

Speciation and fate of As in calcite formed under anoxic condition

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Speciation analyses for arsenic (As) in natural calcite, precipitated in fracture of deep underground sedimentary strata (Hokkaido, Japan), were performed using micro X-ray fluorescence and XAFS (μ -XRF-XAFS) technique to infer how calcite limit As migration in groundwater system.

Chemical data of pore water and groundwater collected from the sedimentary strata showed that arsenite (As^{III}) is predominant aqueous As species in the water phase. Nevertheless, As in the natural calcite is arsenate (As^{V}) [1]. This inconsistency of As species between calcite and water phases has already been observed in our laboratory experiment [2]. In calcite supersaturated solution, aqueous arsenite could be oxidized to arsenate, which is induced by complexation of arsenate with Ca^{2+} ion [2]. On the other hand, other minerals in the sedimentary strata (Fe oxide, siderite, biotite, and pyrite) contain As as arsenide and arsenite species. These Fe (secondary) minerals are frequent in As-contaminated sediments and considered to be effective sink for As. Among the minerals formed under anoxic condition, only calcite immobilized arsenate even in the arsenite system by selective incorporation of arsenate produced by the complexation-induced arsenite oxidation.

This property differentiates calcite from other minerals as a unique scavenger for As under anoxic condition. Calcite could preserve As as relatively insoluble arsenate from anoxic groundwater, while the arsenide and arsenite in the Fe secondary minerals easily leach from host minerals into aqueous phase depending on the change of the environmental condition such as redox. Mobilization of arsenate from calcite to aqueous phase hardly occur regardless of redox condition. Calcite seemed to be a rare mineral scavenging As as arsenate in groundwater system with low risk of As leaching to natural water. The present study about distribution behavior of As to calcite is also expected to lead a understanding of incorporation mechanism of redox sensitive oxyanions into calcite, which might be a useful tool for reconstruction of paleo-redox environment in which the calcite precipitated.

[1] Yokoyama et al. (accepted) *J. Phys.: Conf. Ser.* [2] Yokoyama et al. (2012) *Geochim. Cosmochim. Acta* **91**, 202–219.

Adsorption experiment of rare earth elements on clay minerals: Implication to the formation of ion-adsorption type REE deposit

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Supply of rare earth elements (REE), especially heavy rare earth elements (HREE), highly depends on China. REE are essential for advanced environmental protection technology. HREE ore is mainly produced from ion adsorption type deposit. In order to clarify the role of the surface of clay minerals on the adsorption of REE, the adsorption and desorption (sequential extraction) experiment of REE were demonstrated in this study. Kaolin minerals such as kaolinite and halloysite were focused as adsorbents. In addition to the above experiment, some of hydrothermally altered rocks and clay vein were applied to the desorption experiment.

The adsorption experiments were conducted at room temperature and pH 6 with magnetically stirring in NaNO_3 or NaCl solutions (0.025M and 0.5M). At 0.5M, significant fractionation of REE on clay minerals from LREE to HREE was observed (HREE rich). However, no significant effect of the different electrolyte could be observed on any clay minerals at 0.5M. In order to understand an adsorption mode on clay minerals, the desorption (extraction) experiment were subsequently carried out. Three types of samples are used: REE on montmorillonite, 10Å-halloysite and pyrophyllite. Most of REE, especially LREE were preferentially extracted from montmorillonite and halloysite by neutral salt extraction step, suggesting that those extracted REE are considered to be concentrated by ion exchangeable form. Relatively more strongly adsorbed REE by forming chemical adsorption may be extracted by the following proton exchangeable step.