# TRACING BIOLOGICAL AND ABIOLOGICAL PROCESSES IN THE EARLY EARTH USING SILICON ISOTOPES

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A Si-rich ocean, resulting from the absence of marine Si-secreting organisms, was a prominent feature of the early Earth. It has become increasingly evident that Si had played an important role in modulating marine cycles of several biogeochemically significant elements, such as P, during the Precambrian ocean [1], and in controlling formation of banded iron formations (BIFs) and cherts [2], two of the major archives through which the environment of the early Earth is studied, as well as geochemical signals preserved in these rocks (e.g., Fe isotopes [3]).

Silicon isotopes ($\delta^{30}$Si) are promising proxies for the Precambrian Si cycle. Existing $\delta^{30}$Si data measured from BIFs and cherts show an overall ~2‰ increase from ~3.8 to 1.5 Ga, with significant scattering of up to serveral per mil at any given geological time point [4]. Although temperature and Si sources can exert the first order control on $\delta^{30}$Si values of seawater, as emphasized by most previous studies, potential Si isotope fractionations associated with different pathways of BIF and chert formation, as well as diagenetic alteration, have rarely been considered. This limitation prevents a mechanistic and quantitative understanding of temporal and spatial variability of the Precambrian $\delta^{30}$Si records.

Our goal was to explore the important role of Fe in the behavior of Si isotopes in Fe–Si gels. Based on numerous experimental studies, Fe(III)–Si gels are the most likely primary marine chemical precipitate in the Archean oceans where hydrothermal Fe(II) has been oxidized to Fe(III) in the presence of a Si-saturated solution. A series of abiologic and biological experiments in artificial Archean seawater (AAS) were conducted to constrain Si isotope exchange kinetics and fractionation factors between aequous Si and amorphous Si gel, or Fe–Si gel, the two presumed precursors to cherts and BIFs, respectively.

Equilibrium Si isotope fractionation factors between Fe(III)–Si gel and aqueous Si ($\Delta^{30}Si_{gel\text{-}aq}$), estimated by a three-isotope method with a $^{29}$Si tracer, are -2.3‰ in the absence of aqueous Fe(II), and -3.2‰ in the presence of Fe(II) in the solution [5]. Aqueous Fe(II) catalyzes Si isotope exchange, and causes larger Si isotope fractionation due to incorporation of Fe(II) into the solid that may have changed Si bonding. In addition, we found that the Fe:Si ratio of Fe–Si gel has a profound impact on Si solubility. This observation has an important implication for estimating Si concentrations in the Precambrian oceans, assuming the Precambrian seawater was saturated with respect to easily formed Fe-Si precipitates.

In contrast, our preliminary experimental results, using the three-isotope and multiple directional methods, show that the magnitude of Si isotope fractionation between pure Si gel and aqueous Si at equilibrium ($\Delta^{30}Si_{gel\text{-}aq}$ within ~ ±1‰) is considerably simaller than that found in the Fe–Si system. The contrast in $\Delta^{30}Si_{gel\text{-}aq}$ between Fe-Si and pure Si systems highlights a significant impact of Fe on Si isotope fractionations. These results provide a brand new explanation for generally lower $\delta^{30}$Si values observed in Precambrian BIFs as compared to those found in cherts.

Silicon isotope fractionation was also investiaged in experiments that simulated dissimilatory iron reduction of Fe(III)–Si gel by bacteria *Desulfuromonas acetoxidans* in AAS [6], and was found to become larger with progression of Fe reduction. A $\Delta^{30}Si_{gel\text{-}aq}$ of ~-3.5‰ was observed at ~32% reduction of Fe(III). This result explains lower $\delta^{30}$Si values in magnetite-associated quartz as compared to quartz associated with hematite in some BIFs [7]. The large Si isotope fractionation produced in the microbial experiment, even larger than that seen in our Fe(II)-bearing abiologic experiments, suggests that $\delta^{30}$Si can be a potential tracer for magnetite of a microbial origin, or, *vice versa*, for microbial activities in magnetite. Moreover, the difficulty with which Fe(III)–Si gels may be converted to magnetite precursors through interaction with aqueous Fe(II) suggests that the highly negative $\delta^{30}$Si values of magnetite-rich cherts of early Archean age may require biological Fe(III) reduction. Such a conclusion implies that the mere presence of abundant magnetite, in a Si-bearing system, is a biosignature.

**References:**

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