



Effect of pH on chromate incorporation during calcite growth - An experimental approach

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Chromium (Cr) is commonly present in marine environments, whereas e.g. in soils and aquifers it is mostly referred to weathering processes. The toxic Cr(VI) species, occurring as bichromate (HCrO_4^-) and chromate (CrO_4^{2-}) ions, are highly soluble in aqueous solution. Limits of chromate mobility in the aqueous environment can be either induced by its reduction to Cr(III) and/or by incorporation into coprecipitating minerals, f.i.e. carbonates. Although the elemental and isotopic cycling of Cr has been studied in marine and environmental settings, the effect of parameters such as temperature, pH or precipitation rate on chromate incorporation into carbonate minerals is still less explored. We performed calcite precipitation experiments using a mixed flow reactor at ambient temperature and distinct pH values. For this, a KCl and a K_2CO_3 (including chromate) bearing solutions were introduced into the stirred reactor at a constant flow rate using a peristaltic pump. The pH was kept constant by bubbling air or adding KOH solution into the reacting solution throughout the experimental runs. Preliminary results indicate the pH to play a crucial role for chromate incorporation behaviour into calcite. From pH 8.0 to 9.5 the molar chromate of the precipitating calcite decreases from about 0.005 to 0.002. In contrast, from pH 9.5 to 10.5 the molar chromate of the calcite increases from 0.002 to 0.004. This incorporation behaviour might be related to the dominance of CO_3^{2-} in solution and therefore the preferential incorporation of the aqueous CrO_4^{2-} , which is assumed to adopt an off-center position in the CO_3^{2-} site. Ongoing investigation is also focussed on the reaction mechanisms controlling $^{53/52}\text{Cr}$ isotope fractionation during chromate uptake in calcite.