

Application of selenium coprecipitated with barite as a new redox indicator

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Redox potential (Eh) is an important factor controlling chemical processes in hydrosphere on the earth, because redox reaction is related to the behaviors of many major and minor species in natural waters. A number of the previous studies have suggested that Eh was estimated by the solid-water distributions of redox-sensitive elements based on the effect of valence change such as a relative enrichment-depletion profile of particular elements. However, the estimation of redox conditions based on previous indicators may not be reliable because (i) trace elements concentrations are influenced by many factors and mechanisms such as secondary adsorption-desorption and/or diagenetic processes and (ii) the redox condition was relatively evaluated by the depth profiles of particular elements. Thus, the aim of this study is to propose a new redox indicator using the valence ratio of redox sensitive element itself in the mineral which can be directly used to estimate the particular redox condition at the time of the mineral formation. Here, we examined the incorporation behavior of selenium (Se) species to barite. Selenium is well known as a redox-sensitive element which is dissolved in water as selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}) oxyanion under oxic and suboxic condition, respectively. On the other hand, barite can work as a host phase of Se in the environment. Thus, if barite can incorporate both Se(IV) and Se(VI), the ratio of Se(VI)/Se(IV) may possibly reflect the ratio in the coexistent water, which consequently indicates the redox condition in the environment. The aim of this study to understand the incorporation behaviors of Se(IV) and Se(VI) into barite in co-precipitation experiments with the information of the oxidation states both in water and barite to utilize it as a redox indicator for oxic-suboxic condition.

Coprecipitation experiments of Se with barite were conducted to investigate the influence of the Se oxidation state on its immobilization into barite at pH 8.0 and pH 4.0. Barite was precipitated from a mixture of artificial seawater (ASW) and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution. The initial pH of ASW was adjusted to 4.0 and 8.0 before the barite precipitation. These two pH conditions were adopted considering typical pH for hydrothermal water (3.0-4.0) and seawater (8.0). Total concentrations of Se in the remaining solution and precipitates were measured by ICP-MS. The Se(VI)/Se(IV) ratio in the precipitates and water were determined by HPLC-ICP-MS and X-ray absorption near-edge structure (XANES) at Se K-edge, respectively.

It was found that the Se(VI)/Se(IV) ratio in barite reflects the Se(VI)/Se(IV) ratio in water, which suggests that the oxidization state of Se in barite can work as a redox indicator showing redox condition at the time of barite formation. Selenium(IV) is incorporated into barite under suboxic condition below the redox boundary of Se(VI)/Se(IV). Selenium(VI), on the other hand, is incorporated under oxic condition above the redox boundary of Se(VI)/Se(IV). These trends are observed at pH 4.0 and 8.0, regardless of the different distribution behaviors of Se to barite at both pH systems. Based on the distribution behavior of Se to barite in the pH 4.0 and 8.0 systems, we conclude that the Se(VI)/Se(IV) ratio in barite can be used as a redox indicator whether barite was precipitated below or above the redox boundary of Se(VI)/Se(IV), the Eh region of which is different from the Fe(III)/Fe(II) and Mn(IV)/Mn(II) boundaries often employed as a signature of redox condition. Thus, the redox indicator using the Se(VI)/Se(IV) ratio in barite could provide more detailed redox information on the depositional environment.

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