Estimation of redox condition based on the enrichment and speciation of arsenic and selenium oxyanions in barite

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It is possible that the distribution behaviors of redox-sensitive elements between water and authigenic minerals can provide information on the oxidation state of the element in the coexistent water during the deposition of the mineral. For example, our previous study [1] showed that barite-selenium oxyanion system can be used as a redox indicator for oxic-suboxic boundary because the selenate/selenite (Se(VI)/Se(IV)) ratio in barite was primarily correlated with that of the ratio in water. If the method can be applied to other redox sensitive elements coprecipitated with barite, one barite particle can provide more detailed redox information on the environment. Thus, in this study, we focus on arsenic oxyanion as a coprecipitated trace elements because arsenic (As) is dissolved in water as arsenite (As(III)) or arsenate (As(V)) ion under suboxic and anoxic conditions, respectively. If barite can incorporate both As(III) and As(V) as well as Se(IV) and Se(VI), the As(V)/As(III) ratio recorded in barite may possibly reflect the ratio in water, which consequently indicates more accurate redox information whether barite precipitated under oxic, suboxic, or anoxic redox environments.

Coprecipitation experiments of As with barite were conducted to investigate the influence of the oxidation state on its immobilization into barite based on the speciation of As in barite and water phases by As K-edge XANES and HPLC-ICP-MS, respectively. The results showed that both As(III) and As(V) can be incorporated into barite to preserve their initial species in water. Natural barite samples collected in Tamagawa Hot Springs (Akita Prefecture in Japan), where the headwater was very acidic (pH 1.2) with high As concentrations (1000 μg/L), were also analyzed by micro-XRF and XANES to investigate the applicability of barite-arsenic system as a redox indicator in natural systems. The results showed that As in natural barite can be detected by the micro-XRF-XAFS technique, and the presence of As in barite reflects the As(V)/As(III) ratio in depositional water, suggesting that barite-arsenic oxyanion system can work as a redox indicator to estimate E_h range where barite precipitated.

[1] K. Tokunaga, Y. Yokoyama, and Y. Takahashi, *Geochem. Geophys. Geosystems* **14** (2013) 4826-4834.