

ASSESSING THE ANTIQUITY OF MICROBIAL METAL RESPIRATION IN THE GEOLOGIC RECORD. P.R. Craddock¹ and N. Dauphas¹, ¹Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 S Ellis Ave, Chicago, IL 60637, USA (craddock@uchicago.edu)

Introduction: Evidence for early cellular life on Earth has been advanced either on the occurrence of putative microfossils or molecular biomarkers [e.g., 1, 2]. However, the interpretation of such evidence is not without controversy and these techniques are not applicable to Eoarchean samples, which are all metamorphosed. Here, we present coupled iron ($\delta^{56}\text{Fe}$ vs. IRMM-014) and carbon ($\delta^{13}\text{C}$ vs. V-PDB) isotope data of carbonates from Archean Banded Iron Formations (BIFs) that may be used to discriminate biosignatures. BIFs are voluminous and conspicuously-laminated chemical sediments that are rich in iron-oxide, carbonate and silica and whose occurrence is unique to the Precambrian. We present a study of two iron-formations: the late Archean/early Proterozoic (2.5 Ga) Brockman Iron Formation from the Hamersley Basin, Australia, and the early Archean (~3.8 Ga) Isua Supracrustal Belt, Greenland. Our data are used to constrain the probable chemical and biological pathways for the precipitation of iron-bearing carbonates in these formations. We examine specifically whether the range of Fe and C isotope ratios recorded in Fe-rich carbonates in BIFs records evidence for Fe and C cycling by microbially-mediated iron respiration (i.e., dissimilatory iron reduction) throughout the Archean. Our study provides a geochemical perspective on the early development of microbial metabolisms on Earth.

Samples and Methods: The Hamersley Group is of particular significance owing to the presence of four major and several minor conspicuously laminated, Fe-rich stratigraphic units (i.e., BIF), including the Brockman Iron Formation. The Brockman Iron Formation contains up to 15 wt% Fe-rich carbonates (siderite, ankerite) [3]. The Hamersley Group also contains the Wittenoom Dolomite, which comprises between 200 and 300 m of interbedded carbonate, chert and shale [3]. In contrast to that of the overlying iron-formation, the carbonate in the Wittenoom Dolomite is typically Fe-poor (calcite, dolomite). Both Fe-rich and Fe-poor carbonates from Hamersley have been studied previously for their O and C isotopic signatures [4,5]. We couple here new Fe isotopic data for these carbonates to provide further constraints on their formation.

In addition, samples of Fe-rich and Fe-poor metacarbonates from the ~3.8 Ga Isua Supracrustal Belt (ISB) were targeted for their comparison with carbonates from the younger Hamersley Basin. The ISB is one of the oldest metasedimentary-bearing formations on Earth [6-9]. Protolith identification of these rocks

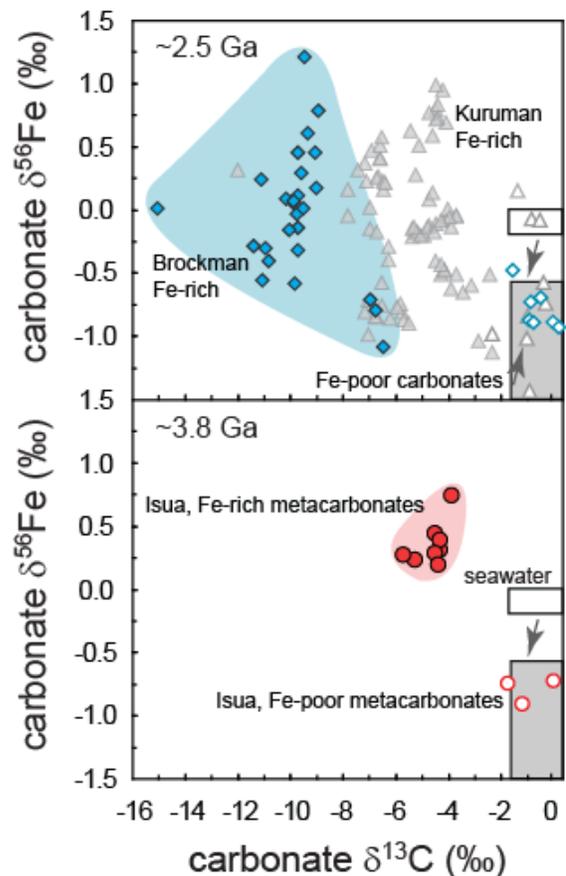


Fig. 1. Coupled $\delta^{56}\text{Fe}$ and $\delta^{13}\text{C}$ ratios iron-rich and iron-poor carbonates from the Brockman Iron Formation [4, this study] and Kuruman Iron Formation [13,14] (top panel) and from the Isua Supracrustal Belt [10, this study] (bottom panel). The white box delineates the estimated isotopic composition of Archean seawater. The gray box is the predicted range of isotopic compositions for carbonates precipitated from and in isotopic equilibrium with Archean seawater.

is, however, complicated owing to metamorphism and metasomatic overprint. The origin of metacarbonates in the ISB is particularly disputed, with interpretations ranging from primary chemical sediments [e.g., 6] to entirely metasomatic [e.g., 8]. We report here new C isotopic data for Fe-rich and Fe-poor metacarbonates to accompany Fe isotopic data for these samples that were previously measured in our laboratory [10]. The isotope data are used to assess a likely chemical sedimentary origin for the ISB metacarbonates, including

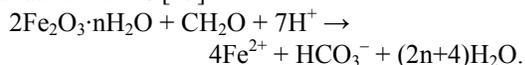
whether the signatures are consistent with microbial metabolisms in their formation.

Iron isotopic analyses were performed on a Thermo Scientific Neptune MC-ICPMS at the University of Chicago following the procedures developed in our laboratory [11,12].

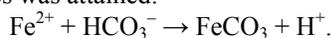
Results: Hamersley Basin: The $\delta^{56}\text{Fe}$ of Fe-rich carbonates analyzed in this study range from -1.1 to $+1.2$ ‰ (Fig. 1). The $\delta^{56}\text{Fe}$ of Fe-poor carbonates from the Wittenoom Dolomite are all negative, between -0.5 and -1.0 ‰ (Fig. 1). Carbon isotope compositions ($\delta^{13}\text{C}$) of these carbonates were previously reported by [4]. All Fe-rich carbonates have light $\delta^{13}\text{C}$ (Fig. 1), with an average of -10 ‰ ($n=43$). Fe-poor carbonates from the Wittenoom Dolomite have a limited range of heavier $\delta^{13}\text{C}$ with an average of -2 ‰ ($n=15$; Fig. 1).

Isua Supracrustal Belt: Fe-poor metacarbonates have light $\delta^{56}\text{Fe}$ (-0.90 to -0.73 ‰), whereas iron-rich metacarbonates have heavy $\delta^{56}\text{Fe}$ ($+0.20$ to $+0.76$ ‰; Fig. 1) [10]. Fe-poor metacarbonates have $\delta^{13}\text{C}$ values between -3 and 0 ‰, whereas iron-rich metacarbonates have distinctly lighter $\delta^{13}\text{C}$ values between -6 and -4 ‰ (Fig. 1).

Discussion: Fe-rich carbonates in BIFs from the 2.5 Ga Hamersley Basin exhibit a wide range of iron and carbon isotopic compositions, in particular light $\delta^{13}\text{C}$ and heavy $\delta^{56}\text{Fe}$ compositions (Fig. 1). The range of light $\delta^{13}\text{C}$ ratios in Fe-rich carbonates requires a source of C in the iron-formation with a light isotopic composition; likely this was from oxidation of isotopically-light organic carbon ($\delta^{13}\text{C} \sim -30$ ‰) [4]. This oxidation must have occurred predominantly within marine sediments in order for the light $\delta^{13}\text{C}$ from organic carbon to have significantly affected the C isotopic composition of DIC ($\delta^{13}\text{C} \sim 0$ ‰). Oxidation of organic carbon requires reduction of a terminal electron acceptor. In the anoxic Archean, this electron acceptor was likely ferric Fe-oxides because oxygen, nitrate and Mn-oxides would have been severely limited or absent whereas ferric Fe (e.g., ferrihydrite) was abundant in BIFs [15]:



This Fe reduction produces both dissolved Fe(II) and carbonate that would accumulate in pore waters until saturation with respect to authigenic Fe-rich carbonates was attained:



The $\delta^{56}\text{Fe}$ values of Fe-rich carbonates provide direct support for these processes. Critically, the $\delta^{56}\text{Fe}$ values are consistent with Fe isotopic fractionations produced during microbially-mediated Fe and C cycling. Fe-rich carbonates with heavy $\delta^{56}\text{Fe}$ values ($+1$ ‰) could only

have precipitated from dissolved Fe(II) also with heavy $\delta^{56}\text{Fe}$. This was not common seawater ($\delta^{56}\text{Fe} \sim 0$ ‰). Instead, this Fe(II) reservoir was from the near-complete reduction in marine sediments of ferrihydrite with a heavy $\delta^{56}\text{Fe}$. Ferrihydrite with heavy $\delta^{56}\text{Fe}$ was produced by partial Fe(II) oxidation in overlying surface ocean waters, possibly via anoxygenic photosynthesis [16], which imparts a large positive Fe isotopic fractionation (up to $+1.5$ ‰ [17]). We thus interpret the coupled Fe and C isotopic signatures of Fe-rich carbonates in the Hamersley BIFs as preserving evidence of microbial Fe respiration at 2.5 Ga. Heimann et al. [14] proposed the same interpretation for the penecontemporaneous Kuruman Iron Formation from the Transvaal Craton, S. Africa.

The origin of Fe-rich metacarbonates in association with BIFs in the ~ 3.8 Ga Isua Supracrustal Belt is disputed. It has been argued that the metacarbonates are metasomatic [8]. However, the heavy Fe isotopic compositions of Fe-rich metacarbonates are inconsistent with light Fe isotopic ratios ($\delta^{56}\text{Fe} \leq 0$ ‰) expected for a metasomatic derivation from leaching of Fe from igneous protoliths. Instead, coupled Fe and C isotopic signatures are similar to those of Fe-rich carbonates from genuine late Archean BIFs of known chemical sedimentary origin (Fig. 1). By analogy, Fe-rich metacarbonates in the ISB appear to have formed as chemical sediments. In particular, these metacarbonates preserve Fe and C isotopic signatures that are consistent with microbial Fe respiration and thus imply the evolution of such catabolism by 3.8 Ga on Earth.

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