



Preferential ³⁰Si uptake during coprecipitation of Fe(III)(oxyhydr)oxide

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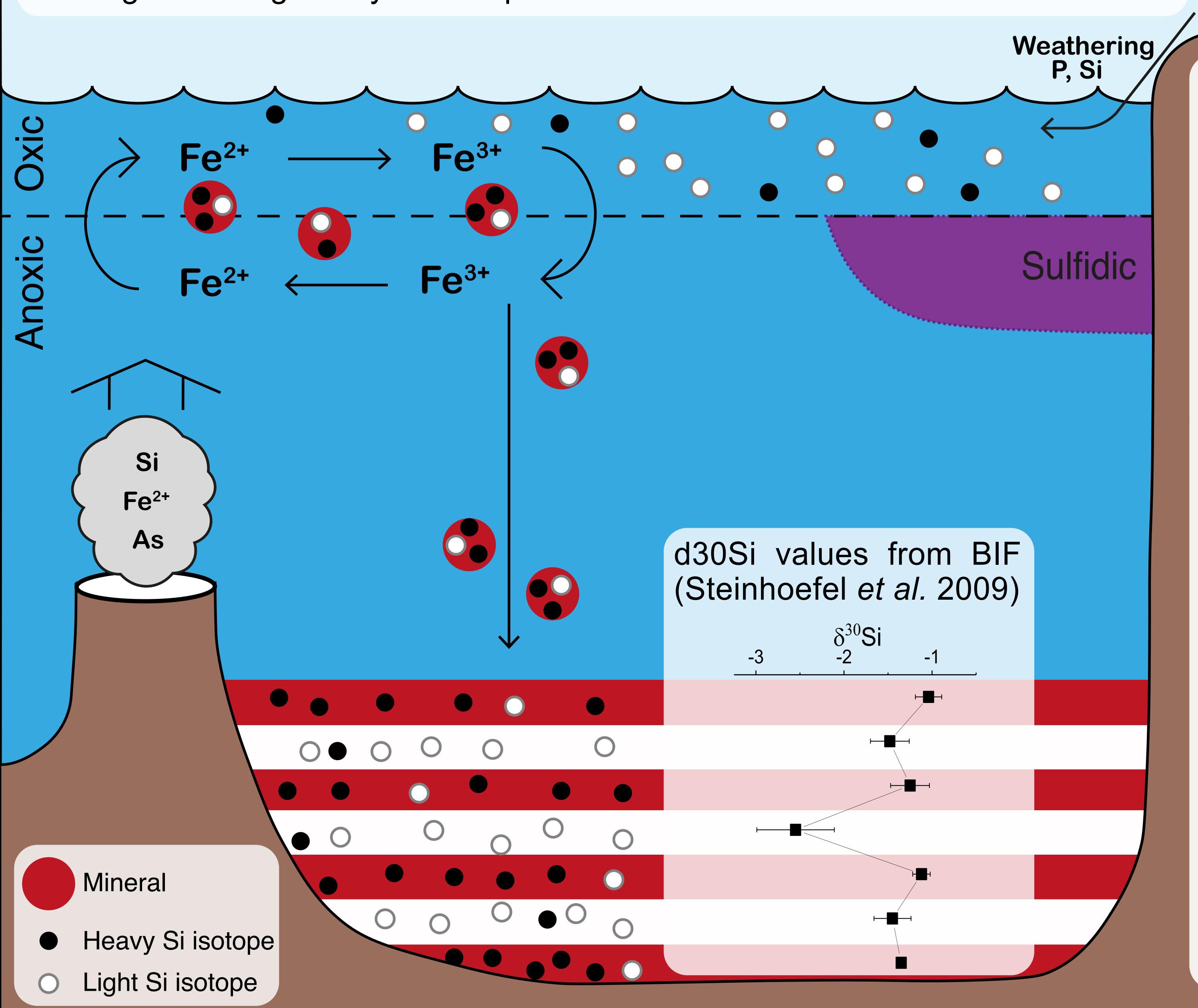




Background

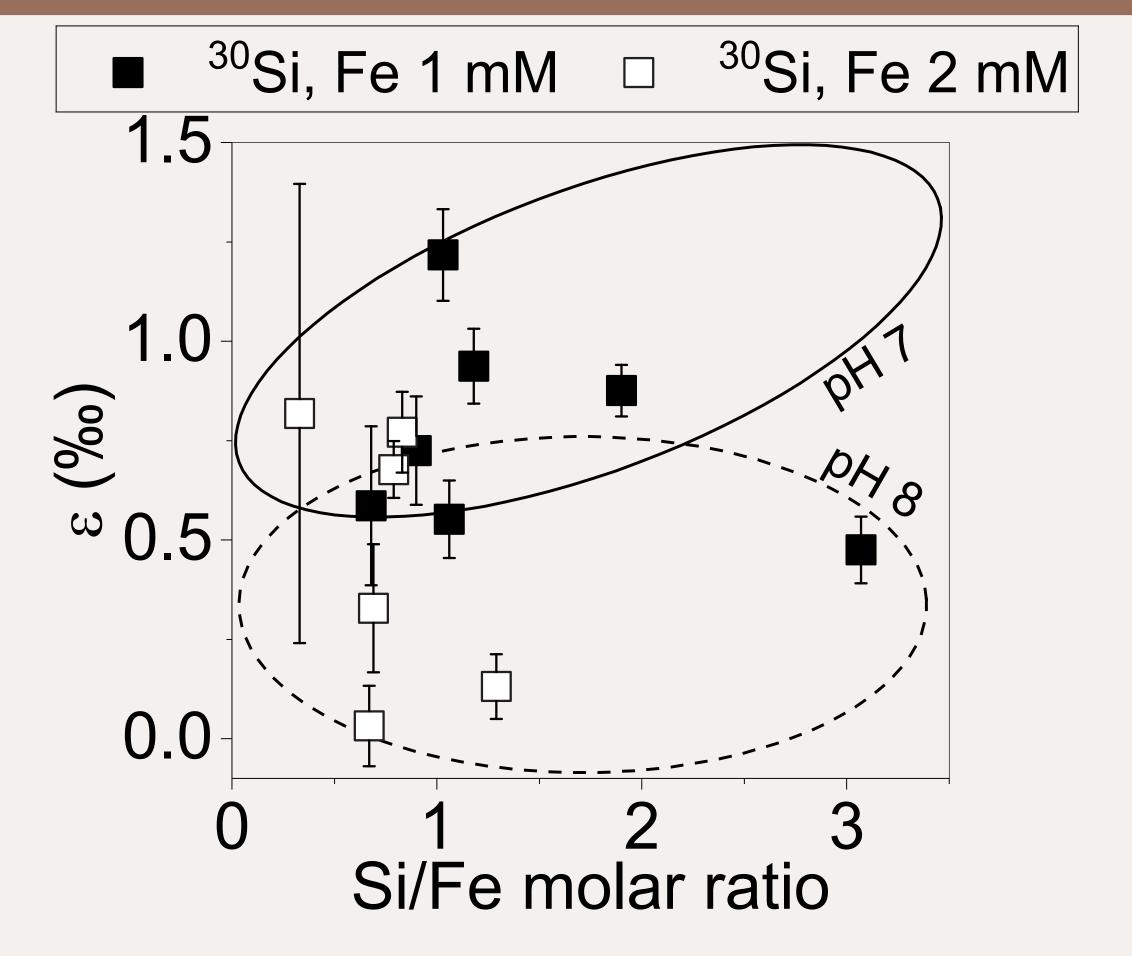
The adsorption of light Si isotopes onto Fe(III)(oxyhydr)oxides is believed to be a dominant feature of the Precambrian ferruginous oceans. The expected outcome is chert bands within banded iron formations (BIFs) that would carry the Si isotope signal of the ocean once the adsorption of Si isotopes ceased. Contrary to the expected outcome, the Fe-rich layers in BIFs carry the heavy Si isotope signal meanwhile Si-rich layers carry a light Si isotope signature leaving a missing heavy Si isotope sink from the current models.

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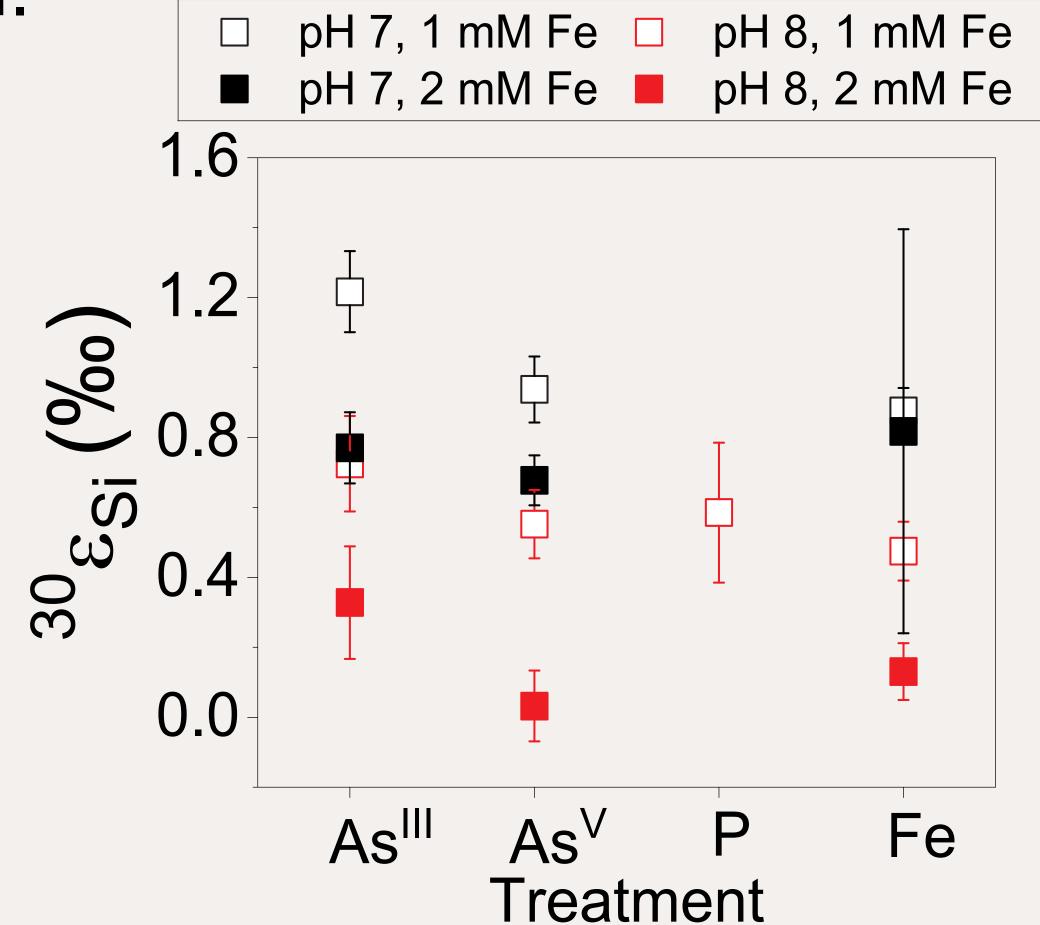


Aims

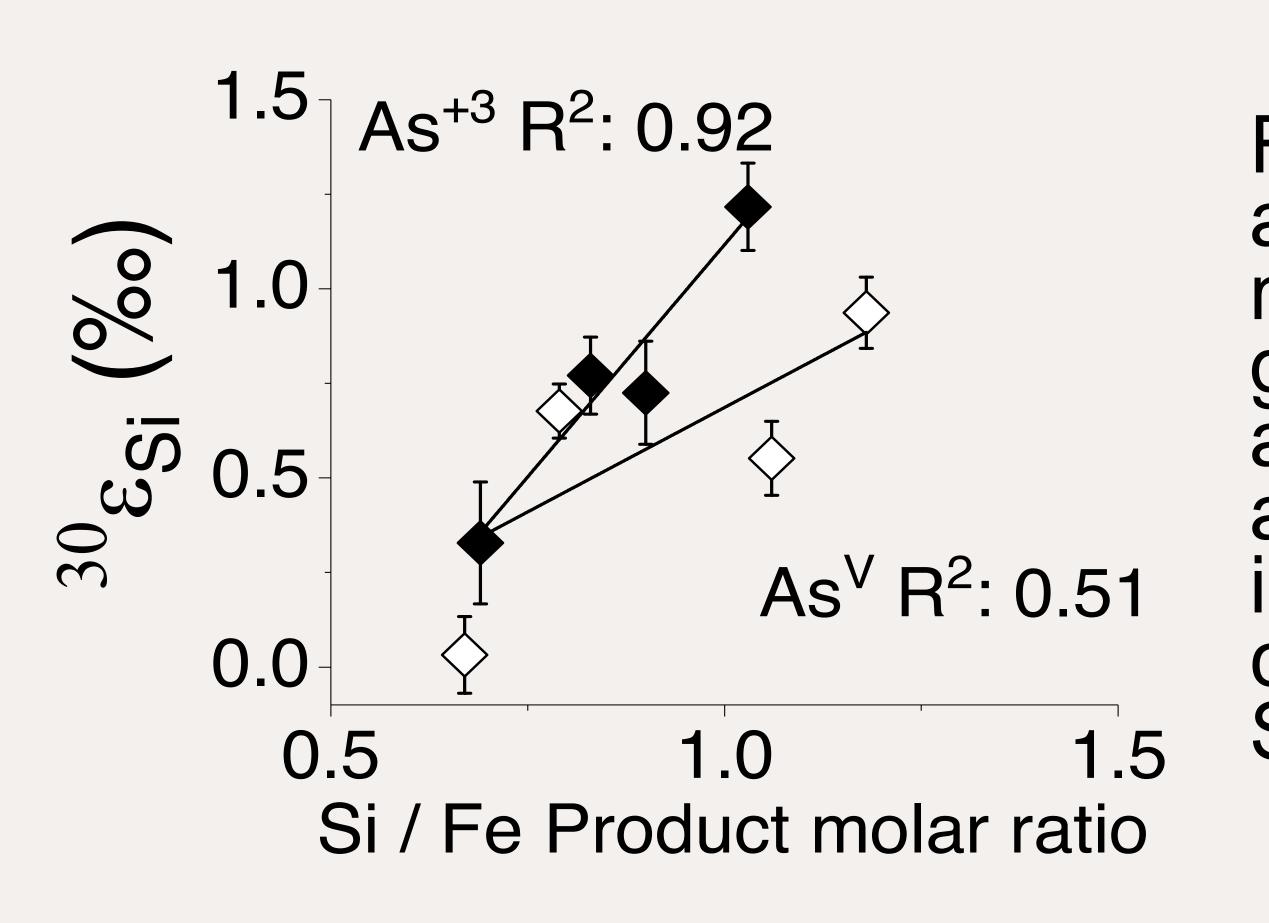
Recent advances in empirical adsorption and coprecipitation models show strong differentiation in ionic uptake between the two models. The Overall aim of this study is to investigate the Si-isotope fractionation during coprecipitation of, rather than adsorption onto, Fe(III)(oxyhydr)oxide. Precipitations were conducted in solutions with elevated Si, Fe, P and As in order to mimick the formation of chemical sediments in the Early Proterozoic ferruginous oceans that lead to the deposits of BIFs, based on earlier adsorption and coprecipitation studies (Bjerrum & Canfield 2002, Chi Fru et al. 2017, Hemmingsson et al. 2018, Jones et al. 2015, Konhauser et al. 2007).



Fractionation factor (ε) ³⁰Si against mineral Si/Fe ratio indicating pH as an important factor for isotopic fractionation.



Fractionation factor (ε) ³⁰Si divided by pH and Fe-content. The effect of Fe content during mineral formation is seen within each pH.



Fractionation factor (ε) ³⁰Si against mineral Si/Fe ratio and matrix composition showing greater fractionation when P and As^{III} is present over As^V. In addition to matrix effects on isotope fractionation a strong correlation is seen for mineral Si/Fe ratios.

Conclusions

- Contrary to the adsorption of light Si isotopes on Fe(III)(oxyhydr)oxides, coprecipitation removes heavy Si isotopes from solution during mineral formation (up to δ^{30} Si +0.994 (2SD: 0.111) % or ϵ^{30} Si +1.217 (2SD: 0.058 %).
- The experimental results show similarities to Si isotope variations in natural BIFs indicating that coprecpipitation is the major contributor to Si isotope fractionation.
- The fraction of Si isotopes is dependent on pH, Si/Fe ratios as well as the composition of the precipitation matrix, in particular the presence of P and As ions.
- The current study potentially explains the "missing heavy Si isotope sink" and add complexity in estimating characteristics of the Early Proterozoic environment, e.g. ocean temperature.

References

Hemmingsson C., Pitcairn I.K. and Chi Fru E. (2018) Evaluation of phosphate-uptake mechanisms by Fe(III)(oxyhydr)oxides in Early Proterozoic oceanic conditions. Environmental Chemistry. (Accepted)