Calcium isotopic fractionation during adsorption and desorption onto common soil phyllosilicates

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Mineral soils constituents play an important role in the storage/release of nutrients due to their cation adsorption/desorption capacity. Previous work has highlighted the potential of Ca isotopes ($\delta^{44/40}$ Ca) to identify secondary processes occurring in soils. Nevertheless, the mechanisms of isotopic fractionation (amplitude, nature) associated with the adsorption/desorption phenomena of Ca onto different constituents of the soil remain poorly understood. This step is fundamental in order to improve our understanding of the biogeochemical cycle of Ca at the watersoil-plants interface.

Consequently, the study of a possible isotopic fractionation during Ca adsorption/desorption was carried out experimentally using "model" substrates representative of the minerals frequently encountered in soils (phyllosilicates: KGa-2 kaolinite, Swy-2 montmorillonite and Tuftane muscovite). The experiments were carried out under abiotic conditions in water-mineral batch systems by controlling the physicochemical conditions of the medium: pH, solid/solution ratio, initial dissolved Ca concentration, ionic strength, particle size distribution, reaction kinetic and cation competition.

Our results show no significant isotopic fractionation associated with adsorption or desorption of Ca onto kaolinite and muscovite regardless of physico-chemical parameters However, during adsorption of Ca onto used. montmorillonite, the light isotope (⁴⁰Ca) is preferentially adsorbed on the clay mineral and a positive isotopic fractionation of 0.25‰ is observed in the solution. The opposite is observed for desorption. This suggests that the isotopic fractionation of Ca is reversible and probably related to the adsorption in the interlayer space of the particles and not to the adsorption onto the sites present on the lateral surfaces (aluminol and silanol edge sites). The amplitude of the fractionation is thus a function of the accessibility of the aqueous major element to the interlayer of the clayey particle and then is dependent of its cristalchemistry.