

Application of selenium in barite as a new redox indicator

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It is possible that the distribution behaviors of redox-sensitive elements such as selenium (Se) between water and authigenic minerals can provide information on the oxidation state of the element in the coexistent water during mineral deposition. Considering the similar chemical characteristics of Se(IV) and Se(VI) oxyanions, we propose that the Se(VI)/Se(IV) ratio in a particular precipitate, such as barite, may enable us to estimate the Se(VI)/Se(IV) ratio in the coexistent water, or indicate the redox condition under equilibrium in term of redox reactions for inorganic Se species.

Coprecipitation experiments of Se with barite were conducted to investigate the influence of the oxidation state on its immobilization into barite at pH 4.0 and 8.0 by Se K-edge X-ray absorption near-edge structure and high-performance liquid chromatography connected to inductively coupled plasma-mass spectrometry, respectively. These two pH conditions were adopted considering typical pH for hydrothermal water (3.0-4.0) and seawater (8.0). The results showed that the Se(VI)/Se(IV) ratio in barite was primarily correlated with that of the ratio in water, which in turn can provide physicochemical, biogeochemical information on the environment where barite precipitated. Especially under equilibrium condition, the Se(VI)/Se(IV) ratio in barite may work as a redox indicator whether it is below or above the redox boundary of Se(VI)/Se(IV). Natural barite samples in marine sediments were also analyzed by μ -XRF and XANES to investigate the applicability of barite-selenium systems as a redox indicator in natural systems. The results showed that Se in natural barite can be detected by the μ -XRF-XAFS technique, where the presence of Se species in barite reflects the ratio of Se(VI)/Se(IV) in the coexistent water. Thus, the consistent results including laboratory experiments and natural samples analysis allow us to conclude that the Se(VI)/Se(IV) ratio in barite can be used as a redox indicator to estimate Eh range where barite precipitated and can be applied to environmental systems where Se was incorporated into barite if it is under equilibrium condition. Various applications of this method can be suggested such as (i) to estimate the redox condition in the past when barite was precipitated and (ii) to estimate the redox condition in environment where we cannot use a Pt electrode to measure Eh such as in hydrothermal water.