

Evaluation of redox condition by selenium speciation coprecipitated with barite

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Barite (BaSO₄) preserved in marine sediments can maintain its crystalline form at wide range of temperature, which can be present in hydrothermal vent. Barite crystals coprecipitated in seawater contain some elements that may reflect the physico-chemical condition of the seawater from which they are formed. Selenium dissolves mainly as selenite (SeO₃²⁻) or selenate (SeO₄²⁻) in seawater, where the valence of selenium depends on the redox condition. Sulfate ion is stable in wide range in the Eh-pH diagram of sulfur, and the range include the Eh-pH boundary of selenite-selenate in the Eh-pH diagram. Therefore, the oxidation state of selenium in barite can provide information on the redox condition in the depositional environment. The purpose of this study is to establish a method to estimate the redox condition in the environment where barite is precipitated.

Coprecipitation experiment of selenium with barite was conducted to clarify the relationship between selenate/selenite rates in synthetic seawater and in barite. After this experiment, the precipitates of barite and aqueous phase were separated by filtration with a 0.20 μm micro-meter filter (mixed cellulose ester, Advantec). Total concentrations of selenium in the remaining solution and precipitates were measured by ICP-MS to determine the apparent distribution coefficient (K_d) of selenium between barite and seawater. The selenate/selenite ratios in the solution and in the precipitates were measured by HPLC-ICP-MS and X-ray absorption near-edge structure (XANES) at the selenium K-edge, respectively. Micrometer scale distribution and oxidation state of selenium in barite formed in marine sediments in Okinawa hydrothermal vent was determined by μ-XRF- XAFS in natural samples.

The XANES results showed that selenite was preferentially incorporated into barite rather than selenate. Selenate can be incorporated only when the selenate/selenite ratio is over 0.9 in the aqueous phase. The apparent distribution coefficient of selenium was reduced by increasing selenate/selenite ratio in the aqueous phase. These results are caused by the preferential incorporation of selenite into barite due to the high stability of Ba-selenite complex compared with Ba-selenate complex.

Based on the relationship, the redox condition of the interstitial water in the sediment was estimated. The μ-XRF-XAFS result showed that selenate fraction was 60% for the barite in the sediment. The result suggests that the seawater from which barite was precipitated was under oxic condition. This result is consistent with the redox condition of the sediment suggested by iron and sulfur XANES results in the same sample, which showed that the environment was highly oxic.

Keywords: barite, selenite, selenate, redox condition