A Study on the Coprecipitation of Arsenite and Arsenate into Calcite Coupled with the Determination of Oxidation States of Arsenic Both in Calcite and Water

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It was found that the amount of arsenite incorporated into calcite is much less than that of arsenate. The result suggests that the sequestration of arsenic by coprecipitation with calcite cannot be an important chemical process under reducing conditions such as in groundwater where arsenite is the dominant arsenic species.

Arsenic is well known as a highly toxic element. Arsenic-rich groundwater leads to serious health problems in some areas, particularly in Bangladesh and West Bengal.[1,2] Many scientists have studied the behavior of arsenic in groundwater and other natural waters to elucidate the mechanism of arsenic contamination in the systems.[1] Among possible processes, sorption and/or coprecipitation reactions from aqueous phase to various minerals are important factors controlling arsenic concentrations in natural waters. Calcite is an important mineral for these reactions, because calcite is ubiquitously found in various environments on the earth's surface.[3] In particular, it has been recently considered that the contribution of calcite to the sequestration of arsenic can be important under reducing conditions,[4] since Fe^{III} hydroxides, the most important host phase of arsenic in the environments,[1] is unstable under such reducing conditions in groundwater.

Arsenic in natural water is mostly found in inorganic forms of oxyanions of trivalent arsenite ($As^{III}O_3^{3-}$) or pentavalent arsenate ($As^{V}O_4^{3-}$).[1] Since the behavior of arsenic in natural water depends greatly on its oxidation state, arsenic interaction with calcite must be investigated with consideration of the dependence on the oxidation state. There have been some studies on the sorption and coprecipitation of arsenic with calcite,[4–6] but the oxidation states of arsenic both in the aqueous and solid phases were not always determined in the previous studies. Thus, the aim of this study is to understand the incorporation of arsenite and arsenate into calcite in coprecipitation experiments with the information of the oxidation states both in water and calcite, since little is known about the influence of the oxidation state on the coprecipitation of arsenic into calcite.

Coprecipitation was conducted by synthesis of calcite in the presence of arsenite and/or arsenate in water. Calcite was synthesized by two methods (see Supporting Information[19] for more details). First was the spontaneous precipitation from a 1:1 mixture of $CaCl_2$ and $NaHCO_3$ solutions (50 mM for both solutions).[7] The initial pH was adjusted to 8.0 with a small amount of an NaOH solution. The mixed solution in a glass vessel was in open air and stirred with a magnetic stirrer at 25 °C for about 22 h. The second was a constant addition method,[8] where the precipitation rate of calcite was kept constant during the coprecipitation experiments. For the second experiment, calcite-supersaturated solution (saturation index (SI, logarithmic scale): ca. 1.0) containing arsenic was constantly pumped into a reactor, in which calcite seeds and the solution were mixed and CO_2 (1.85%) + N_2 (98.15%) gas was bubbled to form calcite overgrowths on the seeds at pH 7.0. This system allowed (i) coprecipitation of arsenic with calcite under equilibrium situation and (ii) determination of the apparent distribution coefficients of arsenic, $K = [As]_{calcite}/[As]_{water}$, from this experiment.

In the both experiments, the precipitates were filtered with a membrane filter and freeze dried. The minerals of the samples obtained were identified using a powder X-ray diffractometer (MultiFlex, Rigaku Co.). Concentrations of arsenic in the precipitates were analyzed by ICP-MS (Agilent 7500cs, Agilent) after dissolution of the precipitates. During the reaction, the As^{III}/As^{V} ratio in the remaining water was measured by HPLC-ICP-MS (column: TSKgel Super IC-AP, Tosoh; flow rate: 1.0 $mL\,min^{-1}$).[9] The As^{III}/As^{V} ratio in the precipitates was determined by X-ray absorption near-edge structure (XANES) at the arsenic K-edge,[10] which was recorded in fluorescence mode at BL01B1 of the SPring-8 (Harima, Japan). XANES data were analyzed by REX2000 (Rigaku Co.). Extended X-ray absorption fine structure (EXAFS) was also measured to confirm the local structure of arsenic in calcite.

Concentrations of arsenic in calcite for the spontaneous method are summarized in Table S1.[19] The precipitates formed in the experiments were all calcite containing arsenic. The EXAFS of arsenic in the calcite recorded in our study (Figure S2 and Table S3[19]) is similar to those obtained for arsenate in calcite reported elsewhere,[11] suggesting that arsenate ion substitutes carbonate in calcite.

Much larger amounts of arsenic were incorporated into calcite when arsenate was added into the system (arsenic concentration in calcite: 2.9 $mmol\,kg^{-1}$), compared with the system with arsenite (0.014 $mmol\,kg^{-1}$). Note that the systems were undersaturated in terms of various calcium arsenate and arsenite compounds.[12] Hence, the results qualitatively showed that arsenate is preferentially incorporated into calcite rather than arsenite.

The oxidation state of arsenic in the precipitates was determined by XANES (Figure 1) based on fitting of the spectra of the samples by linear combination of the spectra of $KAsO_2$ and KH_2AsO_4 as As^{III} and As^{V} reference materials, respectively.[9,10] As a result, only arsenate was found in calcite in any samples even in the sample spiked with arsenite (sp-1). Considering the detection limit of As^{III}/As_{total} by XANES (=4%),[10] more than 96% of arsenic in calcite was pentavalent. For the arsenite system, the arsenate fraction in the remaining solution determined by HPLC-ICP-MS was less than 4%, showing the oxidation of

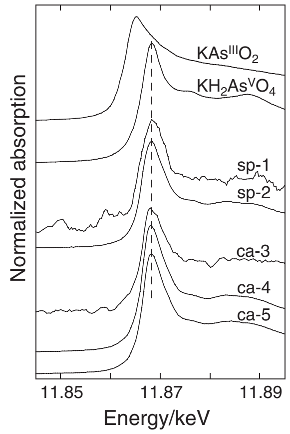

Figure 1. Normalized arsenic K-edge XANES spectra of arsenic reference materials ($KAsO_2$ and KH_2AsO_4) and arsenic in calcite formed by spontaneous (sp-1 and -2) and constant addition methods (ca-3, -4, and -5). Details of the experimental conditions for each sample are in Tables S1 and S2 in Supporting Information.[19]

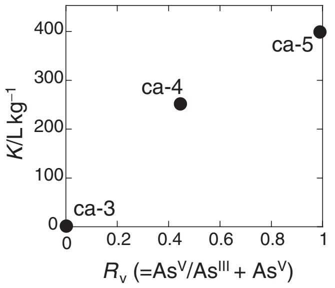

Figure 2. Apparent distribution coefficient (K) at various R_V in the constant addition method.

arsenite in the coexistent water was minimal. Based on the determination of oxidation states of arsenic both in water and calcite, the ratio of distribution coefficients of arsenate (K_{As^V}) and arsenite ($K_{As^{III}}$), $K_{As^V}/K_{As^{III}}$, is larger than $(96/4)^2 = 5.8 \times 10^2$, showing that arsenate selectively coprecipitates with calcite compared with arsenite.

In the constant addition experiments, apparent K value was determined at three As^V/As_{total} ratios ($=R_V$) in water (Figure 2). The apparent K value can be written as $K = (1 - R_V)\ K_{As^{III}} + R_V K_{As^V}$. From the dependence of K on the R_V, it was found that $K_{As^{III}}$ is lower than $1.5\,L\,kg^{-1}$ (=the K value at $R_V = 0.2\%$). Since K_{As^V} was $4.0 \times 10^2\,L\,kg^{-1}$, the $K_{As^V}/K_{As^{III}}$ should be larger than 2.7×10^2.

From the spontaneous precipitation and constant addition experiments, it was clear that the incorporation of arsenic into calcite is practically inhibited when arsenite is the main dissolved species of arsenic in water, since calcite selectively incorporates arsenate during the coprecipitation. Some other studies have suggested that arsenite can also be incorporated into calcite without determination of oxidation states of arsenic in the solid phase.[13,14] In this study, it was clear that arsenite cannot be incorporated into calcite as revealed by the determination of the oxidation state in calcite by XANES.

The reason for the difference between arsenite and arsenate is not clear yet at present, but the speciation of arsenic in water may be crucial. Arsenate is dissolved in water as anionic forms, $H_2AsO_4^-$ or $HAsO_4^{2-}$, but arsenite is not dissociated in the pH range in our experiments.[15] Since Ca^{2+} ion may be more reactive to anions to incorporate the ions into the calcite structure, the difference of their charges may induce selective incorporation of arsenate into calcite rather than arsenite. Similar results were also suggested in a sorption study,[16] where sorption of arsenate was observed, whereas little or no arsenite sorbs on calcite. The results are consistent with our coprecipitation experiments showing a much larger distribution of arsenate into calcite than arsenite.

The present results are important in terms of arsenic behavior in groundwater. Under reducing conditions such as in groundwater, arsenite is usually the main dissolved species in the aqueous phase.[17] According to our present results, arsenic incorporation into calcite may be very limited in such reducing environments. In Bangladesh and West Bengal, the groundwater is saturated or oversaturated in terms of the solubility of calcite,[18] which leads to the suggestion that calcite can be a host phase of arsenic.[4] However, the present results discount the suggestion due to the very limited distribution of arsenite from water into calcite under circumneutral conditions.

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