Chromium isotope fractionation during coprecipitation with calcium carbonate

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The chromium (Cr) isotopic composition of carbonates can potentially be used as a paleoclimate proxy to elucidate past fluctuations of oxygen contents in atmosphere and hydrosphere. The use of Cr isotopes to track paleoenvironmental changes, for example related to the rise of oxygen during the Archaean and Protoerozoic, needs careful assessment of the signal robustness and necessitates a thorough understanding of the Cr cycle in Earth system processes. We conducted experiments testing the incorporation and isotopic fractionation of chromate into the calcite lattice. Our experiments indicate enrichment in Cr concentration and preferential incorporation of heavy Cr isotopes in the precipitates. Further, experiments following the procedure of [1], showed an increasing relative isotope difference between precipitate and initial solution ($\Delta^{53}Cr_{[p\text{-}is]}$) from +0.06 to +0.18 ‰ with increasing initial Cr solution concentration. Another set of experiments conducted in double diffusion silica hydrogel [2] yielded calcite crystals again significantly enriched in heavy Cr isotopes with [$\Delta^{53}Cr_{[p\text{-}is]}$] of +0.29 ± 0.08 ‰ (2σ), whereas silica hydrogel samples show a preferential retention of light Cr isotopes. Previous studies of δ^{53}Cr seawater signals inferred from carbonates may have been too positive. However, considering that seawater Cr concentrations are significantly lower than those chosen for our experiments, a trend towards lower [$\Delta^{53}Cr_{[p\text{-}is]}$] at lower initial Cr concentrations could mean marginal to no Cr isotope fractionation in the oceans. These experiments represent a first step toward understanding the Cr isotope signal of carbonates where fractionations will likely be ≤ 0.3 ‰ and as such, pave the way for future work to enable a reliable application of the Cr isotope proxy.

[1] Hua *et al*, 2007, *Water Air Soil Poll.* **179**, 381-390. [2] Sánchez-Pastor *et al*, 2011, *Cryst. Growth Des.* **11**, 3081-3089.