

Calcium isotope fractionation associated to adsorption and desorption on/from δ -MnO₂

ANNE-DESIREE SCHMITT¹, SOPHIE GANFLOFF¹, JEAN-MICHEL BRAZIER¹, EMMANUEL TERTRE²

¹ Université de Strasbourg, CNRS, ENGEES, LHyGeS UMR 7517, 1 rue Blessig, 67000 Strasbourg, France

² Université de Poitiers/CNRS, UMR 7285 IC2MP/HydrASA, B8 rue Albert Turpain, 86073 Poitiers, France

In this study, we experimentally investigated Ca isotopic fractionation during its adsorption on and desorption from δ -MnO₂, an ubiquitous mineral in soils, at 20°C as a function of time, pH, initial aqueous Ca concentration and nature and concentration of the desorbent (salts of NH₄⁺, K⁺ and cobalt hexamine).

Stationary state for adsorption was achieved rapidly whatever the pH and initial aqueous Ca concentration used. Between pH 4 and 10, Ca-adsorption is pH independent, suggesting that Ca is mainly adsorbed in interlayers and on basal surfaces of the particles. During adsorption step, the light ⁴⁰Ca isotope was preferentially adsorbed with an isotope fractionation $\delta^{44/40}\text{Ca}_{\text{solid-solution}}$ equal to 1.2‰. These data are consistent with a closed-system equilibrium exchange between the solid and the solution, with a $\alpha_{\text{solid-solution}}$ value equal to 0.9988. Furthermore, the amount of desorbed Ca depends strongly on the nature of the desorbent and number of desorption cycles used, and evolves with time. This evolution is probably due to structural modifications during these steps. Isotopic signatures of the desorbed solution evolve then also with time, starting from the composition of the Ca adsorbed after the adsorption step to the composition of the solution used before adsorption. This behaviour suggests that first Ca which is desorbed probably comes from external basal surfaces, while more Ca is extracted from interlayer sites when desorption time increases.

These different results tend to confirm that Ca isotopic fractionation during adsorption is governed by the amount of structural charge in the mineral, and more specifically by adsorption on external basal surfaces, in accord with similar results obtained previously with different clay minerals commonly found in soils (Brazier et al., 2019).

Brazier et al. (2019). *GCA* **250**, 324-347.