

## バライト中のヒ素とセレンのオキソアニオンを用いた新しい Eh 計の開発 Development of Eh meter based on the enrichment and speciation of arsenic and selenium oxyanion 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. Our previous study showed that barite-selenium oxyanion system can be used as a reliable 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 barite-redox-sensitive element systems as well, single barite particles can provide more accurate redox information on the environment where barite precipitated. 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 under various pH conditions (pH=2.0, 5.0, 8.0, or 10.0) 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. These pH conditions were determined to assume the variation of As species in water: (i) As(III) are mainly dissolved as  $\text{H}_3\text{AsO}_3$  from pH 2.0 to pH 8.0, and  $\text{H}_2\text{AsO}_3^-$  at pH 11.0, while (ii) As(V) are mainly dissolved as  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$  at pH 2.0, 5.0, 8.0 and 11.0. The results showed that both As(III) and As(V) can be incorporated into barite depending on their species in water at all pH. These trends are also observed at different chemical composition of water and/or saturation indices of barite. Based on the laboratory experiments, it is suggested that barite-arsenic oxyanion system can be used as a reliable redox indicator to estimate the As(V)/As(III) ratio in water. Moreover, we can estimate absolute Eh value based on the As(V)/As(III) ratio in barite if the oxidation state of As in water was under equilibrium in terms of the redox condition.

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  $\mu\text{g/L}$ ), were also analyzed by micro-XRF and XANES to investigate the applicability of barite-arsenic system as a redox indicator in natural systems. Ogawa et al. (2012) revealed that As predominantly was dissolved as As(III) in this area by anion exchange method. The results showed that As in natural barite can be detected by the micro-XRF-XAFS technique and the presence of As(III) species in barite, suggesting that As(V)/As(III) ratio in barite reflect the ratio in depositional water. Thus, a good correlation between laboratory experiments and natural analysis suggested that barite-arsenic oxyanion system can work as a redox indicator to estimate Eh range where barite precipitated and can be applied to environmental systems where As was incorporated into barite.

Keywords: barite, selenium oxyanion, arsenic oxyanion, redox indicator, XAFS, distribution coefficient