Solubility of calcium carbonate hemihydrate (CCHH): Where does CCHH occur?

M. Suyama, T. Kitajima, K. Fukushi

Supplementary Information

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Materials and Methods

In the following, we use the notation Na, Mg, Ca, Cl, and DIC to express sodium, magnesium, calcium, chlorine, and dissolved inorganic carbon as components. Mixed CaCl$_2$–MgCl$_2$ solutions were prepared in a 1 L plastic bottle to which a stock Na$_2$CO$_3$ solution (1 mol/kg) was poured. The initial concentrations of Ca, Mg, and DIC were 0.05, 0.06, and 0.05 mol/kg, respectively. A duplicate batch experiment (Runs 1 and 2) was performed to confirm the reproducibility. Immediately after the addition of Na$_2$CO$_3$, whitish precipitates formed in the bottle. The bottle was placed on a mixing rotor in an incubator held at 25 °C in a temperature-controlled room (23 ± 2 °C). Aliquots (50 mL) of the homogenised suspensions were collected at ~30 min intervals. Before collecting the aliquots, the pH and temperature of the suspensions were measured with a pH meter (HM-21P, DKK-TOA Corp.) equipped with a pH electrode (GST-5741C, DKK-TOA Corp.) calibrated using three buffer solutions. The errors on pH measurements were less than 0.03 pH units. The collected suspension was then filtered through a 0.2 μm mixed cellulose ester membrane under vacuum. Approximately 10 mL of the filtrates were acidified by adding a small volume of concentrated, ultrapure HNO$_3$ for Ca and Mg analyses. The 30 mL of the filtrates were separated for alkalinity measurements. The collected solid on the filter paper was placed on a polypropylene conical tube. The tube containing the collected sample was immediately placed in a Dewar flask filled with liquid nitrogen to prevent further mineralogical alteration. The frozen samples were stored in the refrigerator prior to freeze-drying. The time required for the pH measurement and sample treatment was typically less than 10 minutes.

Ca and Mg concentrations in the filtrate were measured by using an inductively coupled plasma optical emission spectrometer (ICP-OES, ES-710S, Varian Inc.). The relative standard deviations of triplicate ICP-OES measurements were always less than 1 %. The total alkalinity ([HCO$_3^-$] + 2[CO$_3^{2-}$], where [i] represents the mol/L concentration of the i-th species) of the filtrate was measured by alkalinity titration with 0.1 N H$_2$SO$_4$ solution. Alkalinity was calculated by the Gran function plot method using the USGS web-based Alkalinity Calculator (https://or.water.usgs.gov/alk/). The
errors associated with the alkalinity measurements were at most 10%. The solid residues in the tubes were freeze-dried and stored in a vacuum desiccator before use. The samples were gently crushed manually and mounted on a non-reflective sample holder for mineralogical analysis by X-ray diffraction (XRD, Cu Kα, 40 kV, 30 mA; Ultima IV, Rigaku Corp.). The step size was 0.02° and scan speed was 2°/min for most of the samples. One sample (210 min, run 2) was measured integrated to get a better single-to-noise ratio.

Speciation in the reacted solutions was analysed by using the REACT program in the Geochemist’s Workbench with the thermodynamic database ”thermo.v8.16+.dat” (Bethke et al., 2021). The activity coefficient was calculated using the extended Debye-Hückel equation known as the B-dot method (Helgeson and Kirkham, 1974; Bethke, 2007). The activity model can reasonably account for the ionic strength of the present experiments (I = 0.3 mol/kg) (Bethke, 2007). Input parameters for speciation analyses were pH, alkalinity and Na, Ca, Mg and Cl concentrations. Temperature was assumed to be 25 °C in the calculations. The Na and Cl concentrations (mol/kg) were derived from the initial concentrations of CaCl₂, MgCl₂, and Na₂CO₃. The Ca and Mg concentrations (mol/L) were derived from ICP-OES measurements. Alkalinity (meq/L) was derived from the alkalinity titration.

The dissolution reaction of hydrated calcium carbonate with the stoichiometry of CaCO₃·nH₂O can be written as:

\[ \text{CaCO}_3 \cdot n\text{H}_2\text{O} = \text{Ca}^{2+} + \text{CO}_3^{2-} + n\text{H}_2\text{O}. \]

The corresponding mass action expression is:

\[ K_{\text{sp}} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \cdot a_{\text{H}_2\text{O}}^n}{a_{\text{CaCO}_3 \cdot n\text{H}_2\text{O}}}, \]

where \( a_i \) represents the activity of the \( i \)th species. The activities of water and pure solids can be assumed to be unity for the ionic strength of the solution in the experiments (\( I = 0.3 \) mol/kg). The ionic activity product (IAP) with respect to calcium carbonate was calculated using the activities of \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) determined from the speciation analyses.

**Difference of Lifetime of CCHH Between This Study and Zou et al. (2019)**

This study showed that the CCHH formed from ACC after 60–110 min and completely transformed to aragonite after 400–500 min. Zou et al., also conducted the time resolved synthesis experiments and showed that CCHH formed from ACC after 30 min of duration but completely transformed to MHC after 120 min of duration (Zou et al., 2019). The difference of the lifetime of CCHH and mineralogy after the transformation must likely derived from the difference of initial solution conditions. Fukushi and Matsumiya (2018) examined the mineralogical evolution of carbonates from CaCl₂, MgCl₂, and Na₂CO₃ mixed solution for 650 h to estimate the solubilities of MHC and associated hydrous magnesium carbonate. They showed that the onset of the transformation of MHC to aragonite was delayed with increasing Mg/Ca in the solution, probably because the Mg²⁺ ion in the solution plays a role in inhibiting the dehydration of the hydrous carbonate. The Mg/Ca in the initial solution of present study was 1.2, while that of Zou et al. (2019) was 0.25. The higher Mg/Ca ratio in this study, therefore higher dehydration inhibiting effect, most likely provide the longer lifetime of CCHH than that of Zou et al. (2019). Nishiyama et al. (2013) and Fukushi et al. (2017) carried out the systematic synthesis experiments of calcium carbonate as function of initial concentrations of CaCl₂, MgCl₂, and Na₂CO₃ for 24 to 48 h duration. They showed that the MHC was formed from the solutions of which the ratio of the DIC to Ca was greater than 1 in the presence of a certain amount of Mg which allows to the supersaturation with respect to hydrous magnesium carbonate. The condition is consistent with the solution condition by Zou et al. (2019) (DIC/Ca ratio = 1.25). When the ratio of the DIC to Ca was close to 1 in the presence of Mg, aragonite with small calcite was formed instead of MHC, of which the condition is consistent with this study. The conditions of the DIC/Ca ratio > 1
with a certain amount of Mg can allow the simultaneous formation of MHC and hydrous magnesium carbonate. Because of the higher solubility of hydrous magnesium carbonate, the MHC formation requires the higher saturation state with respect to MgCO₃. On the other hand, this study suggests that the formation of CCHH which is also hydrous calcium carbonate does not require the higher saturation state. Furthermore, Zou et al. (2019) suggested that the CCHH can form from the ACC with the molar ratio of Mg/(Mg+Ca) between 5 and 9%. The molar ratio of the ACC from this study was 20–30%. Therefore, the formation conditions of CCHH in regard with the concentration ranges of CaCl₂, MgCl₂, and Na₂CO₃ are possibly wider than those of MHC. This suggests that the CCHH is more common precursor calcium carbonate in natural water which ubiquitously contain Ca, Mg and DIC as components.

**Selection of Water Chemistry of Alkaline Lakes in the World**

Fukushi and Matsumiya (2018) reviewed the water chemistries of natural lakes around the world with pH > 9 and total dissolved solids (TDS) > 1 g/L (almost equivalent to ionic strength (I) > 0.1 mol/kg) of which water type are Na-Cl type (Table S-2a). They compiled the literature data in which (1) the concentrations of major constituents including Na, Mg, Ca, Cl, SO₄, and DIC (or alkalinity) are reported and (2) the electric charge balances (E.B.) of the solution are balanced to within 10%. Recently, Caumartin et al. (2023) compiled 140 modern microbialite-hosting systems occurring on all continents. We selected the lake water chemistries that met the criteria of the Fukushi and Matsumiya (2018) compilations, i.e., pH > 9, I > 0.1, T < 35°C, Na-Cl type and electric charge balance (E.B.) < 10% (Table S-2b). The E.B. was calculated by using the following equation using the concentration data of Caumartin et al. (2023).

\[
E.B. \ (\%) = \frac{[Na]+[K]+2[Ca]+2[Mg]-[Cl]-[HCO₃]-2[CO₃]-2[S0₄]}{[Na]+[K]+2[Ca]+2[Mg]+[Cl]+[HCO₃]+2[CO₃]+2[S0₄]} \times 100,
\]

where \([i]\) denotes the molar concentration of \(i\)th component. When the concentrations of HCO₃ and CO₃ were not available, the E.B. was calculated by using DIC concentration:

\[
E.B. \ (\%) = \frac{[Na]+[K]+2[Ca]+2[Mg]-[Cl]-[DIC]-2[S0₄]}{[Na]+[K]+2[Ca]+2[Mg]+[Cl]+[DIC]+2[S0₄]} \times 100.
\]

Similarly, the \(I\) was calculated by using the following equations:

\[
I = \frac{1}{2} ([Na] + [K] + [Ca] \times 2^2 + [Mg] \times 2^2 + [Cl] + [HCO₃] + [CO₃] \times 2^2 + [SO₄] \times 2^2),
\]

or

\[
I = \frac{1}{2} ([Na] + [K] + [Ca] \times 2^2 + [Mg] \times 2^2 + [Cl] + [DIC] + [SO₄] \times 2^2).
\]
Supplementary Tables

**Table S-1** List of reacted solution chemistries, log activities of Ca$^{2+}$, CO$_3^{2-}$, and Mg$^{2+}$, log IAP with respect to CaCO$_3$ and crystalline phases from XRD.

**Table S-2a** Water chemistries of alkaline lakes compiled in Fukushi and Matsumiya (2018).

**Table S-2b** Water chemistries of selected alkaline lakes compiled in Caumartin et al., (2023).

Tables S-1 and S-2 are available for download (.xlsx) from the online version of this article at http://doi.org/10.7185/geochemlet.2428.
Supplementary Figures

Figure S-1  (a) XRD pattern of the sample after 210 min in Run 2 (black line). The numbers represent the d-value in units of Å. The red pattern represents the XRD pattern of monohydrocalcite from Fukushi et al. (2017). (b) The XRD pattern of the same sample (red line) of selected range in λ = 0.49596 for comparison with calculated theoretical XRD patterns with different Mg content given by Aufort and Demischelis (2020).
The magnified XRD patterns of selected samples (initial, start of CCHH, end of CCHH and final) for (a) Run 1 and (b) Run 2. The temporal changes of the XRD intensities averaged from 30.3 to 31.0° (yellow lines in panels (a) and (b). Ara, aragonite; Cal, calcite.

**Figure S-2**
Figure S-3  The changes in the XRD peak intensity of CCHH (16.7° at 2θ) and aragonite (26.3° at 2θ) with time for (a) Run 1 and (b) Run 2.
Supplementary Information References


