The mechanism of isotopic fractionation during selenium adsorption on iron oxides: An EXAFS study

HAI-BO QIN[1], JIAN-MING ZHU[2,1], WEN-PO XU[1,4], AND YOSHIO TAKAHASHI[3]

[1] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang, China (qinhaibo@vip.gyig.ac.cn)
[2] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing, China (jmzhu@cugb.edu.cn)
[3] Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Japan
[4] University of CAS, Beijing, China

Selenium (Se) could be used to trace the biogeochemical cycling, and also be regarded as the powerful proxy for paleo-ocean and evolution of atmosphere, based on its multiple valences and six stable isotopes. The content and isotopic composition of Se in modern oxic seawater could be impacted by the adsorption of ferromanganese oxides, however, the study on isotopic fractionations during adsorption of Se on iron oxides is very lacking. Furthermore, previous study has observed that different isotopic varition during Se species adsorption on iron oxides, but they didn't explain this disparity [1]. In this study, the mechanisms of isotope fractionation during Se adsorption on iron oxides were tried to be elucidated at molecular level using XAFS technique. The XAFS results showed that inner-sphere and outer-sphere complexes can be formed in the case of the adsorption of Se(IV) and Se(VI) on iron oxide, respectively. This could be the reason for that Se(IV) isotopic fractionation is larger than Se(VI), which observed in Mitchell's study[1] and ours. This explanation has been proved to be reasonable for molybdenum adsorption to iron and manganese oxides in recent research [2], in which larger isotopic fractionation caused by the structure change from tetrahedral to octahedral inner-sphere during Mo adsorption on manganese oxide. These results indicate that the mechanisms for isotopic fractionations can be well revealed on the basis of their structural information obtained by XAFS technique.

The work was supported by the National Natural Science Foundation of China (41303099), CAS "Light of West China" Program, and Natural Science Foundation of Guizhou Province, China ([2013]2287).

[1] Kashiwabara *et al.* (2011). *Geochim.Cosmochim.Acta* **75**, 5762-5784. [2] Mitchell *et al.* (2013). *Chem.Geol.* **342**, 21-28.