Abiologic silicon isotope fractionation between aqueous Si and Fe(III)–Si gel in simulated Archean seawater: Implications for Si isotope records in Precambrian sedimentary rocks


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Abstract

Precambrian Si-rich sedimentary rocks, including cherts and banded iron formations (BIFs), record a >7‰ spread in 30Si/28Si ratios (δ30Si values), yet interpretation of this large variability has been hindered by the paucity of data on Si isotope exchange kinetics and equilibrium fractionation factors in systems that are pertinent to Precambrian marine conditions. Using the three-isotope method and an enriched 29Si tracer, a series of experiments were conducted to constrain Si isotope exchange kinetics and fractionation factors between amorphous Fe(III)-Si gel, a likely precursor to Precambrian jaspers and BIFs, and aqueous Si in artificial Archean seawater under anoxic conditions. Experiments were conducted at room temperature, and in the presence and absence of aqueous Fe(II) (Fe(II) aq).

Results of this study demonstrate that Si solubility is significantly lower for Fe–Si gel than that of amorphous Si, indicating that seawater Si concentrations in the Precambrian may have been lower than previous estimates. The experiments reached 70–90% Si isotope exchange after a period of 53–126 days, and the highest extents of exchange were obtained where Fe(II) aq was present, suggesting that Fe(II)–Fe(III) electron-transfer and atom-exchange reactions catalyze Si isotope exchange through breakage of Fe–Si bonds. All experiments except one showed little change in the instantaneous solid–aqueous Si isotope fractionation factor with time, allowing extraction of equilibrium Si isotope fractionation factors through extrapolation to 100% isotope exchange. The equilibrium 30Si/28Si fractionation between Fe(III)–Si gel and aqueous Si (Δ30Sigel–aqueous) is −2.30 ± 0.25‰ (2σ) in the absence of Fe(II) aq. In the case where Fe(II) aq was present, which resulted in addition of ~10% Fe(II) in the final solid, creating a mixed Fe(II)–Fe(III) Si gel, the equilibrium fractionation between Fe(II)–Fe(III)–Si gel and aqueous Si (Δ30Sigel–aqueous) is −3.23 ± 0.37‰ (2σ). Equilibrium Si isotope fractionation for Fe–Si gel systems is significantly larger in magnitude than estimates of a near-zero solid–aqueous fractionation factor between pure Si gel and aqueous Si, indicating a major influence of Fe atoms on Si–O bonds, and hence the isotopic properties, of Fe–Si gel. Larger Si isotope fractionation in the Fe(II)-bearing systems may be caused by incorporation of Fe(II) into the solid structure, which may further weaken Fe–Si bonds and thus change the Si isotope fractionation factor. The relatively large Si isotope fractionation for Fe–Si gel, relative to pure Si gel, provides a new explanation for the observed contrast in δ30Si values in the Precambrian BIFs and cherts, as well as an explanation for the relatively negative δ30Si values in BIFs, in contrast to previous proposals that the more negative δ30Si values in BIFs reflect hydrothermal sources of Si or sorption to Fe oxides/hydroxides.

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Keywords: Si isotopes; Fe–Si system; Fractionation factor; Precambrian; BIFs; Chert

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1. INTRODUCTION

The silica cycle in the Precambrian oceans was controlled by silica saturation due to the absence of Si secreting organisms, in marked contrast to the modern marine silica cycle that is dominated by biological utilization (Tréguer and De La Rocha, 2013). Silica concentrations in Precambrian seawater, if determined by solubility of amorphous silica, as well as sorption to silicate minerals, are estimated to have been between ~1 and ~2 mM (Siever, 1992; Maliva et al., 2005; Konhauser et al., 2007). High silica concentrations in the Precambrian oceans, sustained by input from continental and hydrothermal sources (Siever, 1992), have produced abundant Si-rich sedimentary rocks, including cherts and banded iron formations (BIFs) (Maliva et al., 2005; Perry and Leflucaru, 2013). Formation of Si-rich precipitates would also impact cycling of other elements in the Precambrian oceans, including iron (Fe) and phosphorus (P) (e.g., Konhauser et al., 2007; Fischer and Knoll, 2009; Jones et al., 2015), and therefore study of secular change in the silica cycle bears on our general understanding of geochemical cycles in Precambrian marine systems.

Stable Si isotopes are potential tracers for the ancient silica cycle. High-temperature fractionation is limited based on the narrow range (<~0.5‰) of δ30Si values for igneous rocks (see review by Savage et al., 2014). Surface processes, however, including continental weathering (e.g., Basile-Doelsch et al., 2005; Ziegler et al., 2005; Georg et al., 2007) and terrestrial and marine biological uptake (e.g., De La Rocha et al., 1998; Ding et al., 2005; Opfergelt et al., 2006), can fractionate Si isotopes up to several per mil (e.g., see review by Basile-Doelsch, 2006).

Published δ30Si values for Precambrian cherts and BIFs span a range of over 7‰ (André et al., 2006; Robert and Chaussdon, 2006; van den Boorn et al., 2007, 2010; Steinhoefel et al., 2009, 2010; Abraham et al., 2011; Heck et al., 2011; Chakrabarti et al., 2012; Delvigne et al., 2012; Marin-Carbonne et al., 2014; Geilert et al., 2014a; Stefularak et al., 2015). Based on a simple Si mass-balance model, δ30Si values in Precambrian cherts have been interpreted to reflect seawater temperature (Robert and Chaussdon, 2006; Marin-Carbonne et al., 2014). This interpretation, however, was not based on an explicit determination of Si isotope fractionation as a function of temperature, and was challenged by subsequent studies that attributed changes in δ30Si values in cherts to different silica sources (e.g., van den Boorn et al., 2007; Steinhoefel et al., 2009). It has been increasingly recognized that both interpretations are likely oversimplified (Chakrabarti et al., 2012; Stefularak et al., 2015), and some first-order observations remain unexplained. For example, δ30Si values in Precambrian BIFs are often lower than those recorded in broadly coeval cherts (Chakrabarti et al., 2012; Marin-Carbonne et al., 2014; Stefularak et al., 2015), and the cause of this is still debated. Recent discussions on the Si isotope record in the early Precambrian have stressed understanding the processes of Si cycling rather than focusing primarily on Si sources (e.g., Stefularak et al., 2015), and such an approach requires detailed knowledge of stable Si isotope fractionation factors.

Experimental studies of Si isotope fractionations under conditions relevant to the Precambrian oceans have been relatively few. Adsorption experiments suggest that Si isotope fractionation factors (Δδ30Siadsorb–fluid) range between ~3‰ and ~1‰ during adsorption of Si onto Fe and Al oxides (Delstanchte et al., 2009; Oelze et al., 2014). Batch and flow-through experiments yield solid–aqueous Si isotope fractionation factors that vary between ~3‰ and ~1‰ during precipitation from Si-saturated solutions (Li et al., 1995; Geilert et al., 2014b; Oelze et al., 2015; Roerdink et al., 2015), consistent with field studies that document low δ30Si values for siliceous cements and secondary clay minerals (Basile-Doelsch et al., 2005; Ziegler et al., 2005; Georg et al., 2007). Kinetic processes, such as Si precipitation, clearly affect Si isotope fractionation (e.g., Geilert et al., 2015), but all low-temperature experimental work to date has been conducted under conditions associated with strong Si precipitation and/or dissolution, making differentiation between equilibrium and kinetic fractionation challenging. In addition, none of the low-temperature experimental work to date has assessed Si isotope exchange rates.

Here we present the results of Si isotope exchange experiments that involved aqueous Si and amorphous Fe(III)–Si gel, using the “three-isotope method” to rigorously constrain the extent and kinetics of isotopic exchange (e.g., Matthews et al., 1983a,b; Young et al., 2015). In contrast to most previous experiments that explored silica precipitation in simple silica solutions (e.g., Li et al., 1995; Geilert et al., 2014b), our experiments were conducted in a synthetic seawater matrix intended to be analogous to Archean seawater chemistry in key aspects such as high aqueous Fe(II)aq, and that the unique Si isotope properties of Fe–Si formations (Rasmussen et al., 2015). Our results demonstrate that the magnitude of equilibrium Si isotope fractionation as well as the isotopic exchange kinetics are significantly controlled by the presence or absence of Fe(II)aq, and that the unique Si isotope properties of Fe–Si gels can well explain previously puzzling aspects of the Si isotope compositions of certain Precambrian BIFs and cherts.

2. NOMENCLATURE AND EXPERIMENTAL DESIGN

2.1. Notation

Silicon isotope compositions are reported relative to the international standard NBS-28, and are expressed using standard δ notation:
\[ \delta^{29}\text{Si} = \left( \frac{^{29}\text{Si}_{\text{sample}}}{^{28}\text{Si}_{NBS-28}} - 1 \right) \times 1000 \] (1)

\[ \delta^{30}\text{Si} = \left( \frac{^{30}\text{Si}_{\text{sample}}}{^{28}\text{Si}_{NBS-28}} - 1 \right) \times 1000 \] (2)

The Si isotope fractionation factor (\(\alpha\)) between phase A and B is defined as:

\[ \alpha_{A-B}^{29/28} = \left( \frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_A \left( \frac{^{28}\text{Si}}{^{30}\text{Si}} \right)_B \] (3)

\[ \alpha_{A-B}^{30/28} = \left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_A \left( \frac{^{28}\text{Si}}{^{30}\text{Si}} \right)_B \] (4)

More conveniently, Si isotope fractionation between phase A and B can be expressed by \(\Delta_{A-B}\), which directly links the Si isotope compositions of phase A and B to the fractionation factor \(\alpha\) through the following relations:

\[ \Delta_{A-B}^{29}\text{Si} = \delta^{29}\text{Si}_A - \delta^{29}\text{Si}_B \approx 10^3 \ln \alpha_{A-B}^{29/28} \] (5)

\[ \Delta_{A-B}^{30}\text{Si} = \delta^{30}\text{Si}_A - \delta^{30}\text{Si}_B \approx 10^3 \ln \alpha_{A-B}^{30/28} \] (6)

### 2.2. Application of the three-isotope method to Si isotopes

The three-isotope method was initially developed to study isotopic exchange kinetics and to allow estimates for equilibrium fractionation factors for O isotopes (Matsuhisa et al., 1978; Matthews et al., 1983a,b), and, more recently, has been extensively applied to stable Fe and Mg isotopes (e.g., Shahar et al., 2008; Beard et al., 2010; Li et al., 2011; Frierdich et al., 2014a). This method was previously applied to experiments on Si isotope fractionation between silicate melt and Si-bearing Fe metal under high-temperature conditions (Shahar et al., 2009). To the best of our knowledge, the experiments reported here represent the first application of this method to determine Si isotope exchange kinetics and fractionation factors in low-temperature experiments.

The three-isotope method involves isotope exchange between two components (Fig. 1), one of “normal” isotopic composition that initially plots on the primary mass-dependent fractionation line in a three-isotope (i.e. \(\delta\delta\)) diagram, and the other that is enriched in one isotope (\(^{29}\text{Si}\) in this study) and hence initially plots on a distinct mass-dependent fractionation line. Isotopic compositions of the two components gradually evolve during isotopic exchange, and, at 100% exchange, will fall on a secondary mass-dependent fractionation line. For Si isotopes, \(\delta^{29}\text{Si}\) and \(\delta^{30}\text{Si}\) follow a mass-dependent relation of \(\delta^{30}\text{Si} \approx 1.93 \times \delta^{29}\text{Si}\) (Young et al., 2002).

Progressive isotopic exchange is represented on a \(\delta-\delta\) diagram by rotation of the tie-line between the two components towards the secondary fractionation line, the location of which is determined by the isotopic mass balance of the system and the slope of the mass-dependent fractionation line (Fig. 1). Because the three isotope method permits extrapolation to 100% exchange, it provides one of the most robust methods of estimating equilibrium isotope fractionation factors, although it is important to note that 100% exchange may not be the same as attainment of isotopic equilibrium if the mechanism of exchange occurs under non-equilibrium conditions (e.g., Li et al., 2011; Frierdich et al., 2014b).

### 2.3. Preparation of \(^{29}\text{Si}\)-enriched Archean Artificial Seawater (AAS)

Archean Artificial Seawater (AAS) was prepared as the aqueous Si phase in our experiments, and followed the recipe from previous studies (Percak-Dennett et al., 2011; Wu et al., 2012) to mimic some key features of Archean seawater chemistry, including low sulfate and high Si contents. AAS was adjusted and buffered by 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) to a pH of \(\sim 7.4\), consistent with pH estimates for the Archean oceans (Grotzinger and Kasting, 1993). It is important to note that there is no significant change in aqueous Si speciation at circumneutral pH (\(< 6\–8\)) (Alexander et al., 1954; Iler, 1979), although pH may control Si solubility of Fe–Si gel, as demonstrated recently in Fe(II)–Si systems (Tosca et al., 2015). Different batches of AAS with varied aqueous Si concentrations were prepared with or without Fe(II)\(_{\text{aq}}\) (details in Section 2.5). The goal of the exchange experiments was to operate as close to solubility as possible to minimize net precipitation or dissolution, and hence to provide true isotopic exchange information. AAS that contained Fe(II)\(_{\text{aq}}\) was prepared in an anaerobic chamber to prevent oxidation of Fe(II), and this was monitored through controls.

The \(^{29}\text{Si}\) spike added to AAS was prepared from a \(^{29}\text{Si}\) stock solution from 99.9% enrichment \(^{29}\text{SiO}_2\) powders, fused by sodium hydroxide (NaOH, 99.99% purity) in a silver crucible at \(\sim 750^\circ\text{C}\) for \(\sim 13\) min, and followed by complete dissolution in ultrapure (18.2 M\(\Omega\)-cm) water (Georg et al., 2006). The concentrated \(^{29}\text{Si}\) spike solution was mixed with isotopically “normal” sodium silicate (\(\text{Na}_2\text{SiO}_3\)) solution to produce AAS that had a \(\delta^{29}\text{Si}\) value of \(< 99\%_{ee}\), and a \(\delta^{30}\text{Si}\) value of \(< 0\%_{ee}\).
2.4. Preparation of Fe(III)–Si gel

Isotopically “normal” amorphous Fe(III)–Si gel was synthesized following the methods described in Percak-Dennett et al. (2011) and Wu et al. (2012). A solution containing 100 mM Na₂SiO₃, 50 mM FeCl₂ and 100 mM NaHCO₃ was allowed to oxidize under ambient laboratory conditions for ~18 days with continuous shaking. Iron and Si co-precipitated during gradual oxidation of Fe(II) and associated Fe hydrolysis, forming an amorphous Fe(III)–Si gel. The Fe(III)–Si gel was centrifuged and washed with ultrapure water to remove excessive salts before use in exchange experiments. Iron speciation measurements by the Ferrozine method (details in Section 3.1) showed that >98% of Fe present in the solid was Fe(III). Two batches of Fe(III)–Si gel (termed “A” and “B”) were produced during the course of this study. Analysis of Fe and Si contents for both batches of gels yielded a consistent Si:Fe molar ratio of 1.0:475, which, for convenience, we will refer to as 2:1. The Fe(III)–Si gel, therefore, may be stoichiometrically described as Fe(III)Si₂(OH)₁₁ based on charge balance. X-ray Diffraction (XRD) analysis of the Fe–Si gel used in the current study indicates an amorphous nature (Supplementary Information, Fig. S1). Previous spectroscopic studies indicate that co-precipitation of Fe and Si from a mixed solution tends to form an intimately bonded Fe–Si phase, rather than separate Fe and Si phases (Deolsch et al., 2000, 2001, 2003). This is consistent with transmission electron microscopy (TEM) analysis on Fe (III)–Si gel produced with the same synthesis procedure in our previous companion study, which showed a homogeneous distribution of Fe and Si atoms at the nanometer scale in the gel (Wu et al., 2012).

2.5. Experimental details

All experiments were conducted in an anaerobic chamber (Coy Laboratory, MI, USA), filled with ~4% (v/v) H₂ and ~96% Ar mixed gas. Because O₂ was continuously removed by the palladium-catalyzed reaction with H₂ inside the anaerobic chamber, the O₂ level in the chamber was always maintained below the detection limit of the O₂ monitor (<1 ppm). Reagents used in the experiments, including AAS, were sparged using oxygen-free N₂ gas before being transferred into the anaerobic chamber. Both reagents and experimental apparatus were left to equilibrate with the atmosphere in the anaerobic chamber for at least ~24 h prior to use. The lack of oxidation of Fe(II) during the experiments was confirmed by constant Fe(II)aq concentrations measured in control reactors that contained Fe(II)aq-bearing AAS but no Fe–Si gel. Five exchange experiments, differing mainly in initial Si concentrations and the presence or absence of initial Fe(II)aq in AAS, were conducted at room temperature (~23 °C) (Table 1). The pH of starting AAS was not buffered for Experiment 1 (pH ~ 7.8), but was buffered to ~7.4 with HEPES for all other experiments. Each experiment comprised a series of parallel batch reactors, each in 15 ml plastic centrifuge tubes which contained identical amounts of Fe(III)–Si gel and 10 ml of AAS. Reactors that contained Fe(II)aq were wrapped in aluminum-foil to avoid possible photo-oxidation of Fe(II). To avoid cross-contamination, one parallel reactor for each experiment, treated in the same way as sample reactors, was dedicated to monitor pH of the solution. Control reactors paralleled each experiment, and only contained AAS with or without Fe(II)aq; the control reactors allowed for monitoring of changes in Si polymerization and, for Fe(II)aq-bearing controls, oxidation of Fe(II). All reactors were continuously rolled on an end-over-end rotator throughout the experiments.

Experiment 1 was designed to have an initial aqueous Si concentration (2.33 mM) that slightly exceeds the solubility of amorphous Si (1.86 mM at 23 °C; Gunnarsson and Arnórsson, 2000), and did not contain Fe(II)aq. Experiments 2a and 2b used AAS that had a starting aqueous Si concentration of 0.71 mM, a level chosen based on the results of Experiment 1, as well as previous work that demonstrated a lower solubility of Fe–Si gel (i.e., ~0.45–1.5 mM Si) relative to that of pure amorphous Si (Wu et al., 2011, 2012). Experiment 2a used Fe(II)aq-free AAS, but Experiment 2b used AAS that contained an initial Fe(II)aq concentration of 0.92 mM; this concentration was lower than that used in our earlier work (1.8 mM; Wu et al., 2012), but lies closer to the range estimated for Archean seawater (Czaja et al., 2012). Experiments 1, 2a, and 2b all used the same batch of Fe(III)–Si gel, denoted as “Fe–Si gel (A)” (Table 1). Experiments 3a and 3b reacted a second batch of Fe(III)–Si gel, denoted as “Fe–Si gel (B)”, with AAS that had an initial aqueous Si concentration of 0.99 mM, a concentration level slightly higher than that in Experiment 2. Experiment 3a used Fe(II)aq-free AAS, and Experiment 3b used AAS that initially contained 0.96 mM Fe(II)aq. All experiments were started when amorphous Fe(III)–Si gel was added into AAS.

Fe(III)–Si gel and AAS in parallel reactors were left to react for varied durations before sampling, and parallel reactors were sampled as a time series over 53–126 days. The pH of the aqueous phase was checked in the dedicated reactor in each set of experiments with a pH meter at each sampling time point. For sampling, the solid phase was separated by centrifuging at 10,000 rpm (6238g RCF) for ~5 min, and the aqueous phase was filtered through 0.22-μm filters, followed by centrifuging at 10,000 rpm for another ~10 min. The control reactors, which did not contain Fe(III)–Si gel, were typically sampled at the end of the experiments. Although no visible precipitate was observed in control reactors for all experiments, AAS collected from control reactors was centrifuged at 10,000 rpm for ~10 min prior to collection of only the upper portion of the solution for Si and Fe concentration measurements. Sampling, together with subsequent sample dissolution and measurements of Fe contents, was conducted in the anaerobic chamber.

3. ANALYTICAL PROCEDURES

3.1. Analysis of Si and Fe concentrations

Silica concentrations were measured colorimetrically using the heteropoly blue method (Clesceri et al., 1999).
Table 1
A summary of experimental details.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Description</th>
<th>AAS</th>
<th>Fe–Si gel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[Fe(II)_{aq}] (mM)</td>
<td>[Si] (mM)</td>
</tr>
<tr>
<td>Exp-1</td>
<td>Fe(II)_{aq}-free AAS + Fe–Si gel (A)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Initial conditions</td>
<td>–</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>Final conditions (126 days)</td>
<td>–</td>
<td>0.88</td>
</tr>
<tr>
<td>Exp-2a</td>
<td>Fe(II)_{aq}-free AAS + Fe–Si gel (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial conditions</td>
<td>–</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Final conditions (80 days)</td>
<td>–</td>
<td>0.90</td>
</tr>
<tr>
<td>Exp-2b</td>
<td>Fe(II)_{aq}-containing AAS + Fe–Si gel (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial conditions</td>
<td>0.92</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Final conditions (80 days)</td>
<td>0.10</td>
<td>0.83</td>
</tr>
<tr>
<td>Exp-3a</td>
<td>Fe(II)_{aq}-free AAS + Fe–Si gel (B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial conditions</td>
<td>–</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Final conditions (53 days)</td>
<td>–</td>
<td>0.94</td>
</tr>
<tr>
<td>Exp-3b</td>
<td>Fe(II)_{aq}-containing AAS + Fe–Si gel (B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial conditions</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Final conditions (53 days)</td>
<td>0.18</td>
<td>0.79</td>
</tr>
</tbody>
</table>
This method measures molybdate-reactive Si, which comprises monomeric silica, and possibly some low-weight silica oligomers (e.g., dimers, trimers) (Iler, 1979; Tanakaa and Takahashib, 2001). Briefly, Si-bearing solutions were reacted with ammonium molybdate, and were then reduced by 1-amino-2-naphthol-4-sulfonic acid to produce blue-colored Si complexes. Light absorbance of samples was measured on a spectrophotometer at the wavelength of 815 nm. Conversion of absorbance values to Si concentrations was calibrated against gravimetrically prepared Si standards with known concentrations at the beginning of each analysis session. The precision of the method is estimated to be ~5% (1σ).

Ferrous Fe concentrations were measured colorimetrically on a spectrophotometer at the wavelength of 562 nm, using the Ferrozine method (Stookey, 1970). Total Fe concentrations were measured by the same method after adding a reducing reagent, hydroxylamine hydrochloride. Ferric Fe contents are calculated from the difference between measured Fe(II) and total Fe contents. The instrument was calibrated against gravimetrically prepared Fe solutions with known Fe concentrations before each analytical session. The precision of the method is ~5% (1σ).

### 3.2. Sample pre-treatment

Aqueous samples from the experiments were acidified with Teflon-distilled 7 M HCl to pH ~2–3 (checked by pH papers), followed by chromatographic purification for Si. Solid samples of Fe-Si gel were first dissolved in 0.5 M HCl for at least 12 h, and then centrifuged to separate the supernatant (primarily Fe fraction) and insoluble Si gel. The resulting fractions of white Si gel were then dissolved in 0.5 M NaOH, prepared from NaOH beads of 99.99% purity, for another 12 h at least until complete dissolution was achieved, followed by dilution with ultrapure water to a Si concentration of ~30 ppm. The diluted Si fractions were acidified with 7 M HCl, and subsequently combined with the Fe fractions. Final sample solutions had a Si concentration of ~25 ppm and a pH between 2 and 3.

### 3.3. Si isotope analysis

Silicon was purified following the chromatographic approach of Georg et al. (2006), in which sample solutions were passed through Bio-Rad AG 50W–12X (H form, 200–400 mesh) cation-exchange resin. Under the ion-exchange conditions used, Si existed predominantly as uncharged monosilicic acid (H₄SiO₄) in equilibrium with minor anionic species (H₂SiO₄⁻), and therefore Si passes through the resin directly. Ultrapure water was used to elute the remainder of Si from the resin to achieve an average yield of ~100%.

Isotopic compositions for Si were measured on an MC–ICP–MS (Nu plasma II) in the Department of Geoscience, University of Wisconsin–Madison. Polyatomic interferences on Si isotopes, notably 18N⁴O⁺ on 30Si⁺, were resolved in pseudo-high-resolution mode, achieved by narrowing the width of the source defining slit and two alpha slits. Sample solutions were introduced into the instrument via a self-aspirating nebulizer (~40–100 μl/min uptake rate) and a peltier-cooled cyclonic spray chamber (i.e., “wet plasma”). Typical Si concentration for the isotopic measurements was ~3 ppm, yielding an ion intensity of ~5–6 volts of 28Si on Faraday collectors that were equipped with 10¹⁵ Ω resistors. Backgrounds from the instrument and ultrapure water used during sample pre-treatment and chromatographic separation were corrected using an on-peak zero routine, where ion intensities of Si isotopes were determined in the ultrapure water before each analysis and subtracted from their respective beam intensities measured in the subsequent analyte. On-peak zero intensities, accounting for ~1% (usually ~0.2%) of Si signals in analytes, were negligible.

Silicon isotope ratios were measured using a sample–standard bracketing protocol to correct for instrumental mass bias. The international standard for Si isotopes, NBS-28, was used as the bracketing standard, and all Si isotope data reported in this study are relative to NBS-28. Reference materials, including Diatomite and BHVO-2, were routinely processed through the entire ion-exchange column separation along with samples, and measured in each analytical session to check accuracy and precision of the Si isotope analyses. Each sample was typically measured three times during an analytical session. Measured δ²⁸Si and δ³⁰Si values for reference materials and samples that were not spiked with the ²⁹Si tracer fell on a mass-dependent fractionation line. Repeated analyses of Diatomite yielded δ²⁸Si = 0.66 ± 0.12‰ and δ³⁰Si = 1.28 ± 0.20‰ (2σ, n=43), and repeated analyses of BHVO-2 yielded δ²⁸Si = −0.11 ± 0.12‰ and δ³⁰Si = −0.21 ± 0.19‰ (2σ, n = 64). Our results are in good agreement with published consensus values for these materials (Diatomite: δ²⁸Si = 0.64‰, δ³⁰Si = 1.26‰; BHVO-2: δ²⁸Si = −0.15‰, δ³⁰Si = −0.28‰ (Reynolds et al., 2007; Savage et al., 2014). Long-term reproducibility (2σ), based on repeated measurements of the reference materials, is estimated to be ±0.15‰ for δ²⁸Si and ±0.20‰ for δ³⁰Si.

The accuracy of the Si isotope measurements was assessed using cation and anion doping tests. Different amounts of FeCl₃ solution was added into solution of a reference material, Big Batch, to yield Si:Fe molar ratios of 1:1, 1:2.5 and 1:5. The Fe-doped solutions were processed through the ion-exchange column separation and then measured for their Si isotope compositions. Solutions doped with varied amount of Fe yielded Si isotope compositions that were indistinguishable from each other, as well as results measured for pure Big Batch, suggesting that effective removal of Fe was achieved during chromatographic separation. For Big Batch, the pooled δ²⁸Si value is −10.71 ± 0.22‰ (2σ, n = 8), which agrees within error of the inter-laboratory calibration result of −10.48 ± 0.54‰ (2σ) (Reynolds et al., 2007). Because solid samples of Fe-Si gel from the experiments only had a Si:Fe molar ratio of ~1:0.5, the Fe-doping tests indicate that a matrix effect associated with cations during analysis is unlikely.

Anions cannot be separated from Si during the ion-exchange separation due to the use of cation exchange resin. Because Cl⁻ was the predominant anion in AAS
variable amounts of HCl were doped into an NBS-28 solution that had been processed after column separation to produce Cl concentrations ranging from 0.02 M up to 0.5 M; these solutions were then directly measured on the MC-ICP-MS against the same NBS-28 solution that did not contain added HCl. No matrix effect was detected with the increased Cl concentration. Potential matrix effects associated with anions were further evaluated through comparison of the Si isotope compositions measured for pure sodium silicate that was dissolved in ultrapure water, with those measured for AAS that was prepared using the same sodium silicate powers. The measured δ30Si value of 0.13‰ for sodium silicate dissolved in ultrapure water agrees within analytical uncertainty (±0.2‰) with the average δ30Si value of 0.02‰ measured for different batches of AAS that had a more complex anionic matrix. This agreement is expected, because, without a matrix effect, addition of the 29Si spike at the level of enrichment used in our experiments will only shift δ30Si values of AAS by <0.05‰. These tests, therefore, demonstrate that matrix effects are entirely negligible, and the accuracy of the Si isotope measurement is similar to the precision.

4. RESULTS

4.1. Temporal changes in aqueous chemistry and solid phase

The pH of the aqueous phase for Experiment 1, which was not pH-buffered, showed a minor drift from 7.8 to 8.0 over 126 days. For Experiments 2a and 3a, which did not contain Fe(II)aq but were pH-buffered, the pH of aqueous phase remained at 7.4 throughout the experiments (80 and 53 days, respectively). In contrast, there was a rapid ~0.2-unit pH drop after addition of Fe(III)–Si gel in Experiments 2b and 3b, which contained Fe(II)aq, but after this initial drop, pH remained constant at ~7.2 for the duration of these experiments (80 and 53 days, respectively).

Aqueous Si concentrations in Experiment 1 decreased continuously from the initial concentration of 2.33 to 0.88 mM over the 126 day experiment (Fig. 2), indicating a loss of 62% Si from solution. Aqueous Si concentrations in the control for Experiment 1, which contained AAS but no Fe(III)–Si gel, decreased from 2.33 mM to 1.89 mM (Appendix Table A.1). Fe(III)–Si gel dissolved shortly after initiation of Experiments 2a and 2b, as demonstrated by an increase in Si concentration of AAS at the beginning of both experiments (Fig. 2). For Experiment 2a, aqueous Si concentrations increased rapidly from the initial value of 0.71 mM to ~0.9 mM within ~4 h, corresponding to dissolution of ~5% of total Si from the solid, and then gradually increased to ~1 mM within a week before returning to a relatively constant value of ~0.92 mM during the rest of the experiment. In Experiment 2b, which contained Fe(II)aq, aqueous Si concentrations increased from the initial value of 0.71 mM to ~0.9 mM during the first 5 days, corresponding to dissolution of ~4% of total Si from the solid, and then returned to a constant level of ~0.85 mM during the rest of the experiment. For Experiment 3a, aqueous Si concentrations remained at a relatively constant value of ~0.95 mM for the duration of the experiment, essentially the same as the initial Si concentration of 0.99 mM within the analytical uncertainty (Fig. 2). For Experiment 3b, however, which contained...
Fe(II)aq, there was net precipitation of aqueous Si, as demonstrated by a decrease in Si concentration of AAS from the initial 0.99 mM to ~0.80 mM (Fig. 2). Controls for Experiments 2 and 3 showed no change in aqueous Si concentrations, indicating negligible Si polymerization and precipitation (Appendix Table A.1).

Although Si concentrations in initial AAS were different in Experiments 2a and 3a (0.71 and 0.99 mM, respectively), they reached a similar value of ~0.95 mM within a few days (Fig. 2). Similarly, Si concentrations of AAS in the Fe(II)aq-bearing Experiment 2b and 3b, starting at different initial levels, evolved towards a similar final value of ~0.82 mM. The Si solubility of Fe(III)–Si gel in AAS containing ~1 mM Fe(II)aq (Experiments 2b and 3b) is slightly lower than that in AAS without Fe(II)aq (Experiments 2a and 3a). The final equilibrium aqueous Si concentrations for both sets of experiments were significantly lower than the solubility of amorphous Si (1.86 mM) in H2O at room temperature (23 °C) (Gunnarsson and Arnórsson, 2000), but fit well between the solubility determined for Fe(II)–Si precipitates at pH 7.0 and 7.5 (Tosca et al., 2015).

Aqueous Fe(II)aq contents decreased with time for all Fe(II)aq-bearing experiments (Experiments 2b and 3b) (Fig. 3), similar to what was previously observed in Fe isotope exchange experiments with the same Fe(III)–Si gel in AAS (Wu et al., 2012). The lack of changes in Fe(II)aq contents in control reactors that contained Fe(II)aq-bearing AAS but no Fe(III)–Si gel demonstrates that the Fe(II)aq decrease in our experiments is not due to oxidation (Appendix Table A.1). Transfer of Fe(II)aq to Fe–Si gel was also confirmed in Experiment 3b where the measured Fe(II) addition in the solid phase matched the Fe(II) loss from the aqueous phase within the analytical uncertainty at each sampling time point. Our new results may be directly compared with those of Wu et al. (2012) (Fig. 3), where the same amount of Fe(III)–Si gel was used and the reactor volumes were the same, although the initial Fe(II)aq contents of the experiments of Wu et al. (2012) were higher (~1.8 mM) relative to the current study (~1 mM). Despite the different initial Fe(II)aq contents, the absolute amount (i.e., mole) of Fe(II) loss from solution were very similar between the two studies, at ~8 × 10⁻⁶ moles. Wu et al. (2012) did 5 mM HCl and 0.5 M HCl extractions, which provides an assessment of loosely bound Fe(II) sorbed on Fe–Si gel and Fe(II) incorporated into the structure of Fe–Si gel, respectively. They found that a total of ~5 × 10⁻⁶ moles of Fe(II) was sorbed, and ~3 × 10⁻⁶ moles of Fe(II) were contained in the solid phase, equivalent to a change in stoichiometry from that of the initial material, Fe(III)Si2(OH)11, to Fe(II)0.1Fe(III)Si2(OH)11.2 at the end of their experiments. We did not perform HCl extractions in the current study because it was unknown if this would affect Si isotope compositions of the solid, but if we assume the similar Fe(II)aq losses that were observed in the current study as compared to Wu et al. (2012) are apportioned the same between sorbed and solid components, we would estimate the same solid phase stoichiometry Fe(II)0.1Fe(III)Si2(OH)11.2 at the end of the Fe(II)aq-bearing experiments in the current study. Such changes are consistent with visible color changes in the solid phase for Experiments 2b and 3b, where the initial brown color of the Fe(III)–Si gel changed to green, indicating the presence of Fe(II) in the solid.

XRD analysis of the Fe(III)–Si and Fe(II)–Fe(III)–Si gels indicates that the solid remained X-ray amorphous throughout all experiments in this study (Supplementary Information, Fig. S1). This is consistent with the XRD and TEM results of our previous companion Fe isotope study that has shown the amorphous nature of the gel during the course of experiments in a highly similar AAS and Fe–Si gel system (Wu et al., 2012). Our observation is, however, different from a recent study that found nm-size Fe(II)–Si nanoparticles in Fe(II)–Si gel formed in similar experimental settings (Tosca et al., 2015), probably reflecting inhibition of crystallization due to higher Si contents in our Fe–Si gel (Si:Fe = 2:1) relative to those (Si:Fe = 1:1) produced in Tosca et al. (2015).

4.2. Evolution of Si isotope compositions

Extensive Si isotope exchange was evident from an initial rapid and then gradual convergence in δ²⁹Si values of aqueous and solid phases with time in all experiments (Fig. 4). For Experiments 2a and 2b, which involved modest extents of solid dissolution, the aqueous δ²⁹Si values decreased more than those of the aqueous component for Experiments 3a and 3b, which involved negligible, or small amounts of, net precipitation. Overall, the Fe(II)aq-bearing experiments had larger changes in δ²⁹Si values than the Fe(II)aq-free experiments (Fig. 4). Accompanying isotopic exchange, as monitored using the enriched ²⁹Si tracer, there was a divergence in δ²⁸Si values between the two phases, where δ²⁸Si values of the aqueous phase increased (Fig. 4). The magnitude of δ²⁸Si changes was larger in the aqueous Si than the Fe(III)–Si and Fe(II)–Fe(III)–Si gels, because most of the Si mass resided in the gels for all experiments (Table 1). For Experiment 1, δ²⁸Si values of aqueous Si increased from ~0‰ to 2.24‰ over 126 days, and δ²⁸Si
4.3. Calculation of fraction of Si isotope exchange

Following the approach of previous studies (e.g., Cole and Chakraborty, 2001; Johnson et al., 2002; Li et al., 2011; Wu et al., 2012), the fraction of Si isotope exchange ($F$) can be calculated using the following equation:

$$ F = \frac{\delta_i - \delta_e}{\delta_i - \delta_{eq}} $$

(7)

where $\delta_i$ indicates the Si isotope composition of the sample at any given time $t$, $\delta_e$ and $\delta_{eq}$ represent initial and equilibrium Si isotope compositions, respectively. The parameter $F$ quantifies the extent to which the system has moved to complete isotopic exchange, although, in detail, Eq. (7) does not directly quantify the number of atoms in the solid or solution that have been mixed (Frierdich et al., 2015).

The fraction of exchange is useful to investigate the kinetics of isotopic exchange (e.g., Cole and Chakraborty, 2001), as well as to evaluate changes in the instantaneous fractionation factors that might indicate kinetic isotope effects during isotopic exchange (Frierdich et al., 2014a,b).

The $\delta$ values for phase A ($\delta_{eq}(A)$) and B ($\delta_{eq}(B)$) in a closed system can be expressed by the mass-balance equation at equilibrium:

$$ (N_A + N_B) \times \delta_{eq} = N_A \times \delta_{eq}(A) + N_B \times \delta_{eq}(B) $$

(8)

where $N_A$ and $N_B$ indicate moles of Si in phase A and B, and $\delta_{eq}$ represents the mean Si isotope composition of the system. $\delta_{eq}$ can be constrained by a similar mass-balance equation based on initial materials:

$$ (N_A + N_B) \times \delta_{eq} = N_A \times \delta_{eq}(A) + N_B \times \delta_{eq}(B) $$

(9)

where $\delta_{eq}(A)$ and $\delta_{eq}(B)$ represent initial Si isotopic compositions of phase A and B.

If there is no natural, mass-dependent, Si isotope fractionation between the two phases at equilibrium (i.e. $A = 0$), $\delta_{eq}(A)$ equates to $\delta_{eq}(B)$, and $\delta_{eq}$ equates to $\delta_{eq}$. Consequently, $F$ can be calculated based on Eqs. (7)–(9) without uncertainty. In the case where $A \neq 0$, $\delta_{eq}(A)$ and $\delta_{eq}(B)$ depend on $A$, which can be expressed by rearranging Eq. (8) as:

$$ \delta_{eq}(A) = \delta_{eq} + \frac{N_B}{N_A + N_B} \times A $$

(10)

$$ \delta_{eq}(B) = \delta_{eq} - \frac{N_A}{N_A + N_B} \times A $$

(11)

Substituting Eqs. (9)–(11) into Eq. (7), calculation of $F$, which can be based on either phase A ($F_A$) or B ($F_B$), also depends on $A$:

$$ F_A = \frac{\delta_{eq}(A) - \delta_{eq} - \Delta A}{f \times ([\delta_{eq}(B) - \delta_{eq}])} $$

(12)
Results of our experiments show that apparent fractionation factors between starting materials (i.e. $\delta_{B(B)} - \delta_{B(A)}$) relative to $\Delta_{A-B}$, the less influence of $\Delta_{A-B}$ would impose on the calculation of $F$, and hence use of an enriched $^{29}$Si tracer minimizes the effect of $\Delta_{A-B}$ on the calculation of $F$ using $\delta^{29}$Si data. Results of our experiments show that apparent fractionation factors of $\delta^{30}$Si between Fe(III)–Si (or Fe(II)–Fe(II I)–Si) gel and aqueous Si, based on the last $\delta^{30}$Si data in the time series of each experiment, range between $\sim-2\‰$ and $\sim-4\‰$ (Fig. 4). Because the mass-dependent fractionation law predicts $\Delta^{30}$Si $\approx 1.93 \times \Delta^{29}$Si (Young et al., 2002), $\Delta^{29}$Si$_{gel$–aqueous$}$ is likely to be within the range of $-1\‰$ to $-2\‰$. A value of $-1.5\‰$ for $\Delta^{29}$Si$_{gel$–aqueous$}$ was applied to Eqs. (12) and (13) for all experiments to calculate $F$ (Appendix Table A.1); if, instead, a $\Delta^{29}$Si$_{gel$–aqueous$}$ value of zero were assumed, the calculated $F$ values would only differ by $<2\‰$.

Although our goal was to conduct experiments very close to Si solubility to minimize the possibility of kinetic isotope effects caused by net precipitation or dissolution, net Si mass transfer occurred in most of our experiments (Fig. 2), and this produces slightly different $F$ values calculated from aqueous or solid components. For Experiments 2a and 2b, small amounts of net dissolution of the solid during these experiments preferentially transferred isotopically “normal” Si to the solution, producing slightly higher extents of apparent exchange (Appendix Table A.1); in such cases, the fraction of true exchange is best estimated using $F$ values calculated based on the solid phase results, although it should be recognized that solid-phase $F$ values are less precise in the current study given the smaller overall shift in $^{30}$Si/$^{28}$Si ratios due to mass balance. For Experiments 1, 3a and 3b, where net Si precipitation occurred, the fraction of true isotopic exchange is best estimated using $F$ values calculated from the aqueous phase.

### 4.4. Silicon isotope fractionation factors

Inference of Si isotope fractionation factors at 100% exchange is possible via extrapolation of partial exchange results using the three-isotope method. Extrapolation of data is not possible for Experiment 1 because of a non-linear trajectory of $^{30}$Si towards 100% exchange (Fig. 5), suggesting variable kinetic isotope effects (e.g., Friedrich et al., 2014b); a fractionation factor, therefore, was not determined for this experiment. Extrapolation of data for Experiments 2a and 3a to 100% exchange yielded consistent fractionation factors between Fe(III)–Si gel and aqueous Si ($\Delta^{30}$Si$_{solid$–AAS$}$) of $-2.28 \pm 0.17$ ($2\sigma$) $‰$ and $-2.31 \pm 0.19$ ($2\sigma$) $‰$, respectively (Fig. 6). Extrapolation of data for Experiments 2b and 3b also yielded consistent fractionation factors between Fe(II)–Fe(III)–Si gel and aqueous Si, $\Delta^{30}$Si$_{solid$–AAS$}$ of $-3.23 \pm 0.33$ ($2\sigma$) $‰$ and $-3.23 \pm 0.16$ ($2\sigma$) $‰$, respectively (Fig. 6). Importantly, the fractionation between Fe-Si gel and aqueous Si for Fe(II)$_{aq}$-bearing experiments that involved changes in the stoichiometry of the gel is $\sim 1\‰$ larger than that obtained from the Fe(II)$_{aq}$-free experiments that maintained the same stoichiometry of Fe(III)–Si gel.

### 5. DISCUSSION

In following sections, we first discuss the Si solubility of Fe–Si gel and its implications for estimation of seawater Si concentrations in the Precambrian oceans, and then discuss Si isotope exchange kinetics observed in our experiments, followed by a comparison with Fe isotope exchange kinetics observed in a companion study (Wu et al., 2012). In particular, the role of Fe(II) in controlling Si isotope exchange kinetics and fractionation is highlighted. The discussion is then followed by a comparison between the equilibrium Si fractionation factors for the Fe-bearing Si gels determined in this study and those estimated for pure Si gel in the literature, and concluded with the implications of this comparison for interpretation of Si isotope records in the Precambrian BIFs and cherts.

#### 5.1. Silica concentrations in the Precambrian oceans

Estimation of Si concentrations in the Precambrian oceans is required to understand the Precambrian silica
Fig. 6. Calculation of the $^{30}\text{Si}/^{28}\text{Si}$ fractionation factor between Fe(III)-Si gel and aqueous Si in AAS ($\Delta^{30}\text{Si}_{\text{solid-aqueous}}$), determined by extrapolation to 100% isotope exchange, for Fe(II)$_{\text{aq}}$-free experiments (A and B) and Fe(II)$_{\text{aq}}$-bearing experiments (C and D). (A) Results of Experiment 2a. The fraction of isotopic exchange ($F$) is calculated based on the solid phase due to small amounts of dissolution of Fe(III)-Si gel. (B) Results of Experiment 3a. $F$ is calculated based on the aqueous phase due to small extents of precipitation of aqueous Si. (C) Results of Experiment 2b. $F$ is calculated based on the solid phase due to minor dissolution of Fe-Si gel. (D) Results of Experiment 3b. $F$ is calculated based on the aqueous phase due to small amounts of precipitation of aqueous Si. Note that interaction between Fe(II)$_{\text{aq}}$ and the Fe(III)-Si gel in Experiments 2b and 3b produced a change in stoichiometry from Fe(III)$_2$Si$_2$(OH)$_{11}$ to Fe(II)$_{0.1}$Fe(III)$_2$Si$_2$(OH)$_{11.2}$. In all figures, gray horizontal dashed lines represent the $\delta^{30}\text{Si}$ value ($/C^{25}_{\text{Si}}$‰) of initial Fe(III)-Si gel and AAS used for the experiments, and black solid lines indicate the linear regression lines, and black dashed lines indicate the uncertainty of regression resulted from analytical uncertainty (95% significance level).
cycle. There is general consensus that solubility of different Si-bearing phases played an essential role in controlling seawater silica concentrations before the appearance of marine silica-secreting organisms (Sievér, 1992), and it has been proposed that silica concentrations in seawater may have reached saturation of amorphous silica during the Precambrian (Máliva et al., 2005; Konhauser et al., 2007). Recent studies, however, have highlighted the importance of Fe–Si gels in the Precambrian Si cycle (Fischer and Knoll, 2009; Rasmussen et al., 2015), and this potentially changes estimates of Precambrian seawater silica contents.

Our experiments, together with previous experimental studies using Fe(III)–Si gel (Wu et al., 2011, 2012), demonstrate that Si solubility for Fe(III)–Si gels varies between 1.5 and 0.5 mM at room temperature as a function of Fe/Si ratio of gel (Fig. 7), significantly lower than that of pure amorphous silica (1.86 mM) in water (Gunnarsson and Arnórsson, 2000). The difference in the solubility between Fe–Si gel and amorphous silica cannot be explained by a salt effect due to the presence of an AAS matrix, because our aqueous modeling results, using the PHREEQC software (Parkhurst and Appelo, 2013) and Si equilibrium constants at ionic strength similar to seawater (Felmy et al., 2001), suggest that the presence of a AAS matrix with or without Fe(II)aq would lead to a slightly lower solubility of 1.54 mM Si for amorphous silica, but not as low as that observed for Fe(III)–Si gel, indicating that Fe(III)–Si gel has an intrinsically lower solubility than amorphous silica. This is consistent with a recent study that also observed lower Si solubility of ~0.5–1.2 mM, depending on aqueous pH, for Fe(II)–Si precipitates in simulated Precambrian seawater (Tosca et al., 2015). Ferrous iron in Precambrian seawater may have been oxidized by anoxicogenic photosynthesis (e.g., Walker, 1987; Kappler et al., 2005), or by photo-oxidation (e.g., Braterman et al., 1983), or by free O2 (e.g., Morris, 1993), leading to formation of Fe(III)–Si gels. Also, fluctuations in seawater Fe and Si concentrations associated with secular changes in the Fe and Si cycles in Precambrian oceans may have led to formation of Fe–Si gels with different Fe/Si ratios. Because the solubility of Fe(III)–Si gel varies with the Fe/Si ratio (Fig. 7), any temporal changes in aqueous Fe contents in the Precambrian oceans, as might occur due to changes in oxygen contents, may have had an important impact on Si concentrations in Precambrian seawater.

5.2. Silica speciation in AAS and Fe–Si gel

An understanding of mechanisms for the observed Si isotope exchange kinetics and fractionations requires knowledge on Si species involved during the isotopic exchange process. Aqueous modeling, using the PHREEQC software (Parkhurst and Appelo, 2013), indicates that uncharged monomeric silicic acid (H4SiO4) is the dominant species (~97%) in AAS between pH 7 and 8 at 23 °C. Dissociated H2SiO4 (e.g., H2SiO3) species are minor because of the high pKa value of H2SiO4 (~9.5) (Exley and Sjöberg, 2014). Monomeric silicic acid can be expressed as Si(OH)4 to reflect its tetrahedral structure with the Si atom at the center and hydroxyl functional groups at four corners. Polymeric Si species are expected to be minor in AAS, because monomeric silicic acid can remain stable for long periods at low concentrations (<~2 mM) at neutral pH and room temperature (Iler, 1979). This is supported by constant aqueous Si concentrations in control reactors that only contained AAS (with or without Fe(II)aq) but no Fe (III)–Si gel over the course of the experiments, because Si polymerization or complexation would result in formation of Si species that cannot be detected by the heteropoly blue method used in our study (Appendix Table A.1).

One exception is Experiment 1, where aqueous Si concentrations in control AAS decreased by ~20% at the end of the 126-day experiment (Appendix Table A.1), and this is interpreted to be due to polymerization of Si induced by higher initial aqueous Si concentration (2.3 mM) for this experiment. An abrupt ~20% decrease in aqueous Si concentration was observed in the control reactor at the end of Experiment 3b (Appendix Table A.1). This decrease, however, may only reflect a perturbation in this particular control reactor or an analytical artifact, because it was
not accompanied by a similar decrease in aqueous Si concentration, or an anomalous change in Si isotope composition, in the parallel sample reactor at the same time (Fig. 2).

Silanol bonds (Si-OH) are expected to exist at the surface of Fe-Si gel, but Si atoms should be also present in Fe-O-Si and Si-O-Si bonds in the Si-Fe network of bulk Fe-Si gel. Given high initial aqueous Si (100 mM) and Fe (50 mM) concentrations used for Fe-Si gel synthesis, the production of Fe(III)-Si gel must involve both Si polymerization and Fe hydrolysis processes. Despite the tendency of maximizing Si-O-Si bonds during Si polymerization (Belton et al., 2012), Si has a strong affinity to Fe. Hydrolysis of Fe in the presence of Si tends to form Si-O-Fe bonds, which has been proven to significantly inhibit the growth of crystalline Fe oxides or transformation of less crystalline Fe phases to well-crystallized Fe minerals in both natural and controlled laboratory conditions (e.g., Schwertmann and Thalmann, 1976; Carlson and Schwertmann, 1981; Doelsch et al., 2003; Pokrovski et al., 2003; Chatellier et al., 2004; Jones et al., 2009). Using a suite of spectroscopic techniques, previous studies have demonstrated the presence of both Si-O-Si and Si-O-Fe bonds in amorphous Fe-Si gels that were synthesized by a similar approach involving Fe hydrolysis in the presence of Si in solution under a range of Si/Fe ratios (0.25-4) and pH (3 and 10) at room temperature (Doelsch et al., 2000, 2001, 2003). These studies also indicate that Fe-Si gel is present as a single phase with intimately bonded Fe and Si atoms, rather than separate Si and Fe phases, when produced under conditions similar to those of our synthesis protocol (e.g., a Si/Fe ratio of 2, pH > 3). This agrees well with our previous TEM analysis that showed a uniform distribution of Fe and Si atoms at the nm-scale without Fe- or Si-enriched domains in Fe-Si gels produced using the same protocol as used in the current study (Wu et al., 2012). However, an understanding of the exact ways in which Si tetrahedra are linked to Fe remains limited, because the spectroscopic approaches that have been commonly used to detect the locations of Fe atoms in amorphous materials, such as X-ray absorption fine structure spectroscopy, are not able to precisely detect the locations of Si atoms in the vicinity of Fe atoms (e.g., Doelsch et al., 2000; Pokrovski et al., 2003). It is likely that silicon tetrahedra may be linked to Fe in different ways in Fe-Si gels, given their amorphous nature.

5.3. Kinetics of Si isotope exchange and the catalytic effect of Fe(II)aq

The experiments in this study reached ~70–90% Si isotope exchange after periods of ~50–120 days (Appendix Table A.1), in marked contrast to the assumed low Si isotope exchange rate between silicates and Si-bearing fluids (André et al., 2006). The fast exchange of Si isotopes in our experiments is most likely caused by the amorphous nature of Fe-Si gel relative to crystalline silicate minerals. Isotopic exchange rates may be described by a general rate equation (Johnson et al., 2002):

\[
\frac{-d(1-F)}{dt} = k_a(1-F)^n
\]  

(15)

where \(F\) is the fraction of isotopic exchange; \(k_a\) is the rate constant; \(t\) is reaction time, and \(n\) represents the order of the reaction. A simple first- \((n = 1)\) or second- \((n = 2)\) order rate law, derived from Eq. (15), can adequately account for many isotopic exchange reactions (e.g., Criss et al., 1987; Johnson et al., 2002; Li et al., 2011; Wang et al., 2015), but appears to be inadequate in fitting our experimental results (Supplementary Information, Fig. S2). This may be explained by exchange of aqueous H$_4$SiO$_4$ with different Si bonds (Si-OH, Si-O-Si and Si-O-Fe) in the Fe-Si gel, each of which may produce different exchange rates.

Silicon isotope exchange was more extensive in the Fe(II)aq-bearing experiments (2b and 3b) relative to the Fe(II)aq-free experiments (1, 2a and 3a). This is illustrated through a comparison of the fraction of exchange (\(F\)) based on fitting \(F\) data and time (\(t\)) to an empirical power relation in a form of

\[ F = a \times t^b \]  

(16)

where \(a\) and \(b\) are two constants obtained by curve fit. The comparison clearly demonstrates a consistently higher fraction of Si isotope exchange in Fe(II)aq-bearing Experiments 2b and 3b than that of their counterpart Fe(II)aq-free Experiments 2a and 3a, at any given time (Fig. 8).

Our experiments document the first evidence for Fe(II)-catalyzed Si isotope exchange. Fe(II)-catalyzed isotope exchange has been previously observed for Fe and O isotopes during interaction between aqueous Fe(II) solution and Fe minerals (Friedrich et al., 2015). Poulson et al. (2005) documented limited Fe isotope exchange between Fe(III)aq and nm-size ferrihydrite, where exchange was limited to surface Fe atoms. In contrast, using the same Fe(III)-Si gel as in this study, Wu et al. (2011, 2012) documented extensive Fe isotope exchange between Fe(II)aq and Fe(III)-Si gel.

The catalytic effect of Fe(II)aq on the extent of Si isotope exchange can be explained by electron-transfer atom-exchange (ETAE) reactions between Fe(II)aq and Fe(III) (hydro-)oxides. Ample evidence has demonstrated that electrons are transferred from Fe(II) to Fe(III) substrates when Fe(II)aq is adsorbed onto the Fe(III) (hydro-)oxide surfaces (e.g., Jeon et al., 2003; Williams and Scherer, 2004; Yanina and Rosso, 2008; Rosso et al., 2010), which leads to reductive release of Fe from the solid, thereby facilitating Fe atom exchange (e.g., Crosby et al., 2005; Handler et al., 2009, 2014; Gorski et al., 2012). Fe(II)-Fe(III) ETAE reactions should have occurred in our Experiment 2b and 3b during net sorption of Fe(II)aq onto Fe(III)-Si gel. We suggest that Fe(II)-Fe(III) ETAE reactions may cause breakage of Si-O-Fe bonds, and formation of new Si-O-Fe bonds in Fe(III)-Si gel, and this process is envisioned to be the mechanism behind the larger extent of Si isotope exchange in the Fe(II)aq-bearing experiments.

5.4. A comparison of Si and Fe isotope exchange kinetics

Wu et al. (2012) conducted Fe isotope exchange experiments using a similar Fe(III)-Si gel and AAS that contained Fe(II)aq, offering an opportunity to compare Fe
and Si isotope exchange. An identical preparation method for the Fe(III)–Si gel was used in the current study and that of Wu et al. (2012), and an identical Fe:Si ratio of 1:2 was obtained for Fe(III)–Si gel used in both studies, although there are likely subtle differences in the gels between the two studies. As described above, data for the fraction of Fe isotope exchange with time from Wu et al. (2012) were fit by a power law (Eq. (16)), allowing comparison of the extent of exchange in both studies. The results show that the extent of isotope exchange for Si is subtly higher than that for Fe in the AAS–Fe–Si gel system (Fig. 9). This might reflect differences in the properties of the Fe(III)–Si gel used in the two experiments, despite identical preparation. If any difference, however, is expected, the higher Fe(II)aq contents in the experiments of Wu et al. (2012) would be expected to produce higher rates of Fe isotope exchange, yet the opposite is observed. In a comparison of Fe isotope exchange in the presence or absence of aqueous Si, Wu et al. (2011) observed that Fe isotope exchange was inhibited in experiments that contained aqueous Si, which was interpreted to reflect blockage of surface Fe sites by sorbed Si. This may be an alternative explanation for the slightly higher rates of Si isotope exchange, relative to Fe isotope exchange (Fig. 9).

5.5. Si isotope fractionations factors in low-temperature precipitates

Because the Fe–Si gel is amorphous, and a system comprising this amorphous material and AAS is unlikely to reach thermodynamic chemical equilibrium in our experiments, a fundamental question is whether Si isotope equilibrium can be achieved. Formation of Fe–Si gels in nature is ubiquitous, not only limited to the Precambrian oceans, due to the strong chemical affinity between Fe and Si in solutions, and the incorporation of Si into Fe hydroxides has been demonstrated to strongly inhibit transformation of the amorphous phase into a thermodynamically stable crystalline phase (e.g., Schwertmann and Thalmann, 1976; Carlson and Schwertmann, 1981; Châtelier et al., 2004; Jones et al., 2009). The Fe–Si gel clearly did not undergo any significant phase transformation in our experiments spanning over a period of a couple of months, and hence we consider it to be a metastable phase. Reaching relatively stable aqueous Si concentrations (except for Experiment 1) in AAS and stable Fe(II)aq concentrations in AAS in Fe(II)-bearing experiments (Figs. 2 and 3) after ~10 days is indicative of attainment of a metastable chemical equilibrium state in our experiments. It has been long known in high temperature and pressure oxygen isotope exchange experiments that isotope equilibrium can be achieved in systems that contained metastable assemblages (e.g., Clayton et al., 1989), which reflects the fact that isotope exchange kinetics may be faster than chemical kinetics required for phase transformation. It remains unclear if there is a change in Si isotope fractionation during transformation of metastable Fe–Si gels into crystalline Fe–Si minerals, and this may be dependent on the pathways of phase transformation (e.g., solid state versus dissolution–precipitation conversion). It should be noted, however, that the fractionation factors experimentally determined for amorphous materials do not necessarily differ from those determined for more crystalline phases. For example, oxygen isotope fractionation factors determined between amorphous Si gel and water at low temperatures are close to those extrapolated from quartz–water fractionation factors determined at high temperatures (Kita et al., 1985).

The relatively linear trajectories for the Si isotope exchange in Experiments 2a, 2b, 3a, and 3b (Figs. 6) strongly suggest that the inferred fractionation extrapolated...
to 100% exchange reflects equilibrium or near-equilibrium fractionation. Rapid net dissolution of Fe(III)-Si gel at the beginning of Experiments 2a and 2b drove $\delta^{30}$Si values of aqueous Si at early time points towards the initial $\delta^{30}$Si value of Fe(III)-Si gel ($C_{24}/C_{0}$), causing small deviations of these first data points from the linear regression defined by all data points (Figs. 6). Overall, the consistent fractionation factors between Fe(III)$_2$(OH)$_3$ and aqueous Si ($\Delta^{30}$Sisolid–aqueous = $C_{24}/C_{0}$) obtained for Experiments 2a and 3a, as well as consistent fractionation factors between Fe(II)$_2$Fe(III)$_2$(OH)$_5$ and aqueous Si (with Fe(II)$_{aq}$) ($\Delta^{30}$Sisolid–aqueous = $\approx -2.3\%$) for Experiments 2b and 3b, support our interpretation that these reflect equilibrium Si isotope fractionation factors. Our results contrast with precipitation experiments where large changes were measured for the instantaneous Si isotope fractionation factor between aqueous and solid phases (Li et al., 1995; Oelze et al., 2015; Roerdink et al., 2015); such changes are analogous to the large changes seen in Experiment 1, which involved extensive net precipitation (Fig. 5).

The isotopic fractionations obtained in the Fe–Si gel systems studied here are different from those inferred for pure Si systems based on theoretical calculations and experiments. Early studies that calculated equilibrium Si isotope fractionation factors predicted that heavy Si isotopes would preferentially partition in higher polymerized Si phases (Grant, 1954), suggesting that in a pure Si system, the solid–aqueous Si isotope fractionation factor should be positive. Recent low-temperature experimental studies have suggested little Si isotope fractionation between Si gel and aqueous Si ($\Delta^{30}$Sigel–aqueous $\approx 0\%$) under equilibrium conditions (Fig. 10; Oelze et al., 2015; Roerdink et al., 2015), although equilibrium was not rigorously established in these experiments, nor were the isotope exchange kinetics determined using an enriched tracer. A near-zero $\Delta^{30}$Sigel–aqueous fractionation for pure Si gel is consistent with the suggestion of Douthitt (1982), based on the observation of Si isotope compositions of natural quartz, chalcedony, and dissolved Si. In contrast, batch or flow-through experiments observed slightly larger fractionation, $\Delta^{30}$Sigel–aqueous of $\approx 1\%$, between Si gel and aqueous Si during precipitation from oversaturated solutions.
magnitude of Si isotope fractionation should correlate to mean Si–O distances, where the Si isotope fractionation factor becomes larger with increasing mean Si–O distances (i.e., weaker bonds; Méheut and Schauble, 2014; Dupuis et al., 2015). The presence of cations (M), and variations in their electronegativity, in the Si tetrahedron structure can affect mean distances of Si–O bonds, following an electron donation theory (Méheut and Schauble, 2014), where cations that have electronegativity values lower than Si tend to shorten M–Si–O bond. Shortening of the M–Si–O bond is accompanied by lengthening of the other three Si–O bonds, thereby leading to longer mean Si–O distances for the tetrahedron. Because Fe has an electronegativity value of 1.83 (Pauling scale), which is lower than a value of 1.90 for Si, electron donation theory would predict that overall Si–O bond strength in the presence of Fe in Fe–Si gel is weaker than Si–O bonds of the aqueous Si tetrahedron. As heavy isotopes tend to be partitioned into a stronger bond during equilibrium fractionation (Schauble, 2004), $^{30}$Si is preferentially partitioned in aqueous Si in our experiments. In addition, the presence of Fe would cause weaker Si–O bonds in Fe–Si gel as compared to those in pure Si gel, and this may explain the larger Si isotope fractionation factors in our experiments that used Fe–Si gel, relative to previous experiments that used pure Si gel (Li et al., 1995; Geilert et al., 2014b; Oelze et al., 2015; Roerdink et al., 2015), despite the uncertainty about equilibrium in the pure Si systems.

The first-order interpretation of the influence of Fe on the Si isotope fractionation factors can be derived from first-principles calculations of the equilibrium Si isotope fractionation factors, although it is important to note that detailed knowledge on Fe–Si linkages in Fe–Si gels is not currently possible. Broadly, theoretical calculations on the Si isotope fractionation between different silicates or aqueous Si species suggest that the magnitude of Si isotope fractionation should correlate to mean Si–O distances, where the Si isotope fractionation factor becomes larger with increasing mean Si–O distances (i.e., weaker bonds; Méheut and Schauble, 2014; Dupuis et al., 2015). The presence of cations (M), and variations in their electronegativity, in the Si tetrahedron structure can affect mean distances of Si–O bonds, following an electron donation theory (Méheut and Schauble, 2014), where cations that have electronegativity values lower than Si tend to shorten M–Si–O bond. Shortening of the M–Si–O bond is accompanied by lengthening of the other three Si–O bonds, thereby leading to longer mean Si–O distances for the tetrahedron. Because Fe has an electronegativity value of 1.83 (Pauling scale), which is lower than a value of 1.90 for Si, electron donation theory would predict that overall Si–O bond strength in the presence of Fe in Fe–Si gel is weaker than Si–O bonds of the aqueous Si tetrahedron. As heavy isotopes tend to be partitioned into a stronger bond during equilibrium fractionation (Schauble, 2004), $^{30}$Si is preferentially partitioned in aqueous Si in our experiments. In addition, the presence of Fe would cause weaker Si–O bonds in Fe–Si gel as compared to those in pure Si gel, and this may explain the larger Si isotope fractionation factors in our experiments that used Fe–Si gel, relative to previous experiments that used pure Si gel (Li et al., 1995; Geilert et al., 2014b; Oelze et al., 2015; Roerdink et al., 2015), despite the uncertainty about equilibrium in the pure Si systems. The larger magnitude $\Delta ^{30}$Si$_{gel$-aqueous} fractionation we measured in the Fe(II)-bearing experiments may reflect the lower electronegativity of Fe(II) relative to Fe(III), which should have an even stronger effect on weakening Si–O bonds than Fe(III), resulting in weaker Si–O–Fe(II) bonds as compared to Si–O–Fe(III) bonds.

Finally, it is important to note that our experiments are distinctly different from the case of sorption of aqueous Si to pure iron oxides/hydroxides as studied by Delstanche et al. (2009). Sorption of Si to Si-free iron oxides/hydroxides may only involve attachment of aqueous Si species on mineral surfaces, and does not involve formation of Si–O–Fe bonds throughout the mineral. This likely explains the larger $\Delta ^{30}$Si$_{gel$-aqueous} fractionations of $\sim -2.3‰ \sim -3.2‰$ observed in our experiments, relative to that observed during adsorption of aqueous Si to iron oxide/hydroxides, where $\Delta ^{30}$Si$_{adsorbed$-initial} fractionations of $\sim -1.1‰ \sim -1.6‰$ were measured (Fig. 10; Delstanche et al., 2009).

5.6. Implications for Si isotope records in Precambrian sedimentary rocks

Silicon isotope variations in Precambrian cherts and BIFs have been interpreted to reflect changes in seawater temperature (e.g., Robert and Chausson, 2006; Marin-Carmonne et al., 2014) or distinct sources of Si, including continental or hydrothermal (e.g., van den Boorn et al., 2007; Steinhoefel et al., 2009; Heck et al., 2011). These interpretations, however, are limited by a lack of knowledge on Si isotope exchange kinetics and equilibrium fractionation factors in systems analogous to the Precambrian ocean. One puzzling feature of the Si isotope record for Precambrian cherts and BIFs is the fact that $\delta ^{30}$Si values for BIFs tend to be lower than cherts (Fig. 11; e.g., van den Boorn et al., 2010; Steinhoefel et al., 2010; Heck et al., 2011; Chakrabarti et al., 2012; Marin-Carmonne et al., 2014; Stefurak et al., 2015). Common explanations for this contrast invoke the negative sorbed–aqueous Si isotope fractionation factor that is observed for Si sorption to Fe oxides/hydroxides (Delstanche et al., 2009), or infer a higher portion of hydrothermal component in BIFs relative to cherts (Chakrabarti et al., 2012). Assuming an igneous Si source ($\delta ^{30}$Si $\approx 0$‰) and a fractionation factor ($\Delta ^{30}$Si$_{sorbed$-initial}$) of $\sim -1.6‰$ (Delstanche et al., 2009), sorption to Fe oxides, however, can at most produce $\delta ^{30}$Si values as negative as $\sim -1.6‰$, which cannot explain the very low $\delta ^{30}$Si values for BIF cherts down to $-4‰$ or $-5‰$. Our work on Fe–Si gels provides a new means for interpreting very negative $\delta ^{30}$Si values in BIFs, as well as the contrast in $\delta ^{30}$Si values in Precambrian BIFs and cherts.

The effect of distinct Si isotope fractionation factors for pure Si and Fe–Si systems, as applied to formation of Precambrian cherts and BIFs, can be illustrated in a simple mass-balance model (Fig. 11). Although some workers have argued that $\delta ^{30}$Si values in many Precambrian cherts and BIFs may be dominated by kinetic effects (e.g., Roerdink et al., 2015), the relatively fast Si isotope exchange between Fe–Si gel and aqueous Si demonstrated in our experiments suggests that attainment of Si isotope equilibrium is likely, at least for Fe-bearing systems. Our model assumes that Si precipitates in sediments on the seafloor maintain Si isotope equilibrium with seawater in the overlying water column, and the Si precipitates–seawater system has a mean $\delta ^{30}$Si value of $0$‰, similar to that for the bulk earth (Savage et al., 2014); thus the Si isotope compositions of seawater and Si precipitates are dictated by the equilibrium fractionation factor and the relative Si mass balance (Supplementary Information, Fig. S3), which is determined by Si mass in the water column relative to that in the underlying Si-bearing precipitates ($S_{water$-column}/$S_{precipitates}$). Our calculation assumed a density of 3 g/cm$^3$, close to that of BIFs and cherts, for a dense rock equivalent for Fe–Si gel (Fe (II)$_0$.1Fe(III)Si$_2$(OH)$_{11.2}$) or pure Si gel (SiO$_2$), and a thickness of 1 mm of this dense rock in Si isotope equilibrium with overlying seawater. Consequently, the $S_{water$-column}/$S_{precipitates}$ ratio can be equivalent to the ratio of
water-column depth to the thickness of condensed Si-bearing gels (Fig. 11). Variations in actual density or thickness of the rock would proportionately change the \( S_{\text{water-column}}/S_{\text{precipitates}} \) ratio.

The relations in Fig. 11 demonstrate that the different Si isotope fractionation factors associated with Fe–Si gel and pure Si gel will have a major impact on the \( \delta^{30}\text{Si} \) values of these precipitates. In the case of Fe–Si gel, we illustrate the case for a \( \Delta^{30}\text{Si}_{\text{gel–aqueous}} \) fractionation factor of \(-3.2\epsilon\), the maximum fractionation obtained from our study. For pure Si gel, we illustrate two possible \( \Delta^{30}\text{Si}_{\text{gel–aqueous}} \) fractionation factors of \( 0\epsilon \) and \(-1\epsilon\), encompassing estimates from recent experimental studies (e.g., Roerdink et al., 2015; Oelze et al., 2015). For comparison, the compiled distribution of \( \delta^{30}\text{Si} \) values for Precambrian cherts and BIFs, based on compiled literature data, is shown as Kernel density functions on the right (after Stefurak et al., 2015 and refer to references therein for details on the \( \delta^{30}\text{Si} \) data compilation). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Production of BIFs that have highly negative \( \delta^{30}\text{Si} \) values, in a simple equilibrium mass balance model, requires a relatively high \( S_{\text{water-column}}/S_{\text{precipitates}} \) ratio. That the average \( \delta^{30}\text{Si} \) values for 3.8 Ga BIFs from Isua are generally lower than those of the 2.5 Ga BIFs from the Hamersley–Transvaal (H–T) basin (Stefurak et al., 2015) is consistent with the differences in BIF thickness. The Isua BIFs are relatively thin and small deposits, with an Fe footprint of \( \sim 4 \times 10^{11} \) mol km\(^{-2} \) (Czaja et al., 2013), and would be expected to have formed at relatively high \( S_{\text{water-column}}/S_{\text{precipitates}} \) ratios, which would produce relatively low \( \delta^{30}\text{Si} \) values (Fig. 11). The relatively small volume of the Isua BIFs also correlates with modestly positive \( \delta^{56}\text{Fe} \) values for oxide minerals, which is consistent with partial oxidation of Fe (II)\(_{\text{aq}}\) (Czaja et al., 2013), and hence supports potential formation of Fe(II)–Fe(III)–Si gels. In contrast, the very large
Hammersley–Transvaal BIFs are estimated to have an Fe footprint that is two orders of magnitude higher than the Isua BIFs (Czaja et al., 2013), and this should be reflected in lower \( \frac{\text{Si}_{\text{water-column}}}{\text{Si}_{\text{precipitates}}} \) ratios in our model, which in turn would produce, on average, less negative \( \delta^{30}\text{Si} \) values. The less negative \( \delta^{30}\text{Si} \) values for the Hammersley–Transvaal BIFs corresponds with the lower average \( \delta^{30}\text{Fe} \) values for oxide minerals that reflect more extensive oxidation of Fe(II)\(_{\text{aq}}\) (Czaja et al., 2013). It is certainly true that a variety of \( \delta^{30}\text{Si} \) values in individual BIF layers would be expected depending upon Si sources and pathways, but in the broadest context, the average \( \delta^{30}\text{Si} \) values for BIFs of different ages may reflect fundamental mass balance relations that correlate with the size of BIF deposits.

Finally, we note that variations in seawater Si concentrations can also affect \( \delta^{30}\text{Si} \) values of Si-bearing precipitates, because it shifts the Si mass-balance between the solid and solution. For example, a change in seawater Si concentration from \( \sim 2 \text{ mM} \), estimated based on amorphous Si solubility, to \( \sim 0.4 \text{ mM} \), estimated based on Fe–Si gel solubility for gels that have high Fe/Si ratios, may cause up to \( \sim 1\% \) increase in \( \delta^{30}\text{Si} \) values of Fe–Si gel. Depending on the fractionation factor assumed for pure Si gel and aqueous Si, the same decrease in seawater Si concentrations would cause either no change (\( \Delta_{\text{gel–aqueous}} = 0\% \)) or an up to \( \sim 0.5\% \) increase (\( \Delta_{\text{gel–aqueous}} = -1\% \)), in \( \delta^{30}\text{Si} \) values of Si gel (Fig. 11). The long-term trend of increasing \( \delta^{30}\text{Si} \) values in cherts was interpreted to reflect secular seawater cooling (Robert and Chausssidon, 2006), or reduced hydrothermal input (Chakrabarti et al., 2012), but this trend also involves major changes in dissolved Si and Fe abundances. Our data and model suggest that the changes in \( \delta^{30}\text{Si} \) values in cherts and BIFs, in response to secular changes in seawater Si and Fe concentrations, should be considered when interpreting the long-term \( \delta^{30}\text{Si} \) increase in Precambrian cherts and BIFs.

When considering the origin of Si isotope variations in Precambrian cherts and BIFs, diagenetic reactions are clearly important, although our mass balance model does not explicitly include such a process. Marin-Carbonne et al. (2014) proposed a diagenetic model for cherts, which involves two processes: (1) dissolution of opal A and subsequent precipitation of opal CT from the dissolved opal A following a Rayleigh process; (2) formation of microquartz from a Si pool that comprises aqueous Si from dissolution of opal CT and additional diagenetic fluids. It should be noted, however, that this model does not consider a potentially important role of Fe–Si gel, and the associated larger Si isotope fractionation, in the Precambrian oceans. Instead, the model of Marin-Carbonne et al. (2014) focuses on additional sources of dissolved Si with negative \( \delta^{30}\text{Si} \) values, produced from successive dissolution–precipitation processes, to explain very negative \( \delta^{30}\text{Si} \) values (\( \sim -3\% \)) in cherts. Importantly, this model does not consider Si isotope exchange rates between Si-bearing precipitates and fluids. Because our experiments indicate that Si exchange rates are relatively fast, at least for Fe–Si gel, Si-bearing precipitates may undergo isotopic exchange with Si-containing diagenetic fluids in sediments. Depending on the \( \delta^{30}\text{Si} \) value of diagenetic fluid and Si mass balance between precipitates and fluid, the initial Si isotope compositions of Si-bearing precipitates can be altered towards a new precipitate–fluid equilibrium.

### 6. CONCLUSIONS

The results of a series of Si isotope exchange experiments using the three-isotope method demonstrate that Si isotope exchange kinetics are sufficiently rapid at room temperature between amorphous Fe(III)–Si gel and aqueous Si that equilibrium isotope fractionations can be confidently determined. The experiments were designed to simulate anoxic Archean seawater conditions and were conducted at different degrees of Si saturation, and in the presence and absence of Fe(II)\(_{\text{aq}}\). An important finding of these experiments is that Fe(III)–Si gel has a significantly lower solubility than that of amorphous Si, implying that Precambrian seawater Si concentrations may have been considerably lower than previous estimates based on amorphous Si solubility. About 70–90% Si isotope exchange was achieved for all experiments after 53–126 days, but experiments that used Fe(II)\(_{\text{aq}}\)-bearing solutions showed more extensive Si isotope exchange than equivalent experiments that used Fe(II)\(_{\text{aq}}\)-free solutions. This suggests that Fe(II) catalyzes Si isotope exchange through Fe(II)–Fe(III) electron-transfer and atom-exchange reactions that promote breakage of Si bonds in Fe–Si gel.

Possible kinetic isotope effects were evaluated based on the linearity of changes in the \( \delta^{30}\text{Si} \) values of aqueous Si over time. Only in one experiment, which initially contained aqueous Si concentrations that were twice that of solubility for Fe–Si gel, were non-linear changes observed in \( \delta^{30}\text{Si} \) values that would indicate changes in the instantaneous isotope fractionation factor. The majority of experiments were operated close to equilibrium solubility, and under such conditions, no apparent changes in instantaneous Si isotope fractionation were observed, suggesting the absence of kinetic isotope effects during exchange; in such cases, equilibrium Si isotope fractionation factors could be confidently obtained by extrapolation to 100% exchange. Experiments that used Fe(II)\(_{\text{aq}}\)-free Si solution yielded a consistent \( \delta^{30}\text{Si}_{/28}\text{Si} \) fractionation factor between Fe(III)–Si gel and aqueous Si (\( \Delta_{\text{gel–aqueous}} = -2.3\% \)). In contrast, a larger \( \Delta_{\text{gel–aqueous}} \) fractionation factor of \( -3.2\% \) was obtained for experiments that used Fe(II)\(_{\text{aq}}\)-bearing Si solution; in this case, exposure to Fe(II)\(_{\text{aq}}\) resulted in net addition of Fe(II) to the solid, which changed the Fe–Si gel stoichiometry from Fe(III)\(_{1.2}\)Si\(_{0.8}\)(OH)\(_{11.2}\) to Fe(II)\(_{0.1}\)Fe(III)\(_{3}\)Si\(_{2.9}\)(OH)\(_{11.2}\). In all experiments, the solid–aqueous Si isotope fractionation factors were significantly larger in magnitude than previous work on pure Si gel systems, indicating that Fe has a major effect on Si isotope fractionation. This discrepancy is interpreted to reflect weaker Si–O bonds in Fe(III)–Si gel as compared to pure Si gel. The larger Si isotope fractionation between Fe(II)–Fe(III)–Si gel and aqueous Si is probably caused by further weakening of Si–O bonds due to incorporation of Fe(II) into gel structures.

The large Si isotope fractionation factor between Fe–Si gel and aqueous Si may explain the observation that \( \delta^{30}\text{Si} \) values of Precambrian BIFs are broadly lower than those
in Fe-free cherts. In addition, changing Fe and Si balances in the Archean and Proterozoic oceans, reflecting changes in Si solubility and aqueous Fe(II) levels, may help explain the secular trend in Si isotope records in cherts and BIFs during the Precambrian. Finally, depositional settings can affect the mass-balance of amorphous Si-bearing precipitates and seawater Si, and hence control \(^{29}\)Si values in cherts and BIFs. These results indicate that Si isotopes in Precambrian cherts and BIFs are not only affected by Si sources but also by a variety of other parameters, hence they can be potentially useful for tracing a wide range of processes that controlled the Precambrian Si cycle, and its coupling to Fe.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.05.012.

REFERENCES


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