Application of arsenic in barite as a redox indicator for suboxic/anoxic redox condition

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ABSTRACT

Redox condition is an important factor that controls the behavior of various elements in an aquatic environment. Incorporation of redox-sensitive trace elements in minerals describes redox conditions in water and provides information about past environmental changes, unless it is dissolved or recrystallized during sediment burial. In the present study, we explore the application of arsenate/arsenite ratios (As(V)/As(III)) in barite as a new geochemical proxy for paleo-environmental reconstruction. Laboratory experiments showed that both As(III) and As(V) could be incorporated into barite as As(III)- and As(V)-coprecipitated barite, respectively, which could more or less retain the information of the As(V)/As(III) ratio in coexistent water, if under equilibrium in terms of the redox reactions. Furthermore, the As(V)/As(III) ratios in natural barite collected in (i) Tamagawa Hot Spring and (ii) Okinawa hydrothermal vent were determined by micro-X-ray fluorescence and micro-X-ray absorption fine structure analysis to (a) evaluate the reliability of the As(V)/As(III) ratio in barite as a redox indicator in natural system and (b) estimate the depositional redox condition in water whether barite precipitated below or above the redox boundary of As(V)/As(III), or the suboxic/anoxic boundary. Our previous study showed that barite–selenium oxyanion system could also be used as a proxy for the oxic-suboxic boundary because the selenate/selenite [Se(VI)/Se(IV)] ratio in barite is primarily correlated with the ratio in water. Given that the redox boundary of the Se(VI)/Se(IV) ratio has higher redox potential than the As(V)/As(III) boundary, the combination of these two systems can extend the redox condition, which can be specified by the analysis of one single barite grain to a wide region. Thus, one barite particle can provide information on the As(V)/As(III) and Se(VI)/Se(IV) ratios in water, and whether barite precipitated under oxic, suboxic, or anoxic redox environments.

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1. Introduction

Redox potential (E_h, if standardized to hydrogen electrode) is an important physicochemical factor that controls the chemical processes in the hydrosphere because redox reactions strongly affect the behaviors of various chemical species. Previous studies estimated redox condition indirectly and qualitatively based on the solid-water distribution of redox-sensitive elements caused by the variation in their oxidation states, such as the relative enrichment-depletion profiles of particular elements (e.g., iron and manganese) in the environment (Thomson et al., 1993; Calvert et al., 1993; Algeo et al., 2004). However, the estimation of redox conditions based on these profiles may be unreliable because (i) elemental concentrations are influenced by factors, such as secondary adsorption-desorption reactions and subsequent diagenesis, and (ii) only the relative evaluation of the redox condition can be obtained by the depth profiles of particular elements. The present study aimed to propose a redox indicator using the oxidation states of redox-sensitive elements in a certain mineral to directly estimate the redox condition during mineral formation.

In the present study, arsenic (As) oxyanion was selected as a possible element because As is dissolved in water either as arsenite [$As^{III}O_3^{3-}$: As(III)] or arsenate [$As^VO_4^{3-}$: As(V)] ion under suboxic and anoxic conditions, respectively (Jain and Ali, 2000). Arsenite and arsenate are highly soluble ions, but these ions can be retained on various minerals through ion exchange, sorption/desorption, and coprecipitation/dissolution processes. Understanding the distribution process between minerals and

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water is important to predict arsenic mobility on earth surfaces in the presence of water. Previous studies have compared the immobilization mechanism of As(III) and As(V) via coprecipitation with minerals, such as calcium carbonate (Lowers et al., 2007; Sø et al., 2008; Yokoyama et al., 2012; Renard et al., 2015), pyrite (Savage et al., 2000; Andrade et al., 2012), and iron hydroxides (Dixit and Hering, 2003). These studies revealed that the distribution of As(V) on minerals is larger than that of As(III) because of the larger complexation stability of arsenate than that of arsenite. For instance, Yokoyama (2012) demonstrated that in the case of arsenic incorporation into calcite, calcite selectively incorporates arsenate rather than arsenite. This result suggests that As in calcite is not an appropriate proxy to estimate the As(V)/As(III) ratio in water because of the selective incorporation of As(V). Similar phenomena were also observed in other systems with As and sulfide minerals in environments (Savage et al., 2000; Smedley and Kinniburgh, 2002).

In the present study, coprecipitation of As with barite was used as a new geochemical proxy to reconstruct the redox conditions. Coprecipitation is defined as the incorporation of a compound in a host mineral when that compound is otherwise soluble under the conditions of precipitation. Incorporation of trace elements into the crystal lattice can lead to their immobilization and retard their migration in crystal structure than simple adsorption on crystal surface. Thus, coprecipitation is important for paleo-environmental reconstruction because of the high preservation of trace elements in the mineral. For example, coprecipitation of trace elements into calcite provides information about past environmental changes. Barnaby and Rimstidt (1989) showed that the Mn^{2+} and Fe^{2+} contents in calcite are frequently interpreted in terms of the E_h of the depositional or diagenetic environment because of the incorporation of both metals in calcite depending on the redox conditions. Lu et al. (2010) also showed the application of iodine/calcium ratios in marine carbonate as a new geochemical proxy to constrain seawater redox change because of the selective incorporation of iodate under oxidizing conditions, which is not the case for iodide under anoxic conditions.

This work focused on barite ($BaSO_4$) as a host phase of As for our purpose. Barite, which is stable under a wide range of pressure, temperature, E_h, and pH, can incorporate various trace elements that may record geochemical information of coexistent water and depositional condition (Fig. 1(a)). Several elements (e.g., cations: Sr^{2+}, Ca^{2+}, Ra^{2+}, Pb^{2+}, and rare earth elements; anions: SeO_4^{2-}, CrO_4^{2-}, and MnO_4^{2-}) are incorporated into barite by substituting Ba^{2+} or SO_4^{2-} (Guichard et al., 1979; Hein et al., 2000; Prieto et al., 2002; Van Beek et al., 2003; Zhu, 2004; Griffith and Paytan, 2012; Prieto et al., 2016). Barite

formation occurs in various environments, such as seawater, seafloor hydrothermal fluid, groundwater, and onshore hot spring water. In particular, barite is precipitated from hot spring water contains considerable amounts of trace elements in its crystal lattice, such as radium (Ra), As, and other alkaline earth elements (Boyle, 1973; Chao et al., 2009). Several studies characterized the behavior of arsenate in barite in terms of solubility and stability of barium arsenate (Robins, 1985; Zhu et al., 2005). Nevertheless, the distributions of As(III) and As(V) between barite and water remain poorly understood. Thus, in the present study, coprecipitation experiments of As with barite were conducted to investigate the influence of oxidation state on its immobilization into barite through batch experiments. If both As(III) and As(V) are incorporated into barite to a similar degree, the As(V)/As(III) ratio recorded in barite reflects the ratio in water. Particularly, if As(III) and As(V) are under equilibrium in terms of redox reactions, the As(V)/As(III) ratio in barite can be a useful indicator of E_h in natural water (Cherry et al., 1979; Yan et al., 2000). Consequently, the As(V)/As(III) ratio in barite may be adopted to estimate the E_h of the environment, whether the environment is below or above the redox boundary of As(V)/As(III), or suboxic/anoxic boundary (Fig. 1(b)).

Furthermore, natural barite samples collected in high As concentration areas were also analyzed by micro-X-ray fluorescence (μ-XRF) and micro-X-ray-adsorption fine structure (μ-XAFS) to investigate whether this method can be applied to natural systems where barite precipitates. Two natural barite samples were analyzed: (i) one sample was collected from the Tamagawa Hot Spring (Obuki Hot Spring, Tamagawa Geothermal System, Akita Prefecture, Japan) where the depositional E_h-pH condition is known (pH: 3.4; E_h: 0.59 V) (Ogawa et al., 2012); (ii) the other sample was obtained near the hydrothermal vent system at the seafloor in Okinawa Trough (Izena Hole) in Japan without information of the depositional E_h-pH condition. These analyses were carried out to (i) evaluate the reliability of the As(V)/As(III) ratio in barite as a redox indicator based on the analysis of the Tamagawa sample and (ii) estimate the depositional E_h condition in water whether barite precipitated below or above the redox boundary of As(V)/As(III), or the suboxic/anoxic boundary for the Okinawa sample.

Our previous study suggested that barite–selenium oxyanion system could be used as a redox indicator for the oxic-suboxic boundary because the selenate/selenite [(Se(VI)/Se(IV)] ratio in barite is primarily correlated with that of the ratio in water (Tokunaga et al., 2013a). In particular, the Se(VI)/Se(IV) system is sensitive to more oxic condition compared with the As(V)/As(III) system (Fig. 1(c)). Thus, if the As(V)/As(III) ratio in barite can also be applied to the natural system as a
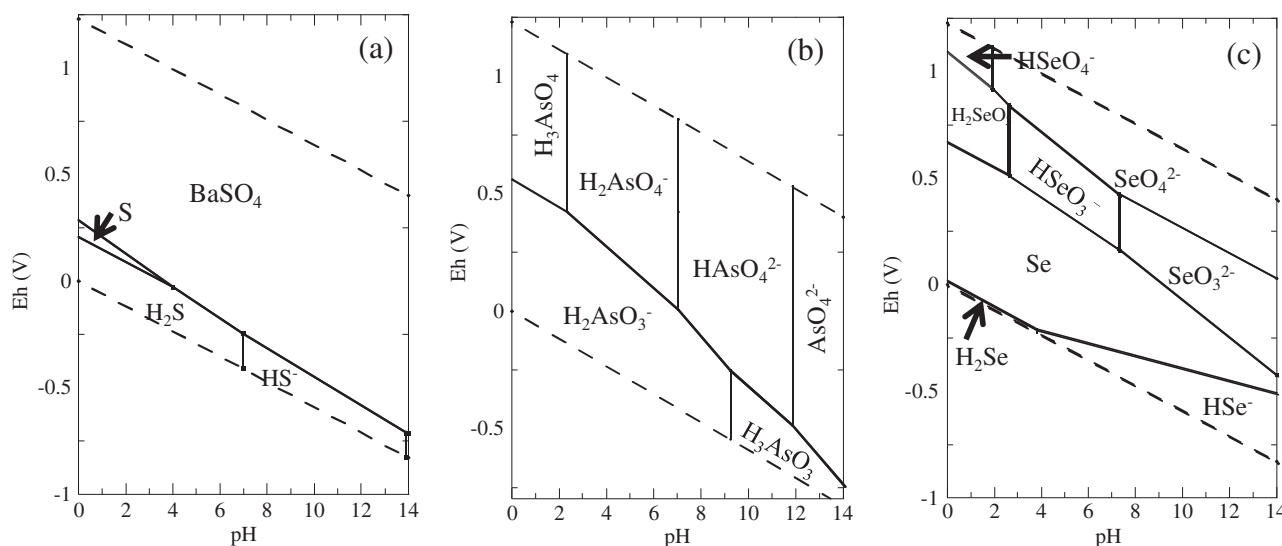

Fig. 1. E_h-pH diagrams for Ba-S-H_2O (a), As-H_2O (b), and Se-H_2O(c) at 25 °C and 1.0 bar calculated based on the Visual MINTEQ. The total dissolved concentrations of Ba, As, Se, and S used for the calculations were 270, 80, 140, and 2600 μg/L, respectively, which corresponded approximately to their concentrations in our experimental systems.