

モノヒドロカルサイトのアラゴナイト相変化における鉛イオンの取り込み挙動の変化

Changes in lead uptake during transformation of monohydrocalcite to aragonite

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INTRODUCTION

Monohydrocalcite is metastable and transformed to aragonite in aqueous solutions [1]. The uptake of phosphate and arsenate, oxyanions, by monohydrocalcite has shown that it depends on the concentration of sorbate whether or not the transformation occurs, and in addition, that the uptake characteristics may vary with the presence or absence of the transformation [2]. This strongly suggests the uptake of oxyanions by monohydrocalcite is not a simple process. On the other hand, there have been few studies for the uptake of cations by monohydrocalcite. We conducted uptake experiments of lead ion by monohydrocalcite to examine changes in uptake behavior of lead ion during transformation of monohydrocalcite to aragonite.

METHODS

To minimize changes in concentrations of carbonate ions and pH, buffer solutions were equilibrated with atmospheric CO₂ using Na₂CO₃, NaHCO₃ and NaNO₃; the solution pHs were adjusted to pH 8.50, 9.00 and 9.50 by NaOH and HNO₃. 2 g/L of synthesized monohydrocalcite was added to each solution for the experiments. The transformation kinetics was examined at 1 μM of initial Pb²⁺ and pH 8.50, 9.00 and 9.50. The apparent sorption isotherm experiments were conducted at 0.5 to 100 μM of initial Pb²⁺ and pH 9.50. The concentrations of Pb were measured at the end of each batch experiment. The durations of the kinetic experiments were up to 15 hours, while all isotherm experiments were carried out for 24 hours.

RESULTS AND DISCUSSION

Monohydrocalcite was transformed to aragonite in several hours in aqueous solutions. Aragonite increased in amount gradually while monohydrocalcite decreased with time. Monohydrocalcite was almost completely replaced by aragonite in 15 hours. The growth rates of aragonite were almost the same between the three different pH conditions. Before, during and after the phase transformation, the amounts of uptake of Pb²⁺ were almost the same at different pH.

The solutions with more than 3 μM of Pb²⁺ were supersaturated with respect to cerussite (lead carbonate) which was, however, not identified by X-ray powder diffraction. Therefore, the precipitation of lead carbonate was not predicted in solutions with less than 3 μM of Pb²⁺. Despite the supersaturation in 10 μM initial-Pb²⁺ solution, SEM observation of the reacted solid showed that the contrast of BSE image was homogeneous, suggesting Pb was associated with aragonite probably by sorption or coprecipitation. At 100 μM of initial Pb²⁺, fine grains with high contrast were observed by BSE, showing the formation of lead carbonate. Some amount of Pb was considered to be associated with aragonite because of the reasons as follows: (1) the Pb²⁺ concentration at the end of the experiment at 100 μM of initial Pb²⁺ was about 4 μM, of which the concentration was similar to that for the 5 μM initial-Pb²⁺ experiment where about a half of Pb was associated with aragonite and (2) the transformation was completed in 15 hours.

The transformation mechanisms of monohydrocalcite to aragonite are dissolution and precipitation [1]. Depending on the initial Pb²⁺ concentrations, portion of Pb forms lead carbonate and some other portion is associated with aragonite after the transformation. Because aragonite increases in amount gradually and because aragonite and cerussite are isostructural to one another, it is possible that the Pb with aragonite forms solid solution during the transformation, which will be clarified in the near future.

REFERENCE

[1], Munemoto and Fukushi, 2008, Journal of Mineralogical and Petrological Sciences, 103, 345-349

[2], Fukushi, et al., 2011, Science and Technology of Advanced Materials, 12, 064702

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