STRONTIUM ISOTOPES OF BANDED IRON FORMATION CARBONATES: AN ARGUMENT AGAINST IRON CARBONATES PRECIPITATING FROM SEA WATER. J.M. Ludois,1,2 A. Heimann,1,2 C.M. Johnson1,2, B.L. Beard1,2 J.W. Valley,1,2 E.E. Roden,1,2 and M.J. Spicuzza.1,2 1University of Wisconsin, Department of Geoscience, 1215 West Dayton Street, Madison, WI 53706, USA, 2NASA Astrobiology Institute, University of Wisconsin, Madison, WI 53706, USA.

Introduction: Constraining the isotopic composition of ancient seawater can give insight into past geologic and oceanic processes. Strontium’s isotopic homogeneity throughout the world’s oceans, its long residence time, and lack of biologically mediated fractionation make it suitable to studying past ocean chemistry [1]. Here we analyze Sr isotopes on the same samples analyzed for Fe, C, and O isotopic compositions by Heimann et al. 2010 [2], and presented at this meeting by Johnson et al. 2010 [3], of banded iron formation (BIF) carbonates (calcite, dolomite, siderite, ankerite) from the Kuruman Iron Formation and underlying BIF platform carbonates from the Gamohaan Formation, Transvall Craton, South Africa. The Kuruman is thought to have undergone a very low degree of metamorphism (T = 110-170 °C, P < 2 kbar) and the carbonates are thought to be authigenic [4]. Three stratigraphically equivalent drill cores encompassing up to 100m depth were taken and the siderite-rich facies within were analyzed. Elemental compositions of carbonates shown in Figure 1, and the average composition of sampled carbonate laminae can be seen in Figure 2. Petrographic analysis revealed that ankerite formed later than siderite and that neither have textures that suggest late, diagenetic recrystallization [2].

Methods: Because sample size was limited and Sr concentrations were very low in the iron rich carbonate minerals, Sr isotopic analysis was done on exceptionally small samples, << 10ng. To get high precision results, analysis was performed by TIMS using Rhenium filaments and TaF activator, similar to the procedures used in Charlier et al. (2006) [5]. Total procedural blank levels were on average <<1% of total sample.

Isotopic Results: Isotopic analysis revealed large Fe isotope variability, (δ13CFe = +1 to -1‰), low δ13C values (-12 to -1‰), and δ18O values of ~21 ‰ [2]. It is essential to analyze Rb contents because the in situ age corrections for these 2.5 b.y. old samples may be significant. Rb concentrations were also used to evaluate possible clay contamination, and samples with high Rb concentration (> 2 ppm) likely reflect shale contamination and are not considered further (Figure 3). Initial 87Sr/86Sr ratios of the BIF carbonates used the measured Rb/Sr ratios and the age of the Kuruman Iron Formation given by Pickard (2003) of 2460±5 Ma [6]. Sr isotope analysis revealed a large range of initial 87Sr/86Sr values (Figure 4), with calcites at or near the 87Sr/86Sr value of ~2.5 Ga seawater (~0.705) and the iron-rich carbonate having initial 87Sr/86Sr values that range from at or near sea water to very high ratios of ~0.745 [1]. Figures 3 and 4 show that the high 87Sr/86Sr values are not due to excess Rb contamination or, passage by diagenetic fluids, which would have shifted the low Sr concentration samples the most. Combining the

Figure 1. Major-element compositions of individual carbonate minerals present in each lamination of carbonate [2].

Figure 2. Average calculated carbonate composition for each carbonate laminae sampled in this study [2].
initial $^{87}\text{Sr}/^{86}\text{Sr}$ with the $\delta^{13}\text{C}$ shows Fe-poor carbonates (calcites and dolomites) have both Sr and C isotopic composition close to or at sea water composition, whereas the Fe-rich carbonates (siderite and ankerite) are farther from equilibrium with seawater (Figure 5).

**Figure 3.** Plot of Rb vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonates.

**Figure 4.** Figure 3. Plot of Sr vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonates.

**Figure 5.** Figure 3. Plot of $\delta^{13}\text{C}$ vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonates.

**Conclusions:** The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonates provide a robust test for formation in equilibrium with ancient seawater. Calcite and dolomite samples from the 2.5 b.y. old Kuruman Iron Formation and the Gamohaan Formation, suggest that they likely precipitated directly from seawater. In contrast, the highly variable and radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Fe-rich carbonates do not reflect seawater compositions. As noted by Johnson et al. (2010) [3], the Fe-rich carbonates do not have C, O, or Fe isotope compositions that reflect formation from seawater, but instead record extensive microbial dissimilatory iron reduction (DIR) in the soft sediment prior to lithification. Because these Fe-rich carbonates are bounded by shale layers, the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios likely reflect small-scale fluid interaction during authigenic mineral formation in the soft sediments. These results demonstrate that multiple isotopic systems, including those not directly cycled by life, provide important constraints on interpreting isotopic biosignatures in ancient rocks.

**References:**