

XAFS法を用いた鉱物への微量元素の取り込みの解明 Factors controlling barite-water distribution of selenium

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Geochemical behavior of trace elements in water is controlled by their interaction with major minerals through ion exchange, sorption/desorption, and coprecipitation/dissolution processes, which finally govern the concentrations of trace elements in natural water. Especially, the coprecipitation into the structure of mineral is potentially important because trace elements is less available and can be immobilized in the crystal lattice at least until the dissolution of the minerals. Previous studies showed that the partitioning behaviors of the trace elements to such minerals were controlled many complex factors, such as crystal constraints of ion substitution, complexation effects in water, crystallization rate, and changes in temperature and/or pressure. For instance, Yokoyama et al. [2011, 2012] demonstrated that, in the case of arsenic (As) and selenium (Se) incorporation into calcite, calcite selectively incorporated arsenate rather than arsenite, and selenite rather than selenate because of their high stability of calcium arsenate and calcium selenite complexes compared with those for arsenite and selenate. In this study, we focused on the Se incorporation mechanism to barite to examine the influence of or chemical effect and structural effect to the solid-water distribution behaviors.

The coprecipitation experiments of Se with barite were conducted to examine the influence of (a) the chemical effect at various pH conditions (pH = 3-8), and (b) structural effect of ion substitution as a function of the reaction time (0-42 days). Barite was precipitated from a mixture of artificial seawater (ASW) and BaCl₂ · 2H₂O solution in the presence of selenite or selenate solution. The total concentration and valence ratios of Se in barite were measured by ICP-MS and X-ray absorption near-edge structure (XANES) at Se K-edge, respectively.

[Chemical effect]

The results showed that Se(IV) was preferentially incorporated into barite at 7 < pH < 8 whereas Se(VI) at 3 < pH < 6, which reveals its correlation with the pH dependence of Se(IV) and Se(VI) speciation. These results suggest that the pH has a strong influence on the coprecipitation of trace elements into barite. Thus, the chemical affinity is an important factor controlling the species of Se incorporated into barite, as also found in Se and As incorporation into calcite.

[Structural effect]

The results showed that both the Se(VI)/Se(IV) ratio and total Se concentration in barite increased at first, and reached constant as time passed, suggesting a strong correlation between the Se(VI)/Se(IV) ratio in barite and crystallinity. The correlation indicates that the aging effect in the first stage was dominated by the chemical effect, or larger affinity of Se(IV) than Se(VI), while the aging in the second stage was influenced by the structural similarity between sulfate (SO₄²⁻) and selenate (SeO₄²⁻). It is considered that the Se(IV) was dissociated at barite due to the low structural affinity, thus, the Se(VI)/Se(IV) ratios in barite relatively increased through crystallization.

Keywords: distribution behavior, selenium, barite, chemical effect, structure effect, XAFS