

Redox- and diffusion-controlled fractionation of Fe stable isotopes in silicate minerals of igneous rocks

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Amongst the non-traditional stable isotopic systems available for study in high temperature geochemistry, Fe isotopes have received particular attention. However, the controls of Fe stable isotope fractionation in high temperature magmatic systems are not fully understood, mainly due to poorly constrained isotopic fractionation factors between silicate minerals and melts.

We present new Fe stable isotope data obtained using a high precision double-spike technique ($\delta^{56}\text{Fe} \pm 0.02\text{‰}$, 2 sd) for minerals from terrestrial (basalt-rhyolite, gabbro-granite, boninite) and extraterrestrial igneous rocks (angrites, eucrites, mesosiderites). Results show that significant mineral isotopic fractionations exist in terrestrial samples that appear to be controlled by Fe redox state ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = -1.0$ to $+0.85\text{‰}$). Fe^{2+} -rich minerals like olivine display enrichments in light Fe ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = -0.35$ to -0.25‰) compared to host melt ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = +0.05$ to $+0.22\text{‰}$). Conversely, Fe^{3+} -rich minerals like plagioclase have heavy Fe ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = +0.25$ to $+0.42\text{‰}$), and alkali feldspar exhibits markedly heavy Fe ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = +0.85\text{‰}$). Clinopyroxene typically has a Fe stable isotopic composition the same or only slightly lower than host melt. In contrast to the terrestrial samples, olivine, pyroxene and plagioclase from basaltic meteorites formed on planetesimals that differentiated in the early Solar System under reducing magmatic conditions do not show measurable Fe stable isotope fractionations. This demonstrates isotopic fractionation between Fe^{2+} and Fe^{3+} in high temperature magmatic systems, which is then captured in terrestrial igneous rocks when minerals incorporate various proportions of these two Fe pools according to their mineral chemistry.

Analyses of single olivine crystals from a basaltic andesite erupted in a subduction zone setting display an extreme isotopic range ($\delta^{56}\text{Fe}_{\text{IRMM-14}} = -0.96$ to $+0.19\text{‰}$). Evidence for chemical zonation in the olivine related to Fe-Mg interdiffusion between olivine and melt suggests that significant stable Fe isotopic fractionation in the olivines may be due to diffusion-driven processes. This dataset will be complemented by Mg stable isotopes of the same grains in order to assess the relative importance of redox- and diffusion-controlled processes on Fe stable isotopic fractionation in high temperature magmatic systems.

Carbon isotope fractionation associated with CaCO_3 precipitation induced by ureolysis

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It is increasingly recognized that carbonate precipitation by microorganisms presents some similarities with the carbonate biomineralization of skeleton-forming organisms. For example, in both processes crystallization often starts with the formation of amorphous carbonate, and the polymorphism and habit of carbonate crystals are influenced by interactions with the cell membrane or with extracellular organic products. However, if the occurrence of vital isotopic effects has been extensively documented for skeleton-forming organisms, so far the potential vital effects associated with microbial carbonate precipitation have remained unexplored. Paleoenvironmental reconstructions based on microbial carbonates therefore rely on the assumption that the carbon isotope fractionation expressed during microbial carbonate precipitation is equal to that expressed during inorganic precipitation at isotopic equilibrium.

We performed an experimental study of the carbon isotope fractionation expressed during CaCO_3 precipitation associated with ureolysis induced by *Sporosarcina pasteurii* used as a model organism for carbonate precipitation by heterotrophic bacteria. The crystallization sequence initiates with the formation of amorphous calcium phosphate followed by vaterite and then calcite, which dominates the CaCO_3 products at the end of precipitation. The carbon isotope composition of CaCO_3 evolves following a typical Rayleigh distillation pattern, which can be modeled assuming precipitation with no isotopic re-equilibration between CaCO_3 crystals and dissolved inorganic carbon (DIC). According to this model, the first stage of precipitation, possibly of vaterite, is characterized by an increasing ^{13}C -depletion of CaCO_3 relative to DIC of up to 2‰. The second stage, probably of calcite, proceeds very close to calcite precipitation isotope equilibrium. These results suggest that vital isotopic effects are probably not limited to skeleton-forming organisms but may also occur during microbial biomineralization, where they might be related to the initial precipitation of metastable mineral phases.