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

M. Suyama 1, T. Kitajima 1,2, K. Fukushi 3*

Abstract

Recently, calcium carbonate hemihydrate (CCHH, CaCO3·1/2H2O) was discovered in a laboratory synthesis experiment. Because CCHH can form from aqueous solutions comprising ubiquitous components under ambient conditions, it is expected to exist in nature and may play an important role in carbon cycling at the Earth’s surface. Here, to constrain its possible formation environments, we investigated the solubility of CCHH for the first time by monitoring the evolving solution and mineralogical compositions of CaCl2–MgCl2–Na2CO3 solutions at 25 °C. During the experimental runs, CCHH formed from amorphous calcium carbonate and transformed to aragonite over time. When CCHH was present as a single reactive solid phase, a constant ionic activity product was reproducibly obtained. The solubility product (log Ksp) was −6.80 ± 0.05, between those of ikaite and monohydrocalcite, and near the upper limit of ionic activity products of calcium carbonates observed in alkaline lakes around the world. These results suggest that CCHH can form in alkaline lakes under evaporative conditions.

Introduction

Calcium carbonate is ubiquitous on Earth and plays an important role in the geochemical carbon cycle. Calcium carbonates have been widely studied in the fields of palaeoenvironmental reconstruction (Alonso-Zarza, 2003), biomineralogy (de Nooijer et al., 2014), and carbon sequestration (Sanna et al., 2014). Six calcium carbonate species have been observed in nature: the three anhydrous polymorphs of CaCO3 (calcite, aragonite, and vaterite), two hydrous species (monohydrocalcite, MHC, CaCO3·H2O; and ikaite, CaCO3·6H2O), and amorphous calcium carbonate (ACC), which is widely recognised as a precursor to the crystalline species (Nielsen et al., 2014). Although the hydrous calcium carbonates are always metastable phases with short lifetimes in aqueous environments, the formation of these phases play an important role in controlling the chemical composition of the systems (Fukushi and Matsumiya, 2018; Zeyen et al., 2021; Tosca and Tutolo, 2023). A new hydrated calcium carbonate (CaCO3·1/2H2O, calcium carbonate hemihydrate, CCHH) was recently produced in the laboratory (Zou et al., 2019) from a solution containing Ca2+, Mg2+, and dissolved inorganic carbon (DIC) at relatively high pH and ambient temperature. Although CCHH does not contain Mg in the structure, the Mg2+ in solutions is required for the formation of CCHH because of the dehydration-inhibiting effect of the Mg2+ ion (Zou et al., 2019; Aufort and Demichelis, 2020). Such conditions are not uncommon at the Earth’s surface (Drever, 1997), and CCHH can be expected to occur in nature and may even play an important role in the carbon cycle. However, the natural occurrence of CCHH has not yet been reported. Because a useful criterion for identifying the formation environment of any mineral phases is its solubility, we here report the first laboratory measurements of CCHH solubility and compare our results to the chemistries of natural waters to predict potential formation environments of CCHH in nature. Methods used in this study are described in Supplementary Information.

Results and Discussion

Evolution of solution chemistry and mineral composition. The solubility of CCHH was investigated by observing the temporal evolution of the solution chemistry and mineralogical compositions in CaCl2–MgCl2–Na2CO3 solutions. Mixed CaCl2–MgCl2 solutions were prepared in a 1 L plastic bottle to which a stock Na2CO3 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. The solution condition allowed for CCHH to exist as a persistent phase for relatively long durations of over 5 hours, thus allowing for reliable offline monitoring of the solution chemistry and mineralogical composition. A duplicate batch experiment (Runs 1 and 2) was performed to confirm the reproducibility. During the experiments of both Runs 1 and 2, the major crystalline phases observed by XRD were CCHH and aragonite (Fig. 1). The XRD patterns confirmed the absence of MHC during the experiments (Fig. S-1a) (Swainson, 2008;
In addition to the dominant phases, small peaks attributed to halite and calcite were observed (Fig. S-2a,b). Because the samples were not washed with the pure water to avoid possible alteration, small peaks of halite (NaCl), which is derived from the dissolved electrolyte in the experiments, were observed in the patterns. The small peak at 29.8° 2θ observed from Run 2 after 480 min came from the strongest peak of calcite. The peak was also observed from Run 1 after 430 min, although it was much smaller than that from Run 2. The position of the peak was close to a peak attributed to CCHH at 29.4° 2θ. A shoulder peak at 29.8° 2θ was commonly associated with the predominant peak of CCHH in Run 2 (Figs. 1, S-1a), which most likely represents the presence of a small contribution of calcite with CCHH. The intensity of the peak at 29.8° 2θ was invariant with the reaction time (Fig. 1). Therefore, we consider that a small amount of the calcite formed at the initial stage of CCHH formation, but it behaved as a chemically inert material during the subsequent reactions.

At the initial stage of the experiments (up to ~100 min), the peak intensity of CCHH increased with time (Fig. 1), and the pH and Mg concentration also increased, but the alkalinity and Ca concentration decreased (Fig. 2a, Table S-1). This stage represents the formation and growth of CCHH from the precursory ACC, which contains a significant amount of Mg (Loste et al., 2003). Based on the mass balances of Ca and Mg between the initial concentrations and the solution concentrations before CCHH formation, the molar ratio of Mg/(Ca + Mg) in ACC was calculated to be 20–30 %. The transformation of ACC to CCHH resulted in rapid decreases of the Ca concentration and alkalinity (Fig. 2b,c). During this transformation, Mg in the ACC was

**Figure 1** XRD patterns of the reacted samples as a function of reaction time for (a) Run 1 and (b) Run 2. The integrated XRD pattern with better signal-noise ratio (210 min, Run 2) is shown in detail in Figure S-1.
released to the solution (Fig. 2d). Indeed, the Mg concentrations in the solutions after the transformation from ACC to CCHH corresponded to the initial (total) Mg concentrations. Based on the mass balances, the molar ratios of Mg/(Ca + Mg) after the Mg release of CCHH were calculated to be 3 ± 4 %. Aufort and Demichelis (2020) simulated XRD profiles of CCHH as a function of Mg substitution. They showed that the introduction of the Mg impurity causes a distortion in the unit cell. Our CCHH XRD patterns are consistent with their Mg-free content (Fig. S-1b), and the molar ratio of Mg/(Ca + Mg) is at most less than 3 %. This result suggests that Mg barely substituted into the CCHH structure. They showed that the introduction of the Mg impurity causes a distortion in the unit cell. Our CCHH XRD patterns are consistent with their Mg-free content (Fig. S-1b), and the molar ratio of Mg/(Ca + Mg) is at most less than 3 %. This result suggests that Mg barely substituted into the CCHH structure, if at all. The intensities of the broad band at around 30° arising from the presence of ACC decreased with the release of Mg to solution (Fig. S-2c). The intensities took a constant value after the complete Mg release to the solutions before the subsequent transformation of CCHH. The coincidence most likely suggests that the ACC almost completely transformed to CCHH at the initial stage until ~100 min. Further decreases in intensities at around 30° after ~350 min coincided exactly with transformation of CCHH. Since ACC must have a different thermodynamic stability from CCHH, the simultaneous transformation of ACC with CCHH is not expected. Therefore, the decreases in XRD background are most likely due to the intrinsic changes of the XRD pattern from CCHH to aragonite without ACC.

When the CCHH peak intensity plateaued and before the appearance of aragonite peaks, the Ca concentration and alkalinity became relatively constant (Fig. 2b,c). This stage, which lasted almost ~300 min, most likely represents quasi-equilibrium between CCHH and the solution. After the aragonite peaks appeared at around 400 min, the pH, alkalinity, and Ca concentration suddenly decreased (Fig. 2a,c,d). This stage represents the transformation of CCHH to aragonite. Zou et al. (2019) also performed time-resolved synthesis experiments and showed that CCHH formed from ACC after 30 min, and completely transformed to MHC after 120 min. The duration of this transformation herein was significantly longer than in their experiments, probably because of the difference in initial solution conditions (see Supplementary Information).

**Solubility of CCHH.** Figure 2e shows the logarithmic form of the IAP with respect to CaCO₃·nH₂O. Due to the negligible Mg content in the CCHH (Mg/(Ca + Mg) < 3 %), the contribution of Mg to the mass action expression was ignored in this study. At the beginning of the experiments, log IAP took relatively constant values at around ~6.0; it then decreased suddenly to ~6.7 by 110 min (Run 1) and 140 min (Run 2), slowly
decreased further to $-6.9$ by 380 min (Run 1) and 410 min (Run 2), and finally decreased suddenly to below $-8.0$ by 400 min (Run 1) and 480 min (Run 2). These temporal changes of log IAP correspond well to those of the mineral compositions (Fig. 1). The first sudden decrease of log IAP (from $-6.6$ to $-6.7$ at around 50–150 min) corresponds to the formation and growth of CCHH from ACC, and the second (from $-6.9$ to below $-8.0$ at around 400–500 min) to the formation and growth of aragonite from CCHH (Fig. 1). In the intervening period, log IAP decreased continuously from $-6.7$ to $-6.9$, most likely because the solution was first approaching equilibrium with CCHH, which was subsequently followed by aragonite formation. It should be noted that the IAP was always significantly higher than the solubility of calcite (log $K_w = -8.48$; Drever, 1997), suggesting that the calcite initially formed with CCHH was chemically isolated from the system during the experiments.

Theoretically, when a solution approaches equilibrium from a state of oversaturation, the change in log IAP per unit time (i.e. the rate of IAP change) gradually decreases because the kinetics of mineral formation depend on the saturation states ($\Delta G$) (Nagy and Lasaga, 1992). In the equilibrium state, the rate of change reaches zero. On the other hand, when a mineral in an (quasi-)equilibrium state begins to transform into a stable mineral, the rate of change must be at a minimum when the transformation begins, and then it gradually increases as the transformation progresses (Fukushi and Matsumiya, 2018). Therefore, periods in which the rate of IAP change was at a minimum most likely approximate the equilibrium state with respect to CCHH. Figure 2f shows the time derivatives of log IAP during the intervals between measurements for both runs. The rate of change was closest to zero during 220–250 min in Run 1 and 250–280 min in Run 2. The corresponding log IAP values during those intervals were consistent in both runs: $-6.79$ and $-6.80$ in Runs 1 and 2, respectively. Based on the possible errors associated with pH, Ca and alkalinity measurements, those log IAP values have maximum uncertainties of 0.04. Therefore, we estimate the equilibrium constant (solvability product; log $K_w$) of CCHH to be $-6.80 \pm 0.05$. This range of log $K_w$ values includes the observed log IAP values during 150–330 min in Run 1 and 150–380 min in Run 2, when the XRD patterns showed CCHH peaks of constant intensity prior to the appearance of aragonite (Fig. 1). According to the solubility product of CCHH and the Gibbs free energies of formation ($\Delta G_f$) of Ca$^{2+}$ ($-552.79$ kJ/mol), CO$_3^{2-}$ ($-527.98$ kJ/mol), and H$_2$O ($-237.183$ kJ/mol) from the thermodynamic database used for our speciation calculations, we calculate $\Delta G_f^\circ$ to be $-1238.2 \pm 0.3$ kJ/mol for CCHH. In the CaCO$_3$-H$_2$O system at ambient conditions, the thermodynamic stabilities of solid phases increase in the order ACC $<$ ikaitie $<$ MHC $<$ vaterite $<$ aragonite $<$ calcite (Hull and Turnbull, 1973; Ogno et al., 1987; Brečičević and Nielsen, 1989; Drever, 1997; Konigsmüller et al., 1999; Mergelsberg et al., 2020). Our estimated $\Delta G_f^\circ$ for CCHH suggests that its stability is between those of ikaitie and MHC. This stability relationship is consistent with the CCHH transformation pathway observed herein (ACC to CCHH to aragonite) and in Zou et al. (2019; ACC to CCHH to MHC).

**Implications for natural occurrences of CCHH.** Zou et al. (2019) showed that CCHH can form from a solution containing Ca, Mg, and DIC at pH $> 10$. Here, we explored more moderate conditions, i.e. pH $> 9$. In nature, the principal aqueous environments rich in calcium, magnesium, and DIC and having high pH are terrestrial alkaline lakes under evaporative conditions (Sekine et al., 2020; Tosca and Tutolo, 2023). Most natural alkaline lakes are characterised by high pH ($>9$) and high Mg and DIC concentrations (Fukushi and Matsumiya, 2018; Zeyen et al., 2021). Figure 3 shows the relationship between the activities of Ca$^{2+}$ and CO$_3^{2-}$ in alkaline lakes worldwide with pH $> 9$ and ionic strengths $>0.1$ (Na-Cl water type; Fukushi and Matsumiya, 2018; Caumartin et al., 2023) (see Supplementary Information and Table S-2). The activities of Ca$^{2+}$ and CO$_3^{2-}$ are negatively correlated, suggesting that lake water chemistry is controlled by formation/dissolution processes of calcium carbonates. Indeed, MHC is considered to be a solubility controlling phase in alkaline lakes (Fukushi and Matsumiya, 2018; Zeyen et al., 2021; Caumartin et al., 2023) based on the ubiquitous presence of MHC in suspended matter and sediments in alkaline lakes in southern Mongolia (Fukushi et al., 2020; Gankhurel et al., 2022). However, the solubility of MHC can explain only the lower limit of the observed trend (grey line in Fig. 3). The red line in Figure 3 represents the solubility of CCHH, which can explain the upper limit of the trend, with 62 of the 68 water chemistry data sets plotting between the solubilities of CCHH and MHC.

The present study showed that the log IAP decreased during the transformation of CCHH to aragonite (Fig. 2e), probably because the rate of the CCHH dissolution is lower than that of aragonite formation. If this is the case for the transformation pathway of CCHH to MHC, the lake waters that are experiencing CCHH formation and alteration are most likely plotted below the solubility line of CCHH. On the other hand, Fukushi and Matsumiya (2018), who studied the mineralogical evolution of MHC to aragonite from CaCl$_2$-MgCl$_2$-Na$_2$CO$_3$, showed that the IAP did not decrease during the transformation of MHC to aragonite, probably because the rate of the aragonite formation is lower than that of the MHC dissolution. If this is the case for the transformation pathway of MHC to other anhydrous calcium carbonates, i.e. calcite, then the lake waters containing the MHC (but not containing CCHH) and the alteration products are most likely plotted on the solubility line of MHC. Therefore, the lake waters that are experiencing the CCHH formation and the transformation to MHC must plot between the two lines.

In alkaline lakes, evaporation or alternative sources (e.g., groundwater input and CO$_2$ volcanic degassing) increase the saturation state with respect to calcium carbonate. This dynamic process can naturally produce CCHH in alkaline lakes. However, CCHH is a short lived species (this study; Zou et al., 2019) that can quickly transform to a stable calcium carbonate species such as MHC under the chemical conditions (i.e. the relationship among Mg, Ca, and DIC in solution) of alkaline lakes. We therefore predict that CCHH is present in alkaline lakes as an initial precipitate during evaporation and exerts an important control on the associated water chemistry. It is solely due to
its short lifetime that the presence of CCHH in alkaline lakes has not yet been reported.

## Conclusions

We investigated the solubility of CCHH, a recently discovered calcium carbonate species. The solubility was obtained from offline temporal monitoring of the solution and mineralogical compositions of mixed CaCl₂-MgCl₂-Na₂CO₃ solutions. We determined the solubility product (log $K_{sp}$) of CCHH to be $\sim6.80 \pm 0.05$ and its Gibbs free energy of formation to be $-1238.2 \pm 0.3$ kJ/mol, suggesting that the stability of CCHH is between those of ikaite and MHC. The solubility of CCHH corresponds to the upper limit of the saturation levels observed in natural alkaline lakes worldwide. From these results, we predict that CCHH forms naturally, though fleeting, during evaporation in alkaline lakes.

## Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research from the Japan Society for Promotion of Science [grant numbers 21K18649, 21H04515 and 24H00268].

## Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2428.

© 2024 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at https://www.geochemicalperspectivesletters.org/copyright-and-permissions.


## References


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

M. Suyama, T. Kitajima, K. Fukushi

**Supplementary Information**

The Supplementary Information includes:

- Materials and Methods
- Difference of Lifetime of CCHH Between This Study and Zou et al. (2019)
- Selection of Water Chemistry of Alkaline Lakes in the World
- Tables S-1 and S-2
- Figures S-1 to S-3
- Supplementary Information References

**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 CaCl₂–MgCl₂ solutions were prepared in a 1 L plastic bottle to which a stock Na₂CO₃ 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 Na₂CO₃, 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 HNO₃ 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 ([HCO₃⁻] + 2[CO₃²⁻], where [i] represents the mol/L concentration of the i-th species) of the filtrate was measured by alkalinity titration with 0.1 N H₂SO₄ solution. Alkalinity was calculated by the Gran function plot method using the USGS web-based Alkalinity Calculator (https://or.water.usgs.gov/alk/).
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 Kirmark, 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 higher Mg/Ca ratio in this study of the hydrous carbonate 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. They showed that the onset of the transformation of MHC to aragonite was 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 MgCO$_3$. 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 CaCl$_2$, MgCl$_2$, and Na$_2$CO$_3$ 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, SO$_4$ 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).

$$E.B. \text{ (}%) = \frac{[\text{Na}]+[\text{K}]+2[\text{Ca}]+2[\text{Mg}]-[\text{Cl}]-[\text{HCO}_3]-2[\text{CO}_3]-2[\text{SO}_4]}{[\text{Na}]+[\text{K}]+2[\text{Ca}]+2[\text{Mg}]+[\text{Cl}]+[\text{HCO}_3]+2[\text{CO}_3]+2[\text{SO}_4]} \times 100,$$

where $[i]$ denotes the molar concentration of $i$th component. When the concentrations of HCO$_3$ and CO$_3$ were not available, the E.B. was calculated by using DIC concentration:

$$E.B. \text{ (}%) = \frac{[\text{Na}]+[\text{K}]+2[\text{Ca}]+2[\text{Mg}]-[\text{Cl}]-[\text{DIC}]-2[\text{SO}_4]}{[\text{Na}]+[\text{K}]+2[\text{Ca}]+2[\text{Mg}]+[\text{Cl}]+[\text{DIC}]+2[\text{SO}_4]} \times 100.$$

Similarly, the I was calculated by using the following equations:

$$I = \frac{1}{2} ([\text{Na}] + [\text{K}] + [\text{Ca}] \times 2^2 + [\text{Mg}] \times 2^2 + [\text{Cl}] + [\text{HCO}_3] + [\text{CO}_3] \times 2^2 + [\text{SO}_4] \times 2^2),$$

or

$$I = \frac{1}{2} ([\text{Na}] + [\text{K}] + [\text{Ca}] \times 2^2 + [\text{Mg}] \times 2^2 + [\text{Cl}] + [\text{DIC}] + [\text{SO}_4] \times 2^2).$$
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 $\lambda = 0.49596$ for comparison with calculated theoretical XRD patterns with different Mg content given by Aufort and Demischelis (2020).
Figure S-2  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-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


