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# The role of $\text{SO}_4$ in the switch from calcite to aragonite seas

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## ABSTRACT

Throughout the Phanerozoic, the primary inorganic marine calcium carbonate mineralogy oscillated between calcite and aragonite, reflecting changes in seawater chemistry. These variations in seawater composition also appear to have influenced the evolution of calcifying organisms. However, the processes controlling these mineralogical and biological changes are poorly constrained. Previous work has focused mainly on the Mg/Ca ratio in seawater as the primary driver. Here, we examine the role of dissolved  $\text{SO}_4$  in these processes by performing controlled laboratory precipitation experiments and geochemical modeling of evaporite formation. We show that an increase in dissolved  $\text{SO}_4$  decreases the Mg/Ca ratio at which calcite is destabilized and aragonite becomes the dominant  $\text{CaCO}_3$  polymorph. Our data suggest that the Mg/Ca and  $\text{SO}_4$  thresholds for formation of calcite seas are significantly lower than previous estimates and are mutually dependent. This shows that our understanding of Phanerozoic changes in seawater chemistry and the models relating this to primary  $\text{CaCO}_3$  mineralogy need reevaluation.

## INTRODUCTION

The primary marine  $\text{CaCO}_3$  polymorph in cements and ooids is documented to have oscillated between calcite and aragonite throughout the Phanerozoic (Sandberg, 1983). The periods recognized when predominantly abiotic calcite or aragonite formed are now known as calcite and aragonite seas. However, the records show that during the Phanerozoic, the  $\text{CaCO}_3$  formed was rarely pure calcite or aragonite (Wilkinson et al., 1985; Zhuravlev and Wood, 2009). Similar patterns in  $\text{CaCO}_3$  biomineral formation have been reported for several, but not all, marine fossils (e.g., bryozoans and rugose corals). Most organisms adopted the dominant mineralogical form from the oceans in which they evolved (e.g., Stanley, 2006; Zhuravlev and Wood, 2009), suggesting that the oceans had a profound effect on the evolution of calcifying organisms (Porter, 2007). Explanations ranging from aqueous Mg/Ca (Davis et al., 2000; Morse et al., 1997; Stanley, 2006), to temperature (Burton and Walter, 1987), to  $p\text{CO}_2$ , and subsequent changes in pH and alkalinity (Sandberg, 1983; Wilkinson et al., 1984), have been invoked to explain the oscillating trends in  $\text{CaCO}_3$  mineralogy. Currently, the aqueous Mg/Ca ratio is thought to have been the major driving force behind the changes (Hardie, 1996; Lowenstein et al., 2003; Morse et al., 1997). Mg substitution for Ca in the calcite structure is a function of the Mg/Ca and temperature (Burton and Walter, 1991). Mg substitution affects the thermodynamic stability of calcite (Davis et al., 2000; Königsberger and Gamsjäger, 1992) and inhibits calcite growth (Davis et al., 2000). In addition, experimental studies have shown that Mg has a negligible effect on the stability of aragonite, causing aragonite to precipitate instead of calcite at an aqueous Mg/Ca higher than  $\sim 1.3$

(Morse et al., 1997). However, models of the chemical changes in seawater suggest that the switch from calcite to aragonite seas occurred at an aqueous Mg/Ca from  $\sim 1$  (Wilkinson and Algeo, 1989) to  $\sim 2$  (Hardie, 1996). These differences indicate that some uncertainty remains about the threshold level of Mg/Ca to induce a mineralogical change.

Coincident with the changes in  $\text{CaCO}_3$  mineralogy, the evaporites that precipitated from marine brines during the same geological periods oscillated between KCl (calcite sea) and  $\text{MgSO}_4$  (aragonite sea) types (Hardie, 1996), which formed from seawater containing higher concentrations of dissolved  $\text{CaCl}_2$  and  $\text{MgSO}_4$ , respectively (Lowenstein et al., 2003). Analyses of halite fluid inclusions indicated that  $\text{SO}_4$  and Mg/Ca covaried during the Phanerozoic in phase with the changes in  $\text{CaCO}_3$  mineralogy (Horita et al., 2002; Lowenstein et al., 2003). These observations support the hypothesis that changes in solution chemistry (e.g., Mg/Ca) were responsible for the oscillations between calcite and aragonite seas (e.g., Stanley, 2006), but they also suggest that other dissolved ions (e.g.,  $\text{SO}_4$ ) might have a significant influence.

The concentration of  $\text{SO}_4$  in the Phanerozoic sea has been determined to have fluctuated between  $\sim 5$  and  $\sim 30$  mM (Horita et al., 2002; Lowenstein et al., 2003), and experimental studies have shown that  $\text{SO}_4$  decreases calcite stability and precipitation rate compared to aragonite (Busenberg and Plummer, 1985; Walter, 1986). This indicates that beside Mg/Ca,  $\text{SO}_4$  may also act as a major influence on  $\text{CaCO}_3$  precipitation (Railsback and Anderson, 1987). However, the influence of  $\text{SO}_4$  in addition to that of the Mg/Ca ratio on the calcite to aragonite seas has so far been largely overlooked (Lee and Morse, 2010).

We quantified the effects of  $\text{SO}_4$  and Mg/Ca ratio on the  $\text{CaCO}_3$  mineralogy precipitated from solutions by performing laboratory-based  $\text{CaCO}_3$  synthesis experiments at a range of  $\text{SO}_4$  concentrations and Mg/Ca values. These experiments were combined with information from geochemical models of changes in evaporite mineralogy caused by fluctuations in seawater composition, allowing us to include  $\text{SO}_4$  in, and reevaluate, the existing models relating seawater chemistry to  $\text{CaCO}_3$  mineralogy throughout the Phanerozoic.

## METHODS

Constant addition experiments were performed at  $21 \pm 1$  °C using the method of Tesoriero and Pankow (1996). Glass spheres (100  $\mu\text{m}$  Biospec Products®) were used to create a surface for nucleation and to mimic the inorganic precipitation of  $\text{CaCO}_3$  on ooids. The initial solution for each experiment (500 mL) contained 10 mM  $\text{CaCl}_2$ , 0–55 mM  $\text{MgCl}_2$ , 0–100 mM  $\text{Na}_2\text{SO}_4$ , and 2 g/L glass spheres. The total Mg and  $\text{SO}_4$  concentrations bracketed proposed Phanerozoic seawater concentrations (Horita et al., 2002). The salinity (ionic strength of  $\sim 0.6$  M) and initial pH ( $\sim 8.2$ , in equilibrium with the atmosphere) were adjusted to seawater values by the addition of NaCl and NaOH, respectively. While being continuously shaken on an orbital shaker (270 rpm), precipitation was induced by continuously injecting two solutions into the initial solutions via a syringe pump at 1 mL/h for  $\sim 48$  h. These input solutions contained 250 mM  $\text{CaCl}_2$  or 230 mM  $\text{Na}_2\text{CO}_3$ ,  $\text{MgCl}_2$  (0–110 mM) or  $\text{NaSO}_4$  (0–200 mM) was added to the input solutions to negate dilution of Mg and  $\text{SO}_4$ . At the start, during ( $\sim 5$  times), and at the end of the experiments, the pH of the reacted solutions was measured. Simultaneously, solution samples ( $\sim 4$  mL each) were removed and filtered through 0.2  $\mu\text{m}$  filters and were either immediately acidified with HCl (for total Ca and Mg measurements) or stored frozen (for total  $\text{SO}_4$  measurements). After the experiments were terminated ( $\sim 48$  h), the precipitated solids were separated from the solutions by filtering through 0.2  $\mu\text{m}$  membrane filters. The resulting solids were washed three times with 18.2 M $\Omega$  Milli-Q grade  $\text{H}_2\text{O}$  equilibrated with calcite, filtered again, and dried at 95 °C for a minimum of 24 h.

The solutions were analyzed for total Ca and Mg using a spectrophotometric method using

calmagite as an indicator (Method 8030, Hach Lange, Düsseldorf, Germany) and for total SO<sub>4</sub> by ion chromatography (IC) with a carbonate/bicarbonate eluent. The equilibrium alkalinity was calculated with PHREEQC (Parkhurst and Appelo, 1999) from the equilibrium pH, assuming equilibrium with the atmosphere. Powder X-ray diffraction (XRD) analyses of the solids were performed using a Bruker D8 X-Ray Diffractometer (Cu Kα<sub>1</sub>) with a silicon internal standard. The obtained XRD patterns were analyzed with Topas4-2® (Bruker\_AXS, 2009) to determine the relative proportions of the precipitated CaCO<sub>3</sub> polymorphs and the CaCO<sub>3</sub> unit cell dimensions. Finally, aliquots of the precipitates were dissolved in 1.2 M HCl, and the resulting solutions were analyzed using IC methods modified after Marini et al. (2006) to measure Ca and Mg, and after Bruno et al. (2003) to measure SO<sub>4</sub>. During most experiments, a mixture of calcite, aragonite, and/or vaterite precipitated (Table 1). If the solid samples contained more than 99% arago-

nite, the total SO<sub>4</sub> and Mg solid composition was assumed to represent the composition of aragonite. These aragonite compositions (as a function of the solution chemistry) were then used to calculate the aragonite composition in samples with less than 99% aragonite. The total composition and the estimated aragonite compositions were then used to calculate the calcite and vaterite composition in the samples where either calcite or vaterite was present alongside aragonite. This approach was used to determine the composition of the CaCO<sub>3</sub> polymorphs in all samples.

PHREEQC (Parkhurst and Appelo, 1999) evaporation simulations were carried out to evaluate the minerals formed from evaporating seawater with varying Mg and SO<sub>4</sub> concentrations, as would have occurred during the Phanerozoic (Hardie, 1996). The method, starting solution compositions, and detailed results from the PHREEQC simulations are described in GSA Data Repository<sup>1</sup> (Tables DR1–DR4; Figs. DR1–DR10).

**RESULTS AND DISCUSSION**

The solution chemistry and solid composition for all experiments are summarized in Table 1. During most experiments, a mixture of calcite, aragonite, and/or vaterite precipitated. The dominant polymorph (>50%) as a function of Mg/Ca and SO<sub>4</sub> concentration is plotted in Figure 1. Note that 100% calcite only formed in experiments without Mg and SO<sub>4</sub> in solution (Table 1).

With increasing Mg in solution, the Mg substitution into calcite increased (Table 1). This change in composition caused the calcite stability to decrease and the aragonite to calcite ratio in the solid to increase (Table 1). In the absence of sulfate, only aragonite precipitated at Mg/Ca > ~1.7 (Fig. 1), which is in accordance with results given by Morse et al. (1997), while at Mg/Ca > ~0.6–0.7, aragonite became the most dominant phase precipitated (Fig. 1). Davis et al. (2000) showed that when Mg exceeds ~1.8 mol% in calcite, aragonite becomes more stable than calcite, which is in agreement with the calculated calcite compositions in the samples

TABLE 1. SUMMARY OF CaCO<sub>3</sub> MINERALOGY AND COMPOSITION FROM THE CONSTANT ADDITION EXPERIMENTS

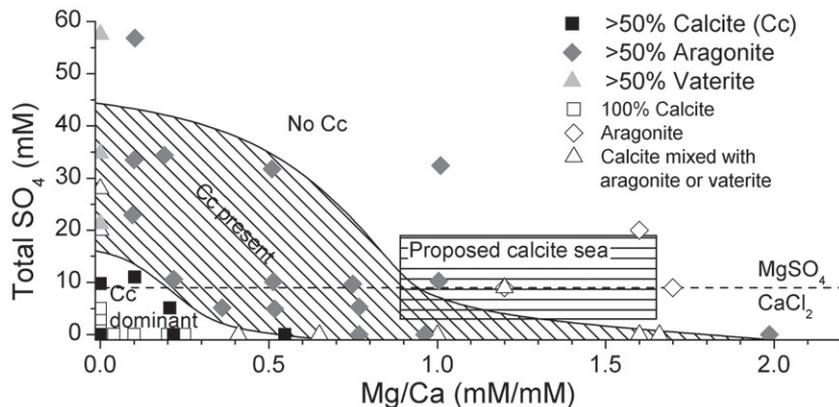
Solution chemistry*		Solid composition after 48 h											
SO <sub>4</sub> (mM)	Mg/Ca (mM/mM)	Polymorph distribution <sup>†</sup>			Total composition		Calcite <sup>§</sup>		Aragonite <sup>§</sup>		Vaterite <sup>§</sup>		
		Calcite (%)	Aragonite (%)	Vaterite (%)	SO <sub>4</sub> (mol%)	Mg (mol%)							
0.0	0.00	100.0	0.0	0.0	0.00	0.000	0.00	0.00	–	–	–	–	
0.0	0.22	97.3	2.7	0.0	0.00	0.627	0.00	0.64	0.00	0.012	–	–	
0.0	0.55	89.9	10.1	0.0	0.00	1.403	0.00	1.81	0.00	0.025	–	–	
0.0	0.77	6.3	93.5	0.0	0.00	0.144	0.00	1.87	0.00	0.031	–	–	
0.0	0.96	<1	99.5	0.0	0.00	0.028	–	–	0.00	0.028	–	–	
0.0	1.99	0.0	100.0	0.0	0.00	0.057	–	–	0.00	0.057	–	–	
0.0	5.22	0.0	100.0	0.0	0.00	0.088	–	–	0.00	0.088	–	–	
5.1	0.21	94.0	6.0	0.0	1.02	0.602	1.07	0.64	0.25	0.012	–	–	
5.1	0.36	37.2	62.8	0.0	0.43	0.361	0.74	0.94	0.25	0.018	–	–	
4.9	0.52	6.6	93.5	0.0	0.25	0.103	0.44	1.25	0.24	0.024	–	–	
5.3	0.77	<1	99.3	0.0	0.24	0.035	–	–	0.24	0.035	–	–	
9.8	0.00	90.4	0.0	10.6	1.62	0.000	1.74	0.00	–	–	0.59	0.00	
11.0	0.10	70.4	29.6	0.0	1.23	0.221	1.56	0.31	0.43	0.007	–	–	
10.6	0.22	46.7	53.3	0.0	0.91	0.274	1.47	0.59	0.42	0.012	–	–	
10.1	0.51	<1	99.1	0.0	0.38	0.022	–	–	0.38	0.022	–	–	
9.7	0.75	<1	99.7	0.0	0.41	0.034	–	–	0.41	0.034	–	–	
10.2	1.00	0.0	100.0	0.0	0.41	0.026	–	–	0.41	0.026	–	–	
22.9	0.10	12.4	52.0	35.7	0.91	0.153	2.08	0.30	0.66	0.006	0.87	0.32	
36.5	0.00	1.5	12.9	85.6	1.22	0.000	3.07	0.00	0.87	0.000	1.28	0.00	
33.5	0.10	1.5	66.5	32.0	0.92	0.107	2.44	0.31	0.83	0.007	1.05	0.31	
34.4	0.19	<1	99.5	0.0	0.86	0.011	–	–	0.86	0.011	–	–	
31.8	0.51	<1	99.6	0.0	0.77	0.023	–	–	0.77	0.023	–	–	
32.4	1.01	0.0	100.0	0.0	0.81	0.034	–	–	0.81	0.034	–	–	
57.6	0.00	0.0	30.2	69.8	1.37	0.000	–	–	1.13	0.000	1.48	0.00	
56.8	0.10	0.0	88.1	11.9	1.11	0.047	–	–	1.11	0.007	1.32	0.35	
110.8	0.00	0.0	69.4	30.6	1.69	0.000	–	–	1.60	0.000	1.88	0.00	
109.9	0.23	0.0	100.0	0.0	1.47	0.013	–	–	1.47	0.013	–	–	
104.8	0.51	0.0	100.0	0.0	1.50	0.023	–	–	1.50	0.023	–	–	
106.4	0.98	0.0	100.0	0.0	1.57	0.046	–	–	1.57	0.046	–	–	

\*The solutions in all experiments also contained 10 mM Ca and had an ionic strength of ~0.6 M.

<sup>†</sup><1 indicates 0%–1% calcite was present.

<sup>§</sup>Dash indicates that the composition for this polymorph is not relevant.

<sup>1</sup>GSA Data Repository item 2011111, method and results for the evaporation modeling (including Tables DR1–DR4 and Figures DR1–DR10) and information on the validation of the experimental setup (including Figure DR11), is available online at [www.geosociety.org/pubs/ft2011.htm](http://www.geosociety.org/pubs/ft2011.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

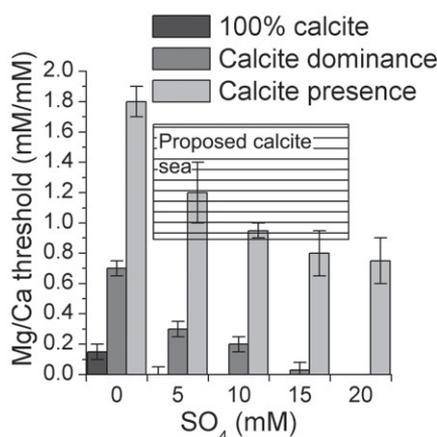


**Figure 1. Polymorph distribution as a function of solution chemistry; closed symbols represent dominant CaCO<sub>3</sub> polymorph as measured in current study; open symbols represent previous research (Doner and Pratt, 1969, 26 °C; Lee and Morse, 2010, 23 °C; Morse et al., 1997, 20 °C; Simkiss, 1964, 22 °C with an increase to 28 °C); diagonally shaded area highlights Mg/Ca and SO<sub>4</sub> field where calcite was present in solid phase after 48 h between 0% and 50%; horizontally shaded area represents proposed calcite sea concentrations (Horita et al., 2002); and dashed horizontal line represents switch from KCl to MgSO<sub>4</sub> evaporites (Lowenstein et al., 2003) as determined from PHREEQC evaporite simulations.**

when aragonite becomes dominant over calcite (Table 1). This suggests that the stability of the CaCO<sub>3</sub> polymorphs is marked by its dominance field in Figure 1.

When the SO<sub>4</sub> concentration in calcite (Table 1) increased, there was an anisotropic change in the calcite unit cell parameters (1.5 mol% SO<sub>4</sub> incorporation caused the *c*-axis to increase by 0.22% and the *a*-axis to decrease by 0.035%). This is indicative of the substitution of tetrahedral SO<sub>4</sub> for planar CO<sub>3</sub> ions in calcite (Kontrec et al., 2004). Hence, changes in pH or alkalinity will affect the incorporation of SO<sub>4</sub> into the calcite structure (Busenberg and Plummer, 1985). The change in the calcite structure by SO<sub>4</sub> incorporation caused calcite solubility to increase (Busenberg and Plummer, 1985) and is likely to have decreased the calcite precipitation rate relative to aragonite (Walter, 1986). Incorporation of SO<sub>4</sub> into aragonite was ~2–4 times lower compared to calcite (Table 1). Furthermore, SO<sub>4</sub> had little effect on the aragonite structure (1.5 mol% SO<sub>4</sub> incorporation caused the *c*-axis to increase by ~0.07% and the *b*-axis to increase by ~0.02%) compared to calcite. This demonstrates that SO<sub>4</sub> influenced the stability of aragonite less than calcite, causing aragonite to become more stable than calcite. This explains the precipitation of aragonite instead of calcite at lower Mg/Ca in the presence of SO<sub>4</sub> (e.g., Mg/Ca = 0.9 at 10 mM SO<sub>4</sub>; Fig. 1).

SO<sub>4</sub> incorporation into vaterite (a rare and unstable CaCO<sub>3</sub> mineral) did not significantly affect the unit cell parameters of vaterite. This indicates that the precipitation of vaterite in the presence of SO<sub>4</sub> and absence of Mg (Table 1; Fig. 2; Doner and Pratt, 1969; Simkiss, 1964) was likely to be caused by a positive effect of SO<sub>4</sub> on the stability of vaterite (Fernández-Díaz



**Figure 2. Mg/Ca thresholds for 100% calcite, calcite dominance, and presence; error bars are estimated from Figure 1, and horizontally shaded area represents proposed calcite sea chemistry (Horita et al., 2002).**

et al., 2010) relative to calcite. Mg incorporation into vaterite (Table 1) caused a significant decrease in the unit cell parameters (0.3 mol% Mg decreased the *a*-axis by 0.06% and the *c*-axis by 0.03%), while it did not affect the SO<sub>4</sub> incorporation. Vaterite inhibition at aqueous Mg/Ca ≥ 0.2 is likely to be due to the changes in the vaterite structure caused by Mg incorporation.

**IMPLICATIONS FOR PHANEROZOIC SEAWATER CHEMISTRY**

The mineralogical and morphological data indicate that SO<sub>4</sub> exerted a significant influence on CaCO<sub>3</sub> polymorphs (Fig. 1; Fig. DR11). In contrary to previous experimental work, the current study used constant solution compositions (e.g., pH, [Ca<sup>2+</sup>]) and a precipitation mechanism

that mimicked ooid formation to give a good representation of abiotic calcium carbonate formation in Phanerozoic seawater (see GSA Data Repository). Our data show that SO<sub>4</sub> needs to be incorporated into the models relating Phanerozoic seawater chemistry with the switch from calcite to aragonite seas. PHREEQC evaporation simulations using input solutions in the experimental range predicted a switch between KCl and MgSO<sub>4</sub> evaporites (coincident to CaCl<sub>2</sub> and MgSO<sub>4</sub> seas and calcite and aragonite seas; Hardie, 1996; Lowenstein et al., 2003) at ~9 mM SO<sub>4</sub>, regardless of the aqueous Mg/Ca (Fig. 1; Figs. DR1–DR8; Table DR1). This SO<sub>4</sub> concentration, combined with experimental results, indicates that the thresholds for calcite presence are within the lower range of the proposed calcite seawater concentrations (e.g., at 9 mM SO<sub>4</sub>, Mg/Ca < ~1.1; Fig. 2). However, the primary CaCO<sub>3</sub> mineralogy during calcite and aragonite seas was rarely exclusively calcite or aragonite (Wilkinson et al., 1985; Zhuravlev and Wood, 2009). We therefore propose that the thresholds for calcite seas are better represented by calcite dominance (e.g., at 5 mM SO<sub>4</sub>, Mg/Ca < ~0.3; Fig. 2). The thresholds for calcite dominance do not overlap with the previously proposed seawater concentrations determined from halite fluid inclusions (Fig. 2; Horita et al., 2002; Lowenstein et al., 2003), but they are in agreement with SO<sub>4</sub> concentrations inferred from δ<sup>34</sup>S isotope records from the Early Jurassic (<5 mM) and Cretaceous (<4 mM) (Newton et al., 2011; Wortmann and Chernyavsky, 2007). The Mg/Ca threshold is also compatible with Mg/Ca ratios from abiotic CaCO<sub>3</sub> minerals from the early Mississippian calcite sea of 0.2–0.3 (Hasiuk and Lohmann, 2008). Finally, the thresholds for the precipitation of 100% calcite (e.g., at 3 mM SO<sub>4</sub>, Mg/Ca < ~0.15; Fig. 2) are unrealistic for seawater; therefore, it is highly unlikely that a pure calcite sea could have formed. The calcite threshold we propose (calcite dominance; Fig. 2) demonstrates that either the primary CaCO<sub>3</sub> mineralogical information from ancient ooids needs reevaluation or that Mg/Ca and SO<sub>4</sub> concentrations were much lower than proposed from halite fluid inclusions as indicated by recent studies (Hasiuk and Lohmann, 2008; Newton et al., 2011; Wortmann and Chernyavsky, 2007).

PHREEQC simulations using Phanerozoic seawater solutions (Horita et al., 2002) revealed a large difference between the switch from KCl to MgSO<sub>4</sub> evaporites (Mg/Ca ≈ 1.9 and SO<sub>4</sub> ≈ 19 mM; Table DR2; Figs. DR9–DR10) and the calcite thresholds (Fig. 2). One explanation is that the KCl and MgSO<sub>4</sub> evaporite types only seem to coincide with the calcite and aragonite seas, respectively, due to low time resolution of the mineralogical records. We could therefore predict that higher-resolution records will reveal

that the switches in evaporites and  $\text{CaCO}_3$  mineralogy are sequential rather than coincident. As shown previously herein, PHREEQC simulations using the experimental solutions did not reveal such a difference. Hence, the absolute Ca and Mg concentrations could have been lower than currently proposed for the calcite seas. Lower absolute Ca and Mg concentrations are not unlikely, because the high concentrations for calcite seas (as proposed from halite fluid inclusions) result from assumptions that the gypsum saturation state did not change significantly (Horita et al., 2002). In addition, PHREEQC modeling indicates that from different starting compositions (i.e., Ca concentrations), equivalent final invariant solutions and similar evaporite sequences are obtained (e.g., simulation runs 14 and 20 in Tables DR1 and DR2).

Our work demonstrates that current seawater chemistry models cannot explain the distribution of inorganic marine carbonate minerals throughout the Phanerozoic. We propose new and lower limits on seawater chemistry during the calcite seas (e.g., at 5 mM  $\text{SO}_4$ , Mg/Ca < ~0.3; Fig. 2) as a result of inclusion of  $\text{SO}_4$  and use of a more representative experimental approach combined with geochemical modeling on evaporite formation. These new limits require reevaluation of the geological evolution of important biogeochemical cycles (Ca, Mg, and S) and their relationship to primary  $\text{CaCO}_3$  mineralogy.

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