

セレン酸・亜セレン酸のバライトへの取り込みを支配する要因の解明 Factors controlling barite-water distribution of selenium oxyanion

徳永 紘平^{1*}; 横山 由佳¹; 高橋 嘉夫¹
TOKUNAGA, Kouhei^{1*}; YOKOYAMA, Yuka¹; TAKAHASHI, Yoshio¹

¹ 広島大学大学院理学研究科地球惑星システム学専攻

¹Department of Earth and Planetary Systems Science, Graduated School of Science, Hiroshima University

Geochemical behavior of trace elements is controlled by their interaction with major minerals through ion exchange, sorption/desorption, and coprecipitation/dissolution processes, which govern the concentrations of trace elements in natural water. Especially, the coprecipitation process with mineral is potentially important because trace elements can be incorporated and immobilized in the crystal lattice at least until the minerals are dissolved. Previous studies showed that the partitioning behaviors of trace elements to minerals were controlled by many complex factors, such as crystal constraints of ion substitution, effects of complexation in the aqueous phase, rate of crystallization, and changes in temperature or pressure. For instance, Yokoyama [2011, 2012] demonstrated that, in the case of arsenic (As) and selenium (Se) incorporation into calcite, arsenate rather than arsenite is selectively incorporated into calcite, whereas selenite (Se(IV)) rather than selenate (Se(VI)) into calcite because of the high stabilities of calcium arsenate and calcium selenate complexes compared with those for arsenite and selenite. In this study, we focused on the distribution behavior of Se into barite to determine the factors controlling the partitioning behaviors of the trace elements to minerals at the molecular scale by X-ray absorption fine structure (XAFS). Our previous results suggested that the distribution behavior of Se into barite was controlled by two factors: the stability of the surface complex between barite and Se species (=chemical affinity) at the initial process and the stability of the ion substitution in the crystal structure (=structural affinity) for the subsequent process. In this presentation, the barite-water distributions of Se controlled by the structural affinity are highlighted.

The coprecipitation experiments were conducted to examine the influence of ion substitution structure on the distribution behavior of Se into barite as a function of the reaction time in term of the variation of barite morphology, total concentration, oxidation states, and coordination structure of Se in barite. The results showed that both total Se concentration and the Se(VI)/Se(IV) ratio in barite increased abruptly within first 24 hour and almost reached equilibrium after 24 hours. EXAFS analysis for the initial and aged samples showed that the coordination number of Se-Ba in the aged sample is larger than that in the initial stage. The results indicate that a larger amount of Se(VI) than Se(IV) was incorporated from adsorption site on the surface into the barite crystal by substituting sulfate site because of their high crystallinity that can exclude Se(IV) to a larger degree than Se(VI) due to the similar structure of sulfate ion and sulfate. Based on these results, it is considered that the Se(VI) was preferentially incorporated into barite due to its high structural affinity than Se(IV), thus, the Se(VI)/Se(IV) ratios in barite relatively increased through crystallization. These results suggest that structural affinity is an important factor for controlling the distribution behavior of Se between barite and water.

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