Si-isotope fractionation during silica precipitation: An experimental approach

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Interpretations of silicon isotope compositions of natural silica deposits suffer from poor constraints on the isotopic fractionation behaviour during precipitation of the silica from a saturated solution. We tested an experimental setup to explore the conditions under which equilibrium precipitation of amorphous silica would occur in the 10-60°C temperature range using flow-through reactors. The objective is to constrain magnitudes and sign of silicon isotope fractionation, the degree of temperature dependence and the sensitivity to non-equilibrium conditions.

Stock solutions, prepared from amorphous silica powder and brought to saturation at 90°C, were forced to pass flow-through reactors, seeded with ca. 200 mg of silica powder with known surface area at well-controlled flow-rates. Precipitation was induced by placing the reactors in a water-bath at the desired temperature. According to a comprehensive set of test runs, our experimental set-up enables us to achieve equilibrium during controlled silica precipitation in the reactors, provided that conditions are carefully tuned. Factors with a strong influence included the applied flow-rate, pH, specific surface area and degree of supersaturation.

Silicon isotope measurements ($^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$), carried out on input and output solutions using a Finnigan Neptune MC-ICPMS, presented insight into the sign and magnitude of isotopic fractionation. Preliminary results for runs where equilibrium was secured demonstrated that, under these experimental conditions, $\delta^{30}Si$ values for SiO_2 remaining in solution were up to 0.5‰ lower relative to the input solution, implying discrimination against the uptake of the lighter isotopes in the solid. The fractionation increased with decreasing temperature.

The observed direction is opposite to what is often seen in natural solid-fluid systems, indicating that equilibrium versus non-equilibrium conditions during precipitation might be a critical factor in the use of Si isotopes as a proxy.

The rusty sink: Impact of Iron on the sedimentary organic biomarker record

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The biogeochemical cycles of iron (Fe) and organic carbon (OC) are strongly linked, each element exerting some degree of control over the other. In the oceans, organic ligands control the concentration of dissolved Fe in the water column. In soils, Fe and OC concentrations are typically correlated, suggesting that they are closely associated. Nevertheless, until now, the role of Fe in the preservation of sedimentary OC has not been clearly established. We recently determined that 20 to 40% of the total OC in marine and freshwater sediments is closely associated to solid reactive Fe phases (operationally defined as the solid iron phases that are reductively dissolved with sodium dithionite). In young and mature sediments, solid reactive Fe phases do not provide sufficient surface area for chemisorption of OC onto Fe oxides. Alternatively, high OC:Fe ratios reflect the existence of largely organic Fe-OC macromolecular structures (through chelation and co-precipitation), attached only minimally to the surface of clay mineral grains. The organic matter in these Fe-OM chelates is 'glued' together by iron ions or nanophases of iron oxide crystals. We also found isotopic and elemental fractionation between Fe–associated OC and the rest of the sedimentary OC pool, with ^{13}C and nitrogen-enriched OC preferentially bound to Fe, and suggesting biochemical fractionation. The presence of iron and the interactions between iron and organic matter also affect the recovery of a broad range of organic biomarkers from sediments. In this communication, we will present and discuss the impact of iron on the recovery of amino, lipid and lignin biomarkers as well as on the environmental message obtained through biomarker analysis. Alternative methods that circumvent the effects will also be presented.