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Experimental studies of REE fractionation during water-mineral interactions

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REE compositions of natural solutions have received particular attention because of their potential as chemical tracers of natural fluid-rock processes (e.g. Sholkovitz, 1993; Byrne et al. 1996; Harlavan and Yigal, 2002), and because REE are believed to exhibit a similar behavior as actinides extracted from nuclear waste. In an attempt to illuminate the behavior of REE in low temperature geochemical processes, the REE release rate was measured during open system apatite dissolution experiments at 25° C and 2.8 > pH > 9.2.

In agreement with previous studies, apatite dissolution rates based on Ca release decrease monotonically with increasing pH. REE release rates, however depend strongly on the rhabdophane (REE(PO₄)·nH₂O) saturation state of the reactive fluid. When rhabdophane is supersaturated, $a_{\text{PO}_4\text{-a}_{\text{REE}^{3+}}} < -26.3$, REE are retained in the solid phase and the middle REE are preferentially retained compared to the light and heavy REE. This observation is consistent with the precipitation of MEE rich rhabdophane during the experiments. When rhabdophane is supersaturated, $a_{\text{PO}_4\text{-a}_{\text{REE}^{3+}}} > -26.3$, REE are released in stoichiometric proportions compared to Ca except during the end of some long term experiments which had previously experienced rhabdophane precipitation. In these latter situations, REE are preferentially released and MREE release is favored, consistent with the dissolution of previously precipitated rhabdophane. Regression of these results was used to determine rhabdophane dissolution and precipitation rates. Combination of retrieved rates and REE solubility calculations indicates that rhabdophane dissolution/precipitation is sufficiently rapid to control the REE concentration and spectra of many near surface waters.

References

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4.2.P05

Fe isotope fractionation in calcium carbonate

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Calcium carbonate precipitates over a range of temperatures in a wide variety of geological environments. Given that Fe(II) is readily incorporated in the structure of calcium carbonate minerals, the stable Fe isotope ratios of the substituted Fe may be useful in understanding carbonate formation. Thus, we have analysed Fe isotopes in a suite of magmatic and metamorphic carbonate rocks by multiple-collector inductively coupled mass spectrometry (MC-ICP-MS) using a ⁵⁸Fe-⁵⁴Fe double spike. $\delta^{56}\text{Fe}$ varies from +0.07‰ for plutonic CaCO₃ samples to $\delta^{56}\text{Fe} = -1.2‰$ for pegmatite samples (relative to IRMM-14; $\pm 0.05‰$, 2 sd). Fe is generally isotopically lighter than the bulk-Earth value, demonstrating that significant abiotic fractionation occurs at higher temperatures during calcium-carbonate formation.

In one hydrothermally-precipitated crystal of calcite, separate analysis of enclosed goethite particles yielded $\delta^{56}\text{Fe}$ of -0.65‰, whereas Fe(II) in the calcite structure has $\delta^{56}\text{Fe}$ of -0.86‰. Based on the high formation temperature and the well-developed calcite morphology, we interpret the small but significant $\Delta^{56}\text{Fe}_{\text{goethite-calcite}} = 0.21 \pm 0.10‰$ (2 sd) to reflect processes occurring while isotopes are at equilibrium. In the literature, reduced partition functions, which describe fractionation for a range of compounds as a function of temperature, have been estimated from Mössbauer (MS) and vibrational (VS) spectroscopy data. For siderite-goethite fractionation, MS-data predicts that the observed $\Delta^{56}\text{Fe}_{\text{goethite-calcite}}$ occurred at 800°C. This formation temperature is inconsistent with mineral assemblages, corroborating the suggestions that MS-data overestimate isotope fractionation. However, the qualitative implications of reduced partition functions, combined from MS and VS data, might suggest that the minerals formed in a solution of (i) isotopically light Fe(II) or (ii) strongly complexed Fe(II) having an isotope composition resembling the bulk-Earth value. Results of laboratory experiments involving precipitation of carbonate under a range of T-X conditions and complementary Mg isotope studies on the natural carbonate minerals will also be presented.