Heat-induced dolomitization of amorphous calcium magnesium carbonate (ACMC) in CO_2

*Shingo Sugawara[1], Wataru Fujiya[1], Hiroyuki Kagi[2], Akira Yamaguchi[3], Ko Hashizume[1]

1. Graduate School of Science and Engineering, Ibaraki University , 2. Geochemical Research Center, Graduate School of Science, The University of Tokyo, 3. National Institute of Polar Research

Amorphous carbonate [$MCO_3 \cdot nH_2O$] is thermodynamically metastable relative to crystalline carbonates (e.g., calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], and magnesite [$MgCO_3$]) and possibly provides a low-energy pathway for carbonate mineralization (e.g., Radha et al., 2012). ACC (Amorphous calcium carbonate) easily crystalizes to calcite by heating in air. This crystallization process is considered to proceed by solid-state transformation (Ihli et al., 2014). On the other hand, ACMC (Amorphous calcium magnesium carbonate) with Mg/Ca ~1 heated in air does not crystalize to dolomite but crystalizes to Mg-calcite and then decomposes to MgO-CO_2. Despite various applications (e.g., control of particle size and dope of impurity), there has been no report on the crystallization of ACMC to dolomite without solution.

The high dissociation pressure (pCO_2) of dolomite likely prevents ACMC from crystallizing to dolomite by heating. We calculated the dissociation pressure from Gibbs free energies (Robie et al., 1978) in each phase, assuming that the decomposition reaction is $CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$. The dissociation pressure is ~1.2 bar around the crystallization temperature of Mg-calcite (700 K). This study investigated if heated ACMC could crystalize to dolomite by suppressing the dolomite decomposition in a closed system filled with CO_2 gas.

The ACMC with dolomite composition was synthesized by mixing 10 ml 0.2 M (Mg + Ca) Cl_2 solution (Mg/Ca = 2.36) and 10 ml 0.2 M Na_2CO_3 solution at 0 ℃. After mixing, precipitates were filtered immediately, washed with acetone, and dried in a vacuum desiccator. We dehydrated this ACMC at 300 ℃ in a furnace evacuated to less than several Pa. Powder X-ray diffraction (XRD) measurements confirmed that the sample was amorphous before and after dehydration. The FE-SEM observation revealed that the particle size after dehydration was <100 nm. These observations are consistent with previous studies (e.g., Rodriguez-Blanco et al., 2015).

We stored the dehydrated ACMC in a stainless-steel vessel filled with CO_2 gas and heated it at 420 ℃. XRD measurements revealed from 101 and 015 reflections that the heated ACMC crystalized to dolomite and did not decompose to MgO. The particle size was about several 100 nm, slightly larger than ACMC particles. Evaporite minerals (e.g., northupite [$Na_3Mg(CO_3)_2Cl$]] and halite [NaCl]) were commonly found in the heated sample and were removed by washing with ultrapure water. The Mg/Ca ratio of this dolomite was 0.83 ±0.04 (2SD) measured with electron probe microanalyzer (EPMA).

To investigate the crystallization process into dolomite, we heated dehydrated ACMC at 360 ℃ for 2, 6, 12, and 24 h, and at 420 ℃ for 2, 12, and 72 h. During the heating of the dehydrated ACMC at 360 ℃ for 2-6 h, 104 reflection in XRD patterns appeared, but 101 and 015 reflections did not occur, indicating incomplete crystallization of dolomite. When increasing heating temperature and/or heating time, diffraction peaks were higher and sharper and, 101 and 015 reflections appeared. In addition, peak positions shifted towards higher angles (e.g., 104 reflection shifted from 30.56˚ to 30.82˚). The shift of peak positions may indicate that the lattice volume varied with increasing Mg/Ca ratios because these

shifts were not observed for ACC. This is also observed for hydrothermal conditions, under which previous experiments on dolomite synthesis have commonly been conducted (e.g., Kaczmarek and Thornton, 2017). Under hydrothermal conditions, dissolution-recrystallization processes result in the increase in the Mg/Ca ratios of the products. This study demonstrates that dolomitization by solid-state transformation without solution also induces the increase in the Mg/Ca ratios.

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