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Silicon isotope fractionation during microbial reduction of Fe(III)–Si gels under Archean seawater conditions and implications for iron formation genesis

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Abstract

Microbial dissimilatory iron reduction (DIR) is a deeply rooted metabolism in the Bacteria and Archaea. In the Archean and Proterozoic, the most likely electron acceptor for DIR in marine environments was Fe(III)–Si gels. It has been recently suggested that the Fe and Si cycles were coupled through sorption of aqueous Si to iron oxides/hydroxides, and through release of Si during DIR. Evidence for the close association of the Fe and Si cycles comes from banded iron formations (BIFs), which consist of alternating bands of Fe-bearing minerals and quartz (chert). Although there has been extensive study of the stable Fe isotope fractionations produced by DIR of Fe(III)–Si gels, as well as studies of stable Fe isotope fractionations in analogous abiologic systems, no studies to date have investigated stable Si isotope fractionations produced by DIR.

In this study, the stable Si isotope fractionations produced by microbial reduction of Fe(III)–Si gels were investigated in simulated artificial Archean seawater (AAS), using the marine iron-reducing bacterium *Desulfuromonas acetoxidans*. Microbial reduction produced very large $^{30}Si/^{28}Si$ isotope fractionations between the solid and aqueous phase at ~23 °C, where $\Delta^{30}Si_{solid-aqueous}$ isotope fractionations of $-3.35 \pm 0.16‰$ and $-3.46 \pm 0.09‰$ were produced in two replicate experiments at 32% Fe(III) reduction (solid-phase $Fe(II)/Fe_{Total} = 0.32$). This isotopic fractionation was substantially greater than that observed in two abiologic controls that had solid-phase $Fe(II)/Fe_{Total} = 0.02–0.03$, which produced $\Delta^{30}Si_{solid-aqueous}$ isotope fractionations of $-2.83 \pm 0.24‰$ and $-2.65 \pm 0.28‰$. In a companion study, the equilibrium $\Delta^{30}Si_{solid-aqueous}$ isotope fractionation was determined to be $-2.3‰$ for solid-phase $Fe(II)/Fe_{Total} = 0$. Collectively, these results highlight the importance of Fe(II) in Fe–Si gels in producing large changes in Si isotope fractionations. These results suggest that DIR should produce highly negative $\delta^{30}Si$ values in quartz that is the product of diagenetic reactions associated with Fe–Si gels. Such Si isotope compositions would be expected to be associated with Fe-bearing minerals that contain Fe(II), indicative of reduction, such as magnetite. Support for this model comes from recent *in situ* Si isotope studies of oxide-facies BIFs, where quartz in magnetite-rich samples have significantly more negative $\delta^{30}Si$ values than quartz in hematite-rich samples.

Keywords: Si isotopes; Fe–Si gels; Microbial reduction; Fractionation; BIFs

1. INTRODUCTION

Iron-rich cherts are common in the Archean and Paleoproterozoic rock record and include lithologies such as jasper and banded iron formations (BIFs). Such deposits

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are commonly used to infer a Precambrian marine system that had high dissolved Fe(II) and Si (e.g., Holland, 1984; Siever, 1992; Klein, 2005), and it is now recognized that oxidation of hydrothermally sourced Fe(II) in the presence of dissolved Si may produce extensive primary Fe(III)–Si precipitates in Precambrian marine environments (e.g., Fischer and Knoll, 2009; Rasmussen et al., 2015). The mechanism for Fe precipitation in BIFs has been attributed to chemolithoautotrophic iron oxidation, anoxygenic photosynthesis (photoferrotrophy), and oxidation by ambient oxygen produced by oxygenic photosynthesis (e.g., Kappler et al., 2005; Klein, 2005). Stable Fe isotope studies of jaspers and BIFs have shown that the extent of oxidation of hydrothermal Fe(II) has increased with decreasing age in the Archean (e.g., Dauphas et al., 2004; Czaja et al., 2013; Li et al., 2013; Satkoski et al., 2015), and recently, combined Fe–Nd isotopes have documented microbial and hydrothermal Fe sources in 2.5 Ga BIFs (Li et al., 2015). The wide range in isotopic compositions of Si in BIFs has been generally interpreted to be a mixture of hydrothermal and continental sources (e.g., André et al., 2006; Robert and Chaussidon, 2006; van den Boorn et al., 2007, 2010; Heck et al., 2011; Chakrabarti et al., 2012), although recent studies have increasingly highlighted the potential role of Si cycling through diagenetic processes (e.g., Stefurak et al., 2015).

Numerous laboratory experiments have constrained stable Fe isotope fractionations associated with interactions between aqueous Fe(II) and various iron oxides/hydroxides in abiologic systems under a variety of pH conditions (e.g., Beard et al., 2010; Wu et al., 2010; Frierdich et al., 2014a, 2014b; Reddy et al., 2015). Stable Fe isotope fractionations are significantly affected by the presence of Si, either as a sorbed species, or in the solid phase as Fe–Si gels, including a major influence by Fe:Si ratios relative to equivalent Si-free systems (Wu et al., 2010, 2011, 2012). In addition, the stable Fe isotope fractionation between aqueous Fe (II) and iron oxides/hydroxides during microbial dissimilatory iron reduction (DIR) has been extensively studied in Si-free (Beard et al., 1999, 2003; Crosby et al., 2005, 2007) and Si-bearing (Wu et al., 2009; Percak-Dennett et al., 2011) systems. The potential importance of DIR in Fe–Si cycling in the Archean lies in the deeply rooted nature of microbial Fe(III) reduction in both the Bacteria and the Archaea (e.g., Vargas et al., 1998). In contrast, there have been few stable Si isotope studies of Fe–Si systems, where, until recently, only the effect of sorption of aqueous Si to iron oxides/hydroxides has been studied (Delstanche et al., 2009), although there has been extensive study of pure Si systems. There have been no studies of stable Si isotope fractionation associated with DIR.

In this contribution, we describe the results of experiments that investigated stable Si isotope fractionation during microbial reduction of Fe(III)–Si gels in artificial Archean seawater. The use of Fe(III)–Si gels in the experiments reflects the recognition that such gels were likely important primary precipitates in the Archean ocean during oxidation of aqueous Fe(II) in the presence of high dissolved Si (Percak-Dennett et al., 2011), and is aligned with the importance of nanometer-scale Fe–silicate phases in iron formation cherts (Rasmussen et al., 2015), which suggest that Fe and Si co-precipitated from anoxic seawater enriched in dissolved Fe and Si. Control experiments are used to determine Si isotope fractionation in the absence of biological production of aqueous Fe(II). The microbially mediated reductive dissolution of the Fe(III)–Si gels results in both solid-phase and aqueous Fe(II), the former of which has a significant effect on Si isotope fractionation, producing very large isotopic fractionations relative to pure silica systems. Our results are compared to those from a companion study (Zheng et al., 2016), where Si isotope exchange kinetics between the same Fe–Si gel and AAS in the presence or absence of aqueous Fe(II) was studied through a series of abiologic ^{29}Si-enriched tracer experiments, and equilibrium Si isotope fractionations in abiologic Fe–Si gel systems were determined through extrapolation to 100% isotope exchange using the three-isotope method. We use the Si isotope exchange kinetics determined by Zheng et al. (2016) to evaluate the likelihood that the biological experiments were close to Si isotope equilibrium. The comparison of the two studies permits us to understand the similarities and differences between Si isotope fractionation imparted by Fe(II) produced as a result of microbial reduction of Fe–Si gels and abiotic introduction of aqueous Fe(II). Our results bear on long-standing puzzles in the Si isotope compositions of BIFs, which tend to have lower δ^{30}Si values for cherts in BIFs, particularly those that have major portions of Fe(II)-bearing minerals such as magnetite.

2. EXPERIMENTAL DESIGN AND ANALYTICAL METHODS

DIR of Fe–Si gel was conducted in an anoxic media of seawater-like matrix (termed "artificial Archean seawater", or AAS). Two sets of experiments (cell and control) were conducted in duplicate, for a duration of 30 d. Experiments that were inoculated with *Desulfuromonas acetoxidans* and 20 mM acetate are termed *cell 1* and *cell 2* (Experiments A and B). Two uninoculated control experiments, *control 1* and *control 2* (Experiments C and D) were run in parallel to the cell experiments. All reactors were maintained under strictly anaerobic conditions. The experiments were conducted and maintained at room temperature (~23 °C). The reactor vessels were agitated at the beginning of the experiments, and caution was taken to ensure homogenous sampling and extractions (see Section 2.4).

2.1. Synthesis of Fe–Si gel (electron acceptor)

The Fe–Si gel was synthesized using the procedure from Percak-Dennett et al. (2011), where a solution containing 100 mM $NaHCO_3$, 100 mM $Na_2SiO_3{\cdot}9H_20$, and 50 mM $FeCl_2{\cdot}4H_2O$ was produced and allowed to oxidize under ambient lab conditions for ~18 d with continuous shaking. The extent of Fe(II) oxidation in the solid was monitored regularly during the synthesis process by *Ferrozine* measurements (Stookey, 1970) on small aliquots of the gel that was dissolved in 0.5 M HCl. The final Fe–Si gel was centrifuged and washed with distilled water, and contained