

IRON, CARBON, AND OXYGEN ISOTOPE COMPOSITIONS OF BANDED IRON FORMATION CARBONATES DEMONSTRATE A MAJOR ROLE FOR MICROBIAL DISSIMILATORY IRON REDUCTION IN 2.5 B.Y. OLD MARINE ENVIRONMENTS. C. M. Johnson^{1, 2}, A. Heimann^{1, 2, 3}, B. L. Beard^{1, 2}, J. W. Valley^{1, 2}, E. E. Roden^{1, 2}, M. J. Spicuzza^{1, 2}, and N. J. Beukes⁴, ¹Department of Geoscience, University of Wisconsin, Madison WI 53706, USA, clarkj@geology.wisc.edu, ²NASA Astrobiology Institute, ³Department of Geological Sciences, East Carolina University, Greenville, NC 27858, USA, heimanna@ecu.edu, ⁴Department of Geology, University of Johannesburg, 2006 Auckland Park, South Africa, nbeukes@uj.ac.za.

Introduction. Carbon isotopes have played a pivotal role in tracing the evolution of life on the early Earth, a central theme of astrobiology. The origin of low- $\delta^{13}\text{C}$ values for Fe-rich carbonates (siderite and ankerite) in banded iron formations (BIFs) has been a topic of great debate, with competing interpretations ranging from i) an abiogenic origin through precipitation from seawater that was vertically stratified in $\delta^{13}\text{C}$ to ii) formation via microbial respiration. If the later is correct, the microbial pathway likely involved dissimilatory iron reduction (DIR), which is deeply rooted in the tree of life and may be one of Earth's most ancient metabolisms [1]. Here we test the hypothesis that Fe-rich BIF carbonates formed by DIR through combined C, O, and Fe isotope analyses of the same samples of the 2.5 b.y. old Kuruman Iron Formation, and platform Ca-Mg carbonates of the Gamohaaran Formation, South Africa. In a separate, but parallel, study, Sr isotope variations in these samples are presented, which provide additional constraints on seawater origins for the carbonates [2].

Results. Vertical intervals of up to 100 m were sampled in three cores that cover a lateral extent of ~250 km. BIF Fe-rich carbonates have a wide range in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 1). In contrast, Campbellrand Ca-Mg carbonates have near-zero $\delta^{13}\text{C}$ values and higher $\delta^{18}\text{O}$ values. It has been proposed that the C isotope variation is due to water column stratification, but recent work comparing coeval deep- and shallow-water carbonates from this section suggests the water column had homogenous $\delta^{13}\text{C}$ values near 0 ‰ [3]. Although the absolute $\delta^{18}\text{O}$ values for Neoproterozoic and Paleoproterozoic seawater are unknown, and subject to extensive debate, the large range in $\delta^{18}\text{O}$ values for Fe-rich (siderite) and Fe-poor (dolomite) carbonates is inconsistent with direct derivation from seawater for all carbonates, and, in fact, is opposite to that expected using siderite-water and dolomite-water O isotope fractionation factors. Although it is possible that $\delta^{18}\text{O}$ values for seawater in the Kuruman basins were stratified, as they are, for example, in the modern Black Sea, such stratification would be expected to produce the lowest $\delta^{18}\text{O}$ values for shallow water carbonates (e.g., dolomite, calcite), reflecting local meteoric water

influences, and yet the trends in Fig. 1 are the opposite. We conclude that although the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the shallow-water calcite and dolomite may reflect equilibrium with seawater, the C and O isotope compositions of the Fe-rich carbonates cannot reflect precipitation from seawater. Instead, the C and O isotope compositions for Fe-rich carbonates are better explained by DIR, where a major control on the measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values reflects inheritance from organic carbon and precursor iron oxides prior to reduction.

The Fe-rich carbonates in the Kuruman BIF have a significant Fe isotope variability ($\delta^{56}\text{Fe} = +1$ to -1 ‰), with an average composition of $\delta^{56}\text{Fe} = 0$ ‰, identical to the average crust. Virtually none of these have Fe isotope compositions that reflect precipitation from seawater. Instead, collectively, the C, O, and Fe isotope compositions of BIF Fe carbonates likely reflect authigenic pathways of formation in the sedimentary pile prior to lithification, where DIR was the major process that controlled the C, O, and Fe isotope compositions of siderite.

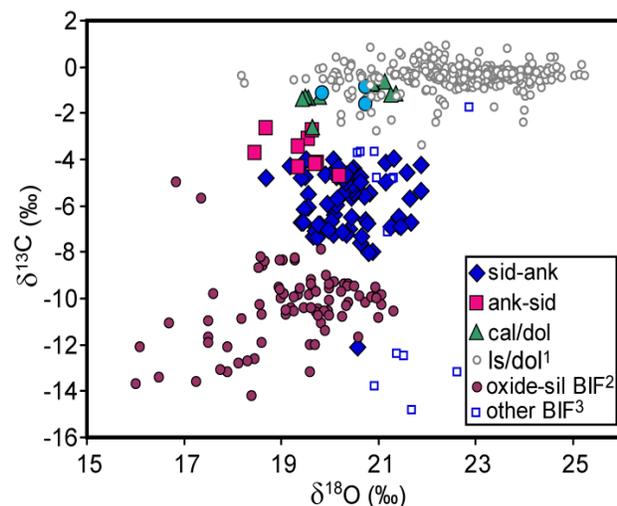


Figure 1. C and O isotope data from BIF carbonates and related Ca-Mg carbonates from the 2.5 b.y. old Kuruman and Gamohaaran Formations. Data from current study [4] and sources cited within.

Isotope mass-balance reactions indicate that the low- $\delta^{13}\text{C}$, low- $\delta^{18}\text{O}$ values of BIF siderite, relative to those expected for precipitation from seawater, reflect inheritance of C and O isotope compositions of precursor organic carbon and ferric hydroxide that were generated in the photic zone and deposited on the seafloor. Carbon-Fe isotope relations suggest that BIF Fe carbonates formed through two end-member pathways (Fig. 2): one group of data, termed “Group I”, has low- $\delta^{13}\text{C}$ and low- $\delta^{56}\text{Fe}$ values and is interpreted to record partial DIR of ferric oxides/hydroxides (“Stage 1” in Fig. 2), followed by mobilization of aqueous Fe^{2+} and interaction with additional carbonate that infiltrated from the seawater/sediment interface (“Stage 2” in Fig. 2). In contrast, low- $\delta^{13}\text{C}$ but high- $\delta^{56}\text{Fe}$ values for Fe-rich BIF carbonates are interpreted to reflect reduction of the residue that remains from “Stage 1” (Fig. 2), which is then followed by addition of seawater-derived carbonate through percolation from the seawater/sediment interface (“Group II” data, Fig. 2, right side). An important observation is the common occurrence of hematite inclusions in the high- $\delta^{56}\text{Fe}$ siderite, supporting a model where such compositions reflect microbial reduction “in place” in the soft sediment (“Group II” data, Fig. 2). Although external seawater carbonate is required in all pathways, the Fe budget was dominated by authigenic mineral formation in the soft sediment, prior to lithification. Limited communication with open seawater during carbonate formation is supported by on-going Sr isotope work, presented at

this meeting by Ludois et al. [2].

Conclusions. The combined Fe, C, and O isotope data from Kuruman BIF carbonates indicate that BIF siderites that have negative, near-zero, or positive $\delta^{56}\text{Fe}$ values may all record biological Fe cycling, where the range in $\delta^{56}\text{Fe}$ values records differential Fe mobilization via DIR in the sediment prior to lithification. Our results demonstrate that the inventory of low- $\delta^{56}\text{Fe}$ in marine sedimentary rocks of Neoproterozoic to Paleoproterozoic age, although impressive in volume, represents only a minimum of the total inventory of Fe that was cycled by bacteria.

References. [1] Vargas M. et al. (1998) *Nature* 359, 65. [2] Ludois J. et al. (2010), *AbSciCon 2010*. [3] Fischer W. W. and Knoll A. H. (2009) *GSA Bull.* 121, 222. [4] Heimann A. et al. (2010) *EPSL*, in press.

Figure 2. C and Fe pathways required to explain $\delta^{13}\text{C}$ and $\delta^{56}\text{Fe}$ values of Fe-rich BIF carbonates from the Kuruman Iron Formation. Groups of data keyed to schematic inset. “Group I” data interpreted to reflect partial DIR (“Stage 1”), followed by carbonate precipitation accompanied by addition of seawater-derived carbonate (“Stage 2”). The residual oxides from “Stage 1” will have positive $\delta^{56}\text{Fe}$ values, and DIR of these will produce “Group II” data; importantly, most carbonates from “Group II” have hematite inclusions, providing support for residual oxides.

