⁵⁴Fe fractionation between Fe(III)-hydroxides and aqueous Fe(II) is ~3-4‰ [5], suggesting that the Fe-poor, shallow-water samples formed from a stronger oxidizing water mass than the deep-water samples. Modeling shows that the maximum dissolved O₂ content that the Fe-rich samples could have formed from is 0.4μM while the low-Fe samples likely formed from waters with higher O₂ content, potentially as high as 10μM, which is the highest content predicted for the Archean [6].

U-Th-Pb isotope data: The concentration of other redox sensitive elements in BIF can also be used to address the oxidation potential of the water from which they precipitated. Here, we use U, which is only soluble in its oxidized U(VI) valence state. Uranium, however, is susceptible to alteration by later metamorphic or hydrothermal circulation. To evaluate the fidelity of the U contents of the samples we

measured U-Th-Pb isotopes. Using these isotopes we were able to assess which samples had preserved their original U contents since 3.23 Ga, and screen out those samples that have been affected by later alteration. While most samples have been affected by Pb addition, some samples remained closed to U alteration and thus preserve their original U contents. For further discussion of original U contents in 3.23 Ga seawater, we only discuss those samples that have remained unaltered with respect to U contents since 3.23 Ga.

U concentration in 3.23 Ga seawater: In seawater, the distribution coefficient of U to Fe(III)-hydroxide is large (10⁴-10⁶), thus the content of U in BIF can be used as a proxy for its concentration in seawater. Once we correct the U data for *in-situ* decay of U to Pb and U from siliciclastic contamination, the remaining component is the U that was absorbed (U_{absorbed}) onto Fe(III)-hydroxides in 3.23 Ga seawater. Using the U_{absorbed}/Fe₂O₃ ratio combined with a conservative 10⁴ distribution coefficient, we calculate that the concentration of U in seawater for the deep water samples was 0.04ppb, while the concentration of U in seawater for the shallow-water samples was 0.14ppb. This, combined with the differences seen in Fe isotope values strongly suggests that 3.23 Ga shallow marine waters were more enriched in O₂ contents than deeper, likely anoxic waters.

Conclusions: For this study, we analyzed the Fe isotope and U contents from deep and shallow water 3.23 Ga BIF from South Africa. The lower δ⁵⁶Fe values and higher U in seawater concentration for the shallow water low-Fe chert samples compared to the deep water high-Fe chert samples implies that the O₂ content of shallow marine waters was higher than that of deep waters, thus the presence of a discrete redoxcline existed in 3.23 Ga seawater. This implies oxygen producing cyanobacteria were present in the photic zone and a discrete redoxcline existed in 3.23 Ga seawater 200 million years earlier than previously proposed.

References: [1] Planavsky et al. (2014) *Nature Geoscience*, 7, 283-286. [2] Crowe et al. (2013) *Nature*, 501, 535-539. [3] Riding et al. (2014) *Precambrian Res.*, 251, 232-237. [4] Anbar et al. (2007) *Science* 317, 1903-1906. [5] Wu et al. (2012) *Geochim. Cosmochim. Acta*, 84, 14-28. [6] Olson et al. (2013) *Chemical Geology*, 362, 35-43.