Ni isotopic fractionation at the interface with mineral phases

I.O. ZELANO[1,2], E. MONTARGES-PELLETIER[1], R. GLEY[1], F. FRAYSSE[1], G. LANDROT[3], C. CLOQUET[2]

[1]LIEC, CNRS-Université de Lorraine, 15 Avenue du Charmois, 54500 Vandœuvre-lès-Nancy, France. isabella.zelano@gmail.com, emmanuelle.montarges@univ-lorraine.fr, renaud.gley@univ-lorraine.fr, fabrice.fraysse@univ-lorraine.fr
[2]CRPG, CNRS-Université de Lorraine, 15 rue Notre-Dame-des-Pauvres, BP20, 54501 Vandœuvre-lès-Nancy, France. cloquet@crpg.cnrs-nancy.fr
[3]Synchrotron SOLEIL, l'Orme Des Merisiers St Aubin, BP 48, 91192 Gif sur Yvette, France
gautier.landrot@synchrotron-soleil.fr

Nickel isotopes have recently been proposed as a new tool to investigate the metal biogeochemical processes. However, a complete comprehension of reaction mechanisms responsible for Ni isotopic fractionation factors is still missing[1,2]. In this study, the isotopic tool was combined with X-Ray Absorption Spectroscopy to associate Ni isotopic fractionation to the modification of its chemical speciation. Nickel sorption isotherms were conducted on pure mineral phases with permanent cation exchange capacity (nontronite) and without (goethite, talc, and calcite). X-ray absorption spectra at Ni K-edge were collected on solid phases in fluorescence mode. Nickel predominantly forms outer-sphere complexes at nontronite surface. The weakness of electrostatic bonds may explain the negligible isotopic fractionation $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ observed for this charged clay mineral. When mineral phases present specific surface sites, e.g. talc and goethite, a preferential sorption of light isotopes was observed, in agreement with previously published data[1,2]. $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ was between -0.29 and -0.86‰ for talc, and -0.43 and -0.94‰ for goethite (2σ=0.05‰). For goethite, the increase of [Ni] promotes the sorption of light isotopes as a consequence of competition for specific surface sites. For calcite, increasing the amount of Ni sorbed from 3 % to 82 %, $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ varied between -0.23‰ and +0.17‰, respectively. The spectroscopic data of Ni-$CaCO_3$ showed the presence of a Ni second neighbor (at 3-3.3 Å) that can be attributed to surface precipitation. These preliminary results suggested that, as goethite, at low % of Ni sorbed, calcite is enriched in light isotopes, but formation of $Ni(CO_3)_2$ in solution and successive precipitation could contribute to the association of heavy isotopes with the solid phase.

[1]Gueguen, B. et al. **2018**. [2]Wang, S.-J.,Wasylenki, L. **2017**