

Zinc isotope fractionation onto reactive minerals: The case of kaolinite

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Zinc is today one of the most widely spread elements in environmental systems as a result of human activities. For 15 years, zinc isotopes appeared to be a powerful tool to decipher Zn sources [1], as well as the processes controlling its transfer to and within the environment. However, part of Zn isotopic cycle at Earth's surface remains poorly known. For example, the isotopic fractionation factors associated to zinc sorption onto organic matter [2] and oxides [3-5] are known with an enrichment in heavy isotopes of sorbed Zn, but are still missing for Zn sorption onto clays.

In this study, we measured the isotope fractionation induced by Zn sorption onto a certified kaolinite (50mg of KGa-2 from CMS was introduced in each batch). A first set of experiments was conducted at two different ionic strengths (0.01 and 0.1M) by varying pH from 3 to 9. A second set was realized at two fixed pH (4 and 6) and constant ionic strength (0.01M) but with Zn concentration ranging between 5 and 1500 μ M. Sorption evolution is correctly fitted by a two-site model including 1/ an ionic exchange reaction at low pH onto permanent negatively charged sites located on basal sheets and 2/ a specific inner-sphere complexation at high pH onto pH-dependent charged sites located on the clay edges.

Zinc sorption is characterized by an enrichment of heavy isotopes on the kaolinite surface with different Δ solid-solution corresponding to the different sites: exchange sites $0.18 \pm 0.04\%$ and edge sites $0.49 \pm 0.04\%$. An agreement was observed between theoretical isotopic evolution predicted using our two-sites model and experimental measurements. Fractionation during ionic exchange is attributed to a change in symmetry for Zn surrounded by water molecules compared to aqueous specie. For edge sites, spectroscopic studies indicated a conservation of average Zn-O bond length and coordination number of Zn during its sorption [6]. We thus explained Zn isotopic fractionation by a shortening of Zn-O bond length at the mineral surface, in opposition to a lengthening of remaining Zn-O bonds.

[1] Chen et al. (2008) *ES&T* [2] Jouvin et al. (2009) *ES&T* [3] Pokrovsky et al. (2005) *JCIS* [4] Juillot et al. (2008) *GCA* [5] Balistrieri et al. (2008) *GCA* [6] Natchegaal et al. (2004) *JCIS*.