

Carbon isotope fractionation in synthetic magnesian calcite

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Abstract

Mg-calcite was precipitated at 25 °C in closed system, free-drift experiments, from solutions containing NaHCO₃, CaCl₂ and MgCl₂. The carbon stable isotope composition of bulk solid and solution were analyzed from subsamples collected during time course experiments of 24 h duration. Considering only the Mg-content and δ¹³C values for the bulk solid, the carbon isotope fractionation factor for the Mg-calcite–HCO_{3(aq)}[–] system (as 10³ ln α_{Mg-cl–HCO_{3(aq)}[–]}) increased with average mol percentage of Mg (X_{Mg}) in the solid at a rate of (0.024 ± 0.011) per mol% MgCO₃. Extrapolation of this relationship to the pure calcite end member yields a value of 0.82 ± 0.09, which is similar to published values for the calcite–HCO_{3(aq)}[–] system. Although 10³ ln α_{Mg-cl–HCO_{3(aq)}[–]} did not vary for precipitation rates that ranged from 10^{3.21} to 10^{4.60} μmol m^{–2} h^{–1}, it was not possible to hold Mg-content of the solid constant, so kinetic effect on 10³ ln α could not be evaluated from these experiments.

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1. Introduction

Mg-calcite is an important constituent of shallow water marine sediments and it comprises the skeletons of many marine organisms. The study of Mg calcites, both biogenic and abiogenic, combined with coordinated measurements of carbon and oxygen isotope composition has grown in recent years because of its potential use to infer depositional and diagenetic processes in sedimentary environments (e.g., González and Lohmann, 1985; Carpenter et al., 1991; Carpenter and Lohmann, 1995; Frank and Lohmann, 1996; Rahimpour-Bonab et al., 1997; Lee and Carpenter, 2001). Paleooceanographic records are inferred from organically precipitated calcite of both low and high Mg-contents. Detailed information on the fractionation factors that describe these systems is critical for an accurate interpretation of the carbon isotope composition of Mg-calcites. Surprisingly, no data exist to date in the literature regarding the effect of magnesium coprecipitation on the isotope compo-

sition of Mg-calcites. It is well known that the isotopic properties of a substance mainly depend on the nature of its chemical bonds. The assemblage of atoms into crystalline solids places additional constraints on isotope fractionation through the generation of lattice vibrational forces. In general, chemical bonds between atoms having relatively low atomic mass are associated with high vibrational frequencies, subsequently, the incorporation of stable isotopes of higher relative mass in the crystal structure lowers vibrational frequency and minimizes the free energy of the system (O'Neil, 1986). For instance, the oxygen isotope fractionation factor (10³ ln α) for the system containing dolomite (CaMg(CO₃)₂) and calcite (CaCO₃) was estimated to be 4–7 by extrapolation of data obtained from high temperature experiments to 25 °C (Northrop and Clayton, 1966; O'Neil and Epstein, 1966). These results were supported by isotope measurements of coexisting dolomite and calcite thought to be in isotope equilibrium in metamorphic marbles (Friedman and Hall, 1963; Weber, 1964; Sheppard and Schwarcz, 1970). A theoretical estimate of the oxygen isotope fractionation factor for the system containing magnesite (MgCO₃) and calcite is greater than or equal to that of dolomite and calcite (Zheng, 1999). The oxygen isotope fractionation factor between Mg-calcite

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and water has been studied by Tarutani et al. (1969) and by Jiménez-López et al. (2004). These authors concluded that Mg-calcite was enriched in ^{18}O compared to pure calcite, although the magnitude of the effect is still debatable (up to 0.17‰ per mol% Mg, respectively).

With respect to carbon isotopes, the isotope fractionation factor ($10^3 \ln \alpha$) for the system containing dolomite and calcite was determined by Sheppard and Schwarz (1970), who concluded that dolomite was enriched in ^{13}C with respect to calcite. Extrapolation of their data to 25 °C yields a value of $10^3 \ln \alpha$ of 2.2. Remarkably, no published data exist on the effect of Mg on carbon isotope partitioning between Mg-calcite and solution. Moreover, this effect has not been considered in the calculations of the carbon isotope fractionation factor for systems containing Mg-calcite and dissolved carbonate species (González and Lohmann, 1985; Carpenter and Lohmann, 1995; Rahimpour-Bonab et al., 1997). However, differences in the carbon isotope composition of high magnesium calcites (HMC) and low magnesium calcites (LMC) have been observed in natural carbonates (González and Lohmann, 1985). These authors determined the carbon and oxygen isotopic composition of Holocene reefal carbonate grains and cements in samples from Enewatak, Bikini, Bermuda and Belize and they found that high magnesian calcite cements (~14 to ~20 mol% MgCO_3) were enriched by ~0.3 to 0.4‰ relative to pure calcite, and by 0.2‰ relative to low magnesium calcite. Finally, no information exists either on potential precipitation rate effect on carbon isotope fractionation in systems containing Mg-calcite.

To evaluate the effect of magnesium on carbon isotope partitioning in calcite, a series of time course experiments were performed in which Mg-calcites (avg Mg-content up to 13 mol%) were precipitated inorganically from solution. The carbon isotope composition of bulk solid and solution were analyzed from subsamples obtained periodically from these experiments. The chemical composition of the solution was chosen to promote the growth of Mg-calcite while minimizing the precipitation of aragonite and vaterite, which are likely to occur at higher aqueous Mg concentrations (Deleuze and Brantley, 1997). These experiments are complementary to those of Jiménez-López et al. (2004), in which the effect of magnesium on the oxygen isotope fractionation for the system Mg-calcite–water was determined. This study reports the carbon isotope fractionation factor ($10^3 \ln \alpha$) for the Mg-calcite– $\text{HCO}_3(\text{aq})^-$ system at 25 °C and the effect of Mg-incorporation on carbon isotope partitioning.

2. Experimental

2.1. Mg-calcite precipitates

Mg-calcite was precipitated from two groups of solutions (referred to here after as master solutions), having a distinct chemical composition: (1) Group I: 0.32 M $\text{NaHCO}_3/0.0023$ M $\text{CaCl}_2 + 0.00053$ M MgCl_2 and (2) Group

II: 0.34 M $\text{NaHCO}_3/0.0023$ M $\text{CaCl}_2 + 0.00105$ M MgCl_2 . The initial Mg/Ca ratio of the master solution was 0.23 for Group I experiments and 0.67 for Group II experiments.

Precipitation experiments were performed in a closed precipitation system, which was a modification of the free drift technique where the chemical composition of the solution drifts toward chemical equilibrium (see Jiménez-López et al., 2001, 2004; for details), while pH was held relatively constant after the first 3 h of an experiment. The system was comprised of cylindrical chambers 7×14 cm in diameter (environmental chamber). Four watch glasses (5 cm diameter) containing master solutions were placed inside the chambers on top of pedestals. The induction of nuclei and growth of crystals was primarily driven by the dissolution of $\text{NH}_3(\text{g})$ into the master solution from a reservoir of ammonium acetate (0.1 M NH_4Ac). The hydrolysis of ammonia to $\text{NH}_4(\text{aq})^+$ in the master solution raised and maintained solution pH at a near steady state within 3 h of the initiation of an experiment. Time step experiments were carried out in a series of 19 isolated environmental chambers held at 25 °C and 1 atm total pressure within a glove box.

This system allowed carbonate precipitation from a solution with a varying state of supersaturation over time (Table 1), but with a higher degree of control of the pH than the conventional free drift technique. Such changes in solution chemistry are known to occur during the biologically induced precipitation of magnesian calcite. For instance, *Myxococcus xanthus*, a Gram-negative soil bacterium, is able to induce the precipitation of Mg-calcite by releasing CO_2 and NH_3 to soil environments as a result of normal metabolic processes. The introduction of dissolved inorganic carbon and ammonium leads to a transient increase in pH, which can result in the local production of carbonate (Gonzalez-Muñoz et al., 2000).

2.2. Experimental set-up

An aliquot of a NaHCO_3 solution (600 mL, initial pH 8.2) was acidified by the slow addition of 1.5 mL of HCl (1 M) until a pH of 7.2 was reached. The solution was allowed to equilibrate with air for 24 h, after which 100 mL of CaCl_2 (0.0184 M) and 100 mL of MgCl_2 solution (0.00424 or 0.0084 M for Group I and Group II experiments, respectively) were added. The resulting final compositions for Group I and Group II experiments are reported in Table 1 ($t = 0$). The precipitation experiments were carried out in nineteen isolated environmental chambers. Master ($\text{NaHCO}_3/\text{CaCl}_2/\text{MgCl}_2$) and stock (NH_4Ac) solutions were placed in a glove box containing the 19 environmental chambers. After purging the glove box with argon to exclude atmospheric CO_2 , 10 mL aliquots of master solution (pre-filtered to 0.05 μm) were loaded into each of four watch glasses housed in each environmental chamber. Each watch glass was supported by a pedestal above the floor of the chamber. Ammonium acetate solution (100 mL) was then poured in the bottom of each chamber, and the cham-

Table 1

Experimental conditions and measured carbon isotope composition of solutions (DIC) and solid for a representative Group I (top) and Group II (bottom) experiment

Time (min)	Mg-cl (%)	pH	X _{Mg,soln}	(X _{Mg,solid}) _{avg}	HCO ₃ ⁻ (mM)	CO ₃ ²⁻ (mM)	CO _{2(aq)} (mM)	δ ¹³ C _{DIC} (‰)	δ ¹³ C _{HCO₃⁻} (‰)	Error δ ¹³ C _{HCO₃⁻} (‰)	δ ¹³ C _{CO_{2(g)}} (‰)	δ ¹³ C _{solid} (‰)	10 ³ ln α _{Mg-cl-HCO₃⁻}	Error 10 ³ ln α _{Mg-cl-HCO₃⁻}	10 ³ ln α _{Mg-cl-CO_{2(g)}}	Ω _{Mg-cl}	log r (μmol m ⁻² h)	Growth rate (mm/y)	
								±0.07‰				±0.07‰							
0		7.22	0.19		275	0.07	30.9	-5.50	-4.65	0.22	-12.58						6.0		
15		8.06	0.23		322	1.3	4.6	-5.12	-4.99	0.09	-12.92						34.0		
30		7.80	0.26		308	0.4	8.3	-4.91	-4.68	0.11	-12.61						15.3		
45	0	8.15	0.38	0	293	0.9	3.4	-4.46	-4.35	0.09	-12.28	-3.65 ^a					18.7		
60	0	8.35	0.48	0	312	2.5	2.3	-4.35	-4.27	0.09	-12.21	-3.43 ^a					18.6		
90	0	8.45	0.46	0	321	2.5	1.8	-4.77	-4.71	0.08	-12.64	-3.37 ^a					28.8		
120	0	8.58	0.54	0	301	5.5	2.9	-4.05	-3.94	0.10	-11.87	-3.21 ^a					19.7		
180	0	8.81	0.57	0	296	6.8	0.7	-4.01	-3.95	0.09	-11.88	-3.24 ^a					34.5		
300	>60	9.00	0.56	0.020	271	17.3	0.9	-4.17	-4.03	0.12	-11.96	-3.36 ^a					32.9		
480	>95	8.96	0.68	0.015	263	12.0	0.5	-4.05	-3.96	0.10	-11.89	-3.21	0.75	0.17	8.74		31.2	3.63	1.11
600	>95	8.84	0.81	0.040	286	7.6	0.7	-4.38	-4.31	0.09	-12.25	—	—	—	—	17.5	4.60	2.34	
720	>95	8.85	0.59	0.061	295	8.9	0.7	-4.24	-4.17	0.09	-12.10	-3.37	0.80	0.16	8.80		26.2	4.18	1.70
840	>95	8.94	0.76	0.028	283	10.6	0.5	-4.21	-4.13	0.10	-12.07	—	—	—	—	15.3	4.35	1.93	
960	>95	9.07	0.63	0.049	286	11.9	0.4	-3.93	-3.85	0.10	-11.78	-3.10	0.74	0.17	8.74		30.0	3.87	1.34
1080	>95	9.13	0.82	0.040	265	14.2	0.3	-3.81	-3.71	0.11	-11.64	-2.72	0.99	0.18	8.98		14.3	4.39	1.99
1200	>95	9.15	0.65	0.059	273	15.4	0.3	-3.97	-3.86	0.11	-11.80	-2.90	0.96	0.18	8.96		28.7	4.06	1.55
1320	>95	9.09	0.63	0.047	258	15.8	0.3	-3.72	-3.60	0.11	-11.54	-2.45	1.16	0.18	9.15		29.0	—	—
1440	>95	9.11	0.69	0.033	257	15.8	0.3	-3.84	-3.72	0.11	-11.66	-2.70	1.03	0.18	9.03		24.6	3.81	1.28
0		7.24	0.31		294	0.1	31.4	-5.49	-4.67	0.22	-12.61						6.7		
15		7.76	0.40		317	0.5	9.4	-4.91	-4.66	0.12	-12.59						15.0		
30		8.09	0.52		312	0.9	4.4	-4.87	-4.75	0.09	-12.68						18.7		
45		8.19	0.57		312	1.6	3.4	-4.82	-4.71	0.09	-12.65						18.3		
60	0	8.24	0.60	0	313	1.9	3.0	-4.61	-4.52	0.09	-12.45	-3.18 ^a					17.8		
90	0	8.38	0.70	0	312	2.9	2.1	-4.64	-4.56	0.09	-12.50	-3.25 ^a					15.1		
120	0	8.48	0.75	0	302	3.7	1.6	-4.51	-4.44	0.09	-12.37	-2.61 ^a					13.2		
180	40	8.61	0.73	0.040	310	5.6	1.2	-4.25	-4.19	0.09	-12.12	-2.80 ^a					21.8		
300	80	8.80	0.76	0.060	287	12.8	0.7	-4.13	-4.03	0.10	-11.96	-2.62 ^a					23.5		
480	>95	8.90	0.83	0.070	275	10.3	0.6	-4.21	-4.12	0.10	-12.06	-2.99	1.14	0.17	9.13		19.8	4.04	1.52
600	>95	8.96	0.70	0.109	254	9.2	0.5	-4.12	-4.04	0.10	-11.97	-2.82	1.23	0.17	9.22		34.7	3.81	1.28
720	>95	9.02	0.71	0.110	261	9.9	0.4	—	—	0.10	—	-2.81	—	—	—		33.0	4.11	1.61
840	>95	9.00	0.73	0.130	271	12.1	0.4	-4.09	-4.00	0.10	-11.93	-2.77	1.23	0.17	9.23		31.1	4.19	1.71
960	>95	9.07	0.82	0.091	268	16.9	0.4	-3.86	-3.74	0.11	-11.67	-2.75	0.99	0.18	8.99		24.7	4.19	1.71
1080	>95	9.07	0.77	0.112	250	15.1	0.3	-3.71	-3.60	0.11	-11.53	-2.60	1.01	0.18	9.00		29.6	3.21	0.81
1200	>95	9.15	0.81	0.091	255	20.6	0.3	-3.91	-3.77	0.12	-11.70	-2.85	0.92	0.19	8.91		27.5	3.90	1.37
1320	>95	9.18	0.76	0.105	254	16.7	0.3	-3.79	-3.66	0.12	-11.60	-2.69	0.97	0.19	8.97		36.0	3.92	1.39
1440	>95	9.16	0.79	0.110	255	18.2	0.3	-3.85	-3.72	0.12	-11.65	-2.65	1.07	0.19	9.07		30.2	3.87	1.34

Isotope compositions of HCO_{3(aq)}⁻ and CO_{2(g)} and carbon isotope fractionation factor, 10³ ln α, for the Mg-calcite-HCO_{3(aq)}⁻ and Mg-calcite-CO_{2(g)} systems are calculated values. The percentage of Mg-calcite in the solid, pH of the master solution, chemical composition of solution and solid, and Mg-calcite precipitation rate are reproduced from Jiménez-López et al. (2004). A dash indicates that data are not available.

^a samples in which monohydrocalcite was detected to be >5%.

bers were securely fitted with lids, sealing and isolating each in a CO₂-free environment (see Jiménez-López et al., 2001; for additional details). The environmental chambers were left to equilibrate for various lengths of time over the course of an experiment (24 h). At predetermined time intervals (see Table 1), a single chamber was vented with argon. Solution (4 × 10 mL) was combined from all four of the watch glasses and filtered through a 0.1 µm Millipore membrane prior to chemical and isotope analysis. Solid was recovered from the filters and watch glasses, rinsed twice with distilled water (~10 s) and air-dried at 40 °C for 6 h. These experiments were replicated three times each for the Group I and Group II experiments. Although the absolute values varied over time from one experiment to the other, the trends in chemical and isotope composition were identical. Therefore, one representative experiment from each group is reported in this study.

2.3. Chemical analyses of solution and solids: characterization of the solids

The experiments reported here are identical to those reported in Jiménez-López et al. (2004) for a study of the effect of Mg on oxygen isotope systematics of magnesian calcites. In short, solution pH was measured with a Cryson combination electrode calibrated with standard buffer solutions for slope correction (pH 7 and 9.26) prior to pH measurement (± 0.05 , reported as one standard deviation, 1σ , in the text). Concentrations of calcium and magnesium in both solution and solid were determined by atomic absorption spectrophotometry (AAS; Perkin-Elmer 1100B, using an air-acetylene flame atomizer) after acid digestion of 1 mg of the solid sample with 1 N HCl and acidification of liquid samples with HCl to prevent further precipitation of carbonate. Average values for the Mg content of the solid, $(X_{\text{Mg, solid}})_{\text{avg}}$ were calculated from AAS measurements of Mg²⁺ and Ca²⁺ from the acid dissolution of the bulk solid. Chemical analyses of DIC (dissolved inorganic carbon in solution) were carried out by acidimetric titration of 10 mL of filtered solution, using the Gran titration method (Stumm and Morgan, 1996). Based on repeated analyses of standards and samples, the analytical uncertainty was ± 0.01 mM for calcium and magnesium and 0.8 mM for DIC ($\pm 1\sigma$). The mineralogy of the solid was analyzed by X-ray diffraction (Philips PW 1730 diffractometer, CuK α radiation, 35 kV, 40 mA), using Al₂O₃ as an internal standard. The percentage of mineral phases in multiminerale mixtures was estimated from the peak area of the reflections for calcite (104), monohydrocalcite (012), aragonite (111) and vaterite (101), using a calibration curve for mixtures of known mineralogical content (e.g., Davies and Hooper, 1963). Error in mineralogical composition was estimated at $\pm 5\%$. The precipitate was observed by optical microscopy and samples were gold-coated and observed by scanning electronic microscopy (Zeiss DMS 950). Thin sections of individual crystals were analyzed by EDX with a HRTEM-AEM (Philips CM20; 200 kV,

56 µA) to determine the Mg and Ca content. Crystals were embedded in resin and cut to 750 Å thickness for analysis. Collection time was 200 s for a 200 × 1000 Å window. Elemental transects were made along diagonals from the center to the vertex of a crystal. Olivine (25.37% Mg) and Titanite (20.44% Ca) were used as internal standards for Mg and Ca, respectively. Experimental uncertainty associated with these measurements was ± 0.05 ppm from the repeated analysis of standards. More than 50 sections were prepared from crystals collected at the 60, 180, 960 and 1440 min time steps of an experiment.

Saturation state with respect to Mg-calcite at any time interval was calculated by dividing the ionic activity product in solution (IAP) by the solubility product for Mg-calcite (Busenberg and Plummer, 1989), considering the value of the Mg content of the overgrowth produced during this particular time interval. IAP was calculated as the product of the activities (a) of calcium, magnesium and carbonate ions as $a(\text{Ca}^{2+})^{1-x}a(\text{Mg}^{2+})^xa(\text{CO}_3^{2-})$ (Morse and Mackenzie, 1990), where x is the mole fraction of Mg in the solution over a particular time interval (Mucci and Morse, 1983, 1984). The activities for each ion were calculated with the EQPITZ program (He and Morse, 1993). The solubility product (K_{sp}) for a solid of particular Mg-content at any time during the time course experiment was calculated using the equation given by Busenberg and Plummer (1989; $A_0 = 6.27$ and $A_1 = 1.77$). Errors in saturation state data with respect to Mg-calcite were calculated from analytical errors in the determination of Ca_{T(aq)}, Mg_{T(aq)}, pH and DIC and were no greater than 15% for Mg-calcite.

Mg-calcite precipitation rate was determined by dividing the mass of solid precipitated over a specified time interval (mass/time) by the average surface area of the cumulative seed material from previous time steps. The mass of solid precipitated was calculated from the consumption of calcium and magnesium at each time interval. Surface area at specific time intervals was determined from the average length of the edge of the crystals observed in SEM photomicrographs and a geometrical model (for details, see Jiménez-López et al., 2001). Time intervals after 480 min were considered in these calculations because the solid was >95% Mg-calcite by this time step. Precipitation rate data were recalculated as mm/y using the molecular weight (100 g/mol) and the density of calcite (2.71 g/cm³).

2.4. Isotope analyses

2.4.1. Isotope composition of solutions and solids

The $\delta^{13}\text{C}$ of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) was determined using a modified version of the technique described by McCrea (1950). Three milliliters of 100% H₃PO₄ were outgassed in a chamber that was connected to a vacuum line. This chamber was isolated and equilibrated in a thermostatic bath at 25 °C for 15 min, after which 1 mL of sample solution was injected through a septum. The mixture reacted for 8 h at 25 °C and carbon diox-

ide was then extracted under vacuum and purified, before introduction to the inlet system of an isotope ratio mass spectrometer for isotope analysis.

The $\delta^{13}\text{C}$ of solid carbonate was determined according to procedures described in McCrea (1950). Carbon dioxide was produced by reacting 5 mg of solid with 2 mL of out-gassed H_3PO_4 (100%) in an evacuated vessel in a thermostated water bath at 25 °C. After 48 h, CO_2 was extracted under vacuum, purified and analyzed.

All isotope measurements were made with an isotope ratio mass spectrometer (Finnigan MAT 251). Isotope ratios are expressed in conventional delta (δ) notation in per mil (‰) units (Craig, 1957). Delta values are calibrated against the V-PDB international standard reference material using an in-house working standard (Reyes et al., 1989). Experimental uncertainty was $\leq \pm 0.07\text{‰}$ (1σ).

2.4.2. Isotope fractionation factors

The carbon isotope composition of individual components of the carbonic acid system (i.e., $\text{CO}_{2(\text{g})}$, $\text{CO}_{2(\text{aq})}$, $\text{HCO}_{3(\text{aq})}^-$, $\text{CO}_{3(\text{aq})}^{2-}$) were computed from measured values of total dissolved inorganic carbon (DIC), pH, Ca^{2+} , Mg^{2+} and the $\delta^{13}\text{C}$ of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) using the EQPITZ speciation model (He and Morse, 1993) and carbon isotope fractionation factors ($10^3 \ln \alpha$) for the $\text{HCO}_{3(\text{aq})}^- - \text{CO}_{3(\text{aq})}^{2-}$ (Turner, 1982), $\text{HCO}_{3(\text{aq})}^- - \text{CO}_{2(\text{g})}$ (Mook et al., 1974) and $\text{CO}_{2(\text{g})} - \text{CO}_{2(\text{aq})}$ (Vogel et al., 1970) systems.

Isotope fractionation factors were calculated for time steps in which Mg-calcite was the only solid detected by XRD. Isotope data for time intervals where monohydrocalcite was present (≤ 300 min in Group I and Group II experiments) were not considered in the calculations of Mg-calcite isotope fractionation relations because of possible kinetic isotope partitioning associated with monohydrocalcite (Jiménez-López et al., 2001). The carbon isotope fractionation factor ($10^3 \ln \alpha$) for Mg-calcite and $\text{CO}_{2(\text{g})}$ or $\text{HCO}_{3(\text{aq})}^-$ was determined from a measured $\delta^{13}\text{C}_{\text{solid}}$ value and a calculated $\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}}$ and $\delta^{13}\text{C}_{\text{HCO}_{3(\text{aq})}^-}$ value, respectively. Thus, the isotope systematics are functionally related through existing fractionation relations reported for $\text{HCO}_{3(\text{aq})}^- - \text{CO}_{2(\text{g})}$ (Mook et al., 1974) and should not be considered independent data sets. The analytical error in measured $\delta^{13}\text{C}_{\text{solid}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ values, as well as those errors generated and propagated in the chemical and isotope speciation analysis were considered in the evaluation of cumulative errors reported in Table 1 and Figs. 3B and C for the determination of $\delta^{13}\text{C}_{\text{HCO}_{3(\text{aq})}^-}$ and $10^3 \ln \alpha_{\text{Mg-cl-HCO}_{3(\text{aq})}^-}$.

2.5. Statistics

Average values reported in this study are followed by one standard deviation ($\pm 1\sigma$) and the number of observations (n). Least square regression analysis was used to fit lines to the data using the program Microcal ORIGIN 5.0. The level of significance chosen for analyses was $p < 0.05$.

3. Results and discussion

3.1. Chemistry, mineralogy and morphology of Mg-calcite

The chemistry of the solution and the solid, and the mineralogy of the solid were originally reported in Jiménez-López et al. (2004) and are reproduced in Table 1. The first solid to precipitate in these experiments was monohydrocalcite that dissolved and reprecipitated as Mg-calcite (>95%) after the 480 min time interval. The average mol% MgCO_3 in Mg-calcite from the 480 to 1440 min time interval ranged from 1.5% to 6.1% in the Group I experiments, and from 7.0% to 13.0% in the Group II experiments. These Mg-calcites had edge lengths of $\sim 17 \mu\text{m}$ at the end of the experiments (1440 min). The crystals displayed prominent {104} forms in which two of the edges of the (104) faces were inhibited by the growth of prismatic (110) and (100) faces. The morphology of Mg-calcites crystals was identical in the Group I and Group II experiments, despite the differing initial magnesium concentration of the master solutions (Fig. 1). The Mg-calcites were chemically zoned, showing varying mol% MgCO_3 along a single sector. The mol% MgCO_3 was highest at the outer corner of each crystal (last layer formed between 22 and 24 h) and it was negligible at the center of the crystal. The increase in mol% MgCO_3 was not constant but showed fluctuations of increasing magnitude from the Group I to the Group II experiments. Although the absolute values of $X_{\text{Mg, solid}}$ differed between the 50 grains analyzed by HRTEM-AEM, the overall trend of Mg-free cores and Mg-rich rims was observed in all the samples. Mg-calcite precipitation rate data for the Group I experiment (480–1440 min) ranged from $10^{3.63}$ to $10^{4.60} \mu\text{mol m}^{-2} \text{h}^{-1}$ for saturation states with respect to Mg-calcite ranging from ~ 14 to ~ 31 , while for the Group II experiment precipitation rates ranged from $10^{3.21}$ to $10^{4.19} \mu\text{mol m}^{-2} \text{h}^{-1}$ for saturation states ranging from ~ 20 to ~ 35 (Table 1).

3.2. Isotope analyses

The isotope composition of the total dissolved inorganic carbon in solution ($\delta^{13}\text{C}_{\text{DIC}}$) increased $\sim 1.5\text{‰}$ during the time course, from -5.5‰ to $\sim -3.7\text{‰}$ for the Group I and II experiments (Table 1). The rate of increase in $\delta^{13}\text{C}_{\text{DIC}}$ was more pronounced within the first 180 min of an experiment (Fig. 2A), while thereafter $\delta^{13}\text{C}_{\text{DIC}}$ averaged $-4.0 \pm 0.2\text{‰}$ for both the Group I ($n = 10$) and Group II ($n = 9$) experiments.

The isotope composition of the aqueous bicarbonate ion, $\delta^{13}\text{C}_{\text{HCO}_{3(\text{aq})}^-}$, increased $\sim 1\text{‰}$ during the time course, from $-5.0/-4.7\text{‰}$ to $\sim -3.6\text{‰}$ for the Group I and Group II experiments (Table 1). Like $\delta^{13}\text{C}_{\text{DIC}}$, the rate of increase in $\delta^{13}\text{C}_{\text{HCO}_{3(\text{aq})}^-}$ was more pronounced within the first 180 min of an experiment, averaging $-3.9 \pm 0.2\text{‰}$ for the Group I ($n = 10$) and Group II ($n = 9$) experiments thereafter. The values for $\delta^{13}\text{C}_{\text{HCO}_{3(\text{aq})}^-}$ and $\delta^{13}\text{C}_{\text{DIC}}$ were similar

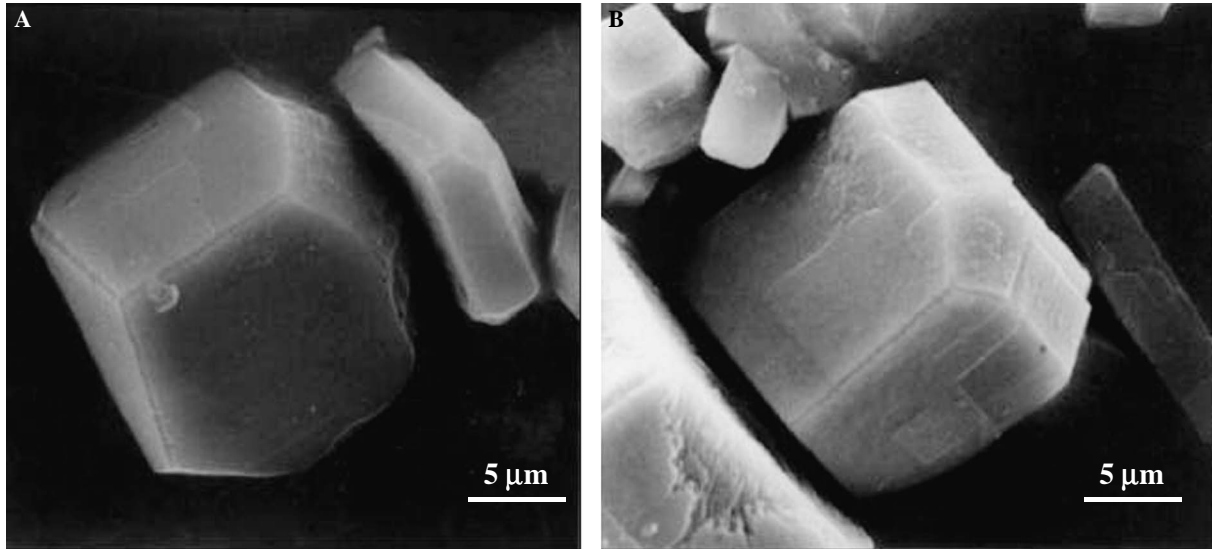


Fig. 1. SEM pictures of Mg-calcite crystals collected at the end of the (A) Group I and (B) Group II experiments.

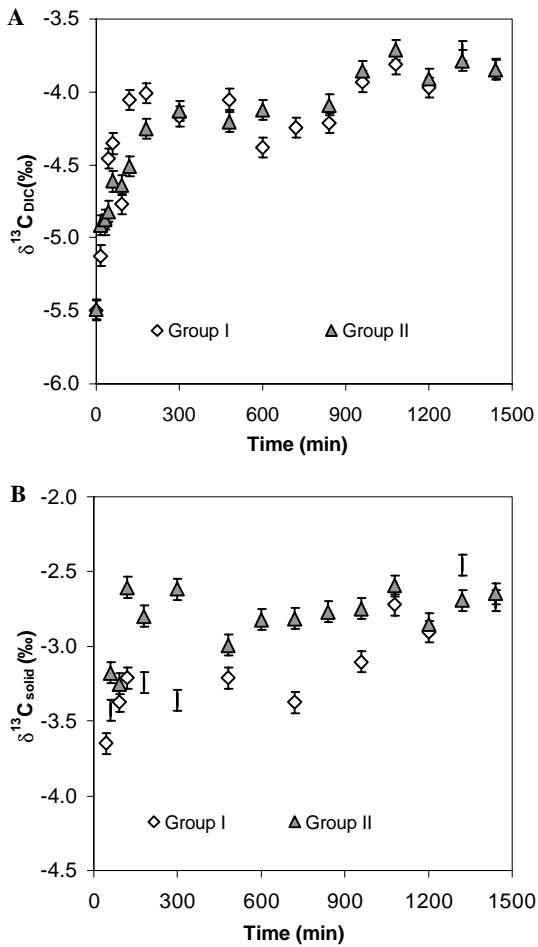


Fig. 2. Changes with time in the measured isotope compositions of the master solutions and precipitates: (A) $\delta^{13}\text{C}_{\text{DIC}}$ and (B) $\delta^{13}\text{C}_{\text{solid}}$.

because bicarbonate ion was the main carbonate species in solution over the limited range of pH (~ 8.8 to ~ 9.2) for these experiments.

The isotope composition of the solid ($\delta^{13}\text{C}_{\text{solid}}$) ranged from -3.7‰ to -2.5‰ for the Group I ($n = 13$) experiment, and from -3.3‰ to -2.6‰ for the Group II ($n = 14$) experiment (Fig. 2B; Table 1). For the Group I experiment, $\delta^{13}\text{C}_{\text{solid}}$ values increased rapidly over the first 180 min and then stabilized at $\sim 3.3\text{‰}$. For the Group II experiment, $\delta^{13}\text{C}$ values for the solid increased over the first 120 min and remained nearly constant thereafter.

Over the time interval where Mg-calcite was the predominant solid (480–1440 min), $\delta^{13}\text{C}_{\text{Mg-cl}}$ values averaged $-2.9 \pm 0.3\text{‰}$ (range: -3.4‰ to -2.5‰ , $n = 7$; mol% Mg in the solid ranging from 1.5% to 6.1%) for the Group I experiment, and $-2.8 \pm 0.1\text{‰}$ (range: -3.0‰ to -2.6‰ , $n = 9$; mol% Mg in the solid ranging from 7.0% to 13.0%) for the Group II experiment (Fig. 2B; Table 1). There was more scatter in the $\delta^{13}\text{C}_{\text{Mg-cl}}$ data for the Group I than the Group II experiments, which was consistent with the greater variation in $\delta^{13}\text{C}_{\text{DIC}}$ values for Group I (-4.4‰ to -3.7‰) compared to Group II (-4.2‰ to -3.7‰). Because the carbon isotope composition of DIC and pH changed during the time course experiments (Table 1), the isotope composition of the solid should reflect that change.

The effect of the Mg-content on the isotope composition of the solid was studied by calculating the isotope fractionation factor between bulk Mg-calcite and $\text{HCO}_3(\text{aq})^-$ for individual time steps after 480 min (Fig. 3B). The isotope fractionation factor $10^3 \ln \alpha_{\text{Mg-cl-HCO}_3(\text{aq})^-}$ ranged from 0.7 to 1.2 for Group I experiment and averaged 0.9 ± 0.2 ($n = 7$). For the Group II experiment, $10^3 \ln \alpha_{\text{Mg-cl-HCO}_3(\text{aq})^-}$ values ranged from 0.9 to 1.2 and averaged 1.1 ± 0.1 ($n = 8$). The slope of the linear fit of $10^3 \ln \alpha_{\text{Mg-cl-HCO}_3(\text{aq})^-}$ data versus $(X_{\text{Mg, solid}})_{\text{avg}}$ was 0.024 ± 0.011 per mol% MgCO_3 ($R^2 = 0.286$; $n = 15$; $p = 0.04$). The y -intercept predicted an isotope fractionation factor for the system containing pure calcite of 0.82 ± 0.09 . For comparison, $10^3 \ln \alpha_{\text{Cl-HCO}_3(\text{aq})^-}$ data reported in the literature for pure

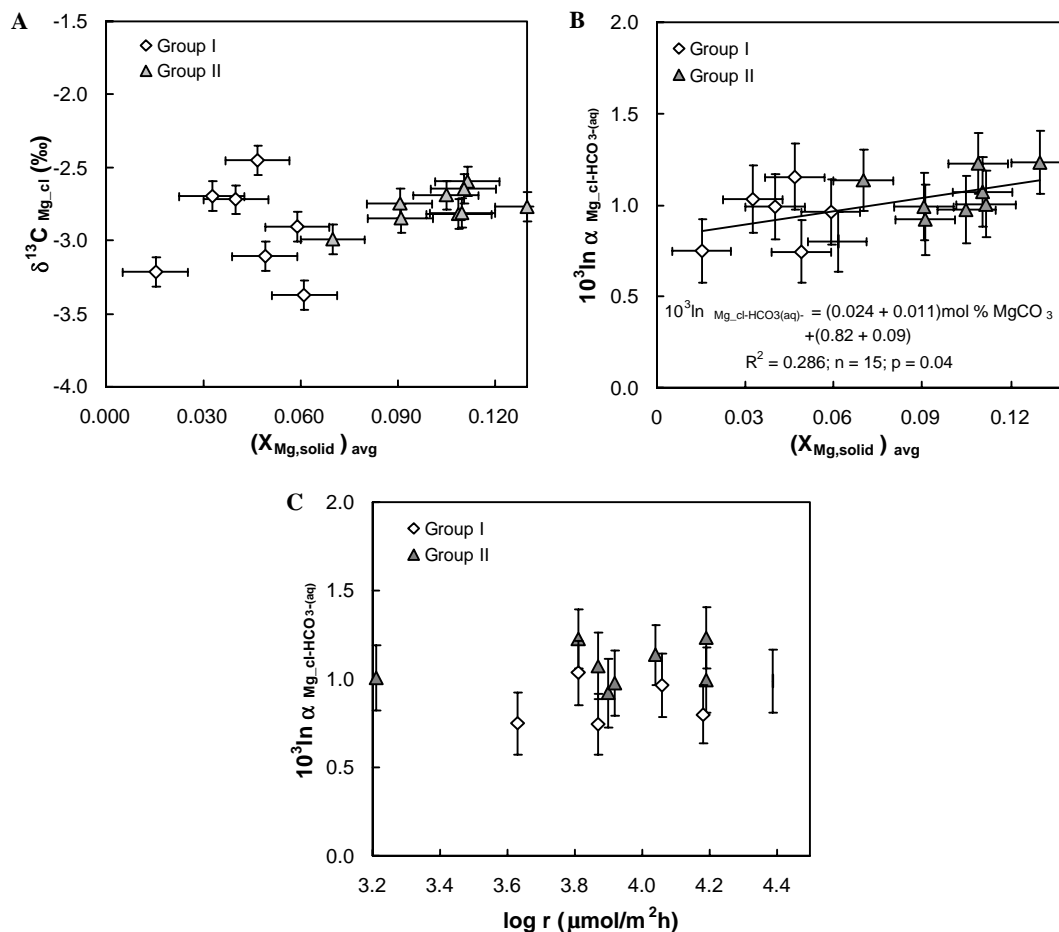


Fig. 3. (A) $\delta^{13}\text{C}_{\text{Mg-cl}}$ values versus $(X_{\text{Mg,solid}})_{\text{avg}}$, where $(X_{\text{Mg,solid}})_{\text{avg}}$ is the average mol fraction of MgCO_3 in the solid at the specified time interval. Calculated values for the carbon isotope fractionation factor, as $10^3 \ln \alpha$, for the $\text{Mg-calcite-HCO}_3(\text{aq})^-$ system versus (B) $(X_{\text{Mg,solid}})_{\text{avg}}$ and (C) Mg-calcite precipitation rate.

calcite at 25 °C are 0.9 (Rubinson and Clayton, 1969), 1.0 ± 0.2 (Romanek et al., 1992) and 0.94 ± 0.06 (Jiménez-López et al., 2001). Results from this study are in good agreement with data in the literature. Our data for $10^3 \ln \alpha_{\text{Mg-cl-CO}_2(\text{g})}$ can be compared to literature values where calcite and $\text{CO}_2(\text{g})$ were independently measured to further evaluate our systematics. The extrapolation of $10^3 \ln \alpha_{\text{Mg-cl-CO}_2(\text{g})}$ data versus $(X_{\text{Mg,solid}})_{\text{avg}}$ to pure calcite yields a value of 8.81 ± 0.09 , which is in good agreement with the following values published in the literature: 9.3 at 22 °C (Vogel, 1961), 9.0 at 25 °C (Romanek et al., 1992) and 8.9 at 25 °C (Jiménez-López et al., 2001).

To our knowledge, there are no published data on carbon isotope partitioning for a system containing Mg-calcite and calcite. As pointed out by numerous studies (for a review, see O'Neil, 1986), the substitution of atoms of lower mass in the crystal structure of minerals (e.g., Mg^{2+} versus Ca^{2+} in Mg-calcite) favors the enrichment of the isotope of greater mass in the solid (i.e., ^{13}C versus ^{12}C in the carbonate anion) to decrease the vibrational energy of the lattice. For instance, Sheppard and Schwarcz (1970) determined an isotope fractionation factor, $10^3 \ln \alpha$, for the dolomite-calcite system of ~ 2.2 , which is consistent with

the preferential incorporation of ^{13}C as Mg^{2+} content in the crystal increased. Our results show a slight enrichment of ^{13}C as $0.024 \pm 0.011\text{‰}$ per mol% of Mg^{2+} incorporated in the crystal structure. This enrichment follows the trend predicted for the substitution of cations in carbonates of lower relative atomic mass (O'Neil, 1986) and it is also consistent with the trend observed by Sheppard and Schwarcz (1970), although the extrapolation of our data to the mol% MgCO_3 for dolomite predicts a lower enrichment of ^{13}C in dolomite of 1.2 compared to calcite than that of 2.2 predicted by the extrapolation of the data of Sheppard and Schwarcz (1970) to 25 °C. Our data are also consistent with the results observed by González and Lohmann (1985) for natural carbonates. Compared to pure calcite, our results predict an enrichment in ^{13}C of 0.38‰ for magnesian calcite containing 16 mol% MgCO_3 (HMC) and of 0.12‰ for magnesian calcites containing 5 mol% MgCO_3 (LMC). These results are in accordance with the increases in $\delta^{13}\text{C}$ observed by González and Lohmann (1985) of 0.3‰ to 0.4‰ for HMC (~ 14 to ~ 20 mol% MgCO_3) cements relative to pure calcite, and of 0.2‰ relative to LMC.

The effect of Mg -content on the carbon isotope composition of Mg-calcite is slight and much lower than that ob-

served for oxygen isotope partitioning (Tarutani et al., 1969; Jiménez-López et al., 2004). As such, these results do not significantly impact interpretations based on the $\delta^{13}\text{C}$ of low magnesian calcites (e.g., Saller and Moore, 1991; Carpenter et al., 1991; Carpenter and Lohmann, 1995; Rahimpour-Bonab et al., 1997). However, studies based on high magnesian calcites (Aghib et al., 1991; Dutkiewicz et al., 2000) should take into account the effect of magnesium in the interpretation of carbon isotope signatures, as deviations of 0.4‰ are expected compared to partitioning with pure calcite. Excursion of similar magnitude have been observed in carbon isotope stratigraphies and diagenetic alterations that can now be attributed, in part, to the effect of Mg incorporation in calcite.

The carbon isotope fractionation factor for $10^3 \ln \alpha_{\text{Mg-cl-HCO}_3(\text{aq})}$ did not display a dependence on Mg-calcite precipitation rate, within the range of precipitation rates ($10^{3.21}$ – $10^{4.60}$ $\mu\text{mol m}^{-2} \text{h}$) and $(X_{\text{Mg,solid}})_{\text{avg}}$ values (0.02–0.13) (Fig. 3C). However, due to the fact that rate data were intimately tied to the chemical composition of the solid, the potential effect of precipitation rate could not be separated from the effect of Mg-content. The effect of precipitation rate on the carbon isotope fractionation factor between natural carbonates and solution remains controversial. McConnaughey (1989) sampled skeletal material from corals that grew at two different sites and reported an effect of growth rate on the carbon isotope composition of the coral. Also, Owen et al. (2002) concluded that seasonal variation in shell growth rate was a governing factor influencing carbon isotope composition of shell carbonate. However, Romanek et al. (1992) and Jiménez-López et al. (2001) studied rate effect on carbon isotope fractionation between calcite and $\text{CO}_2(\text{g})$ and showed no precipitation rate effect over a range of precipitation rates from $10^{3.44}$ to $10^{5.63}$ $\mu\text{mol m}^{-2} \text{h}$. Additional work is sorely needed to reconcile laboratory studies and natural samples.

The precipitation rate data of this study were converted to growth rate data (mm/y; see Table 1) using the molecular weight and density of calcite to facilitate a comparison with published growth rates for sclerosponges, which are slow growing organisms that sometimes precipitate skeleton composed of magnesian calcites. These organisms are important because they may serve as global climate proxies for unusually long time scales (e.g., 500–1000 years) by virtue of their slow growth rate (0.1–0.2 mm/y; Benavides and Druffel, 1986). Although the precipitation rate data for our experiments is an order of magnitude greater than that of sclerosponges, the extrapolation of our data to these low rates suggest that rate effect if present should not hamper the interpretation of climatological information. If the mechanism of carbonate precipitation changes with the approach to chemical equilibrium, the potential exists the extrapolation of rate effect may not be appropriate and other methods are needed to evaluate rate effect. Nevertheless, the effect of Mg-content on the carbon isotope composition of sclerosponges and other biological precipitates

may be evaluated within the context of the present results. For mol MgCO_3 % contents greater than $\sim 5\%$ (e.g., sclerosponges and echinoderms) the effect of magnesium should be taken into consideration.

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