Speciation of As in calcite by micro-XAFS: Implications for remediation of As contamination in groundwater

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Abstract. To evaluate the role of calcite as a host phase of arsenic (As) in As-contaminated groundwater, distribution behavior 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 μ-XRF-XAFS analyses showed (i) preferential arsenate uptake by calcite, and (ii) promptness of arsenate uptake by minor iron (Fe) carbonate minerals coprecipitated with calcite. These findings suggest that the effect of calcite on As remediation of the As-contamination systems strongly depends on arsenite to arsenate ratio (i.e., redox condition) in groundwater, and maybe governed by the amount of Fe coprecipitated with calcite.

1. Introduction
The natural occurrence of arsenic (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 iron (Fe)hydroxides containing As (e.g., [1]). However, in general, the correlation between As and Fe concentrations in the As-contaminated groundwater is poor (e.g., [2]), suggesting that As mobilization/immobilization processes controlling the As concentration in groundwater are also related to other minerals.

Carbonate minerals are ubiquitously found in various surface environments including areas under reducing conditions. Many As-contaminated groundwaters are slightly saturated with various carbonate minerals [3]. Thus, carbonate minerals have been recently of great interest as host phases of As in groundwater under reducing conditions. Arsenic in natural water is dissolved as trivalent arsenite (I) and pentavalent arsenate (V). Our previous experimental study found that the affinity of arsenite with calcite (CaCO₃) is higher than that of arsenate [4]. Siderite (FeCO₃) and carbonate greenrust (Fe²⁺Fe³⁺₂(OH)₁₂)[4H₂O·CO₃] were also found to interact more strongly with arsenite than with arsenate [5]. These properties were only observed in laboratory studies, whereas there have been few studies investigating As interaction with natural carbonate minerals at different oxidation states. In this
paper, we report the results of speciation analyses of As both in natural carbonate minerals and in groundwater by micro X-ray fluorescence and X-ray absorption fine structure (μ-XRF-XAFS) analyses and high-performance liquid chromatography-ICP-MS (HPLC-ICP-MS), respectively, with the aim of estimating the As-scavenging capability of carbonate minerals in groundwater systems.

2. Materials and Method
Natural carbonate minerals, which occur as fracture-filling (FF) secondary minerals at 450 m below ground level (mbgl), were collected from a drilling core (HDB-10) of Neogene marine sedimentary rocks (Wakkanai Formation) in the Horonobe area, northern Hokkaido, Japan. These carbonate minerals originated from carbon dioxide gas produced by diagenetic processes (e.g., sulfate reduction by sulfate-reducing bacteria and biochemical maturation of organic matter) [6] and saline groundwater (total dissolved solids (TDS) < 22 g/L) which is inferred to originate from fossil seawater [7]. Groundwater sample was collected at 250 mbgl while maintaining anaerobic conditions in the shaft off the Horonobe Underground Research Center located near the HDB-10 drillingsite.

Concentration of As in the FF carbonate minerals was measured by ICP-MS (Agilent 7700cx, Agilent Technologies) after dissolution in ammonium acetate adjusted to pH 5.0 with acetic acid. Speciation of As in the groundwater sample was performed using HPLC-ICP-MS (pump: Pu-2089 Plus; oven: Co-2065 Plus, JASCO) with anion exchange columns (TSK gel Super IC-AP, Tosoh). A thin section of natural carbonate samples was prepared for electronmicroprobe microanalyzer (EPMA) and μ-XRF-XAFS analyses. Microscopic chemical distribution on the thin section was observed by EPMA (JXA-8200, JEOL). The μ-XRF-XAFS analyses using an X-ray micro beam were performed at BL-4A in KEK-PF (Ibaraki, Japan) and BL37BXU in SPring-8 (Hyogo, Japan).

3. Results and Discussion
Chemical data from groundwater in the HDB-10 borehole indicate that groundwater at about 450 mbgl is nearly saturated or oversaturated with respect to calcite and siderite under reducing condition (pH 6.8; Eh = −234 mV to −148 mV) [8]. Thermodynamic speciation of As in the groundwater shows that arsenite is the dominant dissolved As species, with the ratio of arsenite to total As being above 99.99%. The predominance of arsenite in groundwater was directly observed by the HPLC-ICP-MS analysis of the groundwater samples collected near the HDB-10 borehole (Figure 1).

![Figure 1. Chromatogram of 75As in the groundwater sample measured by HPLC-ICP-MS. Retention times of arsenite [As(III)], arsenate [As(V)], and 40Ar35Cl species are indicated as dashed lines identified by NaAsO2, NaH2AsO4, and NaCl solutions, respectively. In this measurement system, 40Ar35Cl produced by a large amount of chlorine in groundwater does not interrupt identifications of As(III) and As(V).](image-url)

The FF carbonate minerals were identified as calcite with a bulk X-ray diffraction pattern. These minerals also include 1wt.% Fe and 0.7wt.% magnesium (Mg). Bulk Fe K-edge EXAFS spectra for the FF-calcite exhibit a similar oscillatory structure to ankerite [Ca(Mg,Fe)(CO3)2], indicating that minor ankerite is formed in the FF-calcite (Figure 2).

Two-dimensional μ-XRF maps show that the thin section consists both of the FF-calcite and the rock matrix areas (Figure 3a). Mineral phases of the rock matrix were found to be quartz, silicate, sulfide, and carbonate minerals by the electron microprobe analysis. Distribution of As on the μ-XRF
map partially corresponds to that of Fe, and that of pyrite on a backscattered electron (BSE) image. However, the mineral phases where As accumulates could not be identified completely on the BSE image because the probing depth of XRF imaging is deeper than that of electron imaging. Arsenic μ-XANES analysis for the FF-calcite was conducted to investigate As-immobilization to calcite based on its oxidation state. Micro-XANES spectra of As show that As was incorporated into the FF-calcite as arsenate (Figure 3b). In addition, the distribution of As within the FF-calcite phase correlates most closely with that of Fe on the XRF maps. These results may suggest that arsenate was distributed in minor Fe carbonate phase of the FF-calcite, as identified by the bulk Fe K-edge EXAFS analysis. However, such Fe carbonate minerals could not be found microscopically in the FF-calcite phase.

![Figure 2. Normalized k^3-weighted EXAFS spectra at the Fe K-edge for Fe in the FF-calcite and the reference compounds (ankerite and siderite).](image)

The FF-calcite incorporated arsenate despite arsenite is the main species of As in the groundwater. The preference for arsenate has been observed experimentally in previous studies on calcite and Fe carbonate minerals regarding their importance as host phases of As [4, 5]. In the case of calcite, no interaction of arsenite with calcite at circumneutral pH had been observed in the laboratory [9]. These properties indicate that calcite plays a role as a sink of As by incorporating minor arsenate even under reducing conditions, and that its ability depends heavily on arsenite to arsenate ratio in groundwater.

A static groundwater system in the deeper sedimentary rocks at the Horonobe area is expected to result in a nearly equilibrium state between groundwater and surrounding sedimentary rocks (minerals). Thus, based on the concentration of arsenate both in the FF-calcite and groundwater, an apparent distribution coefficient (K) of arsenate could be calculated (K = [As^V]_{calcite}/[As^V]_{groundwater} = 920 L/kg). This value is higher than the K value of arsenate between calcite and water (K_{arsenate-calcite} = 490 L/kg) determined in our laboratory experiments [9], indicating that the FF-calcite includes a larger amount of arsenate (160 μg/kg) than the predicted value for the immobilization of arsenate by calcite. As noted above, the existence of minor Fe carbonate minerals in the FF-calcite may be related to As incorporation. According to the previously reported K values for arsenate sorption reaction [3], arsenate strongly interacts with siderite rather than calcite. Thus, micro-scale Fe carbonate minerals (e.g., siderite or ankerite) in the FF-calcite contribute to the immobilization of arsenate, which consequently enhances the capacity of the FF-calcite for As-scavenging. In the rock matrix, authigenic siderite along with pyrite was found, which is also assumed to expand the capability of carbonate minerals as a sink for As in deep underground systems. A similar occurrence of siderite has been reported in sediments of As-contaminated areas [10]. Future work should focus on the evaluation of such siderite based on microscopicspeciation using μ-XAFS technique.
Figure 3. (a) ABSE photograph and XRF maps for Ca, Fe, and As in the thin section of the FF-calcite and the rock matrix. A cross in the element distribution maps indicates an analytical point of As μ-XANES. (b) Micro As K-edge XANES spectra for the point in the FF-calcite and reference compounds (arsenopyrite, NaAsO$_2$, and NaH$_2$AsO$_4$).

4. Summary
The results of μ-XRF-XAFS analyses for the FF-calcite formed in deep underground suggested that calcite could be a host phase of As in As-contaminated groundwater through selective incorporation of arsenate. However, the effect of calcite in the remediation of As-contamination systems strongly depends on arsenite to arsenate ratio (i.e., redox condition) in groundwater. The amount of As incorporated into carbonate minerals can also be enhanced by the amount of Fe carbonate minerals coprecipitated with calcite because minor Fe carbonate minerals in calcite can enhance the capacity of calcite for As immobilization.

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