

# Using Ge/Si ratios to decouple iron and silica fluxes in Precambrian banded iron formations

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## ABSTRACT

**Banded iron formations are prominent sedimentary deposits of the Precambrian, yet the source of their silica remains unresolved. Here we show that Ge/Si ratios preserved in banded iron formation chert layers are indicative of weathering of continental landmass. This conflicts with the accumulation of evidence suggesting that chemical components were sourced at mid-ocean-ridge hydrothermal systems. Instead, it implies that the sources of silica and iron were decoupled during banded iron formation deposition, silica being dominantly derived from weathering of continental landmass and iron having a hydrothermal origin. Thus, the chemistry within banded iron formation depositional basins underwent clear switching that varied on a periodic basis and is recorded in the alternation of iron- to silica-rich layers.**

**Keywords:** Hamersley banded iron formation, Ge/Si ratios, Archean-Proterozoic ocean chemistry.

## INTRODUCTION

Banded iron formations are defined as laminated chemical sediments containing >15 wt% iron and commonly comprising as much as 35%–50% chert (James, 1954). The banding is generally defined by alternating layers of Fe-rich minerals and layers of chert. At the characteristic mesoband scale (centimeter-thick units) there is a continuum from Fe-rich layers (compare as much as 100% magnetite-hematite) through varved layers of iron and chert (micrometer- to millimeter-scale laminated units) to those that are almost pure chert. Previous studies have shown that the Fe components of banded iron formations have a depleted rare earth element (REE) pattern and Nd isotopic signature, suggesting that mid-ocean ridges and/or hotspot activity were the major sources of the iron (e.g., Holland, 1973; Morris and Horwitz, 1983; Jacobsen and Pimentel-Klose, 1988) and that deposition of the Fe-rich mesobands took place during periods of intense hydrothermal activity (Morris, 1993). In contrast, chert-rich sequences likely reflect hydrothermal quiescence, the formation of varved mesobands being controlled by intermittent (possibly storm

induced) upwelling of Fe-rich waters from the deeper ocean, followed by a return to iron-poor background conditions. The periodicity and magnitude of these upwelling events determine the relative proportions of iron and chert layers (Morris, 1993).

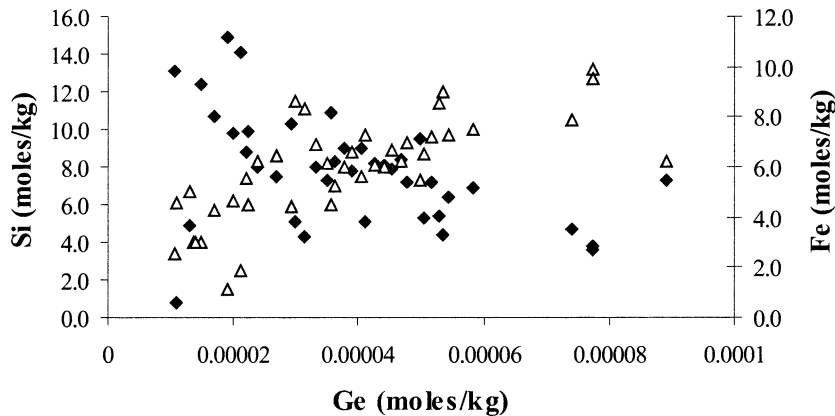
Much of the previous work on banded iron formations has focused on the sources of Fe<sup>2+</sup> and the oxidation processes, but few studies have attempted to determine the origins of the chert layers. Our current understanding is limited to the suggestion that silica concentrations in Precambrian oceans would have been much higher in the absence of silica-secreting organisms, possibly close to saturation with respect to amorphous silica (Sievier, 1992). Silica precipitation therefore would have been induced by evaporative supersaturation (Garrels, 1987) or coprecipitation with solid-phase iron minerals (Ewers, 1983). More problematic, however, is determining the provenance of the silica and whether it is like Fe—hydrothermal—or is continental in origin. Ge/Si ratios offer the potential to address this issue because the Ge/Si ratio preserved in iron formation silica should reflect the ratio of the water from which it precipitated and hence reflect its source.

The geochemical behavior of inorganic Ge

in low-temperature processes is analogous to that expected for a superheavy stable isotope of Si (Froelich and Andreae, 1981; Froelich et al., 1985; Mortlock and Froelich, 1987). Inorganic Ge exists as the same chemical species as Si in natural waters (Pourbaix, 1966; Potrovski and Scholt, 1998) and, due to similar atomic radii (Si 1.46Å and Ge 1.52Å) and Si-O, Ge-O bond lengths (1.63Å and 1.64Å, respectively), substitutes for Si in the SiO<sub>2</sub> lattice. The current marine Ge/Si ratio of  $0.7 \times 10^{-6}$  (hereafter expressed as an atomic ratio or mole/mole) is the result of the relative fluxes of Ge and Si to the oceans. Although there is some variation in the concentrations of Ge and Si vertically and laterally within the oceans, the Ge/Si ratio is preserved (Froelich and Andreae, 1981).

Silica enters the ocean via two compositionally distinct sources: (1) hydrothermal fluids produced during alteration of basalts at mid-ocean ridges, which have Ge/Si ratios on average between  $8$  and  $14 \times 10^{-6}$  (Mortlock et al., 1993) and (2) continental runoff, which has Ge/Si ratios of  $\sim 0.6 \times 10^{-6}$  (Froelich et al., 1992). Si and Ge are dominantly removed from the oceans during precipitation of biogenic opal, which shows little or no fractionation of Ge with respect to Si; the subsequent

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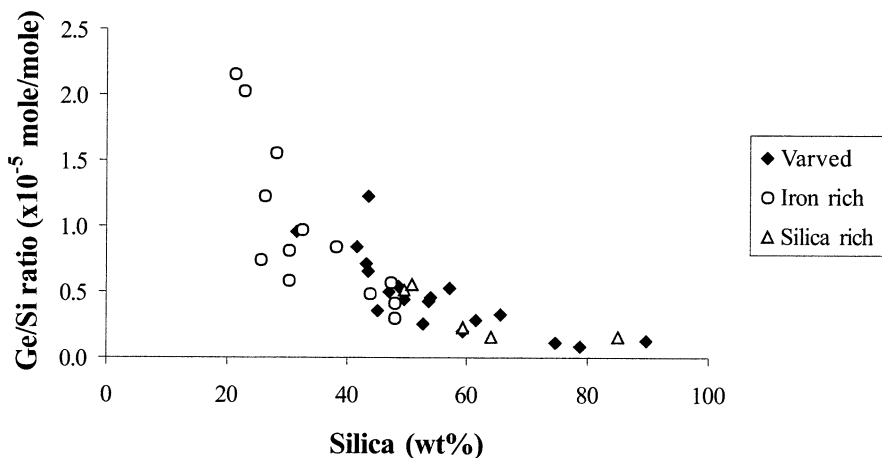
**Figure 1. Concentration of Ge vs. Fe and Si.** Ge concentration is plotted as function of both Fe (triangles) and Si (diamonds) concentrations. Note that Ge concentrations increase as Fe increases and Si decreases. Analyses of powdered mesobands were by wet plasma inductively coupled plasma-mass spectrometry for Ge. Ge concentrations in reagent blanks were found to be at least three orders of magnitude less than in samples and thus corrections were unnecessary. Precision was determined by replicate analysis and accuracy by repeated analyses of certified standard SDO-1 (precision to 95% confidence limit was  $\pm 0.61 \times 10^{-6}$  moles/kg and accuracy  $\pm 0.83 \times 10^{-6}$  moles/kg). Fe and Si were determined by standard X-ray fluorescence analysis on fused beads.

Ge/Si ratio in solution is preserved (Shemesh et al., 1988; Froelich et al., 1992; Bareille et al., 1998). Ge is thought to have an additional sink in Fe-rich sediments during the precipitation of Fe-oxides and sulfides. In this study we report the first Ge/Si ratios for Precambrian cherts and show that these ratios can be effectively used to differentiate the fluxes of silica within the depositional basins.

#### SAMPLES AND METHODS

We collected and subsampled four ~30 cm sections of pristine banded iron formation of the ca 2.5 Ga Dales Gorge Member, Hamersley Group, Western Australia, from DDH 44 core, drilled at Paraburdoo. These samples were selected because they exhibit well-defined banding and are thought to have un-

dergone minimal postdepositional alteration, below greenschist facies (Kaufman et al., 1990). Ge analyses were carried out first by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) on 300  $\mu$ m areas of chert in polished sections, and second by wet plasma ICP-MS analysis of powdered mesoband couplets digested using the standard HF/HNO<sub>3</sub> method. U.S. Geological Survey standard Devonian Ohio Shale (SDO-1) was analyzed by the HF/HNO<sub>3</sub> method to assess possible loss of Ge and Si as GeF<sub>4</sub> and SiF<sub>4</sub>. No appreciable loss was noted when compared to the average value given by the U.S. Geological Survey (2002). Clean areas of chert were identified by scanning electron microscope for point analysis by LA-ICP-MS; therefore silica was assumed to be 100 wt%.



**Figure 2. Silica (wt%) vs. Ge/Si ratio.** Ge/Si ratio is plotted as function of silica. Note that as silica increases, Ge/Si ratios tend to be lower (continental end member), and as silica decreases, Ge/Si ratios tend to be higher (hydrothermal end member).

Mesoband Fe and silica were determined by X-ray fluorescence analyses on fused beads. The band couplets analyzed consist of Si- and Fe-rich as well as varved mesobands, and represent adjacent Fe- and chert-dominated layers within the banded iron formation.

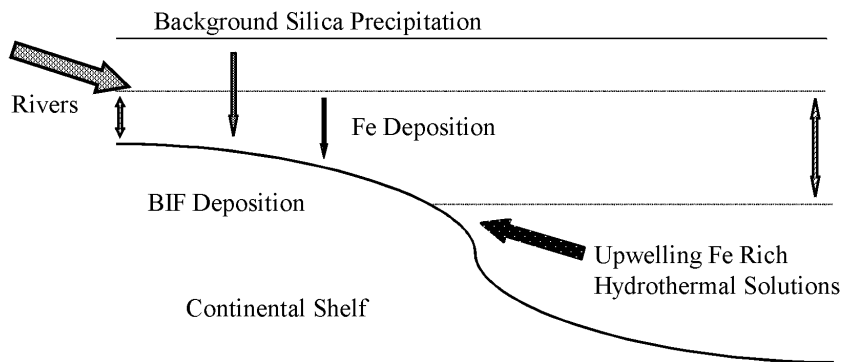
#### RESULTS AND DISCUSSION

Analyses of consecutive mesoband couplets show that Ge varied from 10.7 to 89.0 moles/kg and SiO<sub>2</sub> varied from 3.8 to 14.9 moles/kg. Ge/Si ratios range from 0.82 to  $21.63 \times 10^{-6}$  and average  $6.30 \pm 0.17 \times 10^{-6}$ . These values suggest a strong inverse proportionality between the concentrations of Ge and Si and a strong proportionality between Ge and Fe (Fig. 1).

Ge/Si ratios in banded iron formations can be used to define mesoband type (Fig. 2). Ge/Si ratios in Si-rich mesobands (not necessarily pure chert) average  $3.22 \times 10^{-6}$ , in Fe-rich mesobands average  $9.77 \times 10^{-6}$ , and in varved bands average  $4.74 \times 10^{-6}$ . The varved mesobands show a wide spread in their ratios due to the variability in the amount of iron and silica present. In all cases, as silica increases, the Ge/Si ratio decreases. The most silica-rich samples trend toward ratios close to those measured in pure chert by LA-ICP-MS (average of  $0.82 \times 10^{-6} \pm 0.16 \times 10^{-6}$ ). Conversely, as silica decreases (and Fe increases), the Ge/Si ratio increases to values similar to those associated with present-day mid-ocean-ridge solutions and metalliferous sediments (Froelich et al., 1985). Thus there appear to be two end-member compositions that can be defined in terms of either silica and iron concentrations or by their Ge/Si ratio.

The Ge/Si ratios of  $0.82 \times 10^{-6}$  in pure chert plot close to the present-day marine ratio ( $0.7 \times 10^{-6}$ ). Ratios measured within Si-rich mesobands, although higher ( $\sim 3.22 \times 10^{-6}$ ), tend toward similar continental ratios as the concentration of silica increases and that of iron decreases (Fig. 2). This indicates that chert precipitated from solutions that were dominated by inputs of silica sourced from the weathering of continental landmass. Variations within adjacent microbands, thought to represent yearly deposition, are identical within the error calculated by multiple analyses within a single band, and show that annual variation is negligible.

Ge/Si ratios for varved mesobands show a wider spread (Fig. 2). This is consistent with the wider variations in the relative concentrations of iron and silica present within the band. The proportions of iron to silica relate to the magnitude and periodicity of upwelling events in the Precambrian depositional basin. It is clear from the data that as the dominance of silica within the mesoband increases, the



**Figure 3. Possible model for banded iron formation (BIF) deposition on stable continental shelf. Background precipitation of continentally derived silica takes place due to evaporation. Upwelling of deeper Fe-rich hydrothermally derived waters causes formation of varves, which may represent seasonal storm mixing events. More sustained hydrothermal activity and/or upwelling causes formation of iron-rich mesobands.**

Ge/Si ratio tends toward that of the continental end-member source. Fe-rich varved mesobands tend toward hydrothermal end-member compositions as iron increases.

The Fe-rich mesobands, representing periods of large-scale inputs of hydrothermally influenced waters, have much higher Ge/Si ratios (average  $9.77 \times 10^{-6}$ ). These ratios, while similar to those of present-day hydrothermal solutions and sediments (Froelich et al., 1985), do not necessarily represent the presence of hydrothermal silica, but rather higher concentrations of Ge associated with the iron phases.

This interpretation of Ge/Si ratios as a tracer for silica in banded iron formations assumes the following: (1) the Ge/Si ratios of the sources have remained the same; (2) there is no fractionation of Ge relative to Si during inorganic precipitation of silica; and (3) no postdepositional redistribution of Ge relative to Si takes place during diagenesis and metamorphism.

First, the consistency of Ge/Si ratios of the sources is likely to be robust at least back to the Archean-Proterozoic boundary, given that the compositions of both continental crust and oceanic basalts are thought to have remained constant. Second, although no previous studies, to our knowledge, have assessed the possibility that Ge is fractionated relative to Si during inorganic precipitation of silica, biological processes are, in general, far more efficient at exploiting the energy gains associated with mass-dependant isotopic fractionations (Schidlowski, 2001). It therefore seems unlikely that Ge would have been fractionated relative to Si during the Precambrian, at least before the onset of silica-secreting eukaryotes. Third, King et al. (2000) and Hammond et al. (2000) showed that Ge in pore-water profiles of present-day sediments decouple from silica; they have calculated that  $55\% \pm 9\%$  of Ge

released from the dissolution of biogenic opal is sequestered in near-surface reducing sediments. The sequestering phase has not been identified, but reduced iron, which would have been abundant in Fe-rich sediments, is thought to be necessary. Mesoband couplets (both Fe and Si rich) were analyzed to allow an upper limit to be placed on the Ge/Si ratio, assuming that some small-scale repartitioning of Ge from silica takes place. However, the Ge/Si ratios measured in various Si-rich varved and unvarved mesobands are consistent, and tend toward the ratios measured in pure chert. This suggests that any repartitioning of Ge from silica into iron phases was minimal, and the spread in the ratios measured is a reflection of the Ge associated with the initial iron precipitate. King et al. (2000) and Hammond et al. (2000) also suggested that Ge may diffuse into present-day sediments at rates of as much as  $2.5 \text{ pmol}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$  and removed during precipitation of this unidentified sequestering phase. However, hydrated silica and iron-oxyhydroxide gels would have had considerably less porosity than present-day sediments, and would have acted as aquitards to ion migration (McConchie, 1987). This, coupled with high annual rates of deposition calculated for banded iron formations (Trendall and Blockley, 1970), would minimize the Ge diffusing into the buried sediment. Thus, although some remobilization during early diagenesis cannot be discounted, the Ge fluxes calculated for present-day sediments probably represent an overestimate when related to banded iron formation precipitates. In either case, it seems unlikely that the Ge/Si ratio measured in Precambrian cherts would be significantly shifted away from a continental end-member source.

When considering the validity of Ge/Si ratios of Precambrian cherts as a paleorecorder of oceanic conditions, it must be noted that,

with the exception of plumes adjacent to mid-ocean spreading centers (Mortlock et al., 1993), the present marine ratio of  $\sim 0.7 \times 10^{-6}$  is uniform throughout the ocean. This indicates that oceanic mixing times are faster than the residence times for both Si and Ge ( $\sim 20 \text{ k.y.}$  and  $10 \text{ k.y.}$ , respectively) (Froelich et al., 1992; Hammond et al., 2000). The oceanic inventory of Si during the Precambrian is thought to have had a residence time of 5–10 times greater than present, with fluxes possibly twice that of today (Siever, 1992). To maintain a similar Ge/Si ratio in the Precambrian, as recorded in banded iron formation cherts, the residence time of Ge would have to have remained half that of Si. This implies a residence time for silica of between 50 and 100 k.y. and thus 25–50 k.y. for Ge. Even if slower mixing times than present are assumed for this period, it seems unlikely that the ocean would have been stratified with respect to its Ge/Si ratio. It seems counterintuitive that the residence time of Ge should have remained half that of Si, given that Fe-rich reducing environments, which are important sinks for Ge, would have been more prevalent and would probably have acted as a major sink in the Precambrian. This has important implications for extrapolating the Ge/Si ratios measured in banded iron formation chert to represent the entire Precambrian ocean, because the ratios indicate that banded iron formation basins were chemically isolated from the ocean during periods of silica precipitation, or that the hydrothermal plumes reached the depositional basin still maintaining their distinct ratio relative to the bulk oceans. However, it seems certain that the Ge/Si ratios measured in Hamersley cherts indicate that continental weathering was the dominant source for the silica. This is at odds with the REE and Nd isotope data for the iron component, which indicate a hydrothermal source.

## CONCLUSIONS

The results from this study can be used to better define banded iron formation depositional models; e.g., the Dales Gorge Member is thought to have been deposited on a semi-isolated, submerged marine platform on the continental shelf of the Archean Pilbara craton (Morris and Horwitz, 1983; Morris, 1993). Deposition of Fe-rich mesobands with a depleted-mantle REE pattern and Nd isotopic signature would have taken place within banded iron formation basins during periods of intense hydrothermal activity along oceanic spreading centers. Upwelling of these Fe-rich deep waters onto the shelf would have exerted a dominant control on the basin chemistry, and both hydrothermal and continentally derived Ge would coprecipitate with, and would

have been scavenged by, the iron hydroxides during deposition (Burton et al., 1959). Although Ge/Si ratios do not necessarily indicate a source of the Fe component of banded iron formations, the resulting ratios of these units are close to the hydrothermal end member and similar to those in present-day metalliferous sediments forming at mid-ocean ridges. Varved mesobands represent conditions that fluctuate between dominantly hydrothermal and continental control. Evaporative precipitation of silica would have been periodically interrupted by pulses of Fe-rich waters upwelling onto the depositional shelf, thus creating the Fe-oxide laminations. Higher concentrations of Ge associated with these inputs and scavenged by the Fe-oxyhydroxide precipitates would create the spread observed in the Ge/Si ratios. Ge/Si ratios for Si-rich varved and unvarved mesobands indicate periods when weathering of the continental landmass exerted a dominant control on the basin chemistry, silica precipitation taking place as evaporation caused it to become supersaturated within the basin.

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