Texture-specific Si isotope variations in Barberton Greenstone Belt cherts record low temperature fractionations in early Archean seawater

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Abstract

Sedimentary cherts are unusually abundant in early Archean (pre-3.0 Ga) sequences, suggesting a silica cycle that was profoundly different than the modern system. Previously applied for the purpose of paleothermometry, Si isotopes in ancient cherts can offer broader insight into mass fluxes and mechanisms associated with silica concentration, precipitation, diagenesis, and metamorphism. Early Archean cherts contain a rich suite of sedimentological and petrographic textures that document a history of silica deposition, cementation, silicification, and recrystallization. To add a new layer of insight into the chemistry of early cherts, we have used wavelength-dispersive spectroscopy and then secondary ion mass spectrometry (SIMS) to produce elemental and Si and O isotope ratio data from banded black-and-white cherts from the Onverwacht Group of the Barberton Greenstone Belt, South Africa. This geochemical data is then interpreted in the framework of depositional and diagenetic timing of silica precipitation provided by geological observations. SIMS allows the comparison of Si and O isotope ratios of distinct silica phases, including black carbonaceous chert beds and bands (many including well-defined sedimentary grains), white relatively pure chert bands including primary silica granules, early cavity-filling cements, and later quartz-filled veins. Including all chert types and textures analyzed, the $\delta^{30}Si$ dataset spans a range from $-4.78\%_\text{oo}$ to $+3.74\%_\text{oo}$, with overall mean $0.20\%_\text{oo}$, median $0.51\%_\text{oo}$ and standard deviation $1.30\%_\text{oo}$ ($n = 1087$). Most samples have broadly similar $\delta^{30}Si$ distributions, but systematic texture-specific $\delta^{30}Si$ differences are observed between white chert bands (mean $+0.60\%_\text{oo}$, $n = 750$), which contain textures that represent primary and earliest diagenetic silica phases, and later cavity-filling cements (mean $-1.41\%_\text{oo}$, $n = 198$). We observed variations at a $\sim$100 $\mu$m scale indicating a lack of Si isotope homogenization at this scale during diagenesis and metamorphism, although fractionations during diagenetic phase transformations may have affected certain textures. We interpret these systematic variations to reflect fractionation during silica precipitation as well as isotopically distinct fluids from which later phases originated. SIMS $\delta^{18}O$ values fall in a range from $16.39\%_\text{oo}$ to $23.39\%_\text{oo}$ ($n = 381$), similar to previously published data from bulk gas source mass spectrometry of Onverwacht cherts. We observed only limited examples of texture-related variation in $\delta^{18}O$ and did not observe correlation of $\delta^{18}O$ with $\delta^{30}Si$ trends. This is consistent with hypotheses that Si isotope ratios are more resistant to alteration under conditions of rock-buffered diagenesis (Marin-Carbonne et al., 2011). Our results indicate that low temperature processes fractionated silicon isotopes in early Archean marine basins, a behavior that probably precludes the application of chert $\delta^{30}Si$ as a robust paleothermometer. The values we observe for facies that sedimentological and petrographic observations indicate formed as primary and earliest diagenetic silica precipitates from seawater are more $^{30}Si$-rich than that expected for bulk silicate Earth. This is consistent with the hypothesis that the silicon isotope budget is balanced by the coeval deposition of $^{30}Si$-enriched cherts and $^{30}Si$-depleted iron formation lithologies.

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Precipitation of authigenic clay minerals in both terrestrial and marine settings may have also comprised a large $^{30}\text{Si}$-depleted sink, with the corollary of an important non-carbonate alkalinity sink consuming cations released by silicate weathering.

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1. INTRODUCTION

The apparent overabundance of sedimentary chert is a signal of the early Archean geological record that is thought to reflect the absence of biological controls on the early silica cycle (Siever, 1957, 1992; Maliva, 2001; Maliva et al., 1989, 2005; Perry and Lefticariu, 2003). The Phanerozoic silica cycle was dominated by biologically-mediated precipitation (Maliva et al., 1989; Siever, 1991), so it can be understood as a variation on the modern cycle (Treguer et al., 1995), wherein the evolution and ecology of silicifying organisms played a major role in the distribution of sedimentary chert. The Precambrian silica cycle was dominated by processes of chemical precipitation (Siever, 1957, 1992; Perry and Lefticariu, 2003); in the absence of biological precipitation, early diagenetic replacement of shallow tidal flat carbonates was a common mode of silica precipitation in late Archean and Proterozoic carbonate sequences, likely driven by evaporative processes (Maliva, 2001; Maliva et al., 1989, 2005). However, early Archean sedimentary successions, such as the Barberton Greenstone Belt (3.5–3.2 Ga), South Africa, contain abundant sedimentary cherts that capture different modes of silica precipitation; these cherts occur throughout a variety of paleoenvironments and include some forms that were likely primary precipitates in addition to diagenetically silicified siliciclastic or organic-rich sedimentary rocks, volcaniclastic units, and silicified volcanic flow tops (Knauth, 1994; Lowe, 1999). These cherts also present a major mass balance problem in early Archean time. The silica must have been ultimately sourced from silicate weathering, but what of the corresponding alkalinity sink for cations also released during weathering and concentrated in seawater? Was it in salts precipitated from seawater or did the precipitation of authigenic clay minerals also play an important role? In addition to constraining the early silica cycle, a better understanding of Si sinks from Archean seawater also provides insight into the fundamental mass balance between weathering and the production of sedimentary rocks (Milliken et al., 2009), and the possible operation of a silicate-weathering feedback on the early Earth (Walker et al., 1981).

Previous studies have found that trace and rare earth element (REE) geochemistry of early Archean sedimentary cherts are consistent with a strong hydrothermal source (Paris et al., 1985; Kato and Nakamura, 2003; van den Boorn et al., 2010). This can be interpreted in two ways: (1) that cherts are exhalative deposits formed adjacent to hydrothermal vents, or (2) that silica was precipitated from seawater that carried a “hydrothermal” signature. In other words, did hydrothermal fluids interact with ambient seawater before precipitating silica? Answering this question is only a first step toward understanding the Archean silica cycle. If all Archean cherts formed directly from hydrothermal fluids that had not reacted with seawater, we could stop there. But if fluid interactions did occur, we must also ask how silica is partitioned during these interactions: were there other important silica inputs, what reactions occurred in seawater, and what were the principal silica outputs? These questions have been difficult to resolve with traditional trace and REE geochemical analyses.

Silicon isotopes offer a useful tool for studying the fluxes and processes of the Archean silica cycle. Though the mechanics of the fractionating processes are still not well understood, it is generally observed that silica precipitates are depleted in the heavy isotope of silicon ($^{30}\text{Si}$) relative to the residual fluid by 1–2‰ (Ding et al., 1996; Basile-Doelsch et al., 2005; Fripiat et al., 2007) and kinetic Si isotope fractionations dominate in low temperature Earth surface environments (Ziegler et al., 2005a,b; Georg et al., 2007b, 2009; Delstanche et al., 2009); it is reasonable to suspect that similar kinetic fractionations occurred in Archean marine basins.

Previous studies have used chert $\delta^{30}\text{Si}$ to estimate seawater $^{30}\text{Si}$ composition (Robert and Chaussidon, 2006; van den Boorn et al., 2007, 2010; Abraham et al., 2011), but this required assuming a simple isotope mass balance model (cf. Fig. S2 in Robert and Chaussidon, 2006) in which silica inputs from crustal weathering are balanced by the outputs of hydrothermal silicification and amorphous silica precipitation from seawater. Only two significant isotope fractionations were considered in this simplified framework: the preferential incorporation of light silica into precipitates during (1) hydrothermal and (2) seawater silica precipitation. Robert and Chaussidon (2006) hypothesized that chert $\delta^{30}\text{Si}$, considered to be a seawater silica precipitate and a measure of seawater $^{30}\text{Si}$, was primarily controlled by the temperature gradient between hydrothermal fluids and ambient seawater, with cooler seawater, for example, resulting in a larger fraction of silica output as isotopically light “hydrothermal” silica, leaving the “seawater” silica fraction relatively heavier. Several authors (van den Boorn et al., 2007, 2010; Abraham et al., 2011; Marin-Carbonne et al., 2012) have interpreted the range of $\delta^{30}\text{Si}$ in their chert samples to reflect mixing of isotopically distinct seawater and hydrothermal fluids incorporated into cherts via primary precipitation and/or silicification. The implicit assumption in these interpretations is that seawater Si was not isotopically fractionated by other processes and does not have any additional fractionating sinks. If, as observed in the modern cycle, additional fractionations occurred, then the framework becomes more complex, with the corollary that chert $\delta^{30}\text{Si}$ need not reflect the balance of hydrothermal and seawater precipitates and cannot be uniquely inverted for temperature. In support of this possibility, Chakrabarti et al. (2012) observed an isotopic contrast between peritidal chert and basinal banded iron
formation (BIF) samples within Proterozoic basins, perhaps reflecting the existence of a $\delta^{30}\text{Si}$ chemocline related to fractionation associated with iron oxide adsorption in seawater (Delstanche et al., 2009). A further test of this hypothesis requires additional basin-scale studies to identify large-scale silicon isotope patterns and paleoenvironmental differences. At the same time, measuring $\delta^{30}\text{Si}$ at a much finer spatial scale tied to petrographic textures with secondary ion mass spectrometry (SIMS) supplies complementary information about the processes responsible for primary and diageneric silica precipitation with a small but worthwhile tradeoff in terms of reduced analytical precision. Previous studies using SIMS Si isotope analyses have observed meaningful $\delta^{30}\text{Si}$ variations at small spatial scales (Robert and Chaussidon, 2006; Heck et al., 2011; Marin-Carbonne et al., 2011, 2012).

Oxygen isotopes provide another, independent tool for constraining diageneric fluid interactions in cherts. Chert $\delta^{18}\text{O}$ has been employed as paleothermometer (Knauth and Epstein, 1976; Knauth and Lowe, 1978, 2003), albeit with non-unique complicating issues: (1) the possibility that seawater $\delta^{18}\text{O}$ has changed over time (Kasting et al., 2006; Jaffres et al., 2007) and (2) the possibility that chert $\delta^{18}\text{O}$ has been wholly or partially reset during diagenesis and metamorphism (Robert and Chaussidon, 2006; Marin et al., 2010). This susceptibility to re-equilibration with formation waters makes $\delta^{18}\text{O}$ a good indicator of fluid interactions during diagenesis and metamorphism and therefore potentially useful for evaluating the impact of post depositional processes on $\delta^{30}\text{Si}$ values (Marin-Carbonne et al., 2011). Knauth and Lowe (2003) presented multiple lines of evidence that chert $\delta^{18}\text{O}$ in post-3.445 Ga Barberton cherts was set during burial and not affected by metamorphic re-equilibration. They argued that the maximum values in their data set provided a constraint on seawater temperature, while the ca. 7% spread of values below the maxima resulted from maturation of amorphous silica to chert during burial and diagenesis.

Petrographic textures and cross-cutting relationships reveal that early Archean cherts in the Barberton belt contain an array of micro-scale textures (e.g., sedimentary grains, matrix, early cavity-filling cements, late quartz veins), many of which reflect different generations of silica (primary, early diageneric, late diageneric). These textures record multiple generations of silica mineralization, but whether or not they record and preserve the isotopic signatures of their original fluids remains an open question. Many previous chert Si isotope studies provided only limited geological/sedimentological and petrographic context for their analyses (Robert and Chaussidon, 2006; van den Boorn et al., 2007, 2010; Abraham et al., 2011), making it challenging to confidently compare analogous lithofacies and/or silica generations across different studies. Heck et al. (2011) and Marin-Carbonne et al. (2012) emphasized the importance of Si isotope analysis at the micro-scale in BIF and chert due to the micro-scale complexity of these rocks. Marin-Carbonne et al. (2012) suggested that cherts selected for Si and O isotopic analyses should be mostly composed of microquartz, while also pointing out that microquartz can have a variety of origins and suggesting additional geochronological criteria for determining the preservation of Si and O isotopic signatures. Geological and sedimentological observations were omitted from this list of criteria even though they provide fundamental efficient and effective methods for identifying a paragenetic sequence of phases within a sample by determining primary composition (e.g., silicified ashes vs. organic-rich sediments) and using cross-cutting relationships to ordinate the timing of emplacement of different silica phases. Integrating petrographic and in situ geochemical information can also help assess the possibility of seawater Si isotope fractionation and its implications for the Archean silica cycle and chert petrogenesis by allowing explicit comparisons between the isotopic compositions of different generations of silica (potentially representing distinct fluids and/or precipitation processes). We investigated the uniformity of silicon isotopes in cherts from the Barberton Greenstone Belt, South Africa, by comparing micro-scale texture, composition, and high resolution Si and O isotopic analyses.

2. GEOLOGIC BACKGROUND

Previous Si isotope studies of early Archean rocks have focused on cherts from the Pilbara block (van den Boorn et al., 2007, 2010; Marin-Carbonne et al., 2012) and the Isua greenstone belt (Andre et al., 2006; Heck et al., 2011); fewer studies have examined materials from the 3.5–3.2 Ga Barberton Greenstone Belt in South Africa (Abraham et al., 2011; Marin-Carbonne et al., 2012; Geilert et al., 2014b).

We analyzed samples collected from two stratigraphic levels (Table 1) in the Onverwacht Group, an 8–10 km thick sequence of ultramafic and mafic volcanic rocks with thin interbedded sedimentary chert-rich units (Lowe and Byerly, 1999): the Buck Reef Chert and the upper Mendon Formation chert (Fig. 1). The 3,416 ± 5 Ma (Kroner et al., 1991) Buck Reef Chert is a thick (150–350 m) sequence of banded carbonaceous and ferruginous cherts at the base of the Kromberg Formation (Lowe and Byerly, 1999; Tice and Lowe, 2006). The 3,298 ± 3 Ma (Byerly et al., 1996) uppermost Mendon Formation, present in many structural belts, although variable, can be broadly characterized as ~50 to 75 m of mostly black, banded black-and-white, and ferruginous chert (Lowe and Byerly, 1999). The sedimentary and volcanic rocks of the Onverwacht Group have been heated to lower greenschist grade (~300 °C) (Xie et al., 1997; Tice et al., 2004). Despite metamorphism, petrographic textures are commonly well preserved. Onverwacht cherts span a broad range in apparent petrogenesis, from silicified ash to carbonaceous chert to banded ferruginous chert (Lowe, 1999; Lowe and Byerly, 1999). There has been some debate as to whether some or all Barberton cherts formed as hydrothermal exhalites (de Ronde and Ebbesen, 1996; De Ronde et al., 1994; Hofmann, 2005; Hofmann and Harris, 2008) or as a common mode of marine sedimentation and early diageneric silica cementation (Knauth and Lowe, 1978; Lowe, 1999; Lowe and Byerly, 1986). Indeed, the single proposed example of an Archean hydrothermal vent in Barberton (de Ronde and Ebbesen, 1996; De Ronde et al., 1994) was subsequently shown to be Cenozoic in age (Lowe and
Table 1
Sample stratigraphic information.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation</th>
<th>Stratigraphic Position (m)</th>
<th>Location coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRC-01-2</td>
<td>Buck Reef Chert, Kromberg Formation</td>
<td>LBW</td>
<td>S 25° 55.875'E   30° 55.386'</td>
</tr>
<tr>
<td>BRC-01-3A</td>
<td>Buck Reef Chert, Kromberg Formation</td>
<td>LBW</td>
<td>S 25° 55.868'E   30° 55.389'</td>
</tr>
<tr>
<td>BH-03-7</td>
<td>Upper Mendon Formation</td>
<td>11.6</td>
<td>S 25° 54.916'E   30° 55.962'</td>
</tr>
<tr>
<td>BH-03-9</td>
<td>Upper Mendon Formation</td>
<td>8.8</td>
<td>S 25° 54.916'E   30° 55.962'</td>
</tr>
<tr>
<td>SAF 521-14</td>
<td>Upper Mendon Formation</td>
<td>0.6</td>
<td>S 25° 54.037'E   31° 0.361'</td>
</tr>
<tr>
<td>SAF 521-15</td>
<td>Upper Mendon Formation</td>
<td>1.1</td>
<td>S 25° 54.037'E   31° 0.361'</td>
</tr>
<tr>
<td>SAF 521-16</td>
<td>Upper Mendon Formation</td>
<td>2.6</td>
<td>S 25° 54.037'E   31° 0.361'</td>
</tr>
</tbody>
</table>

* LBW – samples were collected from the lower black-and-white banded chert facies of Tice and Lowe (2006). This facies immediately overlies the 0–80 m thick basal evaporitic facies and is recognized as up to 60 m thick unit of banded black-and-white cherts in with the black chert bands are relatively coarse and composed of up to granule-sized carbonaceous grains. Brecciation or soft-sediment deformation of white chert bands is common, which Tice and Lowe (2006) interpreted to result from disruption by storm events, indicating deposition between 15 and 200 m water depth.

b Stratigraphic position below the top of the Mendon Formation.

Byerly, 2007). In this study, we focus on a particular lithofacies, banded black-and-white chert, which provides the best geological evidence for primary silica in the form of silica granules (Stefurak et al., 2014) and synsedimentary silica cementation. These observations are discussed in more detail below.

The sample suite was selected to leverage sedimentological and/or diagenetic cross-cutting relationships observed at outcrop- and thin section-scales, which provide key constraints on the relative timing of emplacement of various silica phases. Banded black-and-white cherts (Fig. 2a), defined by the alternation of cm-scale relatively pure white or translucent chert bands and black carbonaceous chert bands, form the focus of this study because they commonly contain multiple generations of silica (Fig. 3). Both black and white chert bands are essentially pure SiO₂ (Walsh and Lowe, 1999), but they are texturally distinct due to crystallographic differences and trace-level inclusions of organic carbon and iron oxide phases within black bands. However, beyond these slight geochemical distinctions, black and white bands are easily distinguishable at outcrop- and thin-section-scales due to their substantially different sedimentology. Stefurak et al. (2014) recently discovered that many and perhaps all white chert bands originated as sedimentary deposits of sand-sized primary silica granules. Black bands are sedimentary layers of sand-sized carbonaceous grains, in some cases admixed with volcanic grains (typically lithic fragments of microquartz and fine phyllosilicates, such as sericite or chlorite) and/or silica granules, with matrix material composed of varying amounts of microquartz cement and finely dispersed carbonaceous material (Fig. 2b).

Both physical and geochemical observations highlight that white chert bands probably represent the best examples of primary and earliest diagenetic silica precipitates, and thereby offer target phases from which to constrain seawater silica Si isotope compositions, minding the process fractionations associated with precipitation of solid silica phases. Many white chert bands can be identified as sedimentary deposits of primary silica granules and contain silica precipitated directly from seawater (Stefurak et al., 2014). White chert bands are often locally brecciated due to disruption and reworking by storms (Lowe, 1999; Tice and Lowe, 2006), indicating that they were lithified and thus deformable as rigid, coherent layers when located close to or at the sediment–water interface and while the surrounding carbonaceous layers were still soft and un lithified. This suggests that cementation occurred rapidly during earliest diagenesis. White chert bands also tend to have higher δ¹⁸O values than surrounding carbonaceous chert, suggesting lower precipitation temperatures and better preservation (Knauth and Lowe, 1978, 2003; Hren et al., 2009). Cavity-filling cements (here termed “cavity fills”) are also common; the relative timing of their formation is constrained by the lack of truncations of sedimentary grains along boundaries with adjacent black chert and geopetal relationships. Much of this cavity fill is developed beneath white chert bands and, in breccias, beneath individual clasts of white chert, where it fills what were originally pockets of fluid trapped beneath the relatively impermeable white bands and clasts, respectively (e.g., Fig. 2a). Cherts also often contain late, cross-cutting coarsely crystalline quartz veins and cements (Fig. 2c). This common co-occurrence of primary and early diagenetic phases with later silica phases allows us to examine a time-series of silica precipitation and potential fluid changes with micro-scale isotope ratio measurements tied to petrographic textures using SIMS. Walsh and Lowe (1999) presented a suite of major and trace element geochemical analyses of banded black-and-white cherts from the Onverwacht Group. They found that banded black-and-white cherts had extremely low Al₂O₃, a mean value of 0.05% (n = 11) and a maximum of 0.10%; K₂O, mean value 0.03% and maximum 0.06%; and TiO₂, mean value 0.01% and maximum 0.06% (Walsh and Lowe, 1999). In the discrimination of silica precipitates by Si isotopic composition vs. Al₂O₃, K₂O, or TiO₂ content used by several previous studies (van den Boorn et al., 2007, 2010; Marin-Carbonne et al., 2012), these compositions place banded black-and-white cherts along the array of seawater precipitates (high δ³⁰Si) and hydrothermal precipitates (low δ³⁰Si), distinctly separate from silicified volcanic material (intermediate δ³⁰Si, non-trivial Al₂O₃ content).
3. METHODS

Seven samples of banded cherts capturing a range of sedimentological and diagenetic textures were collected from measured stratigraphic sections in the Onverwacht Group. The samples also provide a measure of stratigraphic (both secular and environmental) variability: five samples from the Mendon Formation—three from one field location (SAF 521) and the other two from another (BH-03), each collected several meters apart in the stratigraphic section (see Table 1 for sample locations and names). The remaining samples were collected from the Buck Reef Chert. Each sample was made into a 1-inch circular polished thin section with quartz standard grains embedded in epoxy as close to the analytical domains of interest as possible, and then carefully polished to obtain a flat analytical surface for light and electron microscopy, electron microprobe, and SIMS analyses. We used Caltech Rose Quartz ($\delta^{18}O = 8.45\%$ and $\delta^{30}Si = -0.02 \pm 0.10\%$) (Georg et al., 2007a) and NBS-28 pure quartz sand ($\delta^{18}O = 9.58\%$, $\delta^{30}Si = 0\%$) as standards for both Si and O analyses.

Sample textures were mapped and imaged in reflected and transmitted light using a polarizing microscope to

identify and document regions of interest. Wavelength-dispersive spectroscopy on the electron probe was used to produce geochemical maps of specific trace elements within sample domains of interest, which allowed us to qualitatively compare trace element patterns with petrographic textures and isotopic patterns. Since microquartz can originate via diagenetic replacement of a wide range of precursor mineral phases, trace elements can be used to identify remnant evidence of replaced primary phases (e.g., carbonate minerals). Selected areas on carbon-coated samples were mapped in elements of interest (Ca, Mg, Fe, Al, and P or Ti; half of samples mapped in P, the other half mapped in Ti) using a JEOL JXA-8200 Advanced Electron Probe Micro-analyzer at the Division of Geological and Planetary Sciences Analytical Facility at the California Institute of Technology (Pasadena, CA). Qualitative intensity maps without background corrections were collected on carbon-coated samples, operating the electron probe in wavelength dispersive X-ray spectrometer (WDS) mode at 15 kV accelerating voltage, 100 nA beam current, and 100 ms dwell time. Grey-scale cathodoluminescence (CL) of areas of interest were mapped using a JEOL JSM-5600.
Scanning Electron Microscope (SEM) fitted with a Hamamatsu Photo Multiplier Tube (PMT), at the Stanford-USGS Microanalysis Center at Stanford University (Stanford, CA). Samples were coated with 15 nm of Au (subsequent to the SIMS gold coat being removed by gentle polishing). Analysis settings were: 15 kV accelerating voltage, 38 μm spot size, and 39 mm working distance.

High-resolution silicon and oxygen isotope analyses were performed with the Cameca IMS-7f-GEO ion microprobe at the Caltech Microanalysis Center (California Institute of Technology, Pasadena, CA) over four sessions (November 2011, April 2012, October 2012, and March 2013). Samples were sputter-coated with 30 nm of Au for SIMS analysis. Though it is possible in principle to measure Si and O isotope ratios at the same time on the 7f-GEO by dynamic peak hopping using a Cs⁺ ion beam, satisfactory precision on Si isotope ratios was not attained (1σ error), so O isotopes and Si isotopes were measured separately, allowing improved precision on Si by using an O⁻ ion beam. Each set of 12–16 sample unknown measurements was bracketed with 3–4 standard measurements. Isotope ratios are reported as permil deviations from VSMOW (Vienna Standard Mean Ocean Water) for oxygen and the NBS-28 quartz standard (defined as 0‰) for silicon using delta notation: 

\[ \delta^{18}O = 1000 \times \left( \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) \]

and

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

Each grain of NBS-28 quartz sand accommodated 4–10 separate spot analyses, while the larger grains of Caltech Rose Quartz typically accommodated >20 separate spot analyses. Typical 1σ external (standard-corrected) errors were ±0.25‰ for δ¹⁸O measurements and ±0.30‰ for δ³⁰Si measurements determined by the variation of multiple spot measurements on known standards. Errors are reported as 1σ for ease of comparison with previous SIMS Si isotope studies (Robert and Chaussidon, 2006; Marin et al., 2010; Marin-Carbonne et al., 2011, 2014).

3.1. Si isotope analysis conditions

Gold-coated samples were sputtered with an O⁻ primary beam of 3–4 nA with 9 kV acceleration. Analysis spot diameters were 30–40 μm, varying slightly between sessions. A mass resolving power of ca. 2400 was achieved, sufficient for excluding contributions from the ²⁹SiH hydride peak in ³⁰Si measurements (Fig. EA1). ²⁸Si and ³⁰Si were detected using fast peak switching with one Faraday cup (resistor value 10 × 10⁻¹¹ ohms). The primary beam aperture size was ~400 μm in diameter. Critical illumination was used, with the diameter of the focused beam of ~15 μm. The focused beam was rastered across an area for the measurements, producing effective analyzed areas of ~30 μm width. The energy bandwidth was 45 eV. Count rates were typically between 5–7 × 10⁶ counts/s. Total analysis time for each spot was 8 min, including 60 s pre-sputtering, field and beam centering, and analyses (20 cycles). Count times were 0.96 s for ²⁸Si and 8.00 s for ³⁰Si.

3.2. O isotope analysis conditions

Gold-coated samples were sputtered with a Cs⁺ primary beam of 2–4 nA with 9 kV acceleration. Analysis spot diameters were 20–30 μm, varying slightly between sessions. A mass resolving power of ca. 1200 was achieved. An electron beam was used for charge compensation and settings.
were optimized for each session. $^{16}$O and $^{18}$O were detected using two Faraday cups (resistor values: FC1 10 x 10–10 ohms, FC2 10 x 10–11 ohms). Total analysis time for each spot was 7 min, including 90 s pre-sputtering, field centering, and analyses (20 cycles). Count times were 0.96 s for $^{16}$O and 4.96 s for $^{18}$O.

For some samples, O isotope measurements were made after Si isotope measurements, leading to the possibility of sample contamination by $^{16}$O implanted by the O$^{-}$ beam during Si isotope analyses. We experimented with distances between Cs$^{+}$ spots and previous O$^{-}$ spots on standard grains and found no evidence for contamination due to analytical spot proximity, even with tangential spots. Furthermore, O isotope values match those previously determined from bulk gas spectrometry measurements of Onverwacht cherts (Knauth and Lowe, 1978, 2003; Hren et al., 2009).

4. RESULTS

4.1. Geochemical mapping

Ca, Mg, and Fe most commonly co-occur in discrete, euhedral crystals within our samples (Figs. EA2-EA4). Ca and Mg are present principally as carbonates. Fe also occurs in carbonates, where it co-localizes with Ca and Mg, and in oxide or sulfide phases, where it maps without textural boundaries visible in light microscopy. These phases appear in matrix materials surrounding primary sedimentary grains, but were not distributed evenly and did not correspond to sedimentological petrographic textures. Based on cross-cutting relationships, we interpret these as later ingrowths of ankeritic dolomite, sulfides, and hematite, respectively.

P is present exclusively in discrete apatite grains (also associated with Ca), which were rare and showed no correlation with specific textures.

Al was the only trace element assayed that highlighted textural boundaries visible in light microscopy. In particular, Al maps pick out differences between white or pure chert grains, cavity fills, and veins (all of which have almost no Al) and carbonaceous grains and matrix material, which contain more Al, present as small dispersed phyllosilicate grains (Figs. 5b, 7c, 8b, and EA2-EA4). Ti co-occurred with Al in some carbonaceous matrix material, but is less abundant and did not capture sample textures as clearly.

Our in situ observations of the distributions and relative abundances of these elements are consistent with prior bulk major element analyses of banded black-and-white cherts presented by Walsh and Lowe (1999). They reported extremely low ($\leq 0.2\%$) abundances of Al$_2$O$_3$, MgO, CaO, TiO$_2$, and P$_2$O$_5$, with still relatively low Fe$_2$O$_3$ contents – mean 1.3\% ($n = 11$) with a minimum measured value of 0.46\% and a maximum of 3.54\%. Our mapping data confirms that these elements are only trace components of the cherts selected, even in layers with a mixture of sedimentary grains (Figs. 6b and EA2).

Consistent with the microprobe analyses, microquartz did not luminesce strongly. CL images in all white or black chert bands and some coarse cavity-filling cements were dark and did not correspond to petrographic textures. Another subset of megaquartz cement in cavity fills was the only phase to produce variable, bright CL images with complex euhedral growth zonation.

4.2. Si isotopes

$\delta^{30}$Si values from all samples span a range of $\geq 7\%_{\text{v}}$ from $-4.78$ to $+3.74$, with overall mean $0.20\%_{\text{v}}$ and standard deviation 1.30\% (Table 2). Individual samples show overlapping $\delta^{30}$Si distributions (Fig. 4e, Table 3), although performing an unbalanced n-way ANOVA and a multiple comparison test indicates that some sample means are significantly different at a 95\% confidence level (Table EA1). Cavity fills (mean $-1.41\%_{\text{v}}$ and standard deviation 0.70\% $n = 198$) are lighter than coexisting white chert bands and grains (mean $0.60\%_{\text{v}}$ and standard deviation 0.70\% $n = 750$) or carbonaceous chert (mean $0.70\%_{\text{v}}$ and standard deviation 0.79\% $n = 104$) (Fig. 4a-b, Table EA1). The $\delta^{30}$Si distribution of sample BRC-01-3a is notable in its divergence from the patterns displayed by the other samples; most of the analyses from this sample were spots located in cavity-filling cements. Analytical grids of white chert bands or grains and adjacent cavity fills or veins (Figs. 5 and 6) display this pattern in context, with the later cavity fill or vein quartz having lower $\delta^{30}$Si values than the earlier white chert phase. Fig. 6 highlights a contrast of approximately $3\%_{\text{v}}$ between the two textures. Fig. 7 also illustrates a contrast in the isotopic composition of spots located in a coarse quartz cavity fill. Grain size increases toward the interior of the cavity (Fig. 7d), a feature common in void-filling cements. $\delta^{30}$Si values within the coarser quartz grains located toward the cavity center (average $\delta^{30}$Si $0.38\%_{\text{v}}$ all but the leftmost point) are heavier than at the cavity edge ($\delta^{30}$Si $-1.10\%_{\text{v}}$ in the leftmost data point).

4.3. O isotopes

$\delta^{18}$O values from all samples span a range of $\geq 7\%_{\text{v}}$ from 16.39\% to 23.39\%, with overall mean 19.64\% and standard deviation 1.42\% ($n = 381$, Table 2). Each individual sample shows a smaller range of 2–3\% (Fig. 4d, Table 4) and performing an unbalanced n-way ANOVA and a multiple comparison test indicates that many sets of sample means are significantly different at a 95\% confidence level (Table EA1). These values fall in the same range as previous bulk gas source measurements of oxygen isotopes in Onverwacht cherts made by fluorination (Knauth and Lowe, 1978, 2003; Hren et al., 2009). In general, $\delta^{18}$O variations did not correspond to petrographic textures (Fig. 4e, Table EA1), with a few notable exceptions. We observed an isotopic contrast between a white chert band (higher $\delta^{18}$O) and the adjacent carbonaceous black chert (lower $\delta^{18}$O) in one sample (Fig. 8); similar relationships were reported from bulk measurements of banded black-and-white cherts (Knauth and Lowe, 2003; Hren et al., 2009). Oxygen isotopic values are also lower toward the center (average $\delta^{30}$Si $20.33\%_{\text{v}}$, rightmost 4 data points) than near the edge (average $\delta^{30}$Si $22.10\%_{\text{v}}$) of the same coarse quartz cavity fill that shows an internal $\delta^{30}$Si contrast (Fig. 7). Oxygen isotope values do not show an
Fig. 4. Si and O isotope ratio data from Barberton Greenstone Belt cherts. (a) Stacked histogram of $\delta^{30}\text{Si}$ data graduated by the three main types of petrographic textures analyzed in this study, from top to bottom: white chert bands and grains (red), black carbonaceous bands and grains (grey), and cavity fill (blue), respectively. Binned by 0.25‰ increments. (b) Kernel-smoothing probability density estimates of the same texture-differentiated data sets as in (a). (c) Kernel-smoothing probability density estimates of $\delta^{30}\text{Si}$ data from the six samples analyzed for silicon isotopes in this study. Five of the samples are from the upper Mendon Formation, representing two sections (BH-03 and SAF 521) from different structural belts with two samples each, located several meters apart stratigraphically. The remaining sample (BRC-01-2) is from the Buck Reef Chert. (d) Kernel-smoothing probability density estimates of $\delta^{18}\text{O}$ data from the five samples analyzed for oxygen isotopes in this study. Note that O isotope data was not collected from sample SAF 521-14, which is shown in (c), due to limited standard material on the thin section. (e) Stacked histogram of $\delta^{18}\text{O}$ data graduated by the three types of petrographic textures in (a), with the addition of veins and cracks (yellow). (f) $\delta^{30}\text{Si}$ vs. $\delta^{18}\text{O}$ graph showing a subset of paired Si and O spots from three samples (BH-03-7, BH-03-9, and BRC-01-2). Each type symbol corresponds to a particular data grid (e.g., BH-03-7 grd2 is grid 2 from sample BH-03-7) and each point represents a Si analytical spot and its adjacent O analytical spot. Note that paired analyses reflect adjacent spots placed in similar locations within a texture, not simultaneous measurements or re-analysis of the same spot. Areas that display considerable isotopic variability over small scales (e.g., between spots located 100 μm apart) are not included in this graph because we cannot be confident that these measured values provide a valid comparison for spots 100–200 μm away. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
analogous trend in the superficially similar cavity-filling cement shown in Fig. 6.

4.4. Si and O comparisons

A comparison of probability distributions reveals that \( \delta^{30}\text{Si} \) distributions are similar across all samples, while \( \delta^{18}\text{O} \) distributions display distinct modes (Fig. 4c–d). ANOVA and multiple comparison tests indicate that some sets of sample means are significantly different for both \( \delta^{30}\text{Si} \) and \( \delta^{18}\text{O} \). However, the sets of significantly different sample means between the two data sets do not perfectly match; for example, the \( \delta^{30}\text{Si} \) mean of sample BRC-01-2 is significantly different from samples BRC-01-3a, SAF 521-14, SAF 521-15, and SAF 521-16, while the \( \delta^{18}\text{O} \) mean of sample BRC-01-2 is significantly different from samples BH-03-7, BH-03-9, and SAF 521-16 (Table EA1). This, along with the observations that texture-differentiated \( \delta^{18}\text{O} \) means are not significantly different, suggests that \( \delta^{30}\text{Si} \) and \( \delta^{18}\text{O} \) are not correlated, consistent with the findings of Marin-Carbonne et al. (2012). Correspondingly, plots of \( \delta^{30}\text{Si} \) and \( \delta^{18}\text{O} \) for selected paired analysis spots (Fig. 4f) show no overall relationship.

Significant heterogeneities exist within and between textures in both Si and O isotopes, but the Fig. 7 is the only example from our study of Si and O showing similar (but opposite sign) behavior: higher \( \delta^{30}\text{Si} \) and lower \( \delta^{18}\text{O} \) are associated with larger grain sizes in a cavity-filling cement. In the only other compelling example of texture-dependent oxygen isotope contrasts (Fig. 8), \( \delta^{18}\text{O} \) values decrease across the edge of the carbonaceous band, while \( \delta^{30}\text{Si} \) values vary within the band but not across its edge. For the remaining observations, oxygen isotopes do not track silicon isotope trends. In analytical grids where cavity fills or veins have significantly lighter \( \delta^{30}\text{Si} \) values than the adjacent white chert, the corresponding oxygen points do not change systematically across these boundaries (Figs. 5 and 6).

5. DISCUSSION

We observed systematic, texture-specific silicon isotope variation in our samples, suggesting that the Si isotopic differences were not caused by late alteration but rather reflect primary differences in the mechanisms of precipitation and Si isotope composition of environmental fluids. If this is
broadly correct, we can invert our observations of the $\delta^{30}$Si of specific lithofacies for processes characterizing the ancient silica cycle and also provide new insight into previous measurements of Si isotopes in Early Archean cherts.

5.1. Relationships between petrographic texture and Si isotopic composition

5.1.1. Early silica precipitates—evidence of low-temperature Si isotope fractionations in seawater

Current understanding of fractionations in the Si isotope system suggests that SiO$_2$ precipitates are $^{30}$Si-depleted, with a fractionation factor of ca. 1‰ enriching the residual aqueous silica in the fluid in $^{30}$Si (Basile-Doelsch et al., 2005; Ziegler et al., 2005a,b; Fripiat et al., 2007; Delstanche et al., 2009). Recent flow-through experiments by Geilert et al. (2014a) indicated that Si isotope fractionation of silica precipitation induced by a sharp drop in temperature were dependent on ambient temperature, ranging from $-2.1_{\text{‰}}$ at 10°C to $+0.2_{\text{‰}}$ at 60°C. Considering their paleoenvironmental context, temperature-dependent changes in solubility may not be the silica precipitation mechanism that formed many cherts, but nevertheless these experiments suggest that actual Si isotope fractionation factors were likely functions of key environmental parameters like temperature and dissolved silica concentration. These parameters, particularly Archean seawater temperature, remain issues of debate (e.g., Knauth and Lowe, 2003; Sleep and Hessler, 2006; Hren et al., 2009). For ease of the following discussion, we will follow previous convention (Varela et al., 2004; Andre et al., 2006; Robert and Chaussidon, 2006; Demarest et al., 2009; Marin-Carbonne et al., 2011, 2012) and assume that the Si isotope fractionation factor associated with silica precipitation was ca. $-1_{\text{‰}}$; further experimental and/or geological constraints should enable better speculation on its actual value.

Robert and Chaussidon (2006) suggested that the temperature difference between hydrothermal fluids and ambient seawater played a principal role in setting seawater $\delta^{30}$Si by controlling the relative size of a $^{30}$Si-depleted silica sink formed by precipitation from hydrothermal fluids. But the range and spatial patterns of $\delta^{30}$Si in our data cannot be simply explained by fluctuations in ambient seawater temperature during mixing of hydrothermal fluids with seawater because it would require rapid non-physical climate changes. The concept of applying chert $\delta^{30}$Si as a proxy for fluid $\delta^{30}$Si, where fluctuations are a function of silica cycle mass balance, is reasonable, but the observations in our study suggest the hypothesis that additional low temperature fractionations associated with silica precipitation also played a significant role in the Early Archean silica cycle.

Based on our data from both black and white chert bands, the fluid from which they precipitated, likely seawater, was isotopically heavy ($\delta^{30}$Si $+2_{\text{‰}}$ to $+3_{\text{‰}}$). It is difficult to
explain such heavy values without substantial low temperature fractionations associated with the marine silica cycle. Igneous silicate minerals are the ultimate source of the silicon to the Earth surface cycle and have a relatively small range of Si isotopic compositions with a mean of ca. $^{28}\text{Si} / {}^\text{Si}=0.4$ (Douthitt, 1982; Ding et al., 1996; Georg et al., 2007a,b). Release of dissolved silica during alteration of these primary igneous silicate minerals does not appear to be associated with Si isotopic fractionation (Douthitt, 1982; Basile-Doelsch, 2006), which is consistent with limited analyses of modern hydrothermal fluids $^{28}\text{Si} / {}^\text{Si}=-0.3$ (De La Rocha et al., 2000). Additional isotopic fractionations would have been necessary to drive seawater $^{28}\text{Si}$ from the igneous/hydrothermal value to the $^{28}\text{Si}$-enriched value indicated by our chert data. It is also important to note that the heavy Si isotopic composition of these cherts supports the substantial geological and sedimentological observations that these deposits were not hydrothermal exhalites (Lowe, 1999), but rather suggests low temperature fractionations occurring in environmental fluids (seawater, pore fluids, etc.). In addition, a substantial fraction of Si leaving seawater must also have been associated with a $^{28}\text{Si}$-depleted Si sink. The nature of this sink will be discussed below in Section 5.4.2.

The chert data presented here also exhibit a degree of variability that is not readily captured by sample texture or stratigraphic position. This variance is likely a result of a few factors, including: contribution of precipitates from later, $^{28}\text{Si}$-depleted fluids that were not identified petrographically (e.g., filling micro-scale porosity); local fluid $^{28}\text{Si}$ enrichment resulting from partially closed system mass balance in the precipitating fluid; measurement uncertainty ($\sim 0.30_{\text{en}}$); and differential $^{28}\text{Si}$-depletion during diagenetic transformation from amorphous silica to chert. The text-independent micrometer-scale variations observed here are similar to those reported by Marin-Carbonne et al. (2012).

Chert petrogenesis is a complex process that could have produced much of the non-texture-related Si isotopic variability, as some previous authors have suggested (Marin et al., 2010; Marin-Carbonne et al., 2012). Primary silica precipitation probably occurred via coagulation or gelation of colloidal silica (Iler, 1979). Transformation of this initial hydrated amorphous silica phase into rigid, fully-cemented microcrystalline quartz would have required one or more stages of dissolution and re-precipitation and, in some cases, the input of additional silica. Although physical and geochemical evidence supports early cementation of white chert bands, phase transformations likely continued into later diagenesis (Knauth and Lowe, 1978, 2003; Lowe, 1999; Hren et al., 2009). The diagenetic fluids interacting with primary silica during phase transformations probably originated via dewatering of primary sediments during burial. Interstitial water released during compaction of underlying sediment is an unlikely source because carbonaceous grains in most black bands show little evidence of compaction. However, dewatering through cementation could have produced large volumes of fluid. Basile-Doelsch et al. (2005) suggested that the $^{28}\text{Si}$-depletion of
primary opal would be enhanced during its diagenetic transformation to quartz, increasing the observed fractionation factor between the fluid and diagenetically-stabilized chert by up to 1%. This process could explain the occurrence of anomalously light data points within some chert analysis grids (e.g., Figs. 5 and 9c), as well as the slightly asymmetric tails of the distributions of chert $\delta^{30}$Si values (Fig. 4a).

Though diagenetic phase transformations may have introduced local variability in early chert $\delta^{30}$Si values, such effects did not eclipse the signals left by fluid Si isotopic composition and precipitation mechanisms. Furthermore, enhanced fractionation due to diagenetic transformations would have decreased the preserved $\delta^{30}$Si below some primary $\delta^{30}$Si value, implying that the measured values are minimum estimates of primary composition. Therefore, the $\delta^{30}$Si contrast we observe between early chert and cavity-filling cements would only have been increased by accounting for additional fractionations during diagenesis; the contrast is real and significant. Importantly, the resolvable distinction in $\delta^{30}$Si between chert associated with primary sedimentary textures and later cavity-filling cements indicates two types of fluids with distinct Si isotopic compositions: (1) $^{30}$Si-enriched seawater and shallow pore fluids, which provided silica for primary precipitation and phase transformations and (2) $^{30}$Si-depleted diagenetic or hydrothermal fluids that provided the silica for macroscopic cavity-filling cements. If the $^{30}$Si-depleted fluids had contributed a significant amount of silica during phase transformations of early chert, we would expect more $^{30}$Si-depleted values, particularly in black cherts, which were cemented later and thus had a more protracted diagenetic history during which $^{30}$Si-depleted silica could be incorporated.
Silica present in cavity-filling cements presents an opportunity for comparison with primary sedimentary textures because the cements can capture the later stages of silica diagenesis. Spot analyses in cavity fills yield $\delta^{30}$Si values ranging from $-4.8_{\text{vo}}$ to $+0.9_{\text{vo}}$ (mean $-1.4_{\text{vo}}$), consistent with precipitation from more $^{30}$Si-depleted fluids than

Table 3
Statistics for $\delta^{30}$Si data by sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$</th>
<th>Mean ($^{\circ}$vo)</th>
<th>Median ($^{\circ}$vo)</th>
<th>Minimum ($^{\circ}$vo)</th>
<th>Maximum ($^{\circ}$vo)</th>
<th>Standard deviation ($^{\circ}$vo)</th>
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<tr>
<td>SAF 521-14</td>
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<td>0.72</td>
</tr>
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<td>SAF 521-16</td>
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<td>0.95</td>
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<td>3.74</td>
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</table>

Table 4
Statistics for $\delta^{18}$O data by sample.

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<th>Median ($^{\circ}$vo)</th>
<th>Minimum ($^{\circ}$vo)</th>
<th>Maximum ($^{\circ}$vo)</th>
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<td>23.39</td>
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</table>

Fig. 9. Kernel-smoothing probability density estimates comparing early Archean chert $\delta^{30}$Si analyses from previous studies and this study. A combined data set from all previous studies ($n = 187$) are denoted by the thick black line (Andre et al., 2006; Robert and Chaussidon, 2006; van den Boorn et al., 2007, 2010; Abraham et al., 2011; Marin-Carbonne et al., 2012). Data from Marin-Carbonne et al. (2012) early Archean (Mendon and Dresser Formations) samples, van den Boorn et al. (2007, 2010) C-cherts and S-cherts, and Geilert et al. (2014a,b) black and translucent chert bands from the Buck Reef Chert are distinguished. From this study, $\delta^{30}$Si analyses from primary silica granules ($n = 195$) and cavity-filling cements ($n = 198$) are distinguished.

5.1.2. Cavity-filling quartz cements – diagenetic fluid circulation
Silica present in cavity-filling cements presents an opportunity for comparison with primary sedimentary textures because the cements can capture the later stages of silica diagenesis. Spot analyses in cavity fills yield $\delta^{30}$Si values ranging from $-4.8_{\text{vo}}$ to $+0.9_{\text{vo}}$ (mean $-1.4_{\text{vo}}$), consistent with precipitation from more $^{30}$Si-depleted fluids than
adjacent white or black chert. The data from cavity-filling cements also has a bimodal distribution, reflecting that multiple fluid $\delta^{30}\text{Si}$ compositions were involved with their formation. What is the origin of the fluid from which the cavity fills precipitated? Some cavity fill $\delta^{30}\text{Si}$ values are consistent with precipitation from fluids with average igneous $\delta^{30}\text{Si}$ composition, but the observed minima imply substantially lighter fluid $\delta^{30}\text{Si}$ compositions. Previous studies generally considered light chert $\delta^{30}\text{Si}$ to have resulted from precipitation from hydrothermal vent fluids, but the implied fluid Si isotopic composition is non-unique and the ubiquitous occurrence and sedimentary context of cavity fills precludes their necessary proximity to hydrothermal vents. There are no observations to support an association with hydrothermal vents or circulation systems; cavity-filling cements in the Buck Reef Chert, for example, occur with similar regularity both laterally and vertically throughout the stratigraphy. Furthermore, cavity-filling cements have similar $\delta^{18}\text{O}$ to the adjacent chert (Figs. 4e and 6c), rather than the depleted $\delta^{18}\text{O}$ that previous authors ascribe to hydrothermal precipitates (Knauth and Lowe, 2003; Marin et al., 2010; Marin-Carbonne et al., 2012). However, the scale of the cavity fills—up to several cm thick, often tens of cm in length, and likely interconnected (e.g., Fig. 2a)—does indicate the operation of a fluid flow system to both provide and occlude the porosity. As suggested above, the Si isotopic contrast between early chert and macro-scale cavity-filling cements indicates that they precipitated from fluids with distinct Si isotopic compositions.

Our isotope ratio observations indicate that there are at least two types of macrocrystalline cavity-filling cements present in our samples. Figs. 6 and 7 are representative examples of superficially similar coarse quartz cavity fills with distinct Si isotopic and CL patterns. There is almost certainly a third type—cements filling micro-scale interstitial pore space, but such cements are not easily distinguished petrographically from microcrystalline quartz in other textures. It is possible that the variable presence and timing of micro-scale cements contributed to the $\delta^{30}\text{Si}$ heterogeneity within samples.

The cavity fill in Fig. 6 shows no distinct internal isotopic trend within the macrocrystalline quartz, although a few points in the chart at the upper cavity edge (mean $\delta^{30}\text{Si} = -1.0_{\%\text{o}}$) are distinct from both the surrounding white chert (average $\delta^{30}\text{Si} 0.4_{\%\text{o}}$) and the main cavity cement (mean $\delta^{30}\text{Si} = -2.7_{\%\text{o}}$) and probably represent the remnants of an earlier cement. Most of the analyses in this cavity fill are also particularly $^{30}\text{Si}$-depleted, with a mean $\delta^{30}\text{Si}$ over $2_{\%\text{o}}$ lighter than the igneous average. Such low $\delta^{30}\text{Si}$ values suggest enhanced apparent fluid-precipitation fractionation due to the isotopic composition observed in macrocrystalline quartz silcretes ($\delta^{30}\text{Si} = -7.5_{\%\text{r}}$). In this case, an early cement, represented by a rim along the cavity edge (mean $\delta^{30}\text{Si} = -1.1_{\%\text{r}}$), could have been dissolved by a later silica-undersaturated fluid that subsequently precipitated a yet more $^{30}\text{Si}$-depleted cement (mean $\delta^{30}\text{Si} = -2.6_{\%\text{r}}$). This latter $\delta^{30}\text{Si}$ value is within the range that would be expected ($\delta^{30}\text{Si} = -3_{\%\text{r}}$ to $-2_{\%\text{r}}$) for silica precipitating from a fluid with a Si isotopic composition similar to the cement edge ($\delta^{30}\text{Si} = 1_{\%\text{r}}$). The $^{30}\text{Si}$-depletion of the secondary fluid may have been enhanced due to the transient preferential release of $^{28}\text{Si}$—a process observed by Ziegler et al. (2005a) during partial dissolution of silicate grains. It is also possible that the $\delta^{30}\text{Si}$ contrast resulted from two unrelated fluids, although the question of how such a low $\delta^{30}\text{Si}$ fluid was generated remains.

The $\delta^{30}\text{Si}$ contrast between the early and late cement in Fig. 7 is consistent with closed-system behavior for a kinetic fractionation process (Ding et al., 1996; Kendall and Caldwell, 1998); a finite supply of reactant (dissolved silica) and negligible back-reaction (minimal dissolution of precipitated silica) leading to progressive isotopic enrichment of precipitates and residual fluid. The apparent Si isotopic enrichment in the later generation of cement suggests that this system was probably relatively isolated from seawater or any other large buffering reservoir.

What causes the difference in observed $\delta^{30}\text{Si}$ evolution in these two cements? The cavity-filling cement in Fig. 6 has particularly depleted $\delta^{30}\text{Si}$ values, consistent with significant dissolution of early silica phases, and a dark CL pattern, a common observation in authigenic quartz cements with relatively low defect concentration resulting from slow growth or precipitation (Götze, 2012). The example in Fig. 7, on the other hand, has a $\delta^{30}\text{Si}$ pattern indicating negligible dissolution and a bright CL pattern with complex euhedral growth zones, similar to those observed in epithermal hydrothermal quartz deposits (Rusk, 2012). Both cements have similar oxygen isotope values, so it is unlikely that differential fluid temperatures are responsible for the different precipitation behavior observed in Fig. 7. Instead, the principal distinction between the two processes seems to be whether or not significant dissolution of early silica phases occurred, which may have been related to the rate and timing of precipitation.

5.2. Comparisons with data from previous chert Si isotope studies

A number of previous papers have presented Si isotope compositions in pre-3.0 Ga cherts (Andre et al., 2006; Robert and Chaussidon, 2006; van den Boorn et al., 2007, 2010; Abraham et al., 2011; Marin-Carbonne et al., 2012). Robert and Chaussidon (2006) applied $\delta^{30}\text{Si}$ as an indirect measure of ancient seawater temperature, while others used $\delta^{30}\text{Si}$ to compare cements in a framework of three types of microquartz: (1) diagenetic microquartz originating from seawater, (2) direct hydrothermal precipitates, and (3) silicification of pre-existing rocks (e.g., carbonates, volcanic rocks) (van den Boorn et al., 2007, 2010; Marin-Carbonne et al., 2012). Although previous authors emphasized the importance of lithology in sample selection and interpretation, descriptions of sample lithologies, petrographic textures, and depositional environments were limited.

Many early Archean cherts are silicified sediments or volcanic rocks. Primary textures can be well-preserved and provide significant information regarding depositional and diagenetic history. For example, many black cherts...
are essentially silicified lithic sandstones where the dominant framework grains are sand-sized organic-rich grains rather than monocrystalline mineral grains (e.g., Figs. 2b, 5a and 6a). These textures are often defined by trace inclusions of organic matter, carbonates, iron oxides, or phyllosilicates and while they are readily identified with standard transmitted light microscopy, which integrates 30 µm of sample thickness, they are often obscured or undetectable when samples are imaged with reflected light, SEM, or electron probe techniques (e.g., Fig. 5a–b). Petrographic observations like these, combined with geological observations (e.g., the common early brecciation of white chert bands indicating their early lithification), provide valuable context for interpreting geochemical data from Archean cherts.

Without petrographic context, we can only draw limited direct comparisons between the texture-resolved $\delta^{30}$Si data presented in this study and analyses from similar cherts presented in previous studies. Van den Boorn et al. (2007, 2010) present data from older cherts of the Pilbara Block in Western Australia: the ~3.46 Ga Marble Bar Chert, the ~3.45 Ga Kitty’s Gap Chert, and the ~3.49 Ga North Pole Chert. The study of Marin-Carbonne et al. (2012) includes samples from the ~3.3 Ga Mendon Formation of the Onverwacht Group in the Barberton Greenstone Belt (also a focus of this study) in addition to the ~3.48 Ga Dresser Formation from the Pilbara Block. Geilert et al. (2014b) analyzed banded black-and-white cherts of the ~3.42 Ga Buck Reef Chert (Onverwacht Group, Barberton Greenstone Belt); samples of the Buck Reef Chert were also analyzed in the present study. In this study, we show that early chert textures (e.g., white chert bands, black cherts composed of silicified organic grains) have heavier $\delta^{30}$Si than a common later texture, cavity-filling cements, suggesting that these two textures precipitated from different fluids. Previous authors have also interpreted that the distributions of their Si isotopic data represented precipitation from two isotopically distinct fluids, which they suggested were seawater and hydrothermal fluids (van den Boorn et al., 2007, 2010; Marin-Carbonne et al., 2012; Geilert et al., 2014b).

The early chert textures from this study (e.g., white chert bands and grains; see Fig. 4b) have a nearly identical $\delta^{30}$Si distribution to the S-cherts of van den Boorn et al. (2007, 2010), which are interpreted to have been formed via silification from seawater (Fig. 9). The distribution of samples from Marin-Carbonne et al. (2012), which includes samples from the Mendon Formation, also has a shoulder that lies in the same domain, which those authors interpreted as a mixing relationship between end-member marine diagenetic silica and silification of some pre-cursor rock. The main peaks of the Marin-Carbonne et al. (2012) data, the C-cherts of van den Boorn et al. (2007, 2010), and the translucent chert bands of Geilert et al. (2014b), interpreted by those authors to represent silica precipitated from hydrothermal fluids, also overlap with the cavity-filling cements from this study, which we interpret to have precipitated from $^{30}$Si-depleted fluids distinct from seawater. Without better sedimentologic and petrographic context of these previous studies, we cannot evaluate whether these $^{30}$Si-depleted measurements were from analogous cements. Nor do we feel it is appropriate in the case of our samples to confidently interpret these $^{30}$Si-depleted fluids as hydrothermal fluids.

The $\delta^{30}$Si data presented here is consistent with the approximately bimodal distribution of the most extensive previous chert Si isotope studies (Fig. 9) (van den Boorn et al., 2007, 2010; Marin-Carbonne et al., 2012). Although we present a different interpretation on the nature of the more $^{30}$Si-depleted fluid, the overall implication of two isotopically distinct fluids, one of which was seawater, is the same. The implied $^{30}$Si-enriched seawater composition indicates that the precipitation of secondary silicate phases has modified seawater $\delta^{30}$Si subsequent to the initial mineral dissolution or alteration reactions that released dissolved silica into solution. Previous authors implied that this $^{30}$Si-enriched signal mainly resulted from authigenic clay precipitation during continental weathering (van den Boorn et al., 2007, 2010). We add that significant low temperature fractionations need not have been limited to continents, particularly given the reduced volume of continental crust pre-3.0 Ga (Cawood et al., 2012; Dhuime et al., 2012), and present an additional model below (Section 5.4.2).

### 5.3. Decoupling of Si and O isotopic systems on small scales

Robert and Chausidon (2006) and Abraham et al. (2011) both observed a positive correlation between $\delta^{30}$Si and $\delta^{18}$O in their chert data sets, although with different conclusions about the origin of this relationship. The former suggested that the isotopic systems were coupled via seawater temperature, while the latter proposed that the correlation was coincidental because the two isotope systems reflected different processes. From the perspective of alteration, O and Si isotope ratios could covary as a result of water–rock interaction during diagenesis, but for different reasons: $\delta^{18}$O is controlled by temperature and fluid composition, while $\delta^{30}$Si is controlled by fluid composition, precipitation process, and mass balance.

Due to the differential elemental abundance in marine and/or formation waters, O isotopes are more susceptible to diagenetic or metamorphic resetting by later fluids than Si isotopes, which, in principle, are better rock buffered and less susceptible to change from secondary fluids. Knauth and Lowe (2003) provided several lines of evidence that $\delta^{18}$O in post-3.445 Ga cherts from the Barberton Greenstone Belt was not strongly affected by peak metamorphism, which is corroborated by our data. The range of $\delta^{18}$O between samples indicates that some O isotopic compositions were altered during early burial and diagenesis, while $\delta^{30}$Si is remarkably consistent across all samples. $\delta^{30}$Si data from white chert bands indicates that early-formed cherts can preserve a record of the Si isotope composition of the fluids from which they precipitated without significant alteration during later burial and metamorphism. The offset in the timing in which cherts record their Si and O isotopic compositions challenges hypotheses for paleoenvironmental coupling of the two isotopic systems.
5.3.1. Origin of oxygen isotope variability

$\delta^{18}O$ varies by $\gamma_{\text{iso}}$ in our sample set, similar to ranges reported in previous studies of samples from the same units in the Barberton Greenstone Belt (Knauth and Lowe, 1978, 2003; Hren et al., 2009). These differences are too large to be explained by changes in either the temperature or oxygen isotopic composition of seawater. Instead, differential resetting of oxygen isotope ratios during burial and diagenesis offers a more reasonable explanation for the observed patterns. The differences between Si and O isotopic patterns in the different textures supports the hypothesis that chert $\delta^{18}O$ is more susceptible to alteration during diagenesis than chert $\delta^{30}Si$.

Although the silica in our samples occurs principally as microquartz with some megaquartz associated with coarse cavity-filling cements, quartz was almost certainly not the primary silica phase, which is an important consideration for interpreting the oxygen isotope ratio data. Mechanisms of chert formation are not well constrained, but it is likely that amorphous silica was usually the precursor to microquartz (Hesse, 1989; Kastner et al., 1977; Knauth, 1992, 1994; Hattori et al., 1996), either as opal-CT or an amorphous silica gel. The diagenetic transformation to microquartz involves dissolution of the primary phase and precipitation of the secondary phase, during which the oxygen isotopic composition can be altered (Knauth and Epstein, 1975; Kolodny and Epstein, 1976; Murata et al., 1977; Jones and Knauth, 1979; Behl and Garrison, 1994; Knauth, 1994). Therefore, most chert $\delta^{18}O$ is likely set early during stage of diageneis: maximum values thus provide a constraint of maximum ambient seawater temperature, while lighter values commonly reflect warmer temperatures experienced during comparatively deeper burial or during interaction with meteoric fluids.

The variability in our $\delta^{18}O$ data is consistent with asynchronous timing of O isotope setting during burial. Sample BH-03-7, for example, shows textural and O isotopic evidence that the white chert band was silicificed before the surrounding carbonate chert (Fig. 8), but, the $\delta^{18}O$ values imply that both phases experienced silica diageneis deeper or at higher temperatures than samples from the SAF 521 locality (Fig. 4d). The effects of differential diaeneis on chert $\delta^{18}O$ can be observed at every scale in our sample set, although the cause is not always apparent, particularly in several examples where $\delta^{18}O$ patterns do not correspond to texture or composition. On the smallest scale, $\delta^{18}O$ can vary between analysis spots located 100 μm apart (Fig. 6d), seemingly independent of the primary texture. As discussed in Section 5.1.1, the complex, multi-phase process of chert petrogenesis may have generated Si isotopic heterogeneities not reflected clearly by petrographic texture. Similarly, spatial and temporal heterogeneity of silica precipitation and phase transformation could have contributed to small-scale $\delta^{18}O$ variability. At a slightly coarser scale is the isotopic contrast in sample BH-03-7 between a white chert band and the adjacent carbonaceous chert, on the order of 1$\gamma_{\text{iso}}$ (Fig. 8d), reflecting that the final $\delta^{18}O$ composition of the white chert band was set earlier than that of the surrounding carbonaceous chert. Differential diaeneis timing also occurred at a bed scale: the two sets of samples collected from within 3-meter stratigraphic intervals (BH-03 samples and SAF 521 samples, see Table 1) yielded only partially overlapping $\delta^{18}O$ distributions. The BH-03 (lighter values) and SAF 521 (heavier values) samples also were collected from stratigraphic sections in two different structural belts, located ~10 km apart, suggesting that O isotope ratios reflect diageneic processes that varied on a regional scale. Consequently, $\delta^{18}O$ patterns are best explained as products of differential setting during diagenesis and burial, at micro- to basinal scales.

5.3.2. Comparison of paired Si and O analyses

Our data set does not show an overall relationship between $\delta^{30}Si$ and $\delta^{18}O$ (Fig. 4f). Using linear regression (ordinary least squares) to assess the relationship between $\delta^{30}Si$ and $\delta^{18}O$ (averaging across the three sample sets in Fig. 4f) yields no significant relationship ($R^2 = 0.01$), indicating that $\delta^{30}Si$ and $\delta^{18}O$ vary independently. If we model by sample, there is also no indication of a relationship between $\delta^{30}Si$ and $\delta^{18}O$: for BH-03-7, $R^2 = 0.07$; for BH-03-9, $R^2 = 0.02$; and for BRC-01-2, $R^2 = 0.01$. Rather, comparing $\delta^{30}Si$ and $\delta^{18}O$ highlights the similarities of $\delta^{30}Si$ across samples and the differences in $\delta^{18}O$ between samples (see also Fig. 4c–d). We hypothesize that any apparent correlation over longer temporal or spatial scales (Robert and Chaussidon, 2006; Abraham et al., 2011) results from independent processes, an interpretation put forward by Abraham et al. (2011) and Chakrabarti et al. (2012).

The data from one sample (BH-03-9 gr6) are tightly clustered in both $\delta^{30}Si$ and $\delta^{18}O$, while the data from the other samples (BH-03-7 and BRC-01-2) show similar $\delta^{18}O$ ranges but a greater range in $\delta^{30}Si$, characterized by relatively sharp upper boundaries with a diffuse “tail” of lighter values. Much of the isotopic variation observed in this distribution can be explained by texture: many of the points with $\delta^{30}Si \leq 0_{\text{per}}$ are from cavity fills, while BH-03-9 gr6 was measured using closely-associated analysis spots in a homogeneous chert band area with no cavity fills. This tight clustering of data points around positive $\delta^{30}Si$ reflects two factors: (1) the inclusion of more spot analyses in white chert bands (which have higher mean $\delta^{30}Si$) and (2) the smaller range of $\delta^{30}Si$ in white chert bands compared relative to cavity fills, the latter likely associated with smaller scale fluid systems more susceptible to shifts in fluid $\delta^{30}Si$ composition during precipitation. Although the BH-03-7 and BRC-01-2 grids show similar $\delta^{30}Si$ ranges but a greater range in $\delta^{18}O$ than the BH-03-9 includes more $\delta^{30}Si$-enriched values, which could be related to variation in the $\delta^{30}Si$ of the fluid from which the silica originally precipitated or differential $^{30}Si$ depletion during diageneic transformation. This plot illustrates the value of textural context for $\delta^{30}Si$ and $\delta^{18}O$ analyses, which enable evaluation of isotopic composition in the context of different processes of silica precipitation.

The only case of $\delta^{30}Si$ and $\delta^{18}O$ correlation on the micro-scale occurs in a coarse quartz cavity fill (Fig. 7), where higher $\delta^{30}Si$ and lower $\delta^{18}O$ occur toward the cavity center ($R^2 = 0.20$). This observation is consistent with the anticipated behavior of these two systems during late cement precipitation. For $\delta^{30}Si$, the earliest precipitates
(small grains along cavity edges) record the lightest values, while subsequent precipitates are increasingly enriched in $^{30}$Si, reflecting concentration of $^{30}$Si in the residual fluid. $\delta^{18}$O, on the other hand, likely recorded increasing temperature, perhaps reflecting the effect of burial as the cavity fill was precipitating. This behavior implies that Si and O isotopic systems recorded by these cherts do not record the same processes, even when $\delta^{30}$Si and $\delta^{18}$O values covary.

### 5.4. Developing a conceptual model for the Archean Si isotope cycle

#### 5.4.1. Process constraints from the modern Si isotope cycle

The modern silicon isotope cycle remains a subject of active research, particularly the study of Si fluxes associated with soil forming processes (Ziegler et al., 2005a,b; Opfergelt et al., 2009, 2010; Bern et al., 2010; West et al., 2011) and various types of biologically-mediated silica precipitation and dissolution (De La Rocha et al., 1997; De La Rocha, 2003; Varela et al., 2004; Delstanche et al., 2009), biogenic silica precipitation (Basile-Doelsch et al., 2005), seawater silica precipitation (this study), and iron adsorption (Delstanche et al., 2009). Fluxes are color-coded by type: particulate (yellow arrows), dissolved (red arrows), precipitation (green arrows), and dissolution (blue arrows). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Fig. 11. Comparison of distributions of the Si isotopic composition of key reservoirs (a) and the major silicon isotopic fractionations (b). (a) Kernel density functions of $\delta^{30}\text{Si}$ distributions of quartz (Douthitt, 1982; Ding et al., 1996; Ziegler et al., 2005b; Georg et al., 2009; Savage et al., 2012), olivine (Douthitt, 1982; Georg et al., 2007a; Savage et al., 2011), basalts (Douthitt, 1982; Ding et al., 1996; Ziegler et al., 2005a; Georg et al., 2007a,b; Opfergelt et al., 2010; Abraham et al., 2011; Savage et al., 2011), granites (Ding et al., 1996; Savage et al., 2012), clays (Douthitt, 1982; Ding et al., 1996; Ziegler et al., 2005b; Opfergelt et al., 2009, 2010, 2012), rivers (Ding et al., 1996; De La Rocha et al., 2000; Alleman et al., 2005; Ziegler et al., 2005a,b; Georg et al., 2007b; Opfergelt et al., 2009), diatoms (De La Rocha et al., 1998, 2000), seawater (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005; Reynolds et al., 2006), primary and early silica phases represented by white chert bands and the subset of primary silica granules (this study), seawater silica as recorded by “S-cherts” (van den Boorn et al., 2007, 2010) and BIF (Ding et al., 1996; Andre et al., 2006; Steinhoefel et al., 2009, 2010; Heck et al., 2011; Chakrabarti et al., 2012; Delvigne et al., 2012). (b) Si isotopic fractionation factors ($\epsilon_{\text{precip-fluid}} = \delta^{30}\text{Si}_{\text{precipitate}} - \delta^{30}\text{Si}_{\text{fluid}}$) for the major processes in the modern and Archean systems: biomineralization by diatoms (De La Rocha et al., 1997; Varela et al., 2004) or sponges (De La Rocha, 2003), dissolution of biogenic silica (Demarest et al., 2009), adsorption onto goethite or ferricydrite (Delstanche et al., 2009), precipitation of authigenic clays (Ziegler et al., 2005a) or groundwater silcretes (Basilé-Doelsch et al., 2005), the maximum high temperature (igneous or metamorphic) fractionation (Meheut et al., 2009), and dissolution of igneous silicates (Ding et al., 1996).
precipitation (Hendry and Robinson, 2012; Hendry et al., 2011; Egan et al., 2012). Broadly, however, the first order controls in the modern cycle are understood and can be outlined in a simple conceptual model (Fig. 10a). Since the Si isotopic composition of dissolved silica can change throughout the silica cycle, it is useful to compare precipitation processes by use of a fractionation factor (ε = δ²⁸Si\textsubscript{precipitate} − δ²⁸Si\textsubscript{fluid}) in addition to range and mean of δ²⁸Si in each silicon-bearing phase (Fig. 11).

Chemical weathering of continental and oceanic crust provides the dominant source of silica to the fluid Earth today with the average δ²⁸Si for bulk silicate earth (BSE) ca. −0.4‰ (Douthitt, 1982; Ding et al., 1996; Georg et al., 2007a,b). Rivers are the principal input of dissolved and particulate silica into modern oceans (Treguer et al., 1995). The processes that fractionate silicon isotopes during continental weathering therefore play a significant role in silicon isotope mass balance in the modern cycle. Dissolution of igneous silicates does not strongly fractionate Si isotopes, with the exception of a possible rapid and transient preferential release of ²⁸Si during dissolution of the outer atomic layers of silicate grains, but this effect disappears as dissolution proceeds (Ziegler et al., 2005a). Precipitation of authigenic silicates, which are ³⁰Si-depleted, is thought to be responsible for increasing riverine δ²⁸Si, which can vary between −0.1‰ to +3.4‰ with a mean value of +1.2‰ (De La Rocha et al., 2000; Ding et al., 2004; Alleman et al., 2005; Ziegler et al., 2005a,b; Georg et al., 2006, 2007b; Opfèrgelt et al., 2009). The key secondary silicate phases include authigenic phyllosilicates, groundwater silicates, and phytoliths (biomineralized opal in plants) (Table 5, Fig. 11).

Surface ocean waters can have highly variable δ³⁰Si, between +0.6‰ and +3.1‰ (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005; Basile-Doelsch, 2006; Reynolds et al., 2006), based on localized factors: river δ³⁰Si and the balance between precipitation and dissolution of biogenic silica. Diatoms, radiolarians, sponges, and silicoflagellates all precipitate siliceous skeletons, with current data showing discrimination against ³⁰Si (Table 5, Fig. 11). Recent experiments have yielded mixed results concerning whether there are Si isotope fractionations associated with dissolution of biogenic silica (Demarest et al., 2009; Wetzel et al., 2014), which have the potential to partially erase the isotopic signature of biogenic silica precipitation.

Dissolution of sinking biogenic silica releases additional ²⁸Si, driving δ²⁸Si of deep waters to lighter values than the surface ocean (De La Rocha et al., 2000). The majority of remaining particulate silica-bearing phases (e.g., quartz, clays, and biogenic silica) mark the surficial Si isotope cycle sinks in marine sediments. Additionally, authigenic cements can be added to sedimentary silica via precipitation from pore fluids. An analysis of a modern marine silica cement yielded δ²⁸Si 0.2‰ (Basile-Doelsch et al., 2005), which is consistent with precipitation from pore fluids that have a Si isotopic composition close to either surface or deep ocean values.

In summary, low temperature kinetic isotopic fractionations drive most of the range of δ²⁸Si observed in the modern silicon isotope cycle (Fig. 11): igneous minerals span a narrow range of values centered on the BSE average, while secondary silicates like clays or biogenic opal and dissolved silica in rivers and seawater span much broader ranges of values. This range results from the complex evolution of fluid and precipitate δ³⁰Si composition during precipitation and dissolution.

5.4.2. The Archean Si isotope cycle

Both modern and Archean Si isotope cycles might be expected to share broad similarities despite clear differences in the exact processes, sources, and sinks. During Archean time, dissolved silica would have been derived from silicate weathering of igneous phases that comprise the crust, with sedimentary sinks in chert, BIF, and possibly secondary clays. Si isotope fractionations occur throughout the modern silica cycle, widely associated with low temperature precipitation of Si-bearing phases through both chemical and biological processes. Biologically-mediated silica precipitation was probably absent from the Archean silica cycle.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Si isotopic fractionations and compositions of key secondary silicate phases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary silicate phase</td>
<td>ε\textsubscript{precipitate-fluid} (‰)</td>
</tr>
<tr>
<td>Terrestrial environments</td>
<td></td>
</tr>
<tr>
<td>Authigenic phyllosilicates</td>
<td>−1.2</td>
</tr>
<tr>
<td>Groundwater silicates</td>
<td>−2.4</td>
</tr>
<tr>
<td>Phytoliths</td>
<td>Unknown</td>
</tr>
<tr>
<td>Marine environments</td>
<td></td>
</tr>
<tr>
<td>Diatoms</td>
<td>−1.1 to −1.6</td>
</tr>
<tr>
<td>Radiolarians</td>
<td>Unknown</td>
</tr>
<tr>
<td>Sponges</td>
<td>−1 to −6</td>
</tr>
<tr>
<td>Silicoflagellates</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

a Recent work has suggested that the Si isotopic fractionation associated with sponges is dependent on silica concentration, with higher silica concentrations corresponding to greater magnitude isotopic fractionations (Wille et al., 2010; Hendry et al., 2011; Hendry and Robinson, 2012).
but chemical processes associated with the precipitation of Si-bearing solid phases would have introduced fractionations.

In principle, it is possible that silica sourced from silicate weathering of Archean crust had a slightly lighter Si isotope composition than modern crust because of differences in the relative proportions of continental versus oceanic crust (Taylor and McLennan, 1981). Mafic silicate minerals like olivine or pyroxene tend to have slightly lighter $\delta^{30}$Si than feldspar or quartz and the average $\delta^{30}$Si in basalt is also slightly lighter than in granites (Table 6). Even if the modern crust was entirely felsic and the Archean crust was entirely mafic (an extreme end-member scenario), the potential difference between modern and Archean igneous inputs would only be about $-0.2\%_{oo}$, which is much smaller in magnitude than most low temperature fractionations ($\varepsilon \approx -1\%_{oo}$). Any effect would be further diminished by the fact that quartz, the most $^{30}$Si-enriched igneous mineral, is also the most resistant to weathering. For this reason, it is probably not possible to diagnose the small to negligible change expected in the average isotopic composition of igneous modern and Archean silicon inputs based on observations from sedimentary cherts.

Nevertheless, the difference in volume of continental crust present on the modern Earth compared to 3.5–3.3 Ga still bears some significance in constructing a model of the Archean silica cycle. Although the continental growth curve over Earth history is still being refined by ongoing studies, there is a common view that there was less continental crust during middle Archean time (Cawood et al., 2012). For example, recent work by Dhuime et al. (2012) suggests that the volume of continental crust present during the time of deposition of samples included in this study was approximately 50% of the modern volume. This is significant because many previous studies of Si isotopes in Archean cherts have interpreted their data in the context of mixing models with two end-members: “continental” silica (heavy $\delta^{30}$Si) and “hydrothermal” silica (light $\delta^{30}$Si) (van den Boorn et al., 2007, 2010; Abraham et al., 2011; Marin-Carbonne et al., 2012). The heavy $\delta^{30}$Si signature of “continental” silica is interpreted to reflect incorporation of $^{30}$Si into secondary phases during continental weathering, while the light $\delta^{30}$Si signature is interpreted to reflect precipitation from hydrothermal fluids that, like modern fluids, had an isotopic composition close to the igneous average. This approach relies on reservoir composition analogies—applying modern $\delta^{30}$Si values to Archean “hydrothermal” and “continental” dissolved silica reservoirs.

These reservoir analogies are problematic because the distributions of $\delta^{30}$Si compositions in modern silica reservoirs result from the complex history of precipitation and dissolution of silicates and their associated isotopic fractionations. For example, the connection between continental silica and heavy $\delta^{30}$Si masks the implicit assumption that most low temperature isotopic fractionations occur during continental weathering, but fractionations in seawater could also have contributed to a $^{30}$Si-enriched marine Si isotopic composition, meaning that heavy $\delta^{30}$Si need not reflect only continental silica input. Likewise, since complete dissolution of igneous silicate minerals does not fractionate Si isotopes, fluid with an “igneous” composition near $-0.4\%_{oo}$ need not necessarily be “hydrothermal”, but simply one that has yet to precipitate a significant fraction of secondary silica phases. Finally, given the much smaller volume of continental crust present during Archean time, we can reasonably suspect that the fluxes of silica derived from continental weathering were lower than modern riverine silica fluxes.

We suggest that a conceptual model based on process analogies is more useful for the Archean system. This is not a radical departure from the previously suggested continental vs. hydrothermal framework, but rather a refinement that explicitly accounts for the complex histories of precipitation and dissolution reflected in cherts, BIF, and clays. This pivot from reservoir analogies to process analogies is particularly relevant in light of recent experimental studies showing that Si fractionation factors associated with some key abiogenic precipitation and adsorption mechanisms are dependent on environmental variables like temperature and silica concentration (Oelze et al., 2014; Geilert et al., 2014a). Many of these environmental parameters have not been constant over Earth history, which is problematic for applying Si isotopic distributions of modern silica reservoirs, fundamentally products of modern conditions, to the Archean silica cycle.

In the modern Si cycle, multiple processes fractionate Si isotopes between the initial release of igneous silicon during weathering and its final removal by sedimentation and cementation. The most significant modern chemical silica
precipitation processes are precipitation of secondary clay minerals (ε ≈ −1.2‰) (Ziegler et al., 2005a,b) and authigenic silica cementation (ε = −2.4‰) (Basile-Doelsch et al., 2005). For Archean time, we must also consider greater contributions from primary silica precipitation and adsorption onto iron oxyhydroxides because of the general prevalence of iron formation as a notable silica sink (ε = −1.1‰ for ferrihydrite and −1.6‰ for goethite) (Delstanche et al., 2009). There are no studies of isotopic fractionations associated with low temperature marine precipitation of primary, non-biogenic amorphous silica because it does not form from modern seawater due to the low concentration of dissolved silica (Siever, 1992; Treguer et al., 1995).

However, groundwater silicretes (ε = −2.4‰) and marine silica cements (ε = −1‰) (Basile-Doelsch et al., 2005) are reasonable analogues and suggest that if, as predicted (Siever, 1992), primary silica precipitation occurred in Archean seawater, it was probably accompanied by isotopic fractionation on the order of −1‰ to −2‰. This is also consistent with recent flow-through experiments measuring Si isotopic fractionations associated with silica precipitation induced by a drop in temperature (ε = −2.1‰ at 10 °C and ε = −1.2‰ at 20 °C) (Geilert et al., 2014a).

Previous authors have suggested that, even in the absence of biomineralization, interaction with organic matter can play a role in silica precipitation and diagenesis (Iler, 1979; Himan, 1990; Siever, 1992). Black carbonaceous chert bands show physical and geochemical evidence of later cementation than adjacent white chert bands (Knauth and Lowe, 1978, 2003; Lowe, 1999; Hren et al., 2009). This observation is consistent with the experimental work of Himan (1990) suggesting that presence of organic matter slows the rate of diagenetic silica transformations. Most modern biologically-mediated silica precipitation is associated with silicon isotope fractionations (Douthit, 1982; Ding et al., 1996; De La Rocha, 2003; De La Rocha et al., 1997), but it remains unclear whether passive reactions between silica and organic compounds also fractionate silicon isotopes. The distributions of δ30Si from white chert and black carbonaceous chert are essentially identical (Fig. 4), suggesting that there is no significant distinction between Si isotope fractionations in the presence or absence of organic matter.

White chert bands from banded black-and-white chert sequences provide the best proxy for seawater Si isotopic composition: they were deposited and silicified/lithified early and they are composed of nearly pure microcrystalline quartz, minimizing the potential effects associated with the presence of trace ferruginous or carbonaceous material. The δ30Si compositions of the white chert bands (average +0.6‰, from this study) are more 30Si-enriched than igneous silicates and can be further inverted to estimate even higher seawater δ30Si values, at approximately +1.6‰ to +2.6‰, which is consistent with estimates from previous studies (van den Boorn et al., 2007, 2010; Abraham et al., 2011; Marin-Carbonne et al., 2012).

Cherts may not be the only significant 30Si-enriched silica sink. Published bulk analyses of δ30Si in Archean basalts span a range from δ30Si = 2.8‰ to +0.8‰ with an average around 0‰ (Andre et al., 2006; van den Boorn et al., 2010; Abraham et al., 2011). The small subset of values lighter than the igneous average are, in principle, consistent with secondary clay formation during basalt alteration. A more important observation, however, is that many of these rocks have been post-depositionally silicified, meaning that they may record a different large sink of seawater silica (Seyfried and Bischoff, 1979; Staudigel and Hart, 1983; Staudigel et al., 1981; Gillis and Robinson, 1988). Most δ30Si analyses of Archean basalts lie between the igneous average and a maximum of +0.8‰, and display a positive correlation between weight percent SiO2 and δ30Si (R² = 0.7775, data from Abraham et al., 2011). This correlation implies a simple mixing relationship between unaltered basalts (45–55% SiO2, δ30Si = −0.4‰) and silicified basalts that have incorporated a considerable amount of additional silica (∼80% SiO2, δ30Si ∼ +0.8‰). This additional silica may have originated from a fluid with a Si isotopic composition similar to the seawater compositions suggested by our chert data. The mechanistic similarities between basalt silicification and chert petrogenesis are evident from isotopic mass balance, with the caveat that basalt analyses from previous studies are complicated by the occurrence of three classes of silica-bearing phases with distinct Si isotopic compositions: primary igneous minerals, secondary clay minerals, and diageneric chert.

From observations of primary cherts and silicified basalts the δ30Si composition inferred for seawater is 30Si-enriched over igneous materials (e.g., bulk silicate Earth, with a mean δ30Si of −0.4‰), and this implies that there were complementary, 30Si-depleted sedimentary silica sinks to achieve Si cycle isotope mass balance. We emphasize here that isotope mass balance for seawater concerns the sum of both terrestrial and marine sinks. For example, the positive δ30Si values inferred for Archean seawater could reasonably reflect the combined processes of a source of silica from silicate weathering and the loss of silica via production of secondary phyllosilicate phases (more on this below). It does not matter whether this weathering takes place in submarine or subaerial settings as its impact on seawater δ30Si values is similar.

Archean and Paleoproterozoic banded iron formation (BIF) has both substantial concentrations of SiO2 and light Si isotopic compositions, ranging from δ30Si = −3.3‰ to +0.8‰, averaging around −1.1‰, suggesting that BIF deposition may have been an important sink in the Archean silica cycle (Ding et al., 1996; Andre et al., 2006; Steinhoefer et al., 2009, 2010; Heck et al., 2011; Chakrabarti et al., 2012; Delvigne et al., 2012). With that in mind, it is unclear whether iron budgets as reflected by BIF deposition were sufficient to drive seawater δ30Si to the composition proposed here. For example, we could assume that the average δ30Si value of +0.6‰, for 3.4–3.3 Ga, based on this study) and BIF (an average δ30Si value of −1.1‰) were the primary Si-bearing components of sedimentary silica and that the average Si isotopic composition of inputs was identical to BSE (δ30Si of −0.4‰). One can then calculate the fraction of Si that must have left the ocean via BIF (assuming steady-state): δ30Siigneous = (1 − fBIF) δ30SiBIF + fBIF
δ^{30}Si_{BIF}, arriving at a value of f_{BIF} = 0.59. Considering that BIFs are 43–56 wt% SiO_2 (Klein, 2005), while chert bands are >95 wt% SiO_2 (Walsh and Lowe, 1999), a considerable amount of BIF would be required to balance the isotopic compositions of the sedimentary clasts we observe.

The previous calculation left out a sink that plays a key role in the modern silica cycle–clay minerals. As discussed in Section 5.4.1, Si isotope fractionations associated with the precipitation of authigenic clay minerals are thought to be the dominant process responsible for the δ^{30}Si-enriched composition of dissolved silica in modern rivers. In other words, authigenic clays represent a significant δ^{30}Si-depleted silica sink on modern Earth. It is reasonable to infer that authigenic clays also precipitated on the Archean Earth and, furthermore, that this need not have occurred solely during the production of soils in terrestrial environments: clay minerals also form during low-temperature, seafloor alteration of oceanic crust (Seyfried and Bischoff, 1979; Staudigel and Hart, 1983; Staudigel et al., 1981; Gillis and Robinson, 1988), subaerial basalt weathering (Ziegler et al., 2005a, 2003), and precipitation from sedimentary pore fluids (e.g., Michalopoulos and Aller, 1995). Clay formation is associated with silicon isotope fractionation similar in magnitude to silica adsorption on iron, so a clay sink could augment the BIF light silica sink, reducing the volume of BIF required to balance chert δ^{30}Si. If the volume of continental crust was substantially less during middle Archean time than on modern Earth (Cawood et al., 2012; Dhuime et al., 2012), the magnitude of the terrestrial authigenic clay sink was also significantly smaller. However, marine authigenic clays could have provided an additional δ^{30}Si-depleted silica sink. Although previous authors have implicitly included a δ^{30}Si-depleted terrestrial silica sink to account for the δ^{30}Si-enriched isotopic signature of “continental” fluids, they have not explicitly considered the potential effects of a smaller volume of continental crust, nor the possibility of authigenic clays produced in marine waters.

Where is this marine clay sink? The general lack of abundant shales in some early Archean sedimentary successions (e.g., the Barberton Greenstone Belt) could be used to argue against a significant role for clays as a silica and alkalinity sink. However, this observation is subject to well-understood biases associated with incomplete preservation of different lithologies and sedimentary environments. Furthermore, Archean shales have not been a focus of most previous silicon isotope studies, although a recent bulk analysis of a 3.4 Ga shale sample from the Gorge Creek Group in the Pilbara Block yielded δ^{30}Si of −0.82‰ (Savage et al., 2013). This value is δ^{30}Si-depleted relative to the igneous average and presents an empirical observation of additional low temperature δ^{30}Si-depleted silica sinks from seawater, and supports the inference of a δ^{30}Si-depleted authigenic clay sink on the Archean Earth.

Authigenic clay production has broader implications for the Earth system because of challenges associated with closing the mass balance of chemical weathering on the early Earth. Broadly, silicate weathering provides a source of alkalinity (balancing cations) and silica to seawater. Traditionally, these cations could be removed from seawater via precipitation of carbonate salts, and if so would have played an important role in a climate feedback via silicate weathering (Walker et al., 1981). Clay minerals (e.g., smectites like montmorillonite (Na, Ca)_{0.5}(Al, Mg)_{0.5}(Si_{2}O_{5})(OH)_{2}·nH_{2}O or saponite Ca_{0.25}(Mg, Fe)_{0.75}(Si_{3}O_{10})(OH)_{2}·nH_{2}O) can provide additional sinks for cations; the degree to which silica back-reacts with the cations is important because these “reverse weathering” reactions do not consume CO_{2} (Mackenzie and Kump, 1995; Michalopoulos and Aller, 1995), a short circuit in the silicate-weathering feedback (Walker et al., 1981). Si isotope data provide a constraint on the size of these silica sinks and thus insights into the extent of “reverse weathering” reactions on the Archean Earth, with implications for alkalinity budgets and climate feedbacks.

6. CONCLUSIONS

When combined with sedimentology and petrography, Si isotopes have the potential to provide a rich record of Earth’s early silica cycle and chert petrogenesis. Observations of micro-scale, texture-specific silicon isotope heterogeneity in Archean cherts provide new insight into some of the previous applications of Si isotopes, particularly the use of δ^{30}Si as a paleothermometer. Outcrop- and thin-section-scale observations indicate a sequence of formation of silica phases in banded black-and-white cherts, which provides useful geological context for interpreting the Si isotopic compositions of different phases present within the samples. White chert bands, many of which formed as sedimentary beds of primary silica granules, have distinctly higher δ^{30}Si than cavity-filling cements, which textural relationships indicate precipitated after white chert beds had lithified. In addition to differences between early and late phases, silica isotope signatures of early well-preserved petrographic chert textures show systematic isotopic contrasts that we interpret to result from complex, multi-phase silica precipitation processes (e.g., primary silica precipitation, silica cementation, phase transformations during diagenesis, and silica addition during metamorphism). These fractionations are challenging to untangle quantitatively and are therefore problematic for the necessary assumption that cherts record a single seawater value, which is required for the application of δ^{30}Si in chert as a paleothermometer. Temperature could have played a role in initial isotopic fractionation when hydrothermal fluids interacted with ambient seawater, but any subsequent low-temperature precipitation processes associated with isotopic fractionations would have overprinted such a signal. In addition to low-temperature Si isotope fractionation processes suggested from petrographic relationships, we cannot rule out additional complexity involving several different generations of fluids and porosity throughout burial diagenesis—a possibility hinted at in several sample textures.

In the modern silica cycle, the broad range of δ^{30}Si observed in various silicon reservoirs results from silicon isotopic fractionations induced by low temperature precipitation of secondary silicates. Excluding biomineralization, the same types of precipitation reactions, associated with the same isotopic fractionations, appear to have operated
during Archean time, producing the range of δ30Si values observed in Archean rocks, which is much broader than that observed in igneous rocks. Sedimentary cherts and silicified basalts appear to represent relatively 30Si-enriched silica sinks, while banded iron formations (BIF) are known to have 30Si-depleted compositions. Authigenic clays formed during continental weathering and low temperature alteration of mafic and ultramafic crust in marine environments likely provided complementary sinks for light silica, in addition to acting as alkalinity sinks. If correct, the precipitation of clays informs a chemical weathering mass balance problem by incorporating the abundant cations (e.g., Mg, Fe, and Ca) that are released during dissolution of mafic and ultramafic rocks.

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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.2014.11.014.

REFERENCES


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