Calcification mechanisms explain why proxies in foraminifera and corals are good recorders of their environment

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Current thinking on biologically controlled calcification involves active and passive transport of calcium from the environment across cell membranes to form cellular storge [1]. The formation of the mineral phase may be intracellular (e.g. coccolithophores) or extracellular, within a delimited space. Calcium is transported from the cellular stores as an free ion or in vesicles, under tight cellular control to the delimited space. The carbonate supply is usually ignored or assumed simple: CO_2 may diffuse freely from the environment, or respiratory CO_2 may provide an internal source for DIC. Given the complete cellular control on the ions supply, it is surprising that trace elements and isotopes are incorporated into marine biogenic carbonates with meaningful relations to the seawater. Furtheremore, despite some deviations from thermodynamic equilibrium, geochemists and paleoceanographers have utilized various proxies in biogenic carbonates (mainly foraminifera, corals, sponges and mollusks) very successfully to reconstruct past oceanic conditions. The current biological thinking (described above) is incorrect. The ions (Ca, Mg, Sr, Ba, DIC, B, Li, and others) and their isotopes are supplied to the delimited calcification space by **direct trasport of ambient seawater** (slightly modified). This has been demonstrated unequivocally in foraminifera [2,3], and more recently has been shown for corals [4]. The pathway of seawater transport to the site of biomineralization is by vacuolization in foramoinifera, and apparently by paracellular leakage in corals. In other marine invertebrates seawater is present at the biomineralization delimited space, but it remains to be shown how this is achieved. Seawater is rich in Ca (~10.5 mM, as opposed to 0.1 μM in live cells), however the DIC concentration (~ 2mM), is much lower.. High Mg concentration (~ 55 mM) inhibits calcite precipitation and hence high supersaturation is needed in order to precipitate the $CaCO_3$ shells. The most common mechanism to increase saturation is elevation of pH at the calcification site. This pH elevation helps to supply DIC both from seawater and from respiration as observed in corals and foraminifera.. The composition of various isotopic and elemental proxies in both groups (e.g. O, C, B, Li, Mg, Sr and others) are best explained using this novel calcification mechanism. Direct seawater transport (DST) explains the usefulnes of paleoceanographic proxies in biogenic carbonates.

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Coupled Ge/Si and Ge isotope ratios as new geochemical tracers of seafloor hydrothermal systems: A case study at Loihi Seamount

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Germanium isotope and Ge/Si ratio systematics were investigated in low temperature hydrothermal vents from Loihi Seamount (Hawaii, USA) and results were compared to high-temperature vents from East Pacific Rise at 9-10°N. Loihi offers the opportunity to understand a low temperature basalt leach system with surface deposits mainely composed of iron oxyhydroxides. The results show that both Ge/Si and $\delta^{74/70}$Ge in hydrothermal fluids are fractionated relative to the host basaltic rock with Ge/Si ~ 30 and 5.7 μmol/mol and δ^{74}Ge ~ 1.9 and 1.55‰ for Loihi and EPR (Bio9) respectively vs. Ge/Si ~ 2.2 μmol/mol; δ^{74}Ge ~ 0.56‰ for basalt[1]. The relative enrichment in Ge vs. Si together with Ge isotope fractionation can be explained by quartz precipitation in the reaction zone at depth. Using Ge mass balance between hydrothermal fluids and fresh basalts, we calculated a $\Delta^{74}Ge_{quartz\text{-}fluid}$ of about -5.0‰. Although the fractionation of Ge isotopes in quartz is presently unknown, such apparent large Ge isotope fractionation at elevated temperature suggests concomitant loss of Ge and Si during fluid upflow resulting in Rayleigh-type effect and/or a fractionation during the basalt dissolution. The study of microbial mats at Loihi Seamount, composed essentially of Fe-oxyhydroxide with minor phases of amorphous silica and volcanic materials, also suggest that Ge isotopes are fractionated upon precipitation at the seafloor during seawater - hydrothermal fluids mixing. We obtained a maximum Ge isotope fractionation between Fe-oxyhydroxide (ferrihydrite) and dissolved Ge in the fluid of about -2.74‰. Isotopic variations observed in the different mats have being interpreted as reflecting the percentage of Ge sequestration in microbial mats; the lower values corresponding with the highest Ge trapping. This result is consistent with recent experimental estimation[2]. This study shows that combining Ge/Si and δ^{74}Ge systematics provide a useful tool to trace hydrothermal Ge and Si sources in marine environments and to understand formation processes of seafloor hydrothermal deposits. Preliminary mass balance of germanium isotope in seawater reveals that the missing Ge sink may correspond to Ge sequestration into Fe-oxyhydroxides within marine sediments.

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