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Mg/Ca Ratios in Synthetic Low-Magnesium Calcite: An Experimental Investigation

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Abstract: The work presented sought to determine the effects of Mg/Ca ratios in solution have on Mg partitioning (K^{Mg}) between precipitated abiotic low-Mg calcite and solution. Experiments were set up so that Mg/Ca in precipitated abiotic calcite would match the Mg/Ca in planktonic foraminifera. This research intended to investigate the effect of Mg/Ca_(Fluid) on K^{Mg} when the molar value of Mg/Ca_(Fluid) was below 0.5, which is below the previously reported Mg/Ca range. The values of pH, salinity, and aqueous Mg/Ca were monitored during calcite precipitation, and Mg/Ca of calcite was determined at the end of experiments. Partition coefficients of Mg were evaluated as a ratio of Mg/Ca in calcite to the averaged ratio of aqueous Mg/Ca for each experiment.

Keywords: low-magnesium; calcite; Mg/Ca; partition coefficient



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1. Introduction

Understanding the means and extent to which external environmental factors control Mg incorporation into calcite is of significant interest to the geoscientific community. The ability of calcite to accommodate trace and minor elements in its crystalline structure has been a topic of interest for inorganic and organic precipitation studies. Calcite precipitated in laboratory settings has been leveraged to better understand the influence of environmental factors that collectively and individually govern Mg incorporation. Biological representative Mg/Ca ratios of foraminifera shells are used to study temperature variations in the oceans over the past 541.0 ± 1.0 Ma (i.e., Phanerozoic). Previous studies have demonstrated that the Mg partition coefficient (K^{Mg}) is temperature-dependent; e.g., [1–7]. Numerous studies have also proposed other parameters that could influence K^{Mg} , such as salinity [8,9], pH [6,10,11], calcite growth rate [12–16], Mg/Ca ratio of the solution [15,17–19], or possibly a combination of calcite growth rate and the Mg/Ca ratio of the solution [16].

For example, Mavromatis et al. [15] assessed the calcite growth rate by conducting a series of experiments in which the pH was maintained constant by bubbling pure CO₂ gas into the precipitation medium. This study found that pH did not have a direct effect on K^{Mg} . However, it is known that the pH of fluids influences calcite growth rate (i.e., fluids with a low pH cause carbonate dissolution), which influences K^{Mg} . The findings of Mavromatis et al. [15] and Gabitov et al. [16] demonstrated that the growth rate was responsible for controlling Mg partitioning. Though the two studies found opposite relationships between K^{Mg} and the growth rate, Gabitov et al. [16] explained that this could

be due to differences in Mg/Ca ratios of the fluid, which would cause a change in the Mg incorporation mechanism.

It is known that the oceanic Mg/Ca ratio is not constant with respect to geologic time, and has varied from ~1 to 5.2 mol/mol between the present day and the Cretaceous [20–32]. The cause or causes for fluctuation of seawater Mg/Ca are not fully understood, but it is thought to be controlled by various parameters, including runoff [33], temperature [34], the rate of oceanic crust production [22,35], a change in the mode of calcium carbonate deposition [36], and the rate of dolomite formation [37]. Although there have been attempts to study variations in oceanic Mg/Ca over the geologic past using coccolithophores [38–40], Mg/Ca in foraminiferal calcite is far more studied. It has been demonstrated that temperature was the primary control on Mg/Ca in the tests of foraminifera [41–44]. Several studies suggested that salinity also influenced Mg/Ca in foraminifera [42,45–47], but in a lesser capacity than the temperature for marine surface waters.

The Mg/Ca ratio of oceanic waters can be inferred by studying Mg/Ca preserved in fossilized marine organisms (e.g., foraminifera, coccoliths, echinoids, corals, and algae) [28,48,49]. It is known that the Mg/Ca ratio in planktonic foraminifera is much lower than what is expected based on the Mg concentration in typical seawaters [50]. It has been postulated that the cause for depressed Mg in foraminiferal calcite is due to biological/physiological factors, which selectively occlude Mg at the site of calcification [50–54]. Moreover, it has been demonstrated by Branson et al. [54] that Mg is uniformly substituted for Ca in the calcite mineral lattice of foraminiferal tests.

In this study, experiments were conducted at 15 °C, a constant titration rate, and variable Mg/Ca of aqueous solutions for precipitating calcite, the Mg/Ca values for which cover the range observed in planktonic foraminifera.

2. Materials and Methods

2.1. Calcite Precipitation

Calcite was precipitated by continuous addition of CaCl_2 , MgCl_2 , and NaHCO_3 titrates into a NaCl solution. These methods were modified from techniques described in several previous works; e.g., [15,55]. In all experiments, titrate fluids were delivered to a reaction vessel at a constant rate using a programmable multichannel peristaltic pump and 1.75 mm inner-diameter (i-d) tubing (Figure 1).

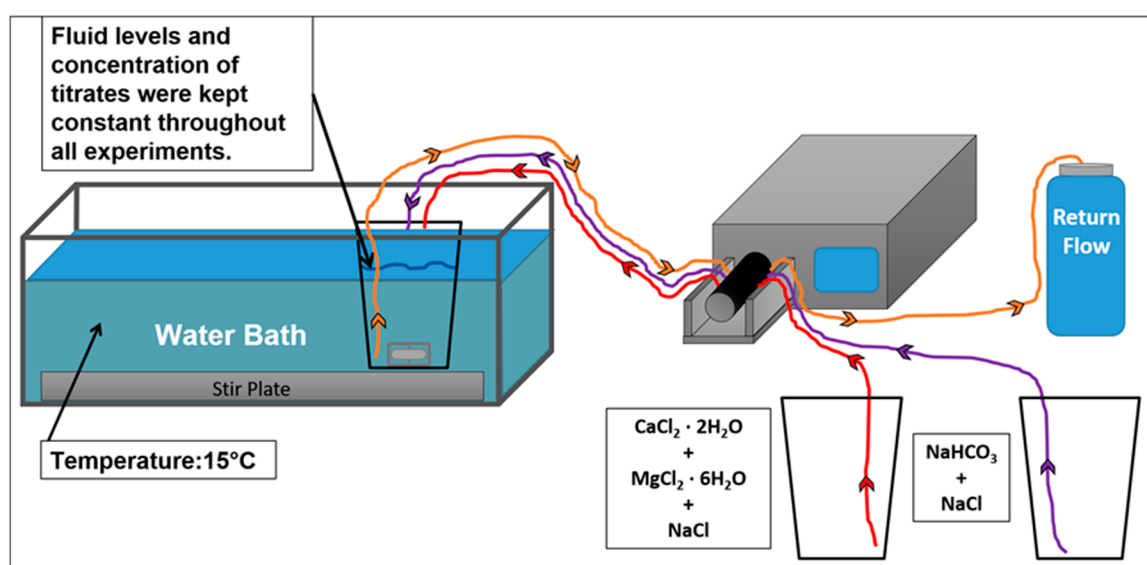


Figure 1. Illustration depicting the experimental set-up for experiments conducted in series 9, 10, and 11. Colored lines and arrows are meant to depict fluid flow directions within tubing.

2.2. Experimental Design

Three series (i.e., series 9, 10, and 11) accounting for a total of 13 experiments were conducted for this study. Series 9 consisted of six experiments, series 10 was one experiment, and series 11 comprised six experiments. All experiments were conducted using a continuous-pumping method by which solutions were contemporaneously pumped into and out of a reaction vessel at a rate of 0.14 mL min^{-1} using a multichannel peristaltic pump. The diameter of the outlet tube was greater than twice the diameter of either inlet tube. To prevent a decrease in solution volume for the reaction vessel, the outlet tube was always kept at a fixed height. Therefore, the volume of the growth media was kept near-constant for the duration of each experiment. Solutions in the reaction vessel were maintained at 15°C in a refrigerated water bath and continuously stirred at 150 rpm using a submersed stir plate and suspended magnetic stir bars (Figure 1). The selected experimental temperature represented the average global sea surface temperature.

For each experiment, three solutions were prepared using Fisher Chemical Certified ACS (American Chemical Society) salts. The first step in preparing all solutions was to mix NaCl with reverse osmosis (RO) H_2O to achieve a concentration of 0.6 M. The solution in the reaction vessel comprised a mixture of NaCl (99.9%) and NaHCO_3 (99.7%) chemical salts (values in parentheses denote chemical purity). For each experiment, two titrate vessels were prepared using the NaCl solution described above. In titrate vessel 1, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salts were added to the NaCl solution. The mass of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salts added for each experiment varied depended on the desired Mg/Ca ratio of the fluid. Titrate vessel 2 was prepared by the addition of NaHCO_3 to the NaCl solution. For each experiment, the molar concentration of NaHCO_3 in titrate 1 was equal to the molar concentration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in titrate 2. The experimental design for the series 11 experiments varied slightly from the previous description, in that the addition of NaOH was used in specific experiments to elevate the pH of the fluid. The concentration of the chemical salts in the titrate solutions for each experiment is reported in Table 1. The fluid Mg/Ca ratio was calculated to have varied from 0.51 to 20.18 (mmol mol^{-1}) between experiments in series 9. For the series 10 experiment, the fluid Mg/Ca ratio was calculated to be 5.0 (mmol mol^{-1}). For the series 11 experiments, the fluid Mg/Ca ratio was calculated to be either 0.25 or 4.41 (mmol mol^{-1}), depending on the respective experiment.

Table 1. Concentrations of salts in the titration solutions.

Run	Concentrations of Salts in Titrate Solutions (mmol L^{-1})					Calculated Aqueous Mg/Ca (mmol/mol)
	NaCl	NaHCO_3	NaOH	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	
9A	600	300		134	166	807
9B	600	300		113	187	604
9C	600	300		50	250	200
9D	600	300		6	294	20
9E	600	300		23	277	83
9F	600	300		66	234	282
10A	600	12		2	10	200
11A-1,2,3	600	300		3	297	10
11AA	600	300	30	3	297	10
11B	600	300	10	3	297	10
11BB-1,2,3	600	300	10	3	297	10
11D	600	300		45	255	176
11E	600	300	10	45	255	176

Subsamples were collected from the reaction vessel every 12–24 h throughout the duration of each experiment to measure pH, salinity, and Mg and Ca concentrations. The collection of subsamples and all other fluids (i.e., return flow fluid and final fluid) was done using a 60 mL syringe. and then the subsamples were filtered using a $0.45 \mu\text{m}$ nylon Whatman syringe filter. All pH measurements were conducted using a Denver

Instrument UB-10 UltraBASIC benchtop meter equipped with a Sartorius PY-P11 pH Combination Electrode, Mississippi State, USA. Salinity measurements were carried out using an HI 5521 benchtop meter equipped with a HI 76312 4-ring platinum EC/TDS probe, Mississippi State, USA. Immediately following measurements, the subsamples were acidified for further chemical analysis. An aliquot of fluid from the return flow vessel was recovered approximately every two to three days and at the end of each experimental run to determine alkalinity of the fluids.

2.3. Analysis of Fluids

2.3.1. Atomic Absorption

Fluid samples from all experiments in series 9 and 10 were analyzed using a Shimadzu, AA-7000 Line-Source AAS, Mississippi State, USA. The LS-AAS was calibrated using 1000 ppm magnesium and calcium analytical standards (Fisher Scientific, Pittsburgh, PA, USA) as stock solutions. Six calibration standards were created for each element. The standards for calcium ranged from 0.5 ppm to 16 ppm, with the concentration of each successive standard being double the previous. The standards for magnesium ranged from 0.05 ppm to 1.6 ppm, with the concentration of each successive standard being double. Calibration curves showed that the actual concentrations measured using LS-AAS were close to the prepared concentration, as the minimum r^2 value for the calibration curves was 0.993.

2.3.2. Alkalinity Titrations

Titration were performed to determine the total alkalinity of each experiment in series 9 and 10 following protocols described by Rounds [56]. Titrations were conducted using a 25 mL burette, 100 mL glass beakers, a pH meter and electrode, magnetic stir plate and stir bars, disposable 10 mL volumetric pipets, phenolphthalein indicator, volumetric flasks, trace-metal-grade H_2SO_4 , RO H_2O , and ACS-grade Na_2CO_3 .

Fluid collected from the return flow vessel at the beginning of each experiment and final fluid collected at the end of each experiment in series 9 and 10 underwent titration with known concentrations of H_2SO_4 to determine the alkalinity of the fluid. Titration was performed in triplicate for each sample, and the average of the three alkalinity values was taken to be the true value. The alkalinity values were converted from mg of $\text{CaCO}_3 \text{ L}^{-1}$ to $\mu\text{mol kg}^{-1}$ of H_2O so that the values would be compatible with the CO2SYS (Version 2.1, U.S. Department of Energy, Oak Ridge, TN, USA), initially developed by Lewis et al. [57] and updated by Pierrot et al. [58].

2.4. Analysis of Solids

2.4.1. ICP-OES

Elemental (Mg and Ca) analyses of calcites were conducted at the University of Cambridge (UK) using an Agilent 5100 ICP-OES) and following protocols described in de Villiers et al. [59] and Greaves et al. [60]. Samples were cleaned prior to analyses by rapid (5–10 s) rinsing of the solids three times with RO H_2O , followed by three rinses with trace-metal-grade methanol, once using 10% ultra-high-purity H_2O_2 , then rinsed three more times using Nanopure H_2O . The storage polypropylene vials were cleaned prior to the addition of the solid samples by soaking them in 10% ACS-grade HNO_3 then 2% trace-metal-grade HNO_3 , and were lastly rinsed with Nanopure H_2O and dried at 40 °C.

2.4.2. X-ray Diffraction (XRD) Analysis

Powdered X-ray diffraction (XRD) analyses were conducted for all solid samples collected from experiments in series 9, 10, and 11 to determine mineral composition. Analyses were carried out using a Rigaku Ultima III X-ray diffractometer. All data interpretations were conducted using the MDI Jade 2010 software package at the Mississippi State University Institute for Imaging and Analytical Technology (I²AT), USA. The XRD pattern for each sample was generated at 40 KV and 44 mA. Scan speed was set at 0.5° per minute with a scan step of 0.02° and an effective scan range of 20–40°.

2.4.3. Scanning Electron Microscopy (SEM) Imaging

Powdered samples were examined with SEM to determine the morphology of precipitated calcites. Imaging was conducted using a Carl Zeiss EVO50VP scanning electron microscope at the Institute of Imaging & Analytical Technologies (I²AT) at Mississippi State University, Mississippi State, USA. SEM imaging of secondary electrons (SE) was performed on platinum-coated crystalline powders while applying 5 KV and 300 pA.

3. Results

3.1. Results for Fluid pH, Salinity, and Saturation State

Graphical representations of pH and salinity data collected as part of series 9, 10, and 11 can be seen in Figures 2 and 3 and Figure 4 for pH, and Figures S1 and S2 for salinity, in which the data was plotted as X–Y scatter plots. Although salinity data was not collected for series 11, the value of ~40 was expected due to the similarity in concentrations of major ions in titration solutions between series 9 and series 11. Additional information regarding salinity and pH can be found in Table S1. The average values of pH and salinity are reported in Table 2. Figure 2 shows that the pH at the beginning of experiments 9A through 9F was between ~6 and ~7. The onset of crystallization was observed approximately 24 h into the experiments for series 9, and it was at this time that the pH began to stabilize for all experiments, demonstrating steady-state conditions. Figure 3 shows the pH at the beginning of experiment 10A was approximately 7.75. Precipitation of crystals was not observed until 75 h into the experiment. After 100 h, the pH of the fluids in experiment 10A began to stabilize, demonstrating steady-state conditions. Figure 4 shows that the pH at the beginning of the experiments in series 11 was between 6.75 and 8.50. Precipitation of calcite was not observed until after 24 h had passed since the start of each experiment.

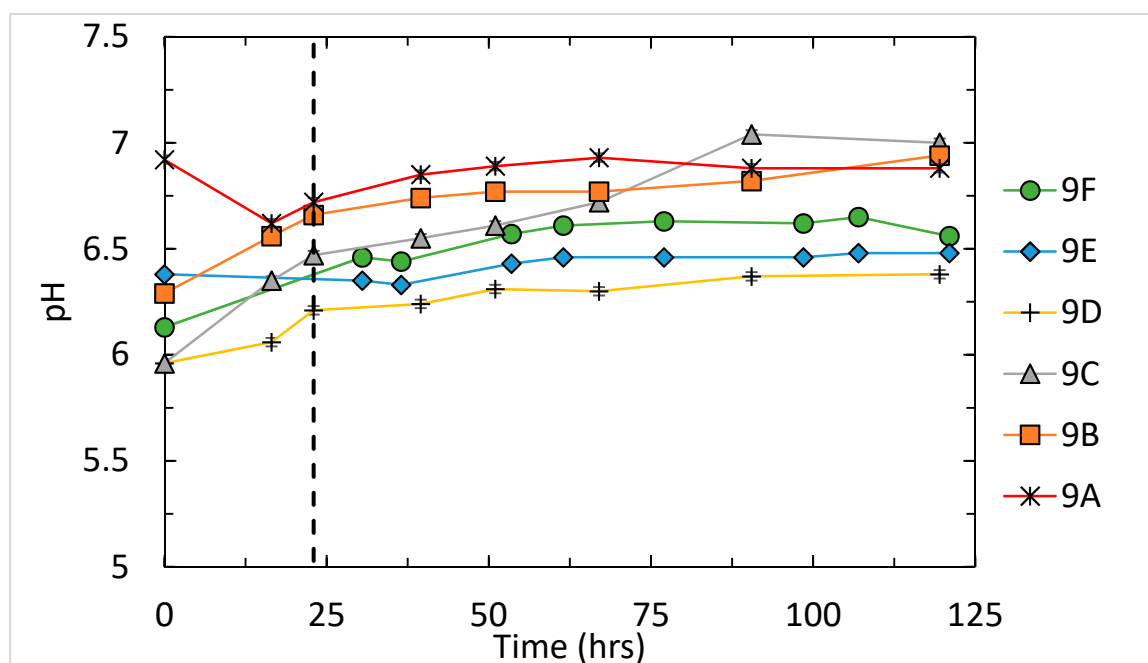


Figure 2. Graphical representation of pH plotted against time for experiments 9A through 9F. The analytical uncertainty was ± 0.02 , and is included in the symbol size. The vertical dashed line indicates the observed onset of crystallization at approximately 24 h.

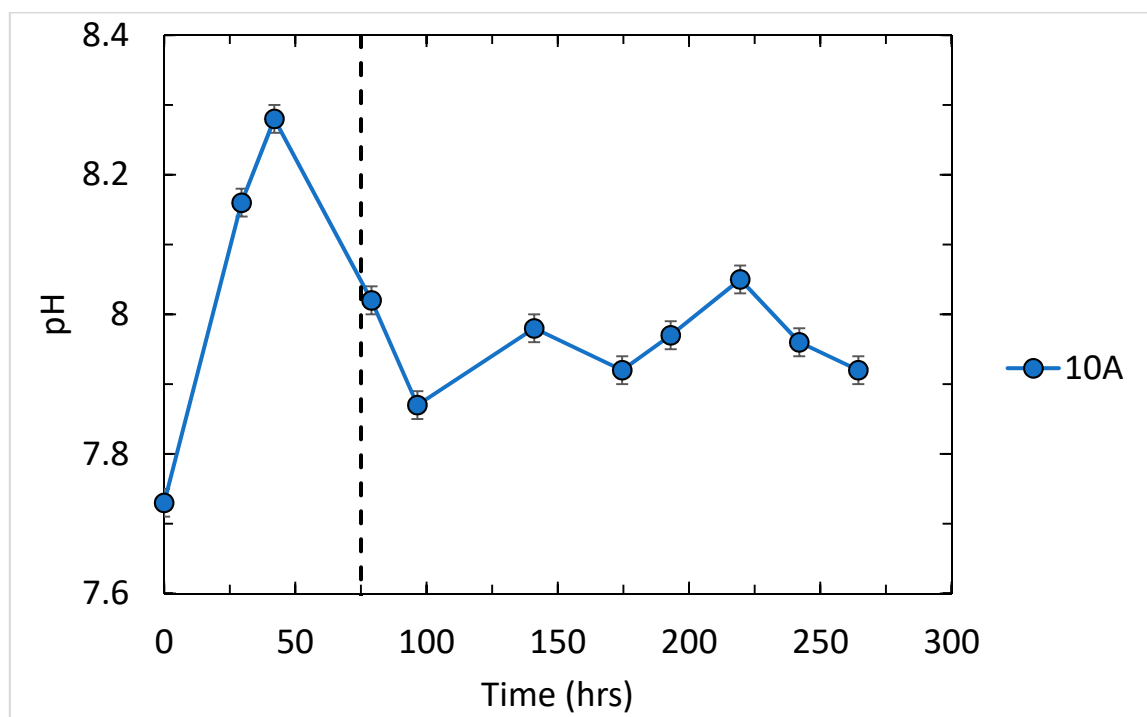


Figure 3. Graphical representation of pH plotted against time for experiment 10A. The analytical uncertainty was ± 0.02 . The vertical dashed line indicates the observed onset of crystallization at approximately 75 h.

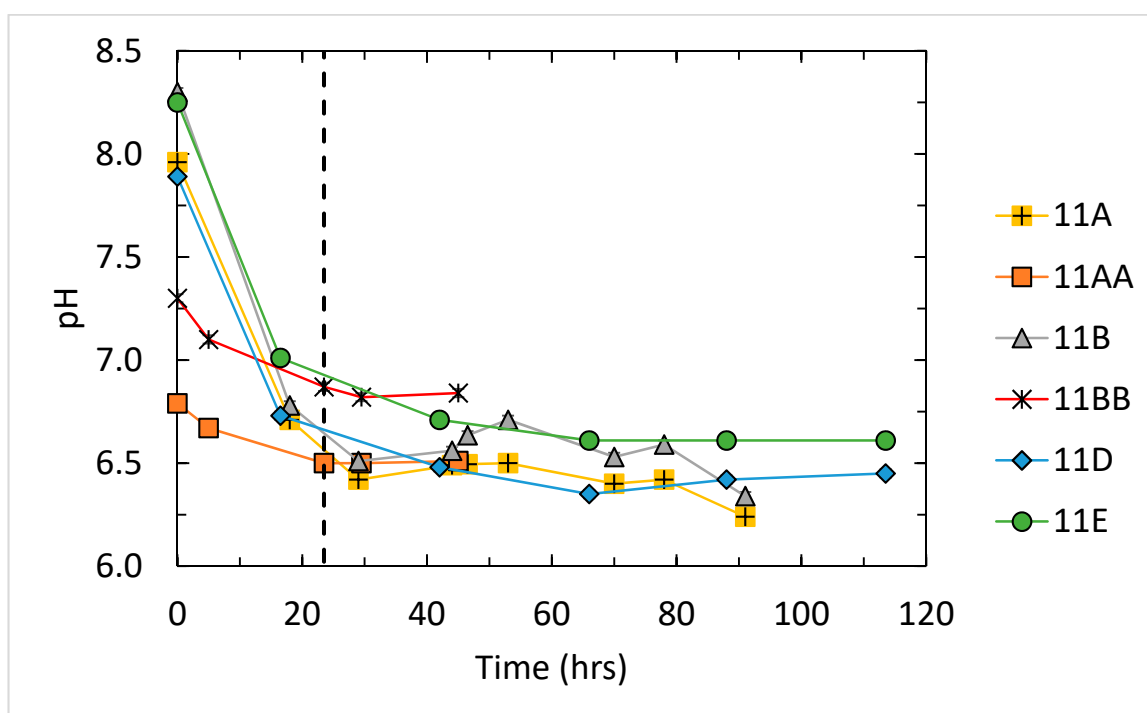


Figure 4. Graphical representation of pH plotted against time for experiments 11A through 11E. The analytical uncertainty was ± 0.02 , and is included in symbol size. The vertical dashed line indicates the observed onset of crystallization at approximately 24 h.

Table 2. Steady-state pH; average salinity; CO_3^{2-} , Ca^{2+} , and Mg^{2+} aqueous concentrations, precipitation, and final saturation state (Ω_c); and mass of precipitated calcium carbonate.

Run		CO_3^{2-}	Ca^{2+}	TA	Ω_c	S (‰)	CaCO_3 (g)
9A	Precip	0.15	14.28	34.25	3.45	45.34	17.74
	Final	0.07	8.09	22.18	1.01		
9B	Precip	0.08	22.28	25.82	3.06	45.08	18.68
	Final	0.11	8.3	22.42	1.57		
9C	Precip	0.04	29.47	11.09	1.8	47.38	19.79
	Final	0.51	16.71	42.01	13.21		
9D	Precip	0.02	61.92	7.22	1.67	45.89	20.59
	Final	0.05	43.59	9.79	3.18		
9E	Precip	0.02	58.51	12.07	1.85	44.81	22.68
	Final	0.04	36.11	17.46	2.27		
9F	Precip	0.04	45.01	13.34	3.21	45.25	22.04
	Final	0.06	33.2	25.96	3.23		
10A	Precip	0.22	2.95	15.83	2.53	22.44	1.53
	Final	0.18	1.62	8.02	1.16		

Ion concentration and total alkalinity (TA) are in mmol per kg of H_2O . S (‰): average salinity. Ω_c : saturation state.

The CO2SYS program developed by Pierrot et al. [58] was utilized using the carbonate dissociation constants developed by Millero et al. [61] and dissociation constant for HSO_4 defined by Dickson [62] to determine CO_3^{2-} .

The terms “precip” and “final” refer to the time at which data was collected and the time at which precipitation began or the end of the experiment, respectively.

The subscript “ss” is an abbreviation of “steady-state”, and was the average of values collected when the standard deviation of the averaged values was less than 13%.

Other values reported in Table 2 include: average salinity, precip and final CO_3^{2-} and Ca^{2+} aqueous concentrations, precip and final saturation state (Ω), and the mass of recovered calcite. The precip and final Ω_c values reported in Table 2 were endmembers for conditions present in each experimental run. To determine the saturation state of the fluid, with respect to calcite or aragonite, the alkalinity, pH, Ca concentration, temperature, and salinity of the fluid must first be known. The calcium carbonate saturation state (Ω) is expressed as:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}^*} \quad (1)$$

where K_{sp}^* is the stoichiometric solubility product for a specific mineral phase of CaCO_3 (e.g., calcite (calc), aragonite (arag), or low-magnesium calcite (lmc)); and $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the total molar concentration of the reacting (free + complexed) ions. The saturation state was calculated for experiments in series 9 and 10 in this manner. $[\text{Ca}^{2+}]$ was determined from the data collected from the fluid samples using LA-AAS. $[\text{CO}_3^{2-}]$ was determined by utilizing the program CO2SYS, initially developed by Lewis et al. [57] and updated by Pierrot et al. [58], using the carbonate dissociation constants developed by Millero et al. [61] for carbonate systems and dissociation constant for HSO_4 defined by Dickson [62] (to be included in alkalinity). The program uses two of four measurable input parameters of the aqueous carbonate system: TA, total dissolved inorganic carbon (TCO_2), pH, and the partial pressure of CO_2 ($p\text{CO}_2$), to calculate the other two parameters at a set of input conditions (e.g., temperature and pressure) and a set of output conditions that included CO_3^{2-} concentration [58]. K_{sp}^* was calculated using the expression developed by Mucci [8] and modified by Zeebe and Wolf-Gladrow [63].

3.2. X-ray Diffraction Results

The mass percentages of each calcium carbonate polymorph precipitated from the various experiments were determined by the MDI Jade 2010 software package, which analyzed XRD patterns of the scans. The XRD scans for series 9, 10, and 11 are shown in

Figures S3–S5, respectively. Scans for all experiments indicated only one polymorph of calcium carbonate—calcite.

3.3. LS-AAS and ICP-OES Results

3.3.1. LS-AAS Results

The data collected from LS-AAS analysis were compiled and are presented in Table S1.

3.3.2. ICP-OES Results

The data collected from ICP-OES and LA-AAS were compiled into a plot of the aqueous Mg/Ca against the calcite Mg/Ca for all experiments (Figure 5). As shown, the calcite Mg/Ca ratio increased in a near-linear manner with an increase in the aqueous Mg/Ca ratio when $23 < \text{Mg/Ca}_{(\text{Fluid})} < 600$ mmol/mol; however dependency became weaker at greater high aqueous Mg/Ca ratios; i.e., when $600 < \text{Mg/Ca}_{(\text{Fluid})} < 4000$. The nonlinear nature of the observed relationship suggested a decrease in Mg partitioning between calcite and fluid with increasing aqueous Mg/Ca ratios, especially at high $\text{Mg/Ca}_{(\text{Fluid})}$ values.

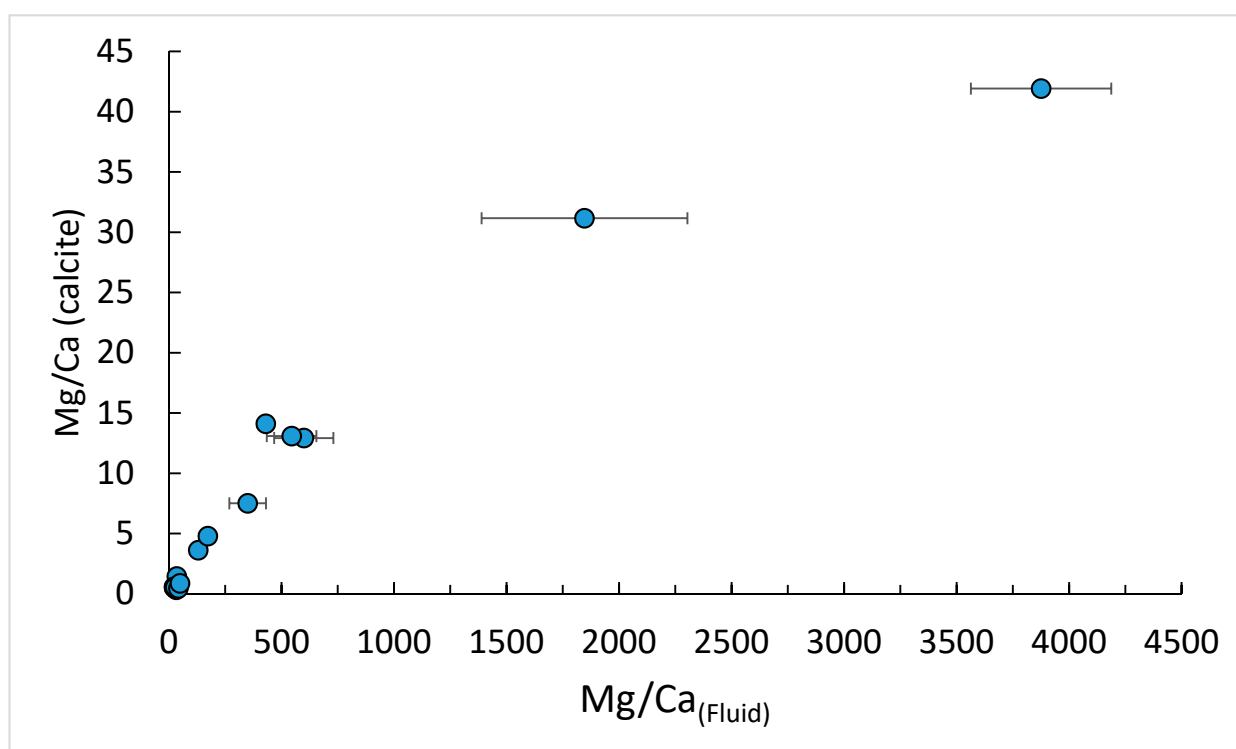


Figure 5. Mg/Ca concentration as a ratio in precipitated calcite plotted as a function of averaged aqueous Mg/Ca concentration as a ratio (in mmol/mol). The $\text{Mg/Ca}_{(\text{Fluid})}$ analytical uncertainty was determined in terms of the standard error.

3.4. SEM Results

Figure 6 shows morphologies of calcite crystals imaged with SEM. Calcite crystals (runs 9A, 9B, and 11E) with relatively high Mg content ($\text{Mg/Ca} = 41.9\text{--}13.1$ mmol/mol) showed somewhat sharper edges compared to other crystals (runs 10A, 9D, and 11AA) with lower Mg content ($\text{Mg/Ca} = 4.78\text{--}0.479$ mmol/mol). In addition, the morphology of high-Mg crystals was pyramidal, whereas low-Mg calcite pyramids were truncated.

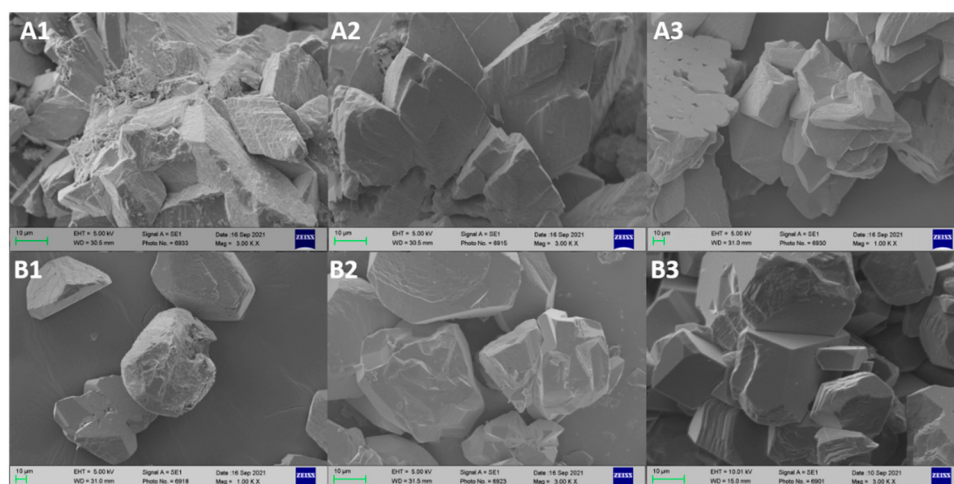


Figure 6. SEM imaging of the crystals (scale bar is 10 μ). The order of the images corresponds to the decrease in Mg content of calcite. (A1–A3) correspond to calcite crystals collected from experiments 9A, 9B, and 11E respectively and are crystals with higher Mg content and sharper crystal edges. Comparatively, (B1–B3) which correspond to calcite crystals collected from experiments 10A, 9D, and 11AA respectively poses lower Mg content and truncated crystal edges.

4. Discussion

Mg/Ca Ratios in Synthetic Low-Magnesium Calcite

For our experiments, K^{Mg} was calculated as a ratio of Mg/Ca in calcite to the averaged Mg/Ca in fluid:

$$\left(K^{Mg} = \frac{Mg/Ca_{(Solid)}}{Mg/Ca_{(Fluid)}} \right) \quad (2)$$

It has been shown that K^{Mg} is not dependent upon the calcium or magnesium concentration in solution, but is dependent on fluid Mg/Ca at $Mg/Ca_{(Fluid)}$ values above 0.35 mol/mol. For comparison, various ranges of Mg and Ca aqueous concentrations have been reported in the literature. Mavromatis et al. [15], reported Ca concentrations from 6.85 to 15.96×10^{-3} M, and Mg concentrations ranged from 1.52 to 14.15×10^{-3} M while Gabitov et al. [16] demonstrated that Ca concentrations ranged from 2.38 to 8.17×10^{-3} M, and Mg concentrations ranged from 0.36 to 0.80×10^{-3} M. In the present study, Ca and Mg concentration ranges were 2.95 to 297×10^{-3} M and 0.32 to 45×10^{-3} M, respectively.

Using the values for $Mg/Ca_{(Solid)}$ and averaged $Mg/Ca_{(Fluid)}$, K^{Mg} was calculated (see Table 3). The values were plotted on a log–linear plot to determine the relationship between $Mg/Ca_{(Fluid)}$ and K^{Mg} . According to the data shown in Figure 7, K^{Mg} decreases by a factor of 3 (from 0.03 to 0.01) when $Mg/Ca_{(Fluid)}$ increases by a factor of 10 (from 0.43 to 3.9 mol/mol) for the crystals on which sharp edges were frequently observed (Figure 6: 9A, 9B, and 11E). No dependence of K^{Mg} on aqueous Mg/Ca ratio was observed at $Mg/Ca_{(Fluid)} < 0.4$. The high scatter of K^{Mg} data at low aqueous Mg/Ca values ($0.02 < Mg/Ca < 0.05$ mol/mol) can be partially explained by the variability of pH values in the growth media (Figure 8). K^{Mg} decreased almost by a factor of four (from 0.041 to 0.014) when pH was increased by 0.7 units (from 6.23 to 6.95). This relationship could be explained by a reverse correlation between K^{Mg} and the growth rate observed by Gabitov et al. [16]; i.e., an increase of pH increased the growth and drove K^{Mg} down, when aqueous Mg/Ca did not vary much ($0.02 < Mg/Ca < 0.05$ mol/mol). Our findings agree with results reported by Mucci and Morse [18] and Mavromatis et al. [15] by replicating the inverse relationship of K^{Mg} on fluid Mg/Ca when $Mg/Ca_{(Fluid)}$ is greater than 0.4 and less than 20 mol/mol.

Table 3. Solid and aqueous Mg/Ca, K^{Mg} .

Run	pH	SE	Mg/Ca _(Solid) (mol/mol)	Mg/Ca _(Fluid) (mmol/mol)	SE	Mg/Ca _(Fluid) (mol/mol)	SE	K^{Mg}	SE
9A	6.84	0.06	41.92	3875	311.9	3.8752	0.3119	0.0108	0.00087
9B	6.77	0.06	31.17	1846	457.1	1.8465	0.4571	0.0169	0.00418
9C	6.74	0.13	12.92	599.1	131.5	0.5991	0.1315	0.0216	0.00474
9D	6.23	0.01	1.441	34.59	2.131	0.0346	0.0021	0.0417	0.00257
9E	6.44	0.02	3.608	129.9	9.531	0.1299	0.0095	0.0278	0.00204
9F	6.51	0.08	14.10	429.8	25.82	0.4298	0.0258	0.0328	0.00197
10A	7.99	0.05	4.785	172.8	8.630	0.1728	0.0086	0.0277	0.00138
11A-1	6.32	0.09	0.5710	21.56	0.850	0.0216	0.0009	0.0265	0.00104
11A-2,3	6.91	0.42	0.3400	32.73	5.160	0.0327	0.0052	0.0104	0.00164
11AA	6.55	0.04	0.4790	23.06	1.009	0.0231	0.0010	0.0208	0.00091
11B-1	6.43	0.09	0.5310	27.36	0.4750	0.0274	0.0005	0.0194	0.00034
11B-2,3	7.05	0.49	0.457	41.4	0.4750	0.0414	0.0005	0.0110	0.00013
11BB	6.91	0.06	0.87	49.0	11.82	0.0490	0.0118	0.0178	0.00429
11D	6.23	0.06	7.508	349.4	81.28	0.3494	0.0813	0.021486	0.00500
11E	6.71	0.08	13.09	544.9	110.0	0.5449	0.1100	0.0240	0.00485

SE: standard error. The SE of Mg/Ca_(Solid) was calculated from the reproducibility of standard measurements using ICP-OES; pH and Mg/Ca_(Fluid) are the average values of the subsamples. The error was determined using the formula: $\sqrt{((\text{Mg/Ca}_{(\text{Solid})} \text{ Error})^2 / (\text{Mg/Ca}_{(\text{Fluid})})^2 + (\text{Mg/Ca}_{(\text{Fluid})} \text{ Std.dev})^2 / (\text{Mg/Ca}_{(\text{Fluid})})^4 \times (\text{Mg/Ca}_{(\text{Solid})})^2)}$.

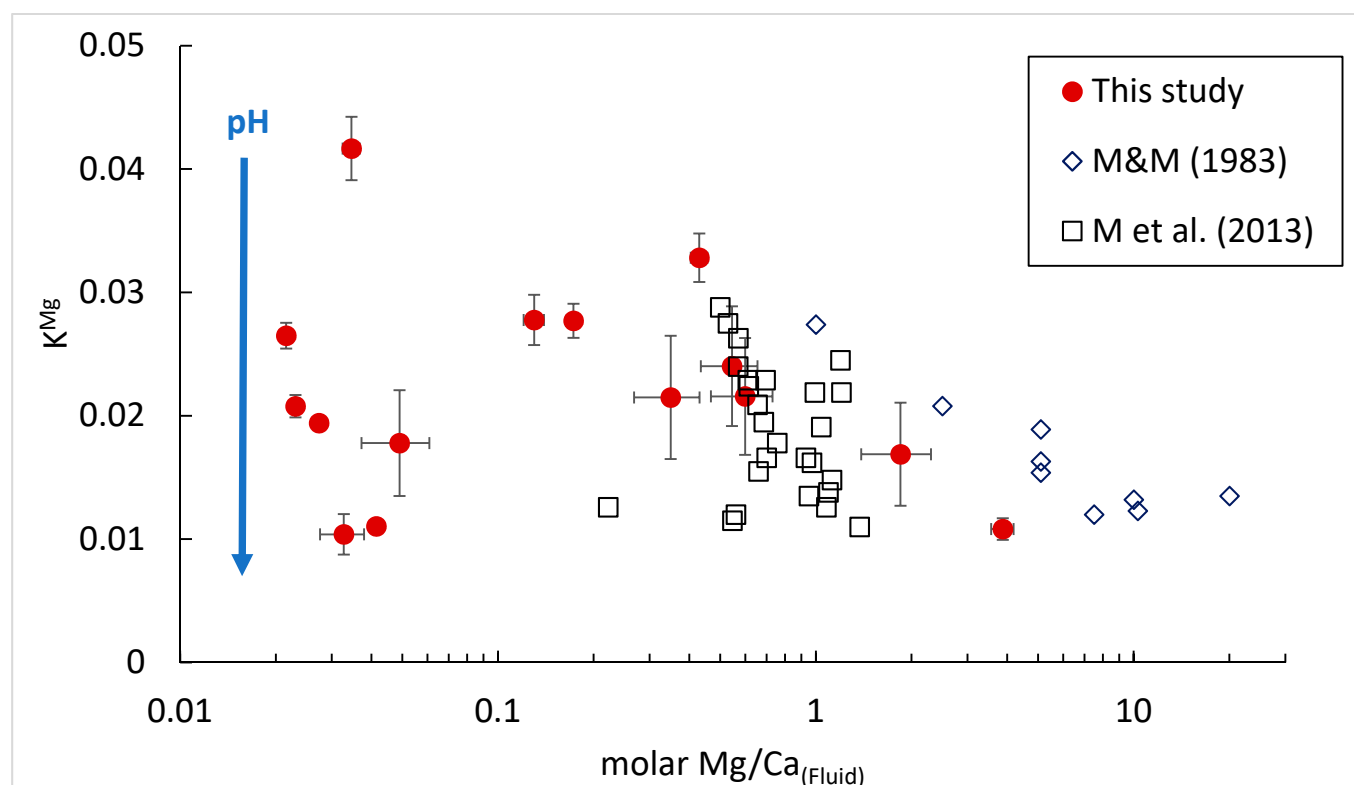


Figure 7. A log–linear plot demonstrating the relationship between aqueous Mg/Ca and K^{Mg} . Red circles represent data from the present study, blue diamonds are data from Mucci and Morse [18], and grey squares are data from Mavromatis et al. [15]. The analytical uncertainty for Mg/Ca_(Fluid) in the present study was determined in terms of the standard error. K^{Mg} analytical uncertainty in the present study was determined using the formula: $\sqrt{((\text{Mg/Ca}_{(\text{Solid})} \text{ Error})^2 / (\text{Mg/Ca}_{(\text{Fluid})})^2 + (\text{Mg/Ca}_{(\text{Fluid})} \text{ Std.dev})^2 / (\text{Mg/Ca}_{(\text{Fluid})})^4 \times (\text{Mg/Ca}_{(\text{Solid})})^2)}$. The method for determining analytical uncertainty was not reported by Mavromatis et al. [15]. The blue arrow indicates a negative effect of pH on K^{Mg} .

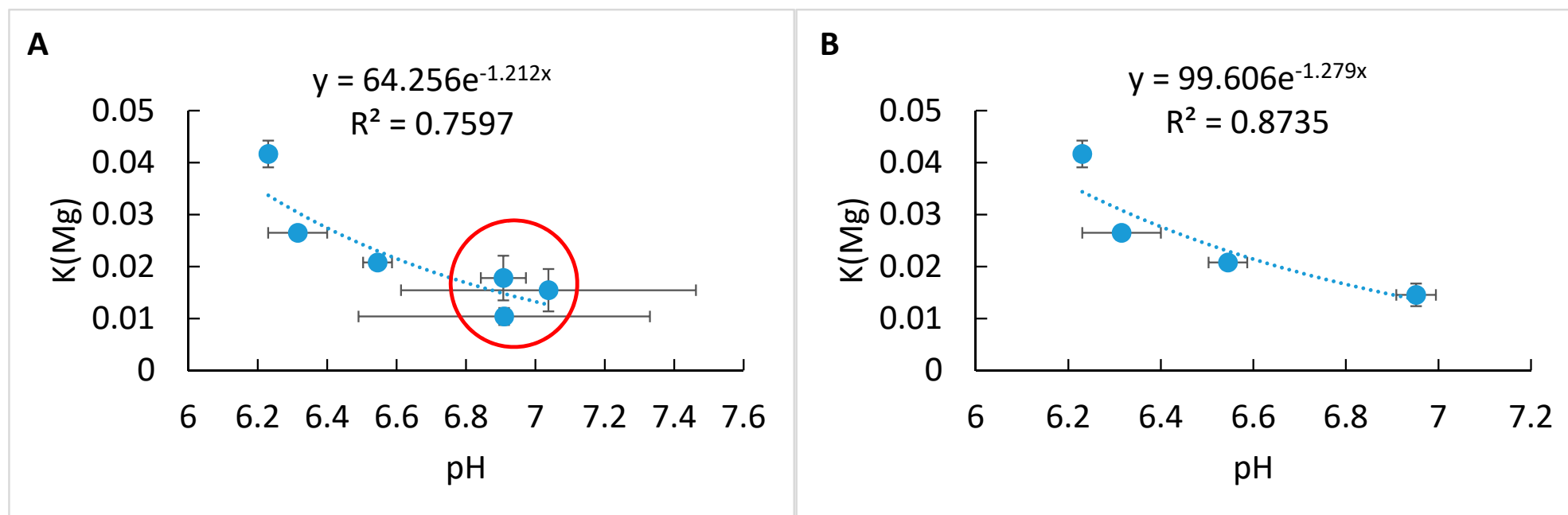


Figure 8. (A) A plot of K^{Mg} versus pH for the experiments run at low aqueous Mg/Ca ($0.02 < \text{Mg/Ca} < 0.05$ mol/mol). (B) The averaging of the three data points with overlapped pH values due to the high error bars (red circle seen in A) yielded a better fit with $r^2 = 0.82$.

5. Conclusions

This study demonstrated that $\text{Mg}/\text{Ca}_{(\text{Solid})}$ increased with increasing $\text{Mg}/\text{Ca}_{(\text{Fluid})}$ when $\text{Mg}/\text{Ca}_{(\text{Fluid})}$ increased from ~ 0.023 to ~ 0.6 mol/mol, implying that Mg uptake in low-Mg calcite was proportional to the Mg concentration in solution. The study results demonstrated that aqueous concentrations of Mg or Ca individually did not influence K^{Mg} .

This study reinforces the previously observed inverse relationship of K^{Mg} on fluid Mg/Ca ratios when $0.5 > \text{Mg}/\text{Ca}_{(\text{Fluid})} < 20$ mol/mol, and extended it down to $\text{Mg}/\text{Ca} = 0.4$ mol/mol, demonstrating that K^{Mg} increased with decreasing $\text{Mg}/\text{Ca}_{(\text{Fluid})}$. However, for $\text{Mg}/\text{Ca}_{(\text{Fluid})}$ concentrations less than 0.4 and greater than 0.023 mol/mol, our results demonstrated a lack of a $K^{\text{Mg}}\text{--Mg}/\text{Ca}_{(\text{Fluid})}$ trend, likely due to the combined effects of Mg/Ca and pH. Although additional research is needed to constrain accurate $K^{\text{Mg}}\text{--Mg}/\text{Ca}_{(\text{Fluid})}$ relationships in low-Mg calcite, our results suggested that the K^{Mg} of low-Mg calcite was less sensitive to $\text{Mg}/\text{Ca}_{(\text{Fluid})}$ compared to calcite with a higher Mg content.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11111158/s1>, Figure S1: Graphical representation of salinity plotted against time for experiments 9A through 9F. Figure S2: Graphical representation of salinity plotted against time for experiments 10A. Figure S3: Series 9. Powdered X-ray diffraction scans with Cu-K α radiation of different calcium carbonate polymorphs. Figure S4: Series 10. Powdered X-ray diffraction scans with Cu-K α radiation of different calcium carbonate polymorphs. Figure S5: Series 11. Powdered X-ray diffraction scans with Cu-K α radiation of different calcium carbonate polymorphs. Table S1: Compiled data documenting time of sample collection in hrs, measured pH value, salinity, and LS-AAS data for Mg and Ca (ppm) and Mg/Ca ratios.

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