

Calcium isotope fractionation during adsorption and desorption on/from soil phyllosilicates and phylломanganates(kaolinite, montmorillonite, muscovite and vernadite)

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Small mineral particles present in soils, such as clay minerals and oxyhydroxides, constitute important nutrient reservoirs due to their negative charges and high specific surface areas allowing them to adsorb cations such as calcium (Ca), a macronutrient that occupies key physiological and structural functions in plant metabolism. Few is known concerning the mechanisms of isotopic fractionation associated with Ca adsorption and desorption onto/from such minerals commonly found in soils. In order to better understand such mechanisms, the possible fractionation between ⁴⁰Ca and ⁴⁴Ca during adsorption and desorption of Ca onto/from an abiotic synthetic phylломanganate (vernadite), and three “model” phyllosilicates (KGa-2 kaolinite, Swy-2 montmorillonite and Tuftane muscovite) with a 0.1-1µm size was studied. Experiments were performed in batch reactors (closed system), and several parameters (time, pH, Ca aqueous concentration) were tested to cover a large range of physicochemical conditions.

The light ⁴⁰Ca isotope is preferentially adsorbed on all the minerals having a permanent charge, with the highest amplitude of isotope fractionation between the reactive solution and the mineral recorded for vernadite. The Ca desorption, induced by reaction with a chloride hexamine cobalt solution, suggest that Ca adsorption and the associated isotopic fractionation are fully reversible for phyllosilicates and vernadite.

For phyllosilicates, the intensity of the isotopic fractionation during adsorption is controlled by the layer charge and the specific surface area, as well as the presence of an interlayer space open to cations. For vernadite, the isotopic fractionation is dependent on the nature of the site involved during the adsorption step (i.e., enriched in ⁴⁰Ca in the interlayer and enriched in ⁴⁴Ca on the edges). Such behavior is likely due to differences in adsorption processes on these two sites with (i) ion exchange of Ca²⁺ with H⁺ in the interlayer sites, and (ii) bidentate nature of the Ca adsorption on edges.

Consequently, adsorption onto phyllosilicate and phylломanganate minerals could be non-negligible contributors