

## Application of selenium in barite as a new redox indicator

The redox potential ( $E_{\rm h}$ , if standardized to hydrogen electrode) is an important physico-chemical factor that controls chemical processes in the hydrosphere in the Earth, because redox reactions are closely related to the behaviors of various chemical species in water. A number of previous studies have estimated  $E_h$  based on the solid-water distribution of redox-sensitive elements reflected in the variation of the oxidation states, such as the relative enrichment-depletion profiles of particular elements (e.g., iron and manganese) in the environment. However, the estimated redox condition based on these profiles may be unreliable because (i) elemental concentrations are influenced by many factors, such as secondary adsorption-desorption reactions and diagenesis, and (ii) only the relative evaluation of the redox condition is possible by the depth profile of particular elements. Thus, the aim of this study is to propose a new redox indicator using the oxidation state of a redox sensitive element in a certain mineral to estimate directly the redox condition at the time of the mineral formation. We focused on the distribution behavior of selenium (Se) oxyanions into barite. Selenium is dissolved in water as selenate (SeO<sub>4</sub><sup>2-</sup>) or selenite (SeO<sub>3</sub><sup>2-</sup>) ion under oxic and suboxic conditions, respectively, and both can be fixed into the sulfate site of the crystal lattice of barite [1]. If barite incorporates both Se(IV) and Se(VI), then the Se(VI)/Se(IV) ratio recorded in barite may reflect the ratio in water, which consequently indicates the redox condition and whether barite precipitated below or above the redox boundary of Se(VI)/Se(IV).

Coprecipitation experiments of Se with barite were conducted at pH 4.0 and 8.0 to investigate the influence of the oxidation state on its immobilization into barite by the Se K-edge X-ray absorption nearedge structure (XANES) measured at BL01B1 and high-performance liquid chromatography connected to inductively coupled plasma-mass spectrometry. These two pH conditions were adopted considering the typical pH values for hydrothermal water (pH = 3.0-4.0) and seawater (pH = 8.0). The oxidation state of Se in the precipitates was determined by XANES based on the fit of the sample spectra by a linear combination of the spectra of BaSeO<sub>3</sub>, BaSeO<sub>4</sub>, and native Se (Fig. 1) [2]. The results show that the Se(VI)/Se(IV) ratio in barite is primarily correlated with that of the Se(VI)/Se(IV) ratio in water at both pH's (Fig. 2), which in turn can provide physicochemical, biogeochemical, and redox information about the environment. All these results are also observed for various chemical

compositions of water and/or saturation indices of barite [2]. These laboratory experiments suggest that the barite-selenium oxyanion system can be used as a reliable redox indicator to estimate the Se(VI)/ Se(IV) ratio in water. If the system is under equilibrium in terms of the redox condition,  $E_{\rm h}$  can be estimated based on the Se(VI)/Se(IV) ratio.

In a natural system, the distribution behaviors of ions between mineral and water are influenced by several factors, such as ionic strength, precipitation rate, etc. [3]. Thus, natural barite samples in marine sediment collected near the hydrothermal vent system in the Izena Cauldron, Okinawa Trough were also analyzed by micro-XRF and XANES to investigate the applicability of the barite-selenium system as a redox indicator in natural systems (BL37XU) [4]. Micro-XRF elemental mapping shows that the distribution of Se is correlated with that of Ba, especially in the left part in Fig. 3, suggesting that Se is incorporated into barite within the sediment. Micro-XANES analysis was performed at a spot with a relatively high concentration of Se in the barite; Se is mainly incorporated as Se(IV) in this marine sediment (Fig. 3 (E)). Based on the aforementioned laboratory experiments barite precipitates under suboxic condition where Se is dissolved as Se(IV). This is consistent with the fact that the pore water of the sample is under a mildly reducing condition ( $E_{\rm h}$  = 150 mV at pH 7.1) where Se(IV) can be the main Se species in the water. Thus, the good correlation between laboratory experiments and natural



Fig. 1. Normalized Se *K*-edge XANES spectra of the reference materials (BaSeO<sub>3</sub>, BaSeO<sub>4</sub>, and native Se) and Se in barite at (**a**) pH 8.0 and (**b**) pH 4.0 as a functions of  $R_W^{VI}$  (= Se(VI)/total Se).



Fig. 2. Relationship between  $R_W^{VI}$  and  $R_B^{VI}$ . Se(VI)/Se(IV) ratios in barite and in solution are measured by XANES and HPLC-ICP-MS, respectively.

analysis suggests that the Se(VI)/Se(IV) ratio in barite can be used to estimate roughly the redox condition of the coexistent water during the formation of barite.

Application of this indicator has several unique characteristics. First, the method is sensitive to the redox condition between the high and low  $E_{\rm h}$  regions as indicated by the MnO<sub>2</sub>/Mn<sup>2+</sup> and Fe(III)/Fe<sup>2+</sup> boundaries, respectively. Second, this method can be used to estimate the redox condition based on the

Se(VI)/Se(IV) ratio using one barite sample, whereas using other data to evaluate the redox condition requires various geochemical data, such as the depth profile of redox-sensitive elements. This method has many potential applications, including (i) to estimate the redox condition when barite was precipitated and (ii) to estimate the redox condition in an environment where a Pt electrode cannot be used to measure  $E_h$ such as in hydrothermal water.



Fig. 3. BSE and  $\mu$ -XRF images and  $\mu$ -XANES of the sample. (a) BSE image of barite. (b, c, d)  $\mu$ -XRF images of Fe, Ba, and Se, respectively. (e) Normalized Se *K*-edge XANES of Se reference materials (BaSeO<sub>3</sub> and BaSeO<sub>4</sub>), Se in barite at pH 8.0 added as Se(IV) or Se(VI), and Se in natural barite at hot spots.

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