

## Iron isotope compositions of carbonatites record melt generation and late-stage volatile-loss processes

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Carbonatites define the largest range in Fe isotope compositions yet measured for magmatic rocks, recording significant isotopic fractionations between carbonate, oxide, and silicate minerals during generation in the mantle and subsequent differentiation. In contrast to the homogeneous  $\delta^{56}\text{Fe}$  values for mantle-derived basaltic magmas, where  $\delta^{56}\text{Fe} = 0.00 \pm 0.05 \text{‰}$ , calcite from carbonatites have  $\delta^{56}\text{Fe}$  values between +0.6 and -1.0 ‰, similar to the range defined by whole-rock samples of carbonatites. Based on expected carbonate-silicate fractionation factors at igneous or mantle temperatures, carbonatite magmas that have negative  $\delta^{56}\text{Fe}$  values can be explained by equilibrium with a silicate mantle. However, positive  $\delta^{56}\text{Fe}$  values for carbonatites are unexpected, and such values likely reflect late-stage exsolution of Fe-bearing chloride fluids, which will have low  $\delta^{56}\text{Fe}$  values at igneous temperatures.

The ranges in  $\delta^{56}\text{Fe}$  values for minerals separated from carbonatites are: magnetite: +0.2 to -0.5‰; clinopyroxene: +0.30 to -0.44 ‰; mica: +0.30 to -0.48 ‰; pyrite: +0.39 to +0.09 ‰. Most samples that have the negative bulk-rock  $\delta^{56}\text{Fe}$  values expected for equilibrium with silicate mantle also have magnetite-calcite and magnetite-silicate fractionations that lie along those expected for either melt eruption or emplacement temperatures. Samples that have the positive bulk-rock  $\delta^{56}\text{Fe}$  values suggesting late-stage loss of Fe chloride solutions generally have disequilibrium magnetite-silicate, magnetite-calcite, and magnetite-pyrite fractionations, consistent with rapid late-stage volatile-loss model under disequilibrium conditions.

The large range in Fe isotope compositions of carbonatites, reflecting their very low Fe contents, make Fe isotopes an exceptionally sensitive tracer of carbonatite melt generation in the mantle and late-stage fluid loss in the crust. During melt generation, the carbonatite melt-mantle fractionation factor should be entirely accommodated by changes in the  $\delta^{56}\text{Fe}$  values for carbonatite magmas, given the relatively high Fe contents of the silicate mantle. Similarly, during late-stage fluid loss, the very low Fe contents of calcite should record large Fe isotope fractionations during fluid exsolution.

## A multi-site ion exchange model to predict contaminants sorption in sediments

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For a better prediction of contaminant migration in environment, over a wide range of chemical conditions, the cation exchange model [1] was particularly improved by considering sorption on multiple sites with different site capacities and sorption affinities [2-4]. Besides of the important development brought by these former authors, our approach is somewhat different [5, 6]. Indeed, for one given pure mineral, the sorption behaviour of each interest cation M is studied by 1) sorption curves obtained by plotting the concentration of sorbed cation in function of pH, under saturation conditions and at trace concentration; 2) sorption isotherm as a function of aqueous cation concentration. The treatment of both types of curves allows us to determine the concentrations of site having strong and weak sorption affinity (in meq/kg dry rock) and selectivity coefficients  $K_{M/H}$  for each of the identified sorption sites.

This study aims to predict the sorption of different cation metals (here: Sr, Zn) on natural sediments for various ionic strengths, pH's and in presence of different competitor cations. In a second step, the predicted results are compared to data issued from sorption experiments carried out in static batches reproducing different physico-chemical conditions.

The experimental study was carried out with a natural sediment constituted from a mixing of illite, smectite, quartz and carbonate. The water chemical conditions are imposed on field by the proximity of sea-water involving high Na, Cl, Ca and  $\text{SO}_4$  gradient concentration in the sediment profile. Experimental results and modelling ones are generally in a good agreement, and particularly well reproduce the effect of ionic strength and the role of competitor cations on the sorption of Sr and Zn. Integration of this approach in a reactive transport model is in progress.

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