

## Interaction of arsenic and carbonate mineral in groundwater system: Effect of oxidation state on arsenic incorporation into calcite

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### 1. Introduction

The natural occurrence of As-contamination in groundwater is a serious problem across southern Asia. The most common and widely accepted mechanism of As release to groundwater in alluvium is reductive dissolution of Fe hydroxides containing. However, in general, there is poor correlation between the concentrations of As and Fe in the As-contaminated groundwater, suggesting that As mobilization/immobilization processes controlling the As concentration in groundwater are also related to other minerals. Among them, carbonate minerals are ubiquitously found in various surface environments including under reducing conditions. Many As-contaminated groundwaters are slightly saturated with some carbonate minerals. Thus, carbonate minerals are recently of great interest as host phases of As in groundwater under reducing condition.

In this study, the influence of oxidation state on As coprecipitation with calcite was evaluated with the information of its oxidation state both in water and calcite, and thermodynamic stability in water. To assess these reactions quantitatively, distribution coefficient (Kd) of As into calcite was determined using reproducible experimental system of their partitions at low precipitation rates such as in natural systems. To evaluate the Kd appropriately, it is essential to determine the Kd for each oxidation state of As, arsenite and arsenate. For this purpose, it is needed to clarify the ratio of arsenite and arsenate, for which XAFS measurement is a powerful tool.

### 2. Experimental

For synthetic system, bulk XAFS spectra were obtained for As incorporated into carbonate, which were recorded in BL9A or BL12C in Photon Factory.

For natural sample, carbonate minerals, which occur as fracture-filling (FF) secondary minerals at 450 m below ground level (mbgl), were collected from a drilling core of Neogene marine sedimentary rocks in northern Hokkaido. A thin section of natural carbonate samples was prepared for electron microprobe and  $\mu$ -XRF-XAFS analyses. Microscopic chemical distribution on the thin section was observed by electron probe micro analyser (EPMA) (JXA-8200, JEOL).  $\mu$ -XRF-XAFS analyses using an X-ray micro beam were performed at BL-4A in KEK-PF.

### 3. Results and discussion

The XAFS measurements showed that calcite selectively incorporated pentavalent As (arsenate) rather than trivalent As (arsenite). However, there was no relationship in their incorporation behaviors into calcite. Interestingly, the XANES analysis detected arsenate in calcite precipitated only from arsenite-spiked system. Moreover, our cyclic voltammetric measurement observed arsenate stabilization in solution containing calcium ion indicating the shift of arsenite/arsenate redox boundary. These phenomena are associated with high stability of calcium arsenate complex compared with those for arsenite. Considering the abundance of calcium in natural water, the valence change effects by calcium is important as a (geo)chemical reaction which may have been overlooked so far. Hence, we conclude that the factor controlling incorporation behavior of As into calcite is the stabilities of the complex with calcium ion. These thermodynamic properties should be explained by quantum chemical approaches. In view of the valence change effects by calcium, ratios of their net Kd into calcite were determined at pH ~7, i.e.,  $Kd_{As(V)}/Kd_{As(III)}$  was > 2500.

To evaluate the role of calcite as a host phase of As in As-contaminated groundwater, distribution behaviour of As between natural calcite and groundwater in deep underground was investigated based on As oxidation state. Speciation analyses of As in natural calcite by  $\mu$ -XRF-XAFS analyses showed preferential arsenate uptake by calcite. These findings suggest that impact of calcite for As remediation on the As-contamination system strongly depends on arsenite/arsenate ratio (i.e., redox condition) in the groundwater.

### Reference

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