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Assessing the potential of *in situ* silicon isotope ratios as palaeo-Si proxy in (re)crystallized material

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The early Phanerozoic has been long thought to have witnessed a decline in ocean dissolved Si, with implications for carbon cycling and climate regulation [1]. The evidence for this decline comes from petrological observations, distribution of fossils, bulk chert Si isotopes (δ^{30}Si) and carbonate lithium isotopes, but direct, quantitative reconstructions of silicon concentrations are missing. In this regard, the magnitude of Si isotope fractionation during growth of siliceous sponge spicules - which depends on ambient seawater Si concentrations - opens a potential window to reconstructions of Si concentrations in geological time, if spicules preserve their initial δ^{30}Si.

Here, we use *in situ* fsLA-MC-ICP-MS to determine the δ^{30}Si and Al/Si ratios of sponge spicules and matrix of four Ediacaran-Cambrian cherts from Yanziqiao section, South China. These cherts formed from seawater with little hydrothermal influence, and are thought to span the stepwise Si decline. All samples are pure cherts (SiO_2>95%) dominated by microquartz. Under transmitted light, white spicules are easily distinguished from the darker matrix and usually exhibit mono- or multiaxial shape.

In all samples, matrix and spicule are very close in composition, with their absolute differences in δ^{30}Si smaller than 0.4‰. In detail, we observe three different δ^{30}Si patterns: (1) spicule δ^{30}Si significantly lighter than matrix; (2) spicules δ^{30}Si significantly heavier than matrix; (3) spicule and matrix of two samples statistically indistinguishable. Differences in Al/Si between matrix and spicule are similarly inconsistent, but display intriguing relationships with δ^{30}Si. We discuss possible mechanisms leading to these patterns, and conclude that δ^{30}Si values reflect a combination of kinetic and equilibrium processes during diagenesis. Overall, caution is required when using Si isotope ratios of ancient spicules that are diagenetically altered from their original amorphous silica as a Si concentration proxy.

[1] Goldschmidt, Isson & Planavsky (2018), Nature 560, 471–475.