

論文の内容の要旨

論文題目

Redistribution of Pb and Zn during phase transformation of calcium carbonate
and its implication for Pb and Zn transport

(炭酸塩鉱物の相変化に伴う鉛と亜鉛の再分配とその元素移動への影響)

氏名 宗本 隆志

The redistribution mechanisms and kinetics of Pb and Zn during phase transformation of monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) to aragonite (CaCO_3) were studied through laboratory experiments. The effects of phase transformation of monohydrocalcite on redistribution behaviors of Pb and Zn were utilized to develop a model for transport of elements at the Earth's surface. My study has been done for a better understanding of determining processes of element transport at the Earth's surface.

For the examination of the effects of phase transformation on element transport in laboratory, appropriate choice of metastable mineral is important to finish experiments in hours or days. I chose monohydrocalcite out of metastable minerals because monohydrocalcite, metastable phase of calcium carbonate, has an advantage that the transformation is completed within several days, which should be compared to, for instance, ferrihydrite, most ubiquitous metastable mineral at the Earth's surface, requiring years for transformation. Monohydrocalcite transforms to more stable calcite and aragonite which accommodate various cations at the 6- and 9-folded coordination crystallographic sites, respectively. Because the distribution behaviors during transformation of monohydrocalcite are possibly different between the above two types of cations, I chose Zn and Pb out of the calcite- and aragonite-type cations, respectively, for the examination of element redistribution during transformation of monohydrocalcite. Batch kinetic and isothermal sorption experiments were conducted at constant Pb and Zn concentrations and for various time duration, and at various Pb and Zn concentrations and for constant time duration, respectively, to elucidate the rates of the transformation and the mechanisms, processes and rates of

Pb and Zn redistribution. All of them are factors to model Pb and Zn transport.

Monohydrocalcite was synthesized from the solution containing 0.06 M CaCl₂, 0.06 M MgCl₂·6H₂O and 0.08 M Na₂CO₃. X-ray diffraction (XRD) analysis shows the absence of impurities in the synthesized monohydrocalcite, Ca_{0.98}Mg_{0.02}CO₃·H₂O, with a spherical shape of ~100 nm in diameter. The transformation experiments of monohydrocalcite in aqueous solutions without metal ions were conducted at temperatures between 10 and 50 °C in order to examine the nature of transformation without metal ions. All sorption experiments were started by the addition of synthesized monohydrocalcite to solutions with given concentrations of initial Pb and Zn. The kinetic batch sorption experiments were conducted at pH 9.5 in 100 μM of initial Pb and Zn concentrations for up to 24 h and 48 h, respectively. The batch isothermal sorption experiments were conducted for 24 h varying initial Pb and Zn concentrations in a range from 1 to 100 μM; 1-30 and 50-100 μM of initial Pb are hereafter referred to as low and high initial Pb concentrations, respectively, and 1-20 and 30-100 μM of initial Zn to as low and high initial Zn concentrations, respectively. The resultant suspensions after the sorption experiments were filtered through 0.22 μm membrane. The resultant solids were air-dried and then analyzed by XRD. The solid morphologies and compositions were analyzed by scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS) and back-scattered electron imaging (BSE). The concentrations of Ca, Pb and Zn in solutions were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES) at the end of each batch experiment. Transmission electron microscopy (TEM) with energy dispersive X-ray analysis (TEM-EDS) was employed for some of the solids. The amounts of sorbed Pb and Zn ([Me]_{sorbed}) were estimated from the mass balance equation. The amounts of sorbed Pb and Zn were divided into those adsorbed on the solid surface ([Me]_{adsorbed}) and incorporated within the solid ([Me]_{incorporated}) by sequential chemical extraction.

In the transformation experiments without metal ions, monohydrocalcite transformed to aragonite with time. There are two rate-limiting steps in the transformation of monohydrocalcite to aragonite: the nucleation and crystal growth of aragonite. The dissolution of monohydrocalcite is a faster process than the nucleation and crystal growth of aragonite. Both the induction time and crystal growth rate of aragonite depend on the temperature. The apparent activation energies are estimated to be 108.1 kJ/mol and 80.7 kJ/mol for the nucleation and crystal growth, respectively.

In the Pb sorption experiments, monohydrocalcite transforms to aragonite of several μm in length with time. The XRD profiles indicate that aragonite begins to form within 3 h and the transformation is almost completed in 15 h. The final solutions with low initial Pb concentrations are in equilibrium with aragonite and those with high initial Pb concentrations are in equilibrium with monohydrocalcite. For the latter case, the presence of a trace amount of monohydrocalcite is confirmed by the TEM observation. Therefore, the transformation of monohydrocalcite is completed in 24 h at low initial Pb concentrations while it is slightly delayed at high initial Pb concentrations. The quantitative change in transformation rate with increase in Pb concentration is not certain. 96% of initial Pb is adsorbed onto monohydrocalcite before the transformation starts, and 95-96.5% of initial Pb is sorbed to solids at any time during the transformation, indicating the Pb redistribution rate is at least as fast as the

transformation rate. The mechanisms of Pb redistribution are different between low and high initial Pb concentrations. For the low initial Pb concentrations, the final solutions are undersaturated with respect to cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$), which were not observed by XRD or SEM, and nearly equilibrium with aragonite. Thermodynamics of the formation of solid solution in aqueous solution for a $\text{CaCO}_3\text{-PbCO}_3\text{-H}_2\text{O}$ system well explains the redistribution of Pb during transformation of monohydrocalcite (Fig. 1). Consequently, the redistribution of Pb occurs by the formation of $(\text{Ca,Pb})\text{CO}_3$ solid solution for the low initial Pb concentrations. On the other hand, for the high initial Pb concentrations, the SEM observation showed the presence of Pb-rich phase(s) (Fig. 2) and the final solutions were near equilibrium with cerussite and supersaturated with respect to hydrocerussite, which is consistent with the analyses by SEM and TEM. Because the extent of the saturation was kept constant through the kinetic experiments and Pb-rich phase(s) were not observed in the early stage of the experiments, the precipitation rate of the Pb-rich phase(s) is slower than the transformation rate. Consequently, for the high initial Pb concentrations, the redistribution of Pb during transformation of monohydrocalcite is explained by the precipitation of Pb-rich phase(s) along with the formation of $(\text{Ca,Pb})\text{CO}_3$ solid solution.

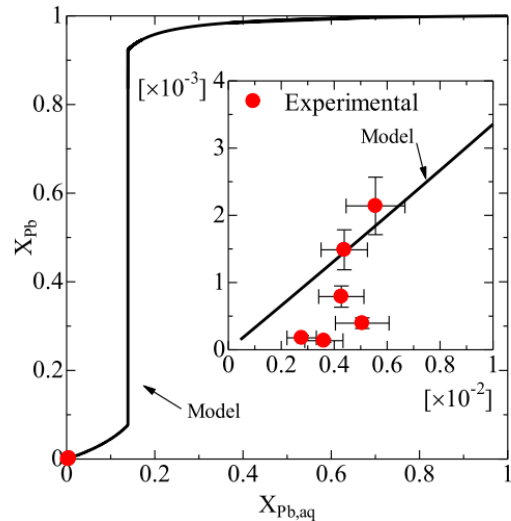


Fig. 1. Solid-solution/aqueous-solution system for $\text{CaCO}_3\text{-PbCO}_3\text{-H}_2\text{O}$.

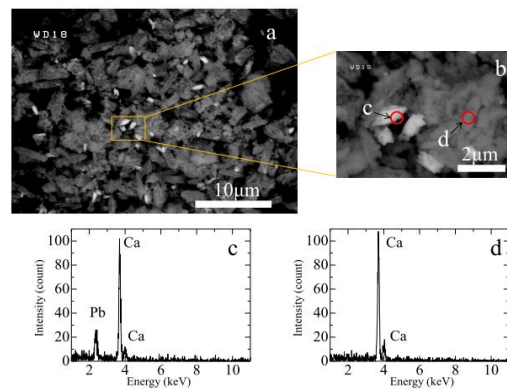


Fig. 2. BSE images of Pb-rich phase(s) (a) and (b). Circles with alphabetical letters present analytical points for EDS (c) and (d).

In the Zn sorption experiments, transformation of monohydrocalcite is slightly slower than that in the Pb sorption experiments: monohydrocalcite transforms to aragonite of a few to several μm in length with time, aragonite begins to form within 3 h and the transformation is almost completed in 24-48 h depending on the initial Zn concentrations. Accordingly, sorbates and their concentrations affect the transformation rate. The final solutions with low initial Zn concentrations are in equilibrium with aragonite and those with high initial Zn concentrations are in equilibrium with monohydrocalcite. The transformation of monohydrocalcite is completed in 24 h at low initial Zn concentrations while it is delayed at high initial Zn concentrations, slower by ~ 2 times than that with the absence of metal ions. The quantitative change in transformation rate with increase in Zn concentration is not certain. 96% of initial Zn is adsorbed onto monohydrocalcite before the transformation starts and 96-99% of initial

Zn is sorbed to solids during the transformation, showing similar, fast redistribution rate to that of Pb. The XRD, SEM and TEM results show the absence of Zn-rich phase(s) during transformation, which is supported by the fact that all solutions are undersaturated with respect to Zn-rich phases such as smithsonite (ZnCO_3) and zinc hydroxide ($\text{Zn}(\text{OH})_2$). The XRD, SEM and TEM results show the presence of only monohydrocalcite and/or aragonite. The amount of sorbed Zn increases with progress in transformation and with increase in initial Zn concentration. The redistribution mechanisms are the same between the low and high initial Zn concentrations. Like $(\text{Ca,Pb})\text{CO}_3$ solid solution, thermodynamics of the formation of $(\text{Ca,Zn})\text{CO}_3$ solid solution in aqueous solution is also applied to a $\text{CaCO}_3\text{-ZnCO}_3\text{-H}_2\text{O}$ system, which indicates approximately 3-5% of Zn can be incorporated into aragonite. Because almost all Zn is incorporated in aragonite, $(\text{Ca,Zn})\text{CO}_3$ solid solution also forms even for the high initial Zn concentrations.

I developed a simple model that shows the changes in the concentrations of monohydrocalcite, and adsorbed metal with time at a given point in a water flow during transformation of monohydrocalcite. Most of the major factors that the model considers are based on the results of the redistribution experiments of Pb and Zn during transformation of monohydrocalcite: (i) transformation rate, (ii) change in metal distribution during transformation, (iii) change in particle size during transformation, and (iv) water flow rate. The model calculations are made to examine the changes in concentrations of monohydrocalcite and sorbed metal with time for the following cases: (1) with and without transformation, (2) with change in water flow rate, (3) with change in particle size of monohydrocalcite, (4) with difference between metal redistribution mechanisms, and finally (5) with difference between metastable minerals (transformation rate, particle size and redistribution mechanism). Major results are: the Zn concentration is lower with transformation than without transformation with water flow of 1 day residence time because of the transformation and subsequent sedimentation. With water flow of 1 year residence time, the Zn concentration is almost null with transformation. 10 and 100 nm of particle size of monohydrocalcite makes no difference with 1 day residence time. The difference in metal redistribution mechanisms (i.e., co-precipitation and solid-solution formation) affect the metal concentration. When monohydrocalcite and ferrihydrite are compared, the Zn concentrations are different between monohydrocalcite and ferrihydrite, for instance, ~ 0 and 0.03 mol/m^3 (two orders of magnitude difference) for monohydrocalcite and ferrihydrite, respectively. My model demonstrates that the transformation rate of monohydrocalcite and metal redistribution during transformation affect metal transport.