

Experimental and computational studies on immobilization of oxyanions at the calcite-water interface

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Geochemical processes at mineral-water interfaces (e.g., mineral growth/dissolution, mobilization/immobilization of trace elements) play a critical role in determining contaminant transport and nutrient availability in natural water environments. Understanding such processes is central to many environmental challenges we are facing today such as the prediction of the long term fate of contaminants for nuclear waste disposal, the design and implementation of carbon sequestration strategies, and trapping of metal contaminants as impurities. Recent advances in computing power and development of computational methods have made possible their physicochemical investigation at the molecular level. This presentation introduces one of the geochemical studies at mineral-water interfaces based both on laboratory experiments and quantum chemical calculations (QCC).

Calcite (CaCO_3) is known as a mineral which can play a role as an effective scavenger of toxic elements in the surface environment. This study focused on the interactions of arsenic (As) and selenium (Se) oxyanions with calcite. The contamination of natural water with them is occurring in various areas in the world. Especially, migration of ^{79}Se from nuclear wastes to biosphere will pose a serious problem for the safe geological disposal of nuclear wastes.

Our coprecipitation experiments and XANES measurements revealed that calcite selectively incorporated arsenate rather than arsenite, and selenite was selectively incorporated rather than selenate. Although molecular geometries of dissolved selenite and selenate are similar to those of arsenite and arsenate, respectively, there is no relationship between their molecular geometries and incorporation behavior into calcite. EXAFS analyses using FEFF shows that these oxyanions are incorporated into calcite through substitution with carbonate ion, which indicated that these impurities are combined with Ca^{2+} ion when they deposit on the calcite surface. In order to determine the factor controlling the preferences of arsenate and selenite for the incorporation of As and Se, respectively, into calcite, their affinities to Ca^{2+} ion, which reflect their reactivities with calcite at the calcite-water interface, were evaluated based on the QCC.

Estimation of intermolecular binding energies between each oxyanion and Ca^{2+} ion by QCC shows that the affinity orders for Ca^{2+} ion are arsenite > arsenate and selenite > selenate. The preference of selenite for incorporation into calcite is related to its higher affinity to Ca^{2+} ion than selenate. On the other hand, though QCC shows that arsenite has higher affinity for Ca^{2+} ion than arsenate, arsenite is hardly incorporated into calcite as shown experimentally. This preference can be attributed to the much lower abundance of deprotonated arsenite as shown in its large dissociation constant ($\text{p}K_a = 9.3$). Other oxyanions (arsenate, selenite, and selenate) dissociate into their anionic forms and can interact with Ca^{2+} ion under pH conditions where calcite can precipitate, whereas neutrally charged arsenite cannot display its high affinity for Ca^{2+} ion except for under high alkaline condition. Hence, the factors controlling their preferences for the incorporation into calcite are different between As and Se; for As, the charge of the aqueous species is important, whereas affinity to Ca^{2+} ion is important for Se. Additional QCC on the interactions between the oxyanions and calcite surface with the cluster models mimicking calcite-water mineral interface is expected to contribute to further investigation at the molecular level. The present findings should provide some insights into natural behavior of As and Se because their oxidation states are variable in subsurface environment, and into physicochemical systematics of oxyanions interaction with calcite.

Keywords: XAFS, Quantum chemical calculation, Mineral-water interface, Calcite