Sedimentology and geochemistry of Archean silica granules

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ABSTRACT

The production of biogenic silica has dominated the marine silica cycle since early Paleozoic time, drawing down the concentration of dissolved silica in modern seawater to a few parts per million (ppm). Prior to the biological innovation of the first silica biominal eralizing organisms in late Proterozoic time, inputs of silica into Precambrian seawater were balanced by strictly chemical silica and silicate precipitation processes, although the mechanics of this abiotic marine silica cycle remain poorly understood. Cherty sedimentary rocks are abundant in Archean sequences, and many previous authors have suggested that primary precipitation of amorphous silica could have occurred in Archean seawater. The recent discovery that many pure chert layers in early Archean rocks formed as sedimentary beds of sand-sized, subspherical silica granules has provided direct evidence for primary silica deposition. Here, we provide further sedimentological and geochemical analyses of early Archean silica granules in order to gain a better understanding of the mechanisms of granule formation. Silica granules are common components of sedimentary cherts from a variety of depositional settings and water depths. The abundance and widespread distribution of silica granules in Archean rocks suggest that they represented a significant primary silica depositional mode and that most formed by precipitation in the upper part of the water column. The regular occurrence of silica granules as centimeter-scale layers within banded chert alternating with layers of black or ferruginous chert containing few granules indicates episodic granule sedimentation. Contrasting silic on isotopic compositions of granules from different depositional environments indicate that isotopic signatures were modified during early diagenesis. Looking to modern siliceous sinter deposits for insight into silica precipitation, we suggest that silica granules may have formed via multiple stages of aggregation of silica nanospheres and microspheres. Consistent with this hypothesis, Archean ocean chemistry would have favored particle aggregation over gelling. Granule formation would have been most favorable under conditions promoting rapid silica polymerization, including high salinity and/or high concentrations of dissolved silica. Our observations suggest that granule sedimentation was often episodic, suggesting that granule formation may have also been episodic, perhaps linked to variations in these key parameters.

INTRODUCTION

The abundance and sedimentary style of chert in early Archean rocks highlight a fundamental distinction between the modern and Archean silica cycles. The early Archean silica cycle lacked the key components that dominate the modern silica cycle: continental weathering as the dominant source and silica biominal eralizing as the dominant sink for dissolved silica in marine waters (Maliva et al., 1989, 2005; Siever, 1957, 1992; Treguer et al., 1995). Although the volume of continental crust during Archean time was much less than on modern Earth (Cawood et al., 2012; Dhuime et al., 2012), Archean oceans had abundant silica sources in the form of weathering and alteration of mafic and ultramafic rocks (Siever, 1992); mass balance requires that abundant sinks must also have been present. Previous authors have suggested that banded iron formations, diagenetic silicification, and authigenic clay precipitation (Maliva, 2001; Maliva et al., 1989, 2005; Siever, 1992; Stefurak et al., 2015) were important sinks in the Archean silica cycle. It has also long been suggested that primary chemical precipitation of amorphous silica phases also played a major role as a silica sink during Precambrian time (Lowe, 1999a; Maliva et al., 2005; Siever, 1992), which is supported by the abundance of chert, especially in pre–3.0 Ga Archean sequences. However, many cherts also formed by diagenetic replacement and metasomatism of nonsiliceous primary material (Lowe, 1999a), making primary silica precipitates difficult to identify unambiguously.

Many pre–3.0 Ga cherty sequences include <10-cm-thick layers of white-weathering or translucent chert composed of nearly pure SiO2 (commonly >99 wt%), now microcrystalline quartz (Lowe, 1999a). These white chert beds are interbedded with compositionally contrast- ing beds containing primary organic sedimentary grains (Lowe, 1999a; Walsh and Lowe, 1999), mixtures of siderite and fine aluminosilicates, or hematite. These alternating lithologies are known as banded black-and-white chert, banded ferruginous (iron-bearing) chert, and banded iron formation, respectively (Fig. 1).

Stefurak et al. (2014) reported that many of the white chert bands in these units are distinct sedimentary beds composed entirely of sand-sized subspherical primary silica granules (Fig. 1) and that silica granules were a common component in other sedimentary layers as well, suggesting that silica granules were a widespread grain type and represented a significant mode of silica deposition in early Archean time. This observation augmented the emerging view that the deposition of mud-, silt-, and sand-sized chemical sand grains composed of silica (Stefurak et al., 2014), iron silicates (Rasmussen et al., 2013), and siderite (Köhler et al., 2013) was involved in the deposition of early Precambrian cherts and iron formations. This study presents additional petrographic and geochemical analyses of silica granules with the goal of providing further insight into controls on their formation and deposition.

GEOLOGIC BACKGROUND

This study focuses on chert samples collected in early Archean strata from both the Pilbara block of Western Australia and the Barberton greenstone belt of South Africa. Samples from the Pilbara block are from the Antarctic Creek Member of the 3470 ± 1 Ma Apex Basalt (Byerly et al., 2002), which forms the middle part of the Warrawoona Group (Febg 2; Van Kranendonk et al., 2002). The Antarctic Creek Member is a 4–14-m-thick unit composed largely of silicified felsic volcaniclastic sediments that also include an event bed of impact spherules and current-deposited layers of silica granules (Stefurak et al., 2014). The spherule bed has been corre-
lated with a similar 3470 ± 2 Ma unit, spherule bed S1, in the Barberton greenstone belt (Byerly et al., 2002; Glikson et al., 2004; Hickman and Van Kranendonk, 2008; Lowe and Byerly, 1986).

Samples from the Barberton greenstone belt were collected from the Buck Reef Chert Member of the Kromberg Formation, the upper Mendon Formation, and the basal Mapepe Formation (Fig. 2; Fig. DR1). Both the Kromberg and Mendon Formations are part of the Onverwacht Group, an 8–10-km-thick sequence of mafic and ultramafic rocks with thin, interbedded sedimentary chert units representing sediments deposited during periods of volcanic quiescence (Lowe and Byerly, 1999). The overlying Fig Tree Group is an ~180-m-thick sequence of immature terrigenous clastic rocks and felsic volcaniclastic units (Condie et al., 1970; Lowe and Byerly, 1999). The Mapepe Formation is the basal unit of the Fig Tree Group south of the Inyoka fault (Lowe and Byerly, 1999).

The Buck Reef Chert is a 200–400-m-thick unit of banded black-and-white and banded ferruginous chert at the base of the Kromberg Formation (Lowe and Byerly, 1999). The age of the Buck Reef Chert is bracketed by two sets of U/Pb zircon ages of 3416 ± 5 Ma from a conglomeratic unit in the lowest part of the Buck Reef Chert (Krüner et al., 1991) and 3334 ± 3 Ma from a felsic tuff from the uppermost Kromberg Formation (Byerly et al., 1996). The basal unit of the Buck Reef Chert was deposited in a shallow, restricted setting, indicated by the common occurrence of wave ripples and evaporite pseudomorphs after nahcolite (Lowe and Fisher Worrell, 1999). The middle Buck Reef Chert, composed of banded black-and-white...
chert, was deposited in a relatively open shelf environment (Tice and Lowe, 2004). The upper Buck Reef Chert represents a deeper, quieter setting marked by finely laminated, banded ferruginous chert (Lowe and Byerly, 1999; Tice and Lowe, 2004). The Buck Reef Chert is exposed in the southernmost structural belt of the Barberton greenstone belt and outcrops for over 15 km along strike, indicating that deposition of banded black-and-white chert and banded ferruginous chert was occurring continuously across relatively large areas on the Archean seafloor.

Previous studies have identified in aggregate at least five episodes of volcanism within the Mendon Formation, punctuated by the deposition of now-silicified sedimentary layers. However, most sections do not contain the full sequence, potentially due to diachronous deposition and/or local topographic highs impeding lateral continuity of volcanic units (Byerly, 1999; Decker, 2013; Lowe and Byerly, 1999; Thompson Stiegler et al., 2010). The overall age of the Mendon Formation is constrained by U/Pb zircon dating: a maximum age of $3334 \pm 3 \text{ Ma}$ from the underlying Kromberg Formation (Byerly et al., 1996); intermediate ages measured within the Mendon Formation of $3298 \pm 3 \text{ Ma}$ (Byerly et al., 1996), $3287 \pm 3 \text{ Ma}$ (Decker, 2013), and $3280 \pm 9 \text{ Ma}$ (Decker, 2013); and several ages from the base of the overlying Mapepe Formation ca. $3259 \pm 3 \text{ Ma}$ (Byerly et al., 1996; Decker, 2013; Krüner et al., 1991).

Throughout the Barberton greenstone belt, the Mendon Formation is capped by a 5–70-m-thick unit of black chert, banded black-and-white chert, and banded ferruginous chert (Lowe and Byerly, 1999). The upper Mendon Formation chert unit is overlain with apparent conformity by the sediments of the Mapepe Formation of the Fig Tree Group, which includes ferruginous shale, locally coarser clastic units, banded ferruginous chert, and hematitic banded iron formation (Lowe and Byerly, 1999). The Mendon-Mapepe contact reflects a change from a relatively quiet, deep-water regime marked by chemical, biogenic, and volcanioclastic sedimentation to a regime dominated by terrigenous and volcanioclastic sediments deposited in a range of depositional environments reflecting the initial stages of uplift and deformation in and around the greenstone belt (Lowe and Byerly, 1999; Lowe and Nocita, 1999).

**METHODS**

Outcrops, polished hand samples, and polished petrographic thin sections were used to examine silica granule properties and occurrence at a variety of scales. Some lower Mapepe Formation samples were collected from the BARB4 core of the 2011 International Continental Scientific Drilling Program (ICDP) in the Barberton greenstone belt.

Granule sizes were measured using thin sections of granules that were only slightly to moderately compacted. For aggregates of granules, individual granules were measured rather than the dimension of aggregates. Apparent grain sizes were corrected using a Matlab script based on the work of Schäfer and Teyssen (1987) to estimate the true grain sizes from observations of spherical segment diameters in thin section cuts through grains. Grains were approximated as oblate spheres. Aspect ratios were measured and averaged in order to compare diameters of volume-equivalent spheres.

Gray-scale cathodoluminescence (CL) images 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–U.S. Geological Survey Microanalysis Center at Stanford University (Stanford, California). Samples were coated with 15 nm of Au. Analysis settings were
15 kV accelerating voltage, 38 µm spot size, and 39 mm working distance.

Elements of interest (Ca, Mg, Fe, Al, and P or Ti) were mapped in carbon-coated (~14-nm-thick) polished thin sections 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, California) and the JEOL JXA-8230 SuperProbe electron probe micro-analyzer at the School of Earth Sciences Mineral Analysis Facility at Stanford University (Stanford, California). Qualitative intensity maps without background corrections were collected, operating the electron probe in wavelength-dispersive X-ray spectrometer (WDS) mode at 15 kV accelerating voltage, 100 nA (Caltech) or 10 nA (Stanford) beam current, and 100 ms (Caltech) or 10 ms (Stanford) dwell time. Color CL images were made simultaneously with WDS elemental maps using the JEOL JXA-8230 at Stanford. The sensitivity of the CL of samples to beam damage made collecting high-quality CL maps challenging.

For Si isotope analysis, select samples were made into 1 in. (2.54 cm) circular polished thin sections with 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 secondary ion mass spectrometry (SIMS) analyses. The sample set of silica granules includes three samples of banded black-and-white chert from the Mendon Formation, one sample of ferruginous chert with lenses of black-and-white chert from the Mendon Formation, and one sample of banded black-and-white chert facies of the Antarctic Creek Member. The sedimentology, lithofacies, and depositional environments adjacent to these more current-active settings. The overall sequence is consistent with deposition in a shallow, current-active setting indicating that granules were forming and being deposited in very shallow water.

RESULTS

Depositional Environments

Antarctic Creek Member

Silica granules in the Antarctic Creek Member occur within a sequence of volcanlastic sandstone, laminated gray chert, granular chert, and translucent chert. The volcanlastic sandstone is current-deposited, moderately to well-sorted, and well-rounded sandstone, often including accretionary lapilli and less often admixed silica granules. Units of volcanlastic sandstone are tens of centimeters to a meter thick, with individual beds of ~1 m thick, but they can be as thin as 10 cm and up to several meters thick. Some granule zones have lenticular geometries, thinning laterally into finely laminated black or gray chert on a scale of ~10 m. The bases of granule zones are often characterized by ferruginous granules, while the tops are characterized by iron-free granules. Dune-scale cross-stratification (~20–30 cm scale) is often observed, but, in contrast with the associated volcanlastic sandstones, grading is absent from granule layers. Some granule layers have erosional caps with evidence of scour and detrital lag deposits containing translucent chert rip-up clasts. Although silica granules occur within some volcanlastic sandstones, volcanlastic grains are not observed in granule layers.

Overall, the Antarctic Creek Member where studied is characterized by current-deposited sediments composed of volcanlastic sand or silica granules interbedded with thin beds of finely laminated chert. The large-scale cross-stratification and lenticularity of granule beds suggest that they formed in a shallow-water setting characterized by periods of moderate- to high-energy wave or current activity. The volcanlastic sandstones represent an adjacent current-deposited facies; the fining-upward character of some volcanlastic units suggests that they could be channel deposits. The finely laminated, fine-grained chert represents lower-energy depositional environments adjacent to these more current-active settings. The overall sequence is consistent with deposition in a shallow, current-active setting indicating that granules were forming and being deposited in very shallow water.

Buck Reef Chert

The sedimentology, lithofacies, and depositional environments of the Buck Reef Chert have been extensively studied by previous investigators (Lowe and Byerly, 1999; Lowe and Fisher Worrell, 1999; Tice and Lowe, 2006). The samples in this study are from the lower banded black-and-white chert facies of Tice and Lowe (2006; cf. fig. 4 of Tice and Lowe, 2006). Black chert bands are composed of coarse sand-sized carbonate grains. Brecciation and/or plastic deformation of white chert bands are common, and coarse quartz cavity-filling cements often occur beneath white chert bands or plates. The lower banded black-and-white chert facies of the Buck Reef Chert overlies the basal evaporitic unit, which includes pseudomorphs after nahcolite and wave ripples (Lowe and Fisher Worrell, 1999). The lower banded black-and-white chert facies is in turn overlain by an upper banded black-and-white chert facies (as defined in Tice and Lowe, 2006; this unit is included in the lower Buck Reef Chert facies of Lowe and Byerly, 1999) and is characterized by
fine-grained, finely laminated, and slightly ferruginous banded chert with less common breciation of the white bands. The succeeding unit consists of the banded ferruginous chert facies, which is composed of intergrown micro quartz and siderite in unweathered subsurface samples (Tice and Lowe, 2006). Locally, the Buck Reef Chert is capped by another unit of banded black-and-white chert up to 60 m thick (Lowe and Byerly, 1999). The Buck Reef Chert samples included in this study are from the lower black-and-white chert unit. Our observations support the interpretation of Tice and Lowe (2006) that this facies represents a shelfal environment above storm wave base at water depths that were probably between 15 and 200 m.

Upper Mendon Formation

Across the Barberton greenstone belt, the uppermost Mendon Formation is composed of ~20–75 m of black, banded black-and-white, and banded ferruginous chert (Lowe and Byerly, 1999). The upper Mendon Formation black chert and the black layers in banded black-and-white chert are dominated by finely plane-laminated, silica-cemented deposits of fine-grained carbonaceous matter and micaceous grains, perhaps representing clays or altered volcaniclastic particles. Many black cherts show a fine-grained granular texture on weathered surfaces and probably represent mixtures of fine ash and carbonaceous matter. Many sections contain <2-cm-thick graded beds of fine ash, but these generally lack current structures and probably represent air-fall material. Graded beds of accretionary lapilli occur in some sections. Current structures are represented mainly by small, widely spaced cross-lamination. Scour features include small, 2–5-cm-deep and 1–15-cm-wide scour pits, but large-scale cross-stratification, scour, and evidence for string current activity and erosion are absent.

Brecciation of white bands in banded black-and-white chert is less common than in the lower black-and-white banded chert facies of the Buck Reef Chert, likely reflecting a lower-energy paleoenvironment. Banded ferruginous chert of the upper Mendon Formation is defined by alternating white chert bands, and finely laminated ferruginous chert bands. Ferruginous chert is often slightly rust-colored on the surface, probably representing a sideritic component at depth.

The upper Mendon Formation represents a relatively quiet depositional setting below storm wave base and therefore a slightly deeper water environment (>~200 m water depth) than the lower black-and-white banded chert facies of the Buck Reef Chert.

Lower Mapepe Formation

Within the study area in the central part of the Barberton greenstone belt, the Mapepe Formation has an apparently conformable contact with cherts of the upper Mendon Formation (Lowe and Byerly, 1999). This contact is widely marked by a bed of spherules formed through a large meteorite impact (Lowe and Byerly, 1986). The Mapepe Formation itself shows a wide variety of facies deposited in a range of environments from shallow to deep water that vary from one structural belt to another within the central and southern domains of the Barberton greenstone belt. These complex facies and depositional settings reflect the initiation of uplift and deformation within the belt, providing sources of clastic sediment and adjacent basins for its deposition and the accumulation of associated deep-water, generally iron-rich chemical sediments. Samples from the Mapepe Formation included in this study are from ferruginous lithofacies representing relatively quiet, deep-water sedimentation—ferruginous cherts and banded iron formation.

Petrography and Sedimentology of Silica Granules

Despite some variability, several key properties characterize granules from all depositional settings. Granules are everywhere sand-sized sub-spherical grains with shapes ranging from nearly spherical to oblate spheroidal. The mean diameters for volume-equivalent spheres from representative samples from a variety of depositional settings range from 216 to 623 μm (fine- to coarse-grained sand; Table 1). In addition, all granules appear to have been relatively soft and easily compacted. Granules are now composed of relatively pure microquartz, and the majority of granules lack internal structures such as concentric laminations, irregular distributions of trace impurities, relict textures reflecting a different primary mineralogy, or cracks formed during dehydration and shrinkage of an initially hydrated gel phase. Some iron-associated granules do display a crude structuring, with interiors containing trace oxides and rims with more abundant iron phases.

Some white bands within banded black-and-white chert of the Buck Reef Chert and the upper Mendon Formation are composed exclusively of granules. These bands are generally 1–10 cm thick. Both matrix-supported (Fig. 1C) and grain-supported (Fig. 3B; Fig. DR1 [see footnote 1]) textures are observed within granule bands. Although structures like cross-laminations and grading are not common, they do occur in rare examples (Fig. DR1 [see footnote 1]). While many white bands are tabular and laterally continuous, others lens out laterally, and local brecciation is common (Fig. 4A). The bands of silica granules have sharp contacts with the adjacent black chert bands, which are composed primarily of silica containing detrital organic grains (Fig. 3B). Compaction of granules is common within the

<table>
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<th>Sample name*</th>
<th>Lithology</th>
<th>Depositional environment</th>
<th>Aspect ratio</th>
<th>μ,raw (μm)</th>
<th>σ,raw (μm)</th>
<th>Φ,raw</th>
<th>μ,corrected (μm)</th>
<th>σ,corrected (μm)</th>
<th>Equivalent sphere diameter (μm)</th>
<th>Φ**</th>
<th>Grain size</th>
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</tr>
</tbody>
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*See supplementary Table DR1 for more detailed stratigraphic and location information for these samples (text footnote 1).

μ—mean granule diameter.

σ—standard deviation of granule diameters.

**Raw** values refer to the grain diameters measured from thin sections prior to being corrected for the effects of the thin section providing random cuts through grains, as described in the methods section.

**Φ = −log (grain diameter in mm); Φ is the Krumbein phi scale, a standard logarithmic expression of grain size.**
white bands (maximum aspect ratios of ~9:1; Fig. 4), often obscuring primary textures. The surrounding matrix is microquartz, visually distinguishable due to trace organic matter or siderite inclusions. In contrast with the common compaction of silica granules in white bands, carbonaceous grains in adjacent black chert bands typically show little to no compaction. This is seemingly in conflict with the sequence of cementation implied by chert plate breccias, where white chert bands are often deformed as relatively rigid and impermeable plates while the surrounding carbonaceous sediment was still un lithified. These observations suggest that, unlike silica granules, many organic grains were at least partially cemented very early, prior to deposition, making them more resistant to compaction. At the same time, in situ silica cementation occurred much earlier in pure layers of silica granules compared to layers of carbonaceous sediment.

Figure 3. Outcrop (A) and thin-section (B–G) images of representative occurrences of silica granules associated with black-and-white banded chert and black chert. (A) Outcrop photo of white chert plate breccia, Buck Reef Chert (locality Buck Reef Chert). (B) Sharp contact between silica granule layer (white chert band) and adjacent detrital organic layer (black chert band), upper Mendon Formation (locality SAF 521). (C) Silica granules mixed with finer-grained detrital organic grains, lower Mapite Formation (locality BHR-02). (D) Large silica granules associated with a variety of organic and volcanic grain types, upper Mendon Formation (locality SAF 521). (E) Silica granule intraclast within an intraclast breccia, upper Mendon Formation (locality SAF 186). (F) Silica granules, intraclasts, detrital organic grains, and volcanic grains within an intraclast breccia bed from the same sample as E, upper Mendon Formation (locality SAF 186). (G) Organic grains and silica granules from a black chert, upper Mendon Formation (locality CQ-01). Silica granules (arrows) occur within the bed and at the base of the overlying graded bed. These granules are similar in size to and in some cases slightly coarser than the associated detrital organic grains. See supplementary Table DR1 for additional stratigraphic information for samples shown and supplementary Figure DR1 for map of sample localities (see text footnote 1).
Sedimentology and geochemistry of Archean silica granules

In the Antarctic Creek Member, coarse sand-sized, slightly compacted silica granules (aspect ratios in the range of 1:2.1–5:1, mean aspect ratio 1.9:1) occur in 10-cm- to 1-m-thick, grain-supported and often cross-stratified beds. Some granules from the Antarctic Creek Member are composed purely of microquartz surrounded by drusy quartz cements (Figs. 5A–5B). Other granules contain iron minerals closely associated with the granules as rims of fine iron-oxide grains (Figs. 5C–5D) and/or dispersed evenly throughout granule interiors (Figs. 5E–5F).

Lenticular centimeter-scale layers of granules occur within ferruginous chert of the Mapepe Formation, which consist of finely laminated sideritic chert (Figs. 1D–1F). Some of these granules are relatively pure silica (Figs. 1F and 5G–5H), while others have trace inclusions of micron-scale iron oxides (Fig. 1E). Most granules are slightly to moderately compacted with mean aspect ratios of ~2:1 (Fig. 4). The surrounding matrix or cement is primarily microquartz, although often containing finely dispersed hematite. The lenticular granule layers could represent cross sections of starved ripples, although the examples examined in this study do not display any cross-lamination.

Silica granules also occur as centimeter-thick lenticular layers within banded iron formation in the lower Mapepe Formation (Figs. 1G–11 and 5I). Excluding the granule lenses, the Mapepe banded iron formation is defined by finely laminated hematitic, sideritic, and cherty layers with some interbedded layers of claystone or mudstone. The banded iron formation-associated granules are composed of relatively pure silica, while the surrounding matrix/cement contains trace hematite and siderite. Granules are slightly to moderately compacted with mean aspect ratios of ~2:1 (Fig. 4). As with granules in the ferruginous chert, the lenticular layers in the banded iron formation may represent starved ripple forms, but we have not observed cross-laminations that would confirm this interpretation, and some granule layers appear to be matrix-supported (e.g., Fig. 1I).

Geochemistry

Electron Microprobe Maps

Electron probe elemental maps confirm petrographic observations showing that granules are essentially pure SiO2 (Fig. 6; Figs. DR4 and DR5 [see footnote 1]). Some granules associated with other iron-bearing facies contain trace inclusions of hematite (Fig. 6). Iron-bearing carbonates, primarily siderite with minor ankerite and ankeritic dolomite, occur within the matrix to the granules, but not within the granules themselves. Granule samples were mapped for either P or Ti, two poorly soluble elements that might reveal possible precursor mineralogy, but there was essentially no P or Ti in any of the samples analyzed. Occurrence of Al was limited to matrix material with trace amounts of clay minerals, but these phases do not occur in granule layers.

Cathodoluminescence

Silica granules and the adjacent matrix or cement are not distinguishable in gray-scale CL (Fig. DR6 [see footnote 1]), but some granules are distinguishable using color CL (Fig. 6C). In the example shown in Figure 6, granules containing fine trace inclusions of hematite are distinguishable from the surrounding cement by their brighter luminescence. Petrographically, the granules appear to be compositionally variable; similarly, CL brightness varies between granules. CL maps do not reveal any internal textures or structuring (e.g., concentric layering) apart from mirroring petrographic textures reflecting slight variations in the abundance of hematite inclusions. The peak emission wavelength is ~640 nm (red). Apart from intensity, there were no distinct or systematic differences between CL spectra within the granules versus within the surrounding cement.

Si Isotope Geochemistry

Si isotopes are fractionated by many low-temperature precipitation processes and can be useful in differentiating different generations of silica and in tracking the cycling of silica (Chakrabarti et al., 2012; Heck et al., 2011; Marin-Carbonne et al., 2012; Stefurak et al., 2015; van den Boorn et al., 2007, 2010). The Si isotopic compositions of silica granules measured in this study had a mean δ30Si of ~0.28‰ and standard deviation of 1.42‰ (n = 338), although analysis of variance (ANOVA) and multiple comparison tests indicated that sample means of granules associated with banded black-and-white chert, banded iron formation, and ferruginous chert were significantly different (Fig. 7; Tables DR2 and DR3 [see footnote 1]). Banded black-and-white chert-associated silica granules had mean δ30Si of 0.77‰ and standard deviation of 0.45‰ (n = 189), while banded iron formation-associated granules had mean δ30Si of ~0.70‰ and standard deviation of 0.67‰ (n = 68), and slightly ferruginous granules occurring in a lens within ferruginous shale had a mean δ30Si of ~2.36‰ and standard deviation of 0.83‰ (n = 81). While neither the banded iron formation–associated nor the ferruginous chert–associated silica granules had significantly different mean δ30Si than the adjacent matrix or cement (Fig. 7), ANOVA and multiple comparison tests indicated a small, but statisti-

Figure 4. Measurements of aspect ratios of silica granules associated with different lithofacies. Mean (circle), standard deviation (line), minimum (diamond), and maximum (square) are given for each data set. Ellipses next to the y-axis indicate dimensions for aspect ratios of 2, 4, 6, and 8. Abbreviations: BBWC—banded black-and-white chert, FC—ferruginous chert, and BIF—banded iron formation.

Within nonbanded chert of the upper Mendon Formation, granules also commonly occur mixed in detrital beds with other sedimentary grain types, including: carbonaceous grains and intraclasts of carbonateous chert, volcanic grains and intraclasts of volcaniclastic sediments, and chert band intraclasts (Figs. 3C–3G). In occurrences with organic grains, the mean aspect ratios of silica granules are similar to other types of occurrences (2:1; Fig. 4), although in some cases, particularly when the organic material occurs as dispersed, very fine-grained inclusions rather than as clearly detrital grains, the silica granules can be quite compacted (~10:1). Within intraclast breccia units, maximum compaction observed (~2.5:1) is much less severe, likely reflecting differences in timing of silica cementation between these lithofacies.

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cally significant difference in the sample means of banded black-and-white chert–associated granules (mean $\delta^{30}$Si = 0.77‰) and the associated microquartz matrix (mean $\delta^{30}$Si = 1.00‰; Table DR2 [see footnote 1]). The three banded black-and-white chert samples and the ferruginous chert sample were all collected from the same continuous stratigraphic section (Fig. DR7; Table DR1 [see footnote 1]; the banded black-and-white chert samples were collected within the upper 3 m of the Mendon Formation, and the ferruginous chert sample was collected from 54 m into the lower Mappe Formation. The granules analyzed in the three banded black-and-white chert samples have similar $\delta^{30}$Si distributions and nonstatistically significant means (Fig. 7B), but they contrast strongly with the ferruginous chert sample, indicating in this case there is some relationship between observed granule Si isotopic composition and lithofacies and/or stratigraphic position. Silica granules from banded black-and-white chert have similar Si isotopic compositions to bulk analyses of samples from van den Boorn et al. (2007, 2010) interpreted to have formed via silicification by seawater silica, while the iron-associated silica granules in banded iron formation and ferruginous chert are broadly consistent with many previous analyses of various Archean banded iron formations finding them to have distinctly low $\delta^{30}$Si compositions (Fig. 7C; Andre et al., 2006; Chakrabarti et al., 2012; Delvigne et al., 2012; Ding et al., 1996; Heck et al., 2011; Steinhoefel et al., 2009, 2010).

DISCUSSION
Petrography and Environmental Distribution

The unstructured nature of iron-free granules and lack of relict textures resulting from diagenetic transformations differentiate silica
Some iron-associated granules do show a rudimentary structuring defined by rims of iron oxides (Figs. 1E and 5C–5F). Some of these granules also include trace iron phases within the granule interiors (Figs. 1E and 5E). Although the distribution of iron within granules is slightly heterogeneous, it does not define concentric laminations as in oolithic iron granules that occur in some granular iron formations (Beukes and Klein, 1990; Dimroth and Chauvel, 1973; Goode et al., 1983; Gross, 1972; Simonson, 1987, 2003). This indicates the coprecipitation of silica and iron phases, rather than alternating deposition of silica and iron layers. The iron-rich rims, on the other hand, appear to have accumulated after silica deposition ceased. These distribution patterns of iron in and around silica granules are both consistent with the hypothesis that granules formed rapidly, in some cases incorporating iron, likely as iron oxyhydroxides or carbonates. Afterwards, additional iron phases could collect on the granule surfaces, perhaps as they were reworked by currents.

Silica granules occur in many depositional settings and water depths, from shallow subtidal (Antarctic Creek Member) to shelfal in the Buck Reef Chert to deep basinal (Mapepe banded iron formation). They also occur in different types of deposits, from lenticular or tabular layers composed purely of granules (Fig. 1), to intraclast breccia units with a variety of grain types (Figs. 3D–3F), to black chert composed mostly of organic grains with a minor component of silica granules (Figs. 3C and 3G). The similarities of granule properties, including size, shape, susceptibility to compaction, lack of internal structure, and composition, across a wide range of depositional environments also suggest that the granules share a common origin. The uniformly sand-sized, subospherical, well-rounded granules are inconsistent with formation as rip-up clasts, which would be expected to display a range of grain sizes, shapes, and internal textures. The occurrence of granules in shallow-water depositional environments indicates that granules probably formed within the shallow water column. Within the deepest-water lithofacies considered here, the banded iron formation of the lower Mapepe Formation, granule layers are relatively thin and irregularly spaced (Fig. 1H). This pattern suggests either that there were some processes preventing the delivery or preservation of granules in deep-water environments (e.g., obliteration during diagenesis) or that conditions for granule formation were more favorable in the shallow water column above shelfal environments, such that current transport was required for granules to be delivered to more basinal environments.

One notable aspect of silica granules is their relationship to the phenomenon of banding: many relatively pure, whitish to translucent chert bands or lenses within banded black-and-white chert and banded ferruginous chert show granular textures and were therefore deposited as beds of silica granules. In theory, hydraulic sorting could explain this juxtaposition of pure granule layers with layers of contrasting composition if both layers were current-deposited and there were density contrasts between granules and other grain types. These conditions are inconsistent with a number of observations, which suggest that the two band types represent separate depositional events. The compositional contrasts between white chert bands composed of silica granules and the adjacent black chert bands (Fig. 3B) or laminated ferruginous sediment (Figs. 5G–5I) are sharp rather than gradational, and silica granules commonly occur as a minor component within black chert bands.
neither of which is consistent with hydraulic sorting of compositionally distinct layers as parts of the same depositional event. Evidence of deposition by currents does not occur consistently throughout banded chert facies: Although the carbonaceous grains in some black chert bands (e.g., within the lower facies of the Buck Reef Chert; see Tice and Lowe, 2006) appear to have been deposited and/or reworked by currents, granular white chert bands can also be juxtaposed with more fine-grained carbonaceous or ferruginous chert facies representing quiet suspension settling. Hydraulic sorting alone cannot explain the occurrence of relatively pure granule layers juxtaposed with different primary sediment types and in different depositional environments. Instead, deposition of silica granules must have occurred only episodically.

Composition of Granules and Associated Grains, Matrix, and Cements

The composition of other grains and matrix materials associated with silica granules depends on the depositional setting. When cements are present, they are always silica cements, supporting the inference that the concentration of dissolved silica in pore fluids was high, either due to the occurrence of primary amorphous silica (e.g., the granules themselves) or as a consequence of a high concentration of silica in seawater. Black cherts are commonly dominated by silicified organic grains and a microcrystalline matrix often containing trace carbonaceous material, while deeper-water iron-rich sediments juxtapose lenticular granule layers with much finer-grained laminated ferruginous sediment composed of mixtures of hematite, siderite, phyllosilicates, and silica. Similarly, the matrix to silica granules within black chert is microquartz that commonly contains trace organic matter, while the matrix within ferruginous settings contains fine hematite, siderite, and silica. The Antarctic Creek granules are notable in the co-occurrence of iron-bearing minerals as trace constituents within granules. Most ferruginous chert-associated and banded iron formation–associated granules in Barberton samples contain little to no iron (Figs. 1F, II, and S5–S1), except for one isolated example, a lens of loosely packed, grain-supported, well-sorted, subangular iron-bearing granules (Fig. 1E) occurring within laminated ferruginous chert (Fig. 1D) within 2 cm of a more typical silica granule layer (Fig. 1F). These granules appear to be current-deposited and may represent a turbidite composed of grains transported from shallower water, which could explain the contrast in composition, sorting, rounding, packing, and compaction with the adjacent granule lens.
The overall CL intensity of microquartz from the cherts in this study is low, but color CL allows the recognition of some contrasts in CL intensity that mirror petrographic textures (Fig. 6). The peak CL wavelength observed using color CL (Fig. 6) is ~640 nm, an intrinsic wavelength observed in most quartz due to nonbridging oxygen hole centers (Götze et al., 2001). Red emissions strongly dominate, and overall CL intensity is relatively low, both of which are common features in low-grade metamorphic rocks (Boggs and Krinsley, 2006; Boggs et al., 2002). The samples do not display spectral peaks indicative of structural substitutions of other elements like Fe$^{3+}$ (705 nm) or Al (several possible peaks in the green or blue range; Götze et al., 2001).

**Granule Compaction**

Most iron-free granules appear to have been soft when deposited, based on the common occurrence of slight to severe postdepositional compaction. The degree of compaction varies between samples (Fig. 4). Silica granules within white bands of banded black-and-white chert include the most severely compacted examples, with black chert precursor sediments would have experienced lower compaction stresses (Bekker et al., 2001). The degree of compaction varies, with the result that granules mixed with black chert precursor sediments would have experienced lower compaction stresses than in grainstone-like granule layers. In the case of intraclast breccias, the abundant lithified intraclasts (Figs. 3E–3F), often including angular chert plate fragments, could have helped protect the relatively minor component of silica granules from the effects of compaction. In the case of deeper-water ferruginous chert–associated or banded iron formation–associated granule lenses, the less-extreme compaction likely resulted from some combination of aging and strengthening of the amorphous silica during transport and/or settling, earlier cementation due to differences in diagenetic conditions, and a slower background depositional rate than that of banded black-and-white chert, resulting in smaller forces exerted by overlying sediment prior to cementation.

Silica granules containing iron from the Antarctic Creek Member (Figs. 5E–5F) and an isolated lens in ferruginous chert of the Mapepe Formation (Fig. 1E) include some oblong grain shapes, but these grains are loosely packed, and the axes of grain elongations are often not aligned, indicating that many of these grains were irregular in shape when they were deposited, rather than being deformed during burial. In contrast with the uniformly rounded nature of iron-free silica granules, some iron-bearing silica granules are angular to subangular. These observations both suggest that coprecipitation of silica and iron resulted in earlier lithification of iron-bearing silica granules, making them less likely to be broken or abraded by grain collisions but less susceptible to postdepositional compaction.

**Relationship to Granular Iron Formation**

The silica granules described here bear some resemblance to granules in granular iron formation in that they are well-rounded, uniquely Precambrian chemical sand grains (Bekker et al., 2010, 2014; Klein, 2005; Simonson, 2003; Trendall, 2002). Some granular iron formations contain oolitic grains with concentric layering, although non-oolitic iron granules are much more common (Bekker et al., 2010; Beukes and Klein, 1990; Dimroth and Chauvel, 1973; Goode et al., 1983; Gross, 1972; Simonson, 1987, 2003). Although granular iron formations are rich in SiO$_2$ (~50 wt%), they also contain a significant amount of iron (>15 wt%, but commonly ~30 wt%) in the form of iron oxides or iron silicates (Bekker et al., 2010, 2014; Klein, 2005; Simonson, 2003; Trendall, 2002). While the silica granules described here co-occur with iron oxides or carbonates in some settings, they also commonly occur without associated iron minerals. Even when iron is associated with the silica granules, it is only a trace constituent within the chert. The silica granules here are clearly distinct from the iron-oxide and iron-silicate granules that occur in granular iron formations.

At the same time, many previous authors have reported the occurrence of silica-rich granules in addition to iron-rich granules within granular iron formations (Bekker et al., 2010; Beukes and Klein, 1990; Dimroth and Chauvel, 1973; Goode et al., 1983; Gross, 1972; Simonson, 1987, 2003). These silica-rich granules appear to commonly have trace inclusions of iron phases, much like the iron-bearing granules we observe in the Antarctic Creek Member (Figs. 1E–1F) and the isolated lens in the Mapepe Formation (Fig. 1E). Furthermore, most granular iron formations are also current-reworked deposits of sand-sized chemical grains representing relatively shallow shelfal environments (Beukes and Klein, 1990; Gross, 1972; Simonson, 1985, 2003). The iron-free and iron-bearing silica granules detailed in this study may therefore represent points on a spectrum of silica granule compositions, with shallow-water granules apparently containing more iron than those deposited in deeper-water environments. The main distinction, therefore, between the shallow-water ferruginous chert–associated silica granules in this study and granular iron formations is the absence of associated iron-oxide or iron-silicate granules. Since most granular iron formations are latest Archean or Proterozoic in age (Bekker et al., 2014; Simonson, 2003), this distinction could be related to the rise of oxygen.

**Si Isotope Geochemistry**

The contrasts between the $\delta^{30}$Si compositions of silica granules and associated matrix and/or cement from banded black-and-white chert (three samples, 316 spot analyses), banded iron formation (one sample, 160 spot analyses), and ferruginous chert (one sample, 105 spot analyses) are striking (Fig. 7), although it is important to point out that this is a relatively small data set and therefore may not reflect the full range of $\delta^{30}$Si variability within each of these lithofacies. At the same time, the data presented here are broadly consistent with analyses from previous Si isotopic studies. The granules from banded black-and-white chert are similar in Si isotopic composition to previous analyses of chert not associated with iron, interpreted to reflect a seawater $\delta^{30}$Si signature (Fig. 7C; van den Boorn et al., 2007, 2010; Stefrak et al., 2015). Similarly, the banded iron formation and ferruginous chert samples are isotopically depleted relative to the mean value of bulk silicate earth ($\delta^{30}$Si = −0.4%), consistent with previous analyses of Archean banded iron formations (Fig. 7C; Andre et al., 2006; Chakrabarti et al., 2012; Delvigne et al., 2012; Ding et al., 1996; Heck et al., 2011; Steinhofel et al., 2009, 2010). There are two main explanations for these distinctions: Either (1) the mechanisms forming these different granule types had drastically different Si isotopic fractionation factors ($\varepsilon = \delta^{30}$Si$_{fluid} - \delta^{30}$Si$_{mineral}$) between fluid and precipitate, or (2) a substantial amount of silica from isotopically contrasting fluids was contributed to each granule association during initial granule formation and/or diagenesis (e.g., the granules associated with ferruginous chert incorporated silica from fluids of much lower $\delta^{30}$Si than the banded black-and-white chert granules).

Previous authors have suggested that Si isotopic fractionation associated with coprecipitation of silica and iron oxyhydroxides (hematite precursor) was responsible for the low $\delta^{30}$Si
values observed in banded iron formations (Chakraborti et al., 2012; Fischer and Knoll, 2009). In theory, this could explain why silica granules with ferruginous inclusions (Fig. 7A, “FC Fe granules”) have lower $\delta^{30}$Si than the iron-free silica granules (Fig. 7A, “BIF granules”), i.e., that Si isotopic fractionation was enhanced by coprecipitation with iron in the former type but not the latter. However, the iron-poor silica granules in the banded iron formation sample still have significantly lower $\delta^{30}$Si than the banded black-and-white chert granules, so differences in fractionation during primary granule formation cannot explain the full range of variability observed in our data.

The different granule types must therefore have incorporated silica from isotopically contrasting fluids: higher $\delta^{30}$Si for the shallower-water banded black-and-white chert–associated granules, intermediate $\delta^{30}$Si for the banded iron formation–associated granules, and surprisingly low $\delta^{30}$Si for the ferruginous chert–associated granules. Since banded iron formation represents the deepest-water depositional environment of these three lithofacies, there is no linear relationship between paleo-water depth and Si isotope composition of silica granules. The lack of isotopic contrast between granules and the adjacent matrix or cement in the iron-associated lithologies (Fig. 7A) furthermore indicates that the cements precipitated from fluids of similar Si isotopic composition to the adjacent granules, perhaps due to exchange of silica during the stages of dissolution and recrystallization characterizing phase transformations from opal-A to opal-CT and finally to microquartz. These inferences fit with the previous suggestion that there was a $\delta^{30}$Si chemocline in Precambrian oceans (Chakraborti et al., 2012), but they are seemingly in conflict with the conclusion that all granules originated in relatively shallow water (Stefurak et al., 2014), which would suggest that they should have shared similar initial isotopic compositions. There are two main scenarios that could have produced the observed patterns: (1) primary Si isotopic variability inherited from depth-related and/or lateral variations in seawater $\delta^{30}$Si, or (2) overprinting of a smaller range of primary granule $\delta^{30}$Si compositions by distinct, locally derived $\delta^{30}$Si signatures during diagenesis.

In reality, both primary and diagenetic processes probably contributed to the observed Si isotopic variability of silica granules, although a larger sample set is required to better evaluate their relative contributions. In one example (Fig. DR8 [see footnote 1]), $\delta^{30}$Si does appear to be sensitive to primary textural boundaries, with lower $\delta^{30}$Si in cements and some granules (mean $\delta^{30}$Si = –3.9‰), while other adjacent granules have higher $\delta^{30}$Si (mean $\delta^{30}$Si = –2.0‰). This distinction indicates that, at least in this case, fluids with a particularly light $\delta^{30}$Si value interacted with these granules during diagenesis. Given the typical fluid-precipitated Si fractionation factor of −1% to −2% (Basile-Doelsch et al., 2005; Ding et al., 1996; Geilert et al., 2014), cements with $\delta^{30}$Si of −3.9‰ likely precipitated from a fluid with a $\delta^{30}$Si value in the range of −2‰ to −3‰, which is significantly lighter than estimates for Archean seawater, with $\delta^{30}$Si in the range of +4‰ to +5‰ (Abraham et al., 2011; van den Boom et al., 2007, 2010), or analyses of modern hydrothermal fluids, which yielded a $\delta^{30}$Si of −0.3‰ (De La Rocha et al., 2000).

Si isotopic compositions of these depleted require light $\delta^{30}$Si generated via one or more previous stages of precipitation/dissolution or adsorption/desorption. Both banded iron formation– and ferruginous chert–associated granules are adjacent to layers that are rich in iron. Adsorption of silica onto iron oxides is known to fractionate Si isotopes (Delstanche et al., 2009). Release of this adsorbed silica with light $\delta^{30}$Si could have contributed to the light isotopic signatures observed in our banded iron formation and ferruginous chert granule samples. The laminated ferruginous chert adjacent to the lenses of granules also contains phyllosilicates. Authigenic clay minerals contain light $\delta^{30}$Si compositions (mean $\delta^{30}$Si = −1.4‰) due to preferential incorporation of $^{30}$Si (De La Rocha et al., 2000; Ding et al., 1996; Douthitt, 1982; Georg et al., 2009; Opfergelt et al., 2010, 2012; Ziegler et al., 2012), so any release of silica from these phases during diagenesis could also have contributed to pore fluids with low $\delta^{30}$Si compositions. The behavior of Si isotope compositions of chert during diagenesis has important implications for determining which silica phases record seawater chemistry rather than diagenetic fluids. The variability of $\delta^{30}$Si compositions of silica granules observed here suggests that future analyses of large silica granule data sets can provide important insights into seawater $\delta^{30}$Si and the fractionation of Si isotopes under different diagenetic conditions.

Processes of Granule Formation

Silicic acid molecules ($H_2SiO_4$) combine and grow into particles by polymerization. This polymerization usually occurs via dehydration reactions that convert two silanol groups into a siloxane bond (i.e., $R$-$Si-O$-$H + H$-$O$-$Si$-$R \leftrightarrow R$-$Si-O$-$Si$-$R + H$-$O$). The aqueous chemistry of silica at low temperatures is dominated by kinetics: Although a solution is technically saturated with respect to quartz at 6–10 ppm SiO2, monosilicic acid is relatively stable in solution up to 100–200 ppm (the solubility of opal-A, depending on temperature; Iler, 1979). In solutions supersaturated with respect to opal-A, silica monomers polymerize first to dimers, then cyclic polymers, and finally to compact spherical particles, which grow via Ostwald ripening to stable colloidal particles 5–10 nm in diameter (above pH 7; Iler, 1979).

Modern siliceous sinters provide a natural system for studying silica precipitation that is potentially analogous to Archean oceans. Some modern and ancient sinter deposits contain siliceous oncocoids 1–10 cm in diameter (Guidry and Chaulet, 2003; Jones and Renaut, 1997; Jones et al., 1999, 2001; Lynne et al., 2008; Renaut et al., 1996) or pisoids (Lowe and Braunstein, 2003; Walter, 1976; Walter et al., 1996). These large siliceous grains are not appropriate analogues for silica granules: Apart from their size discrepancy, these grains are irregular in shape and often contain relatively insoluble impurities (e.g., organic matter, iron oxides, clays) that distinguish the wrinkly or irregular concentric internal laminations visually and geochemically. Although some of these features could be overprinted during diagenesis, it is unlikely that traces of a complex original structure, if similarly defined by insoluble phases, would be eliminated in all grains during lithification.

Opal-A “microspheres” commonly occur in siliceous sinter deposits (Braunstein and Lowe, 2001; Jones and Renaut, 2007; Lowe and Braunstein, 2003; Lynne and Campbell, 2004; Lynne et al., 2005, 2008; Rodgers et al., 2004; Smith et al., 2001, 2003; Tobler et al., 2008). These microspheres are generally <5 μm in diameter, with mean diameters of <2 μm (Jones and Renaut, 2007; Rodgers et al., 2004). Some microspheres show nanoscale substructure (Rodgers et al., 2004; Smith et al., 2003), indicating that they formed via aggregation of nanometer-scale colloidal particles. Once silica colloids reach a certain size (~5 nm), aggregation reduces the interfacial free energy more effectively than individual particle growth, resulting in the formation of microspheres (Iler, 1979; Smith et al., 2003). Smith et al. (2003, p. 577) suggested that the apparent maximum size limit of microspheres in sinter deposits (~10 μm) is a consequence of a similar principle: “Once silica particles grow to a certain size, there is very little change in energy content with surface area, and there is an optimum upper limit on the size to which particles may grow.”

This consistent upper bound on the diameters of microspheres from modern siliceous sinters is two orders of magnitude less than the average size of the Archean silica granules described here. Although there is some systematic size variation observed in sinter microspheres,
thought to be related to variations in environmental conditions (e.g., pH, salinity, temperature, dissolved silica concentration; Rodgers et al., 2004), these variations are still on the order of a few microns. To the extent that the optimum microsphere size appears to be a function of surface free energy and a small range of environmental factors, silica granules cannot be easily explained as extraordinarily large opal-A microspheres.

In the modern Akinomiya siliceous sinter deposit (Japan), examined and sampled as part of this study, sand-sized subspherical granules of amorphous silica occur along the edges of some pools (Fig. 8). Some granules clearly formed around nuclei of β-quartz or other local lithic material (Fig. 8B), but many do not have nuclei identifiable in thin section (Figs. 8A and 8C), although this could be a result of random cuts through grain interiors rather than a true absence of nuclei. The cortices of these granules

Figure 8. Thin-section images of subspherical, sand-sized amorphous silica granules from the modern Akinomiya siliceous sinter deposit in Japan. The sinter is located at 38°57’32”N, 140°33’26”E, and is 0–80 yr old (Nakanishi et al., 2003). (A) Loosely packed sinter granules. The blue coloration in the pore spaces between the samples is epoxy. (B) Sinter granule with a euhedral volcanic β-quartz grain as its nucleus and thin layers of isopachous silica cement along the grain edges. (C) Somewhat irregularly shaped granule. Silica microspheres of 30–50 μm in diameter can be distinguished along the edges of the granule, but the interior is structureless. (D) Distinguishable silica microspheres within a sinter granule. (E) Geopetal fill composed of silt-sized silica microspheres, possibly distinguishable due to extremely thin coatings of impurities. (F) Close-up of layered microsphere fill from E.
appear to have formed by aggregation of silica spheres 10–50 \( \mu \text{m} \) in diameter; these spheres are often clearly visible along granule edges (Fig. 8C) and, in limited cases, in incompletely cemented granule interiors (Fig. 8D). Silica microspheres also settled out of suspension as small geopetal fills (Fig. 8E–8F). Many of the microspheres observed here are larger than the apparent maximum microsphere size (~10 \( \mu \text{m} \)) observed in other sinter deposits. This could be due to differences in environmental conditions or to an additional intermediate stage of aggregation that produced spherical particles tens of microns in diameter. The Akinomiya sinter deposit is only ~80 yr old (Nakanishi et al., 2003), and most of the granules have little discernible internal structure apart from the nucleus/cortex boundary—they lack concentric laminations analogous to ooids. Some granules have finely layered rims of isopachous silica cements that appear to have precipitated after the granules were deposited (Fig. 8B). The Akinomiya sinter granules could potentially be analogous to Archean silica granules, although whether the modern sinter granules can form without nuclei is still an open question.

Polymerization and aggregation are common processes in silica precipitation at multiple spatial scales, be it the initial polymerization of nanometer-scale colloids, the aggregation of nanometer-scale colloidal particles to form microspheres, or, as observed in the Akinomiya sinter deposit, the aggregation of rather large microspheres to form sinter granules. We therefore hypothesize that Archean silica granules may have formed via multistage aggregation analogous to processes observed in siliceous sinters, but including an additional stage or stages of aggregation of microspheres to form macroscopic silica granules (Fig. 9).

These additional stages of aggregation are not common in modern siliceous hot springs—most do not contain silica granules like those in the Akinomiya sinter deposit. Several aspects of the depositional conditions make modern sinters imperfect analogues to Archean marine environments. For example, the maximum water depths in siliceous hot springs are shallow, and currents are variable but generally unidirectional, both of which could affect the length of time during which particles of a particular size stay in suspension. Many siliceous hot springs also have brackish alkali-chloride waters with very high concentrations of silica (400–500 ppm; Jones and Renault, 2007; Rodgers et al., 2004); neither of those conditions is a particularly good fit for Archean oceans, which are thought to have been perhaps supersaline (Knauth, 2005) and only saturated to moderately supersaturated with respect to amorphous silica (Siever, 1992). Salinity and silica concentration are both important parameters for the silica system and could well explain the differences between modern siliceous sinters and Archean marine environments.

Previous authors have suggested that the concentration of silica in the Archean ocean was at or above the saturation of amorphous silica (Maliva et al., 2005; Siever, 1992), meaning that silica would have existed in colloidal, rather than monomeric form (Iler, 1979). Proposed models for Archean primary silica precipitation must therefore take the polymerization behavior of colloidal silica into consideration. Polymerization is most rapid in the range of pH 4–8 (Fig. 10), and higher concentrations of silica translate to more rapid polymerization (Iler, 1979). Polymerization is inhibited from pH 8 to 10 (Fig. 10) because of the increasing particle-particle repulsion caused by negative surface charges due to dissociation of H⁺ from surface silanol groups (R-Si-O-H; Iler, 1979). When electrolyte concentrations are low, circumneutral pH favors gelling, in which colloidal particles link together to form a branched network of chains such that the liquid plus colloid system does not change in silica concentration but becomes increasingly viscous (Iler, 1979). However, when cations are present (Na⁺, Ca²⁺, etc.) in the pH range 6–10, the negative surface charges on colloidal particles are mitigated, and coagulation is favored, in which colloidal particles clump together into relatively dense aggregates (Baxter and Bryant, 1952; Iler, 1979). Although the pH of Archean seawater is poorly constrained, we can reasonably assume that it was not strongly acidic (pH < 4) or alkaline (pH > 10). In addition, the salinity of Archean seawater was almost certainly higher than in the modern alkali-chloride siliceous hot springs discussed here (Knauth, 2005). We can therefore expect that aggregation played a more significant role in Archean marine silica precipitation than in modern siliceous sinters, which perhaps explains why sand-sized silica granules are not common in these modern systems.

**Episodicity of Granule Formation and Deposition**

One of the most striking characteristics of early Archean banded cherts is the regular alternation of layers of contrasting composition, one component of which is the relatively pure chert layer of silica granules, indicating that deposition and probably formation of silica granules occurred episodically. This repetitive nature of granule deposition and the local consistency in thicknesses of silica granule layers and the intervening black or ferruginous chert layers suggest that this cyclic deposition of granules and con-

![Figure 9. Schematic outline of the hypothesis that silica granules formed via multiple stages of aggregation. Silicic acid monomers (H₄SiO₄) polymerize to form dimers and oligomers, which eventually grow to form spherical nanospheres with characteristic diameters on the order of 5 nm. Within modern siliceous sinters, colloidal nanospheres aggregate to form silica microspheres with characteristic diameters on the order of 2 \( \mu \text{m} \). We propose that aggregation of microspheres could produce spherical granules with characteristic diameters similar to those observed in this study, ~200 \( \mu \text{m} \).](image-url)
acidic (pH < 4) or alkaline (pH > 10) values, pH ing between circumneutral and either strongly promoting silica precipitation (Williams and Crerar, 1985) to become supersaturated with respect to silica, driven by periodic fluctuations in key environmental parameters occurring over geologically short time scales. Temperature, salinity, pH, and concentration of dissolved silica, the principal parameters influencing silica polymerization, could all have plausibly varied regularly on seasonal, annual, or multi-annual time scales. A rapid drop in temperature can cause a fluid to become supersaturated with respect to silica, promoting silica precipitation (Williams and Crerar, 1985). However, periodic fluctuations in seawater temperature would not have been the most effective trigger for rapid granule formation because temperature changes would have been gradual and small in magnitude, resulting in only small changes in the degree of saturation with respect to amorphous silica.

As discussed already, there are complicated relationships among pH, salinity, and stability of the colloidal silica-water system (Fig. 10). In general, polymerization of silica is most rapid at moderate pH, and aggregation is favored over gelation in the presence of cations, which would have been abundant in Archean seawater (Knauth, 2005). Unless pH was fluctuating between circumneutral and either strongly acidic (pH < 4) or alkaline (pH > 10) values, pH variations are unlikely to have triggered granule formation. At slightly alkaline pH (8–10), however, increases in salinity can strongly influence polymerization rates (Fig. 10). Finally, the rate of silica precipitation is proportional to the concentration of dissolved silica, so higher silica concentrations produce more rapid precipitation (Rimstidt and Barnes, 1980) and polymerization rates (Iler, 1979). Salinity and silica concentration can therefore both affect polymerization rates and could have fluctuated over seasonal, annual, and/or multi-annual time scales via variations in evaporative concentration and/or fluctuations in inputs (cf. Bekker et al., 2014). We hypothesize that these two parameters are more likely to have triggered silica granule formation than periodic changes in temperature or pH.

If the production and deposition of silica granules were seasonal or annual, an important corollary is that the depositional rates of banded chert must have been quite rapid—several centimeters per year as reflected by both banded chert must have been quite rapid—several centimeters per year as reflected by both banded chert and banded iron formation, could therefore still be relatively slower than shallower-water facies (cf. Tice and Lowe, 2004).

**Effects of Postdepositional Alteration**

The observations presented here suggest that silica granules have been affected physically and chemically by their extended histories of diagenesis and metamorphism. Some of the consequences of this postdepositional alteration relate to the appearance of the silica granules, most notably including widespread compaction. A more subtle but significant change is the obliteration of any primary textural features with smaller length scales than the average size of microquartz domains, ~30 μm. This makes it impossible to directly test our granule formation hypothesis using traditional transmitted or reflected light petrography of Archean silica granules: Microscopic substructures like those observed in the modern granules have been destroyed.

Similarly, the data presented here suggest that the Si isotopic compositions of some silica granules have likely been altered during diagenesis. One likely explanation for the distinct Si isotopic compositions observed in silica granules from different lithofacies is that they resulted from the incorporation of contrasting Si isotopic signatures from local pore fluids, perhaps influenced by the mineralogical and Si isotopic composition of adjacent sediments. In theory, Si isotopic compositions recorded by primary silica precipitates should provide some key insights into any spatial variations in the Si isotopic composition of seawater. At this point, however, we cannot control for the magnitudes and mechanisms of any changes in Si isotopic composition; in other words, the initial Si isotopic compositions of the granules analyzed here are unknown. Notably, if this interpreta-

Figure 10. Schematic diagram illustrating the effects of pH and salinity on polymerization of colloidal silica. The y axis represents stability of the silica sol (the colloidal silica-water system), where higher values correspond to silica being more stable in colloidal form, while lower values correspond to systems favoring polymerization, resulting in coagulation of larger aggregate particles or gelation of branched networks. In the absence of electrolytes, particle repulsion due to negative particle surface inhibits polymerization above pH 7, and the colloidal system is relatively stable. Added cations, however, mitigate surface charges over a greater range in pH and promote coagulation over gelation. For comparison, the concentration of Na⁺ in the modern ocean is 0.47 M (DOE, 1994). Figure is modified after Iler (1979) and Williams and Crerar (1985).
tion is correct, this behavior would contrast with observations that Si isotope compositions of Archean cherts were largely rock-buffered and relatively resistant to resetting during diagenesis and metamorphism (Marin-Carbonne et al., 2012; Stefaefur et al., 2015), perhaps signaling differences in the timing and/or mechanisms of silica diagenesis experienced by silica granules compared to silica cements and other early dia-
genetic chert-precursor silica phases. The most productive future research directions may there-
fore be experimental: evaluating the silica gran-
ule formation hypothesis presented here and
documenting the physical and chemical changes associated with diagenesis and metamorphism.

CONCLUSIONS

Silica granules were a common grain type in early Archean cherty sediments and appear to have represented a significant mode of silica deposition in the Archean chert cycle. Their size, occurrence in non-ferruginous set-
tings, nearly pure SiO2 composition, and uni-
formly subpherical, well-rounded shapes dif-
ferentiate silica granules from other associated detrital grain types or from granular iron forma-
tion. The sharp contacts between pure granule layers and the adjacent detrital organic layers in banded black-and-white chert suggest that the two types of layers were formed from distinct depositional events and that production of silica granules was episodic. We suggest that the gran-
ules were formed via multistage aggregation of silica, in a manner somewhat analogous to silica precipitation observed in modern siliceous silt depositions. In systems with near-neutral to moderately alkaline pH and high concentrations of dissolved silica (saturated to supersaturated with respect to amorphous silica), increased salinity raises the rate of silica polymerization and favors aggregation of silica particles over gelling. Variations in silica concentration and salinity could therefore have triggered episodic production of silica granules.

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