

Differences between immobilizations of arsenite and arsenate by calcite

Arsenic (As) is a highly toxic element. Drinking As-rich groundwater has led to serious health problems in some areas in the world, particularly in Bangladesh and West Bengal. The most common and widely accepted mechanism of As release to groundwater in Bangladesh is the reduction of iron (Fe) hydroxides containing a large amount of As under anoxic condition [1]. However, in general, there is a poor correlation between the concentrations of As and Fe in As-contaminated groundwater, indicating that this mechanism does not fully explain the heterogeneous As contamination in groundwater found in Bangladesh [2]. In anaerobic sediments where Fe hydroxides are unstable, several Fe secondary minerals, clay minerals, carbonate minerals, and sulfide minerals could be present. Recently, the water–mineral interaction for these minerals has received much interest as the key reaction for further investigation of As behavior in As-contaminated groundwater. Calcite (CaCO_3) is the most stable polymorph of calcium carbonate under ambient condition and ubiquitously found in various surface environments. Many As-contaminated groundwater sources are slightly saturated with calcite, suggesting that calcite precipitates in groundwater. Furthermore, once As is incorporated into calcite, a serious environment pollution caused by the leaching of As from calcite could not easily occur, because calcite is unaffected by redox changes unlike Fe minerals. Therefore, calcite has recently received much interest as an effective scavenger of As leached from Fe oxyhydroxides in As-contaminated groundwater.

Arsenic is mostly found in the forms of inorganic

oxyanions, i.e., As(III) (arsenite, AsO_3^{3-}) or As(V) (arsenate, AsO_4^{3-}) in natural water. The toxicity and geochemical behavior of As depend markedly on the oxidation state of As. Thus, As interaction with calcite must be investigated with consideration of the dependence of As reactivity on the oxidation state of As. However, few studies have compared arsenite to arsenate in terms of the scavenging ability of calcite. Previous studies have shown that arsenate could be retained in calcite through sorption and coprecipitation [3]. On the other hand, it remains controversial whether calcite can immobilize arsenite [3,4]. To resolve this controversy, the investigation of the distribution behavior of As between water and calcite needs to be coupled with the determination of the As oxidation state in both water and solid phases.

In this study, laboratory experiments simulating the distribution of As to calcite were conducted for arsenite and arsenate to determine each species' distribution coefficient for calcite [5]. To determine the oxidation state of As in calcite and water, we employed the X-ray absorption near edge structure (XANES) technique and high-performance liquid chromatography-ICP-MS (HPLC-ICP-MS), respectively. In addition, we evaluated the local structure of As in calcite using atomic-scale structural information obtained by extended X-ray absorption fine structure (EXAFS) analysis. Arsenic *K*-edge XANES and EXAFS experiments were performed at beamline **BL01B1**.

The results of the coprecipitation experiment of As and calcite indicated that arsenate is preferentially incorporated into calcite over a wide range of pHs (7–12), whereas the incorporation of arsenite into calcite

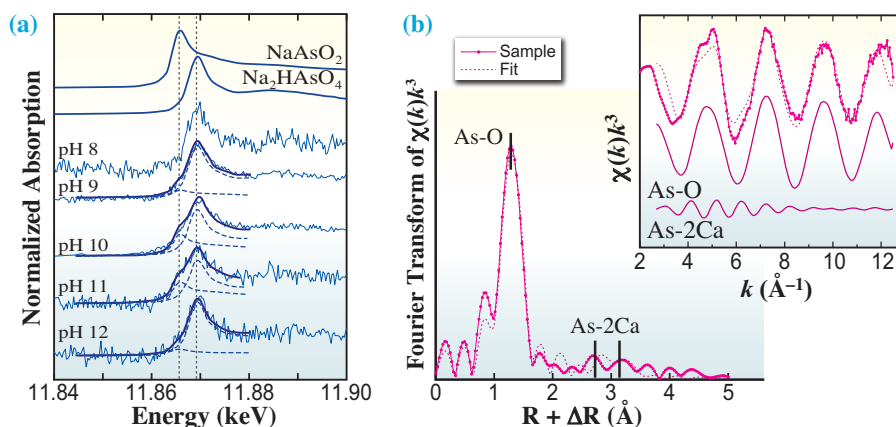


Fig. 1. (a) Normalized As *K*-edge XANES spectra for calcite precipitated in arsenite system at pHs 8 to 12. The spectra obtained by simulation are shown as solid curves, whereas the contributions of arsenite and arsenate are shown as dashed curves. (b) Normalized k^3 -weighted EXAFS spectrum and its Fourier-transformed spectrum for the arsenate incorporated into calcite. Dotted lines are fitted FEFF simulations with an As-O shell and two As-Ca shells.

is not confirmed at circumneutral pH (Fig. 1(a)). This difference between arsenite and arsenate is attributed to the fact that their dissolved species are negatively charged and neutral, respectively, at circumneutral pH (arsenite as H_3AsO_3 ; arsenate as $H_2AsO_4^-$ or $HAsO_4^{2-}$). The ratio of the distribution coefficients of arsenite and arsenate to that of calcite was $K_{As(V)}/K_{As(III)} > 2.1 \times 10^3$ (pH 7). As pH increases (> 9), up to 33% of As(III)/As_{total} ratio is partitioned into calcite. The stronger interaction of arsenite with calcite at an alkaline pH compared with at circumneutral pH is due to the negative charge of arsenite at alkaline pH ($H_2AsO_3^-$). The local environment of arsenate in calcite revealed by EXAFS analysis shows that the AsO_4 tetrahedron is bound to six Ca atoms. This suggests that an arsenate oxyanion is substituted into the carbonate site in calcite during the coprecipitation (Fig. 1(b)).

In the system spiked only with arsenite (arsenite system), the XANES analysis detected arsenate in calcite (Fig. 1(a)), indicating that the oxidation of arsenite to arsenate occurred during the coprecipitation with calcite. To clarify the arsenate-incorporation mechanism in the arsenite system, the stabilities of arsenite and arsenate in the calcite-supersaturated solution were electrochemically investigated using cyclic voltammetry (CV). The oxidation of arsenite to arsenate appears as peak A in the voltammograms of the arsenite solutions in Fig. 2. Peak A shifts to a more negative potential with an increase in Ca concentration, which indicates a decrease in the apparent oxidation potential of arsenite to arsenate in the presence of Ca^{2+} . As a result, it was found that the complexation of Ca^{2+} and arsenate makes arsenate more stable in the solution. This stabilization could induce the oxidation of arsenite to arsenate, which is considered to result in the preferential incorporation of arsenate into calcite in the arsenite system (Fig. 3). The finding of this complexation-induced

redox reaction suggests that the immobilization of As to calcite can occur even under reducing condition via arsenite oxidation to arsenate, although arsenite is hardly distributed to calcite.

The degree of As distribution to calcite may markedly depend on the arsenite/arsenate ratio in solution because of the large difference between the distribution coefficients of arsenite and arsenate, suggesting that the oxidation state of As is a significant issue in considering the scavenging ability of calcite for As in groundwater. In As-contaminated groundwater, arsenite is usually the main dissolved species. Although arsenite is hardly distributed to calcite, the immobilization of As to calcite can occur in groundwater by complexation with Ca^{2+} and the stabilization of arsenate. Considering the high abundance of Ca in natural water, the promotion of arsenite oxidation in the presence of Ca^{2+} is important as a (geo)chemical reaction, which may have been overlooked until recently.

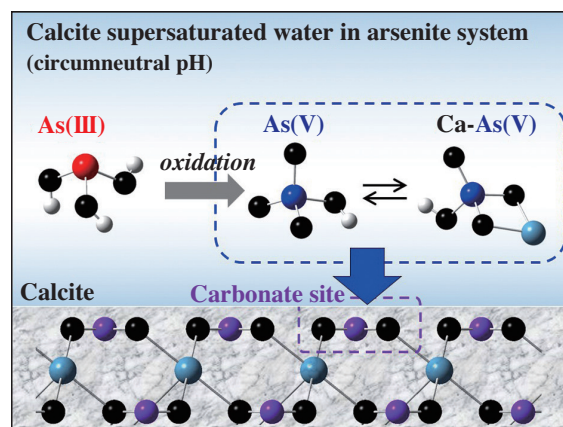


Fig. 3. Conceptual model of the complexation-induced arsenite oxidation and coprecipitation of arsenate with calcite in the arsenite system.

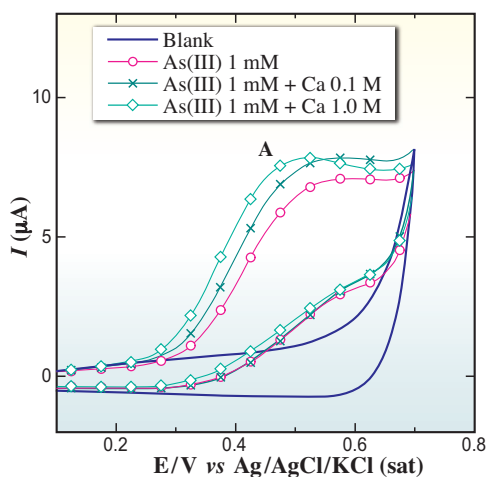


Fig. 2. Cyclic voltammograms for arsenite solution at different Ca concentrations in comparison with a blank solution.

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