

## Exploring Silicon Isotope Fractionation Between Precambrian-Like Artificial Seawater And Fe-Si Gel

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The Precambrian ocean was characterized by unusually high Si concentrations due to the absence of marine Si-secreting species. This Si cycle was maintained by input of Si from continental or hydrothermal sources, balanced by export of Si into sediments, either through direct precipitation or silicification [1]. Cycling of Si in the Precambrian ocean interacted with other biologically important elements, such as Fe and P [2, 3], shaping a unique environment that must have been influenced by the biosphere.

Silicon isotopes in abundant Precambrian Si-rich sediments, including cherts and banded iron formations (BIFs), provide potential access to understanding of the environments of early life. Silicon isotopes have been reported for Precambrian Si-rich sediments [e.g. 4], although unequivocal interpretations of these data are limited by a lack of experimentally determined Si-isotope fractionation factors associated with formation of these sediments and subsequent diagenetic processes.

This study experimentally determined Si isotope fractionation factors between artificial Archean seawater (AAS) and Fe-Si gel, a presumed precursor of BIFs, under anaerobic conditions. Aqueous Si in AAS was spiked with a <sup>29</sup>Si-enriched tracer, and then reacted with isotopically normal amorphous Fe<sup>3+</sup>-Si gel in our experiments. It is the first time that the “three-isotope method” was applied to rigorous determination of Si isotope fractionation factors.

Two parallel sets of batch reactors were set up. The first set used Fe<sup>2+</sup>-free <sup>29</sup>Si-spiked AAS, and second set used <sup>29</sup>Si-spiked AAS containing ~1 mM aqueous Fe<sup>2+</sup>. Both solutions were reacted with the same Fe-Si gel at circumneutral pH and room temperature. After ~30 days, the experiments using the Fe-free AAS showed ~50% Si isotope exchange between the solid and solution. On the other hand, the experiments using the Fe<sup>2+</sup>-containing AAS displayed ~80% isotopic exchange. Extrapolation to 100% isotope exchange predicts a fractionation factor ( $\Delta^{30}\text{Si}_{\text{precip-AAS}}$ ) of  $-2.52 \pm 0.31\text{‰}$  for the experiments without Fe<sup>2+</sup> in the AAS, and a larger fractionation factor ( $\Delta^{30}\text{Si}_{\text{precip-AAS}}$ ) of  $-3.20 \pm 0.30\text{‰}$  for the experiments using 1 mM Fe<sup>2+</sup> in the AAS.

These results suggest that amorphous Fe-Si gel are easily exchangeable with ambient aqueous Si solution,

and the presence of aqueous Fe<sup>2+</sup> in the solution promotes Si isotope exchange and leads to larger Si isotope fractionation during isotope exchange. Presumably, the effect of Fe lies in changes in the Si bonding environment of the gels. The later experimental observation explains field observations that BIFs frequently show Si isotope compositions that are more negative than those recorded in coeval pure cherts [4]. The same three-isotope technique is also applied to determine equilibrium fractionation factors between aqueous Si and Fe-Si gel at ~5°C and 50°C respectively. The results of these experiments allow for better informed interpretations of Precambrian Si isotope data.

### References:

- [1] Siever R. (1992) *GCA*, 56, 3265–3272. [2] Fischer W.W. et al. (2009) *GSA Bulletin*, 121, 222–235. [3] Konhauser et al. (2007) *Science*, 315, 1234. [4] Marin-Carbonne et al. (2014) *Precam Res*, 247, 223–234.