Iron formation carbonates: Paleoceanographic proxy or recorder of microbial diagenesis?

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ABSTRACT
The chemical and isotopic compositions of carbonates are commonly used as proxies for ancient seawater or paleoenvironments. Iron formation (IF) carbonates have been used as evidence for an anoxic, Fe(II)-rich Archean and Paleoproterozoic ocean and high atmospheric CO₂ contents. It has been proposed, however, that microbial Fe cycling dominates the chemical and isotopic compositions of IF carbonates, suggesting less direct applicability as an oceanic proxy. Here we use an isotope tracer that is not affected by biological processes or isotopic fractionation, the radiogenic ⁸⁷Rb-⁸⁷Sr system, to test the applicability of IF carbonates as a paleoenvironmental proxy. We focus on the 2.5 Ga Campbellrand platform, Transvaal Basin, South Africa, that records a shift from Ca-Mg carbonates to IF carbonates during a marine transgression. When coupled with previously determined Fe, C, and O isotope compositions, it becomes clear that the IF carbonates studied here do not reflect seawater compositions, but instead record extensive microbial Fe cycling in the soft sediment prior to lithification. These results question the use of IF carbonates to infer seawater compositions and paleoenvironmental conditions, including estimates for atmospheric CO₂ contents.

INTRODUCTION
Chemical sediments, including carbonates in general, and iron formations (IFs) specifically, have often been used as a proxy for ancient seawater or ambient environmental conditions. The abundance of Precambrian IFs (Klein, 2005) is one of the major lines of evidence for an Fe(II)-rich ocean in the Archean and Paleoprotoreozoic (Holland, 1984). In addition, Fe(II)-bearing minerals in IFs, including siderite and magnetite, have been used to constrain ambient CO₂ contents in the ancient Earth (Ohmoto et al., 2004; Rosing et al., 2010), although such approaches are controversial (Dauphas and Kasting, 2011; Reinhard and Planavsky, 2011). Regarding isotopic compositions, it has been proposed that negative δ¹³C values for IF carbonates reflect vertical stratification of seawater (Winter and Knauth, 1992) or a contribution from microbial respiration (Becker and Clayton, 1972). The δ⁶⁷Fe values of IFs have been interpreted to directly record those of ancient seawater (Planavsky et al., 2012; Rouxel et al., 2005), a mixture of seawater and diagenetic contributions (Steinhaefel et al., 2010), or microbial Fe cycling (Craddock and Dauphas, 2011; Heimann et al., 2010; Johnson et al., 2008a).

The importance of IFs to discussions on the paleoenvironments of the ancient Earth requires an additional perspective to address their applicability for tracing ancient environments. Here we report on ⁸⁷Rb-⁸⁷Sr isotope systematics of IF carbonates from the largest period of IF deposition to test conflicting proposals that IF carbonates may be used as proxies for ancient seawater or may record microbial Fe cycling. Unlike stable isotopes, ⁸⁷Sr/⁸⁶Sr ratios are not significantly fractionated upon precipitation of carbonate, and the Sr isotope composition of 2.5 Ga seawater is relatively well constrained (Shields and Veizer, 2002). These new Rb-Sr data were obtained on the same milligram-size samples previously analyzed for C, O, and Fe isotopes and chemical compositions (Heimann et al., 2010). Integrating these results with the transgressive changes recorded in the Gamohaan Formation and Kuruman Iron Formation provides a view of Fe-poor and Fe-rich marine environments that may be correlated to specific proxy records.

GEOLOGIC SETTING AND SAMPLES
The Campbellrand platform of the western Kaapvaal craton, South Africa, represents a transgressive marine sequence (Beukes and Gutzmer, 2008). Samples are from the Gamohaan Formation and overlying Kuruman Iron Formation (Fig. DR1 in the GSA Data Repository†). Gamohaan Formation samples include carbonaceous limestone and dolomites, as well as carbonaceous siliciclastic units and ankerite and/or ferroan dolomite chert units of the Tsineng Member that reflect a transition upsection to iron-rich units. The overlying Kuruman Iron Formation that was sampled consists of carbonate and oxide facies, chert-rich IF. Miyano and Beukes (1984) estimated that the Kuruman Iron Formation was subjected to only very low grade metamorphism (temperature = 110–170 °C, pressure < 2 kbar). Petrographic relations in the Kuruman Iron Formation indicate that siderite and ankerite are early precipitates (Fig. DR2), and although ankerite may be an early replacement of siderite, we group these minerals in our discussion because of their overlapping isotopic compositions. These chemical sediments are interbedded with thin siliciclastic units in the IF, whereas siliciclastic units in the Gamohaan Formation are generally thicker and interpersed with carbonate units. The Kuruman Iron Formation has been correlated with IFs of the Hamersley Basin, Western Australia, and are interpreted to reflect a large, contiguous marine margin between ca. 2.7 and 2.4 Ga (Beukes and Gutzmer, 2008).

⁸⁷Rb-⁸⁷Sr isotope analysis of carbonate was done on very small samples (~1 mg of carbonate, ~5 ng of Sr) to assess fine-scale Sr isotope heterogeneity. Carbonate laminae that contained <0.5 wt% Al₂O₃ were sampled to minimize the chances of physical contamination from siliciclastic material. A range of carbonates was sampled, including those adjacent to or within shale layers, as well as those in thicker carbonate and chert sections. New ⁸⁷Rb-⁸⁷Sr analyses were done on the same milligram-size powders that were analyzed for chemical and C, O, Fe isotope compositions by Heimann et al. (2010). In addition, ⁸⁷Rb-⁸⁷Sr and ⁶⁶⁷Sm-⁶⁷Nd isotope analyses were done on interbedded shales to constrain potential sources of radiogenic Sr. (For details, see the Data Repository.)

RESULTS
Accurate calculation of initial ⁸⁶Sr/⁸⁶Sr ratios for carbonates requires assessment of physical contamination by siliciclastic material; this can be done using Rb/Sr ratios, providing an additional filter beyond Al₂O₃ contents for screening samples. The majority of carbonates, regardless of FeCO₃ contents, have ⁸⁷Rb/⁸⁶Sr ratios <0.75 (Fig. DR3), and we eliminate samples that have ratios that exceed this from further consideration. A more stringent threshold of 0.1 for

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$^{87}\text{Rb}/^{86}\text{Sr}$ would not change the range in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, although it would eliminate more than half the data set. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for samples that have $^{87}\text{Rb}/^{86}\text{Sr} < 0.75$ produces a data set that has no correlations among Rb, Sr, $^{87}\text{Rb}/^{86}\text{Sr}$, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. DR4). Ca-Mg carbonates that have the lowest FeCO$_3$ and highest Sr contents have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that overlap with the range estimated for 2.5 Ga seawater (Figs. DR3 and DR4), as do some of the Fe-rich carbonates (Fig. 1). The vast majority of Fe carbonates, however, have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are significantly higher than those of 2.5 Ga seawater. Ca-Mg carbonates that have relatively high FeCO$_3$ contents, possibly reflecting a physical mixture of ankerite or ferroan dolomite components, tend to have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that exceed those of 2.5 Ga seawater.

$^{87}\text{Fe}$ values for the majority of siderites are higher and lower than those expected for equilibrium with seawater (Fig. 1), and Heimann et al. (2010) interpreted these to record microbial diagenesis; none of these samples have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are close to those of 2.5 Ga seawater. The $^{87}\text{Fe}$ values for Ca-Mg carbonates extend to highly negative values of $\sim -1.5\%_{\text{o}}$, similar to the results of Czaja et al. (2012) for correlative carbonates from Agouron Institute scientific drill cores GKF01 and GKP01 that are interpreted to reflect those of shallow seawater in the photic zone, produced by extensive, concomitant precipitation of iron oxides in the deeper portions of the basin. $\delta^{13}\text{C}$ values for siderites and ankerites are far from those expected for precipitation from seawater, although all Ca-Mg carbonates have near-zero $\delta^{13}\text{C}$ values that are close to those that would reflect equilibrium with seawater (Fischer et al., 2009). Ca-Mg carbonates have $\delta^{18}\text{O}$ values that overlap those that would reflect seawater precipitation at moderately elevated temperature (50 °C). In contrast, siderites have $\delta^{18}\text{O}$ values that are several per mil lower than would be expected based on the Ca-Mg carbonates, regardless of the $\delta^{18}\text{O}$ value of seawater that is assumed.

**DISCUSSION**

The isotopic data indicate that Ca-Mg carbonates have C, O, and Fe isotope compositions that overlap those of 2.5 Ga seawater, and most Fe-poor Ca-Mg carbonates also have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that reflect 2.5 Ga seawater. Virtually all of the Fe carbonates (ankerite and siderite) have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are far higher than those expected for seawater. Such radiogenic Sr isotope compositions cannot be explained by physical contamination by clay minerals in the carbonates that were analyzed, as noted here.

The highly radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Fe carbonates cannot be explained by post-formation alteration, such as later, regional fluid flow, because petrographic relations show that ankerite and siderite do not have textures that indicate extensive postliithification recrystallization (Fig. DR2). Moreover, there are no correlations among Sr contents, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that would be suggestive of postformation recrystallization (Fig. 1). In a study of Mississippi Valley Type (MVT) Pb-Zn mineralization hosted in carbonates of the Gaap and Griquatown groups at the Pering mine (~200 km east of the White Bank WB-98 core location), units correlative with those studied here, Duane et al. (2004) measured very high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in mineralized carbonates; they noted that initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (calculated at 2 Ga) that exceeded 0.710 were exclusively from highly mineralized vein, fracture, and vug-filling carbonates. A strong correlation between initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr contents for the carbonates (to 100 ppm Sr), associated with increasing mineralization, led Duane et al. (2004) to infer that the mineralizing high $^{87}\text{Sr}/^{86}\text{Sr}$ fluids were also very Sr rich. As noted herein, in the Fe-rich Kuruman Iron Formation carbonates of this study, there is no correlation between initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents (Fig. DR4), and the high $^{87}\text{Sr}/^{86}\text{Sr}$ Fe carbonates have very low Sr contents, generally <20 ppm. These relations, and the fact that the Kuruman Iron Formation carbonates studied here show no evidence for MVT mineralization, rule out explaining the high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios by later fluid-rock interaction and alteration.

All petrographic, chemical, and isotopic data therefore indicate that the highly radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ankerite and siderite in the Kuruman Iron Formation reflect radiogenic Sr that was incorporated into the carbonates at the time of formation. Kamber and Webb (2001) interpreted initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7023 and 0.7049 in Ca-Mg carbonates from the Gamohaan and Kogelbeen Formations, stratigraphically below the samples analyzed in our study, to indicate mixing between deeper, non-radiogenic hydrothermal sources and radiogenic lagoonal and/or estuarine sources. This model, however, does not explain the highly radiogenic Sr measured in the Kuruman Iron Formation carbonates, particularly because the Fe-rich samples, which would normally be thought to represent the hydrothermal end member, have the highest initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In addition, there are large fine-scale changes in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on the centimeter and meter scales in the Kuruman samples analyzed in this study, and such large changes would require very short residence times (<10$^3$ yr), which is highly unlikely.

We therefore propose that the radiogenic Sr isotope compositions of the Kuruman Iron Formation carbonates do not reflect those of seawater, either the open ocean or a restricted basin. We propose that the source of radiogenic Sr was interaction of pore fluids with dispersed clays during early microbial diagenesis in the soft sediment, prior to lithification. Strontium in clays has been shown to be highly exchangeable in the presence of ground waters and pore fluids (Johnson and DePaolo, 1997). It is important to stress that this is not a mechanism of physical clay contamination in the samples analyzed (see preceding), but precipitation from pore fluids that had high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the time of Fe carbonate precipitation, in relative isolation from seawater.

$^{87}\text{Rb}-^{87}\text{Sr}$ isotope analysis of clays from the Kuruman Iron Formation and Gamohaan Formation supports this proposal (Fig. DR5). Specifically, clays in the Kuruman Iron Formation
have \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios, calculated at 2.48 Ga, of 0.730 and 0.757 (Fig. DR5), and shales from the Gamohaan Formation also have very high \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios. Gamohaan shales appear to have undergone some Rb mobilization, which hinders accurate calculation of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios at 2.48 Ga (Fig. DR5), but the very high Rb contents of shales in the Gamohaan Formation make them susceptible to even small amounts of Rb mobilization. Sm-Nd isotope analyses of the Kuruman and Gamohaan shales confirm that these siliciclastic units were derived from older terranes, where Nd model ages range from 2.60 to 2.85 Ga (Fig. DR6), thus providing support for high \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios at 2.48 Ga.

**SEAWATER VERSUS MICROBIAL PROXIES**

Our results suggest that although Ca-Mg carbonates may be useful as seawater or paleoenvironmental proxies, IF carbonates may reflect early microbial diagenetic processes rather than a seawater or paleoenvironmental signal. The contrasting proxy behavior between Ca-Mg and Fe-rich carbonates is well illustrated by the transitions that are recorded in the Neoarchean marine transgression that occurred on the Campbellrand platform, and in Figure 2 we combine our Rb-Sr results with stable isotope data from previous studies. The transition to Fe-rich deposition is clearly accompanied by C isotope compositions that move away from those appropriate for precipitation in equilibrium with seawater toward those that are dominated by organic C. Although some have argued against a role for biological processes in IFs based on low organic carbon contents (Klein, 2005; Planavsky et al., 2012), an initially high abundance of organic carbon is documented by the highly negative \(\delta^{13}\text{C}\) values of IF carbonates. The decrease in \(\delta^{13}\text{C}\) values is accompanied by decreasing \(\delta^{18}\text{O}\) values, which, when considering the distinct \(^{18}\text{O}/^{16}\text{O}\) fractionations between Ca-Mg and Fe-rich carbonates (Carothers et al., 1988; Kim and O’Neil, 1997), highlights the fact that the \(\delta^{18}\text{O}\) values of IF carbonates are far from those expected for seawater. In Heimann et al. (2010) it was proposed that the unusually low \(\delta^{18}\text{O}\) values of IF carbonates reflect inheritance from precursor Fe(III) oxides that were reduced by dissimilatory iron reduction (DIR), and the stratigraphic correlations between \(\delta^{13}\text{C}\) and \(\delta^{18}\text{O}\) values support this (Fig. 2). \(\delta^{56}\text{Fe}\) values for Ca-Mg carbonates are consistently low, reflecting a seawater Fe(II) pool that is residual to the extensive IF deposition that occurred elsewhere in the basin (Czaja et al., 2012). With the transition to Fe-rich deposition on the platform during marine transgression, \(\delta^{56}\text{Fe}\) values shift to an average value of zero, as required for hydrothermally sourced Fe, but the spread in \(\delta^{56}\text{Fe}\) values becomes large, recording extensive fine-scale microbial cycling of Fe in the soft sediment prior to lithification. These changes are accompanied by a dramatic increase in spread of initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios for IF carbonates, far greater than the relatively small spread measured for Ca-Mg carbonates.

Collectively, the transitions in chemical and isotopic compositions in Figure 2 paint a consistent story: the transition from Ca-Mg carbonate to Fe-rich carbonate was accompanied by a change in the nature of what these geochemical proxies record. Ca-Mg carbonates most closely record shallow (photic zone) seawater chemistry and surface-environmental conditions, whereas Fe-rich carbonates are dominated by microbial diageneis, essentially the last thing the rocks underwent before lithification. This reflects the fact that Fe(III) oxidation and CO₂ fixation to organic carbon in the photic zone, produced either from oxygenic or anoxygenic photosynthesis, supplied the reactants required to support extensive DIR on the seafloor. The Neoarchean is inferred to have been a time when DIR was particularly extensive (Johnson et al., 2008b), due to the combination of generation of Fe(III) oxides and organic carbon in the photic zone, but relatively low seawater sulfate contents. These results suggest that IF carbonates, at least those studied here, are excellent proxies for microbial processes, and therefore cannot be used as a direct constraint on the chemical or
isotopic compositions of the open ocean or surface paleoenvironments.

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