

# Dual role of seawater and hydrothermal fluids in Early Archean chert formation: Evidence from silicon isotopes

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## ABSTRACT

The great variety and abundance of chert deposits in Archean terrains constitute one of the most unusual features that mark Earth's early geological history. Proposed explanations for their origin largely relying on field observations, trace element patterns, or oxygen isotope signatures have not yielded an encompassing model. Here we document silicon isotope systematics in cherts from 3.5–3.0 Ga units in the Pilbara Craton (Western Australia) as evidence of their formation by several distinct processes in Early Archean near-surface environments. Our  $\delta^{30}\text{Si}$  results, in combination with geochemical and mineralogical signatures and field relations, point to three end-member sources of silica derivation. One chert type is inferred to have originated through massive transformation of precursor material by silica added from seawater. At least 2‰ differences in  $\delta^{30}\text{Si}$  between the two other types, produced by direct chemical precipitation on the seafloor or in conduits, discriminate seawater from hydrothermal fluid as a source of silica. A virtually continuous Si isotope trend in cherts from this group is consistent with interaction between silica-carrying fluids at submarine vent systems.

**Keywords:** silicon isotopes, Archean cherts, Pilbara Craton, silicification, chemical sedimentation.

## INTRODUCTION

Unusually ubiquitous and voluminous chert bodies are typical phenomena in Archean greenstone belts. Delineating their origin is of fundamental interest, because occasionally preserved sedimentary structures and microbial remains provide critical clues to the evolution of Early Archean marine environments (e.g., Buick and Dunlop, 1990) and the development of early life. Key questions concern the role of ambient seawater versus hydrothermal fluids, and the relative importance of direct precipitation against pervasive silicification of precursor material. Sedimentological and petrological lines of reasoning have been used in support of silica derivation from silica-saturated seawater, providing a rationale for inferring Archean oceanic temperatures from oxygen isotope signatures in cherts (Knauth and Lowe, 2003, and references therein). However, field observations of chert dikes extending into the base of stratiform chert beds have been interpreted as evidence of feeder systems, hinting at a hydrothermal origin for the silica (Nijman et al., 1999; Brasier et al., 2005). Claims for either hydrothermal activity or seawater as the primary silica source have both been supported by trace element characteristics (Kato and Nakamura, 2003; Bolhar et al., 2005).

Silicon isotopes provide a promising tool to unravel the origin of Early Archean cherts, given their susceptibility to fractionation under near-

surface conditions (Douthitt, 1982; Ding et al., 1996, 2004; Ziegler et al., 2005; Basile-Doelsch et al., 2005). André et al. (2006) reported significant Si isotope variations in ca. 3.8 Ga cherts and associated rocks from the Isua Greenstone belt, providing insights into the Early Archean silica cycle. From a correlation between  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  values in a suite of cherts, Robert and Chaussidon (2006) inferred that silicon isotopes signal a significant decrease in oceanic temperatures in the course of the Precambrian era since 3.5 Ga.

We studied a representative set of well-characterized 3.5–3.0 Ga cherts from the Pilbara Craton in order to elucidate chert formation in Early Archean time. Here we report Si isotope results that, in conjunction with other geochemical signatures, enable us to determine the provenance of silica and to discriminate between different modes of chert deposition.

## SAMPLING STRATEGY AND METHODS

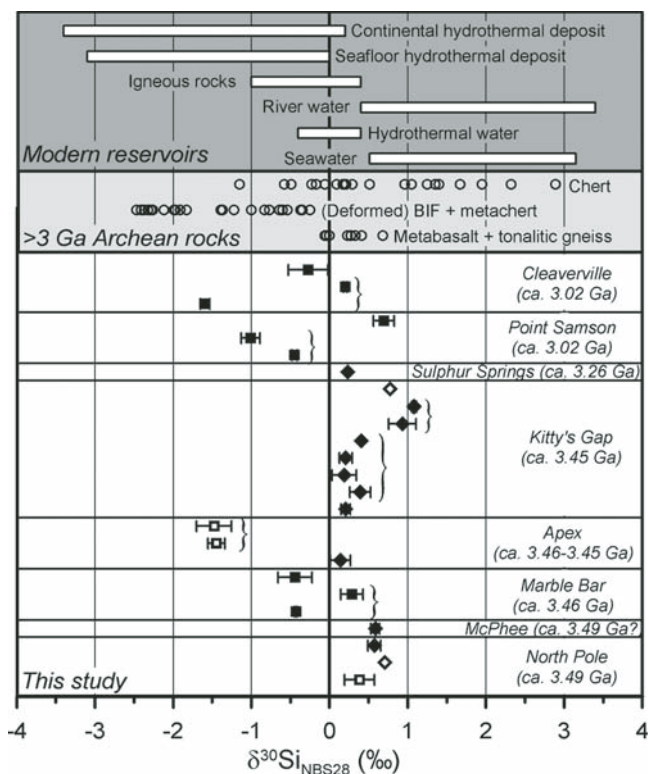
Samples were collected from stratiform chert units and associated chert dikes in eight well-studied settings of the Pilbara greenstone terrain, Western Australia. Nine stratiform samples (ca. 3.5–3.2 Ga) were obtained from the North Pole, McPhee, Marble Bar, Apex, Kitty's Gap, and Sulfur Spring cherts. In addition, four samples were taken from dikes trending at high angles into the Kitty's Gap, Apex, and North Pole stratiform units. In the West Pilbara domain,

four stratiform chert samples (ca. 3.0 Ga) were collected from the Cleaverville Beach and Point Samson outcrops (see Van Kranendonk et al., 2002, for stratigraphic details). A selection of six cherts was subsampled on the scale of laminae, yielding a total set of 25 analyses. The different outcrops cover the entire spectrum of inferred but highly debated depositional settings in the Pilbara block, from mid-ocean ridge chemical deposits (e.g., Marble Bar) to shallow-marine sedimentary environments (e.g., Kitty's Gap). Details on the investigated units and sample descriptions can be found in GSA Data Repository Table DR1.<sup>1</sup> Samples were analyzed for Si isotopes (Van den Boorn et al., 2006) as well as for major and trace elements (Table DR2).

## RESULTS

Observed Si isotopic variations in the investigated Archean cherts are presented graphically in Figure 1, along with ranges for modern terrestrial reservoirs and available data on Archean rocks. The total range in  $\delta^{30}\text{Si}$  values established in this study is 2.7‰. Variations of as much as

<sup>1</sup>GSA Data Repository item 2007231, Table DR1 (origin and description of chert samples) and Table DR2 (compositional data of chert samples), is available online at [www.geosociety.org/pubs/ft2007.htm](http://www.geosociety.org/pubs/ft2007.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1. Si isotope variability in cherts from Early Archean units in Pilbara Craton. Braces group data obtained from single rock slabs. Error bars correspond to 1 standard deviation on duplicate analyses. Published Si isotope data on older than 3.0 Ga Archean rocks, shown for comparison, are from Robert and Chaussidon (2006) and André et al. (2006). Top part summarizes ranges for some of Earth's main reservoirs, based on data from Douthitt (1982), Ding et al. (1996, 2004), De La Rocha et al. (2000), Cardinal et al. (2005), and Reynolds et al. (2006). BIF—banded iron formation. See Figure 2 symbol legend.**

1.5‰–1.8‰ were found among samples from individual outcrops (e.g., Apex, Point Samson, and Cleaverville cherts), and even on the scale of laminae (data points grouped by braces in Fig. 1) differences of as much as 1.8‰ were observed (e.g., Cleaverville sample).

Based on petrography, we distinguished two chert types: (1) silicified precursor cherts (S cherts) and (2) chemical cherts (C cherts). Microcrystalline quartz is the main pervasive component in virtually all of the studied chert samples, but accessory minerals that are disseminated within the siliceous groundmass are distinctive. The S cherts are characterized by the presence of sericite and Ti oxides, and some contain zircon. This assemblage is taken to be indicative of a volcanic precursory rock or sediment, where sericites are alteration products of feldspars, and Ti oxides and zircons represent insoluble residues (cf. Sugitani et al., 1998). C cherts lack sericite but contain abundant Fe(hydr)oxides and minor carbonates and sulfides, inferred to signal an origin as chemical precipitate. The mineralogical differences are clearly reflected in the chemical compositions; S cherts show high  $\text{Al}_2\text{O}_3$  (as well as Ti, Zr, Hf, and Th) contents, in contrast to C cherts, which generally have higher Fe contents. The distinction between C and S cherts is further substantiated by rare earth element and Yttrium (REE+Y) characteristics. While S cherts largely lack diagnostic REE+Y anomalies, C cherts show positive Y/Ho and Eu/Eu\* anomalies (discussed in

the following). C- and S-type cherts appear to occur in both stratiform units and discordant dikes. Isotopic and compositional data are summarized in Table DR.2.

## DISCUSSION

### Multiple Modes of Primary Chert Formation

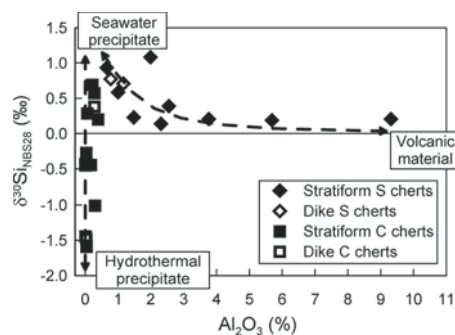
Postdepositional alteration of Archean cherts, possibly affecting their original isotopic signatures (see Knauth and Lowe, 2003, for a review of this problem), is not expected to have a significant effect on Si isotope variations (cf. André et al., 2006). Pervasive secondary modifications by circulating fluids seem difficult to reconcile with the centimeter-scale variations we observed in single specimen. Moreover, assuming that hydrothermal fluids had  $\delta^{30}\text{Si}$  values close to average igneous rocks ( $\sim -0.3\text{‰}$ ; see Fig. 1), pre-metasomatic rocks should have had even more positive  $\delta^{30}\text{Si}$  values (in the case of Kitty's Gap,  $>> 1.1\text{‰}$ ), which would fall outside the known range of Si isotopes in fresh crystalline rocks.

Several lines of evidence also preclude that the cherts are the result of Cenozoic silcrete formation, which is a widespread phenomenon in Australia (e.g., Thiry et al., 2006). This weathering process would produce negative  $\delta^{30}\text{Si}$  values (Basile-Doelsch et al., 2006), whereas the majority of our chert samples have  $\delta^{30}\text{Si} > 0\text{‰}$ . If these were alteration products of originally more positive deposits, then the more mature silcretes (i.e., those with the highest  $\text{SiO}_2$  and

lowest  $\text{Al}_2\text{O}_3$  contents) should have the more depleted values, which is opposite to what our S chert samples show (see following). The orthochemical nature of C cherts is also inconsistent with the typical alteration textures and chemistry of silcretes, despite the negative  $\delta^{30}\text{Si}$  signatures of some samples. Unlike pedogenic silcretes, the chert bodies are not systematically oriented subparallel to the surface, nor do they show typical nodular or columnar structures. Therefore, although weathering-induced silicification may have occurred on a local scale, these observations confirm that our chert samples are of Archean origin.

Three end-member modes of primary chert formation can be recognized when combining Si isotopes with chemical data, as illustrated in the  $\delta^{30}\text{Si}$ - $\text{Al}_2\text{O}_3$  plot of Figure 2. An  $\text{Al}_2\text{O}_3$ -rich end-member chert has a  $\delta^{30}\text{Si}$  value close to or slightly below zero, apparently reflecting a substantial amount of silica from precursor volcanoclastic sediments or crystalline rocks (see Fig. 1). Two other end members are deficient in  $\text{Al}_2\text{O}_3$ , suggesting that they largely represent precipitated silica, one from a  $^{30}\text{Si}$ -enriched fluid reservoir, and the other from a  $^{28}\text{Si}$ -enriched solution. Each of the parental fluids must have had  $\delta^{30}\text{Si}$  values higher than the deposits, because precipitates tend to prefer  $^{28}\text{Si}$  (De La Rocha et al., 1997; Ziegler et al., 2005; Basile-Doelsch et al., 2005).

Our low- $\delta^{30}\text{Si}$  end member is in the range of modern hydrothermal silica deposits, whereas the  $^{30}\text{Si}$ -enriched end member approximates the isotopic composition of modern seawater (see Fig. 1). The strongly positive  $\delta^{30}\text{Si}$  of present-day seawater is generally explained by the activity of diatoms that preferentially remove  $^{28}\text{Si}$  from solution (De La Rocha et al., 1997), and



**Figure 2.  $\text{Al}_2\text{O}_3$  content versus  $\delta^{30}\text{Si}$  for all Early Archean cherts analyzed. Stratiform and dike S cherts form an array between  $\text{Al}_2\text{O}_3$ -rich volcanic material with  $\delta^{30}\text{Si}$  close to zero, and a  $\text{Al}_2\text{O}_3$ -poor, high- $\delta^{30}\text{Si}$  end member representing silica precipitated from seawater.  $\text{Al}_2\text{O}_3$ -deficient stratiform and dike C cherts form an array between low- and high- $\delta^{30}\text{Si}$  end members representing silica precipitated from hydrothermal fluid and seawater, respectively.**

by the continuous supply of isotopically heavy river waters (Ding et al., 2004). In the absence of an efficient biomediated removal mechanism in the Archean, the oceans must have been saturated with silica (Siever, 1992), and because silica precipitation will enrich remaining water in the heavy isotopes, it follows that Archean oceans must have had strongly positive  $\delta^{30}\text{Si}$  values as well (cf. André et al., 2006).

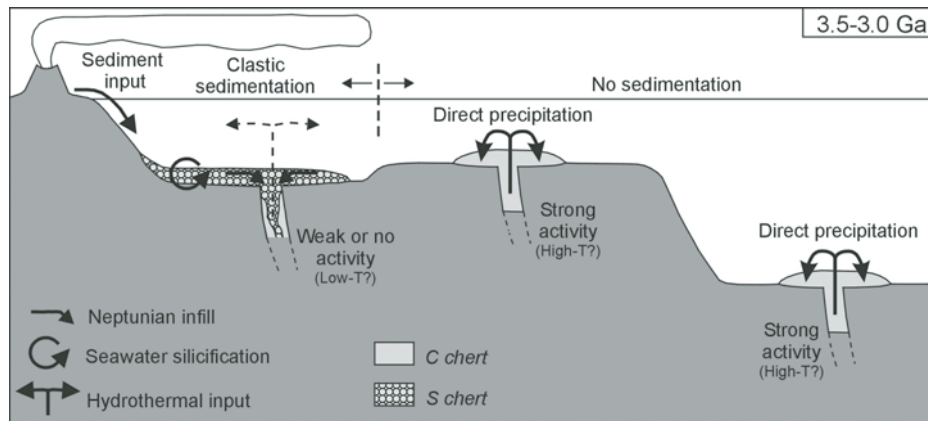
Within the array of C cherts, those with the lowest  $\delta^{30}\text{Si}$  values reflect a predominance of hydrothermally derived silica, whereas precipitation from seawater yielded those with the highest values. We interpret the  $\delta^{30}\text{Si}$  variation in the C chert array to largely reflect mixing of hydrothermal and seawater-dissolved silica, implying dynamic fluid interaction at submarine venting systems. The few C cherts with slightly higher  $\text{Al}_2\text{O}_3$  contents are probably contaminated with minor volcanic detritus.

The trend line of S cherts is remarkable in the sense that it identifies seawater rather than hydrothermal water as the silicifying medium that transformed precursor material. Their isotopic composition thus reflects a mixture of precursor silicates and silica introduced by seawater infiltration.

The distinction between S and C cherts is corroborated by source-characteristic REE+Y anomalies (Table DR2). S cherts have Y/Ho ratios of 26.6–31.3 and Eu/Eu\* ratios of 0.99–1.63, indicating that they have largely retained their precursory igneous rock and/or sediment signatures (assuming chondritic Y/Ho and absence of Eu anomalies), because even a small fraction of such material obliterates any seawater-induced anomalies, due to the orders-of-magnitude higher REE contents in rocks. C cherts, however, show pronounced positive Eu/Eu\* (1.77–5.62) and/or Y/Ho ratios (28.6–72.3) that are characteristic of hydrothermal fluids and seawater, respectively (Bolhar et al., 2005). The REE+Y data are thus in agreement with the proposed genetic grouping, and support the three end-member modes of silica provenance.

### Early Archean Chert-Producing Environments

Combining the geochemical findings with the geological context of the sample units enables us to establish a generalized genetic model for Early Archean chert formation (Fig. 3). It is important to note that subvertical chert dikes often interconnect with the base of stratiform S cherts such as the Kitty's Gap, Apex, and North Pole units. These dikes have been interpreted as former channels for hydrothermal fluids acting as primary silicification agents of overlying sediments and rocks (Nijman et al., 1999; Brasier et al., 2005). Our geochemical data, however, demonstrate that stratiform S cherts do not carry an endogenous hydrothermal signature, and identify



**Figure 3. Schematic representation of chert-forming mechanisms in the Early Archean. Silicification of precursory material by silica-saturated seawater produced stratiform chert units in areas of active volcanoclastic sedimentation (S cherts) and relatively weak or no hydrothermal input. Chert dikes in this environment are predominantly composed of silicified sediments sifted down from overlying seafloor deposits (neptunian infill) and primary precipitated silica, possibly accompanied by silicified wall rock. In sediment-starved environments, either shallow or deep, interaction between (relatively hot?) Si-rich fluids and seawater promoted orthochemical deposition of silica (C cherts).**

seawater as the main source of silica. Two samples collected from chert dikes (Kitty's Gap and North Pole) have a seawater signature as well, and largely lack a hydrothermal imprint. This suggests that seawater gained access along fault systems and silicified volcanic country rock, or that plastically deformable silicified surface sediments slid into cracks during hydrothermal quiescence, and thus formed chert dikes (cf. Lowe and Knauth, 1977). In contrast, we identified other chert dike samples (Apex and North Pole) as purely chemical deposits (C cherts), demonstrating that elsewhere silica precipitated from hydrothermal fluids upon cooling and/or mixing with seawater at depth. Two individual samples (NP-FC8 and NP-FC9) from a dike intersecting the base of the North Pole chert show that neptunian infill and chemical precipitation from mixed fluids may have occurred simultaneously in single systems.

The stratiform C cherts at Marble Bar and Cleaverville Beach represent cases of direct silica precipitation on the seafloor upon mixing of hydrothermal fluids with seawater. This required a different style of hydrothermal activity than at stratiform S chert sites, where fluxes from emanating fluids were insufficient to affect the dominant seawater signature of precipitating silica. We infer that stratiform C cherts formed near relatively active vent systems where fluids entering seawater had relatively high temperatures and silica concentrations, promoting rapid precipitation of silica upon cooling. Scarcity of detrital sediments suggests that such systems predominantly occurred in sediment-poor parts of the depositional environment. S cherts, however, formed where hydrothermal activity was weaker or absent, and direct precipita-

tion was hampered by lower temperatures of fluids that probably contained significantly less silica. Instead, sediments and rocks were largely chertified by continuous exposure to silica-saturated seawater.

Our interpretation is at variance with the hypothesis that seawater temperature controls the Si isotope variations (Robert and Chaussidon, 2006). Robert and Chaussidon (2006) inferred an increase in  $\delta^{30}\text{Si}$  of Precambrian cherts, and explained this in terms of a temperature decrease between 3.5 and 0.8 Ga. In their view, hydrothermal fluids percolating through the crust lost a large portion of dissolved silica, so that remaining silica, which ultimately produced the cherts, was enriched in  $^{30}\text{Si}$  to a degree that depended on the seawater temperature. Our findings favor a different scenario wherein hydrothermal fluids precipitated most of the silica at seafloor level, thus producing chert types with negative  $\delta^{30}\text{Si}$  values, similar to modern hydrothermal deposits (see Fig. 1). In addition, the likelihood that seawater  $\delta^{30}\text{Si}$  was positive and that injection of hydrothermal silica into the silica-saturated seawater induced mixing readily explains much of the observed silicon isotope variability in cherts. The insensitivity of silicon isotopes to postdepositional resetting questions Robert and Chaussidon's (2006) choice to ignore  $\delta^{30}\text{Si}$  data from samples with oxygen isotope signatures that hint at addition of meteoric waters or variable temperatures during diagenesis. An increase in  $\delta^{30}\text{Si}$  during the Precambrian becomes tenuous when considering their entire set of unscreened data. If this trend can be confirmed, it might signal a decrease in the contribution of hydrothermal silica to chert formation rather than a decrease in seawater temperature.

## CONCLUSIONS

In this study we used silicon isotope evidence in combination with geochemical and petrological data to delineate the provenance of silica as the bulk constituent of Early Archean cherts in the Pilbara Craton. Mineral assemblages,  $\text{Al}_2\text{O}_3$  contents, and REE+Y characteristics provided a first-order distinction between chemically precipitated cherts (C cherts) and silicified precursory sediment or rock (S cherts). Positive  $\delta^{30}\text{Si}$  values of S cherts point to silica-saturated  $^{30}\text{Si}$ -enriched Archean seawater as principal agent responsible for pervasive silicification. The absence of an unambiguous hydrothermal signature indicates that formation of stratiform S cherts was largely independent from silica input via submarine vent systems. In contrast, an array of  $\delta^{30}\text{Si}$  values in C cherts from strongly negative to slightly positive provides evidence for a mixing gradient between isotopically light hydrothermal fluids and isotopically heavy seawater, from which we deduce that orthochemical deposition occurred around vents where seawater interacted with relatively hot fluids. Multiple episodes of chert formation and lithification during early burial may add to isotopic heterogeneity on outcrop scale. Our silicon isotope results further suggest that some feeder dikes contain mixed chert types representing silicified sediment entrained from seafloor deposits as well as silica deposited in situ.

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