

THE INFLUENCE OF ALKALINITY AND $p\text{CO}_2$ ON CaCO_3 NUCLEATION FROM
VARIABLE COMPOSITION PHANEROZOIC SEAWATER

A Thesis

by

JANIE LEE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2008

Major Subject: Oceanography

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Approved by:

Chair of Committee,	John Morse
Committee Members,	Niall Slowey
	Ethan Grossman
Head of Department,	Piers Chapman

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ABSTRACT

The Influence of Alkalinity and $p\text{CO}_2$ on CaCO_3 Nucleation from Variable Phanerozoic Seawater. (December 2008)

Janie Lee, B.S., Texas A&M University

Chair of Advisory Committee: Dr. John Morse

There is strong evidence that variations in seawater chemistry occurred during the Phanerozoic Eon. Of particular importance are the changes in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio because they have been attributed to the oscillations between “calcite” and “aragonite seas” over time. In addition to the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio variations, there were also major changes in $p\text{CO}_2$ levels and alkalinity that could also affect the calcium carbonate (CaCO_3) polymorph that precipitates from seawater.

Experiments were conducted in seawater where the initial alkalinity and $p\text{CO}_2$ levels were varied and then slow degassing of CO_2 resulted in a gradual increase of saturation state with respect to CaCO_3 and eventually nucleation. The pH was continually monitored throughout the experiments and it was used in combination with the initial alkalinity to calculate the $p\text{CO}_2$ and saturation state of aragonite (Ω_{arag}) at the time of nucleation. The morphology and mineralogy of the precipitates were determined using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis, respectively.

It was observed that the initial alkalinity greatly affected the nucleation $p\text{CO}_2$ value and the CaCO_3 polymorph that was precipitated. In seawater with $\text{Mg}^{2+}/\text{Ca}^{2+}=1.2$ and ~ 10 mM alkalinity and a $p\text{CO}_2$ below $2,500 \mu\text{atm}$, calcite that was overgrown with aragonite was the dominate polymorph nucleated, while pure aragonite precipitated when the $p\text{CO}_2$ was above $2,500 \mu\text{atm}$. Seawater with $\text{Mg}^{2+}/\text{Ca}^{2+}=1.2$ and a wide range of initial alkalinities (5-50 mM) produced variable results. Seawater with $\text{Mg}^{2+}/\text{Ca}^{2+}=1.7$ produced only aragonite at lower alkalinities, but calcite was nucleated when the alkalinity and $p\text{CO}_2$ values were exceptionally high, typically above 11 mM. These results point to the need to also consider the effects of the carbonic acid system in the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ region of about 1 to 2 for “calcite seas” and “aragonite seas” at various times throughout the Phanerozoic Eon.

DEDICATION

This is dedicated to Mom, Dad, Kyle and Kathlyn. Without you I would not be who I am today or where I am in life. Thank you for always being there for me and putting up with me. I am forever grateful to you and feel blessed to call you family.

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1. INTRODUCTION

Before the late twentieth century, the long standing consensus in the scientific community was that the chemical composition of seawater had not varied significantly for at least the last 500 million years (Ma), but instead had remained close to its present day composition, with the dominant ions being Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- (Holland, 1984; Lowenstein et al., 2001; Tyrrell and Zeebe, 2004). However, marine oöids and cements indicate that there were oscillations between “calcite seas” and “aragonite seas” by preserving the record of deposition of abiotic calcium carbonate (CaCO_3) minerals throughout the Phanerozoic Eon (Fig. 1) (Sandberg, 1983). The periods of oscillations between “calcite seas” and “aragonite seas” occur on about 100-200 Ma time scales (Hardie, 1996; Timofeeff et al., 2006).

Based on experimental studies, it has been hypothesized that marine oöids and cements document changes in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater over geologic time. It has been suggested that “calcite seas” are the result of significantly lower $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios at various times during the past than present day seawater which exhibits higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios and “aragonite seas” dominate (Horita et al., 2002; Mackenzie and Pigott, 1981; Palmer et al., 1988; Tyrrell and Zeebe, 2004; Wilkinson and Given, 1986). Changes in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio throughout time may be the result of removal of calcium from the ocean, which is removed at a much faster rate than magnesium (Sandberg, 1975).

This thesis follows the style of *Geochimica et Cosmochimica Acta*.

In addition to documenting the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios it is believed that changes in oöid mineralogies may reflect changes in carbon dioxide (CO_2) levels throughout time (Mackenzie and Pigott, 1981; Palmer et al., 1988).

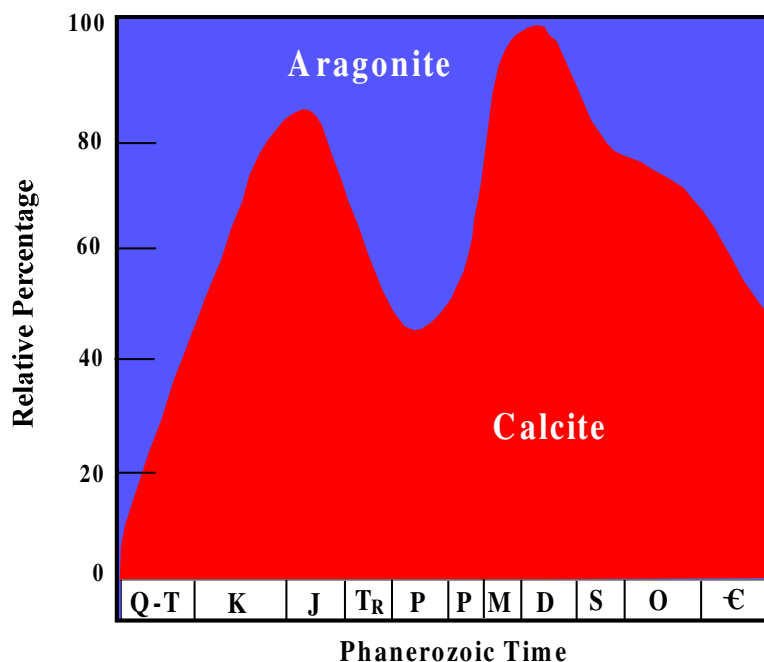


Figure 1. The trend in oöid mineralogies during the Phanerozoic Eon (Mackenzie and Lerman, 2006).

Studies of fluid inclusions in halite from marine evaporites have led to at least semi-quantitative estimates of seawater composition during the Phanerozoic Eon (Fig. 2), which support the hypothesis that oscillations between “calcite” and “aragonite seas” are associated with substantial changes in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater (Fig. 3) (Horita et al., 2002; Timofeeff et al., 2001). These studies also indicate that SO_4^{2-} co-varied with Mg^{2+} and that Ca^{2+} varied in an inverse manner from Mg^{2+} . It is also

believed that K^+ has remained close to constant (Hardie, 1996; Horita et al., 2002; Timofeeff et al., 2006; Tyrrell and Zeebe, 2004). It has been found that the Late Precambrian, Permian, Tertiary, and present day seawaters exhibit higher Mg^{2+}/Ca^{2+} ratios with a present day seawater Mg^{2+}/Ca^{2+} ratio of about 5 (Berner, 1975, Lowenstein et al., 2001). The Cambrian, Silurian, and Cretaceous seawaters have lower Mg^{2+}/Ca^{2+} ratios and it is thought that Cretaceous seawater had the lowest Phanerozoic Mg^{2+}/Ca^{2+} ratio, estimated at about 1 (Hardie, 1996; Lowenstein et al., 2001; Timofeeff et al., 2006).

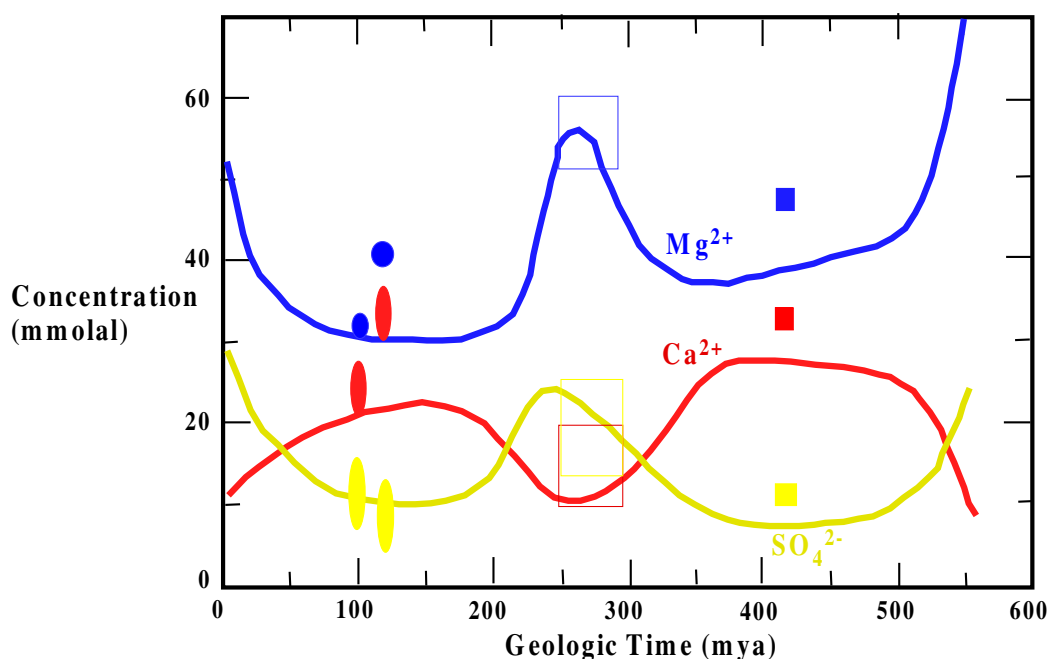


Figure 2. The variation of the three major seawater ion concentrations during the Phanerozoic Eon to present. Solid lines are based on the summary of data from fluid inclusions in marine evaporites (Horita et al., 2002). Circular symbols represent Cretaceous (Timofeeff et al., 2006), open squares represent Permian (Lowenstein et al., 2005) and solid squares represent Silurian (Brennan and Lowenstein, 2002) fluid inclusions.

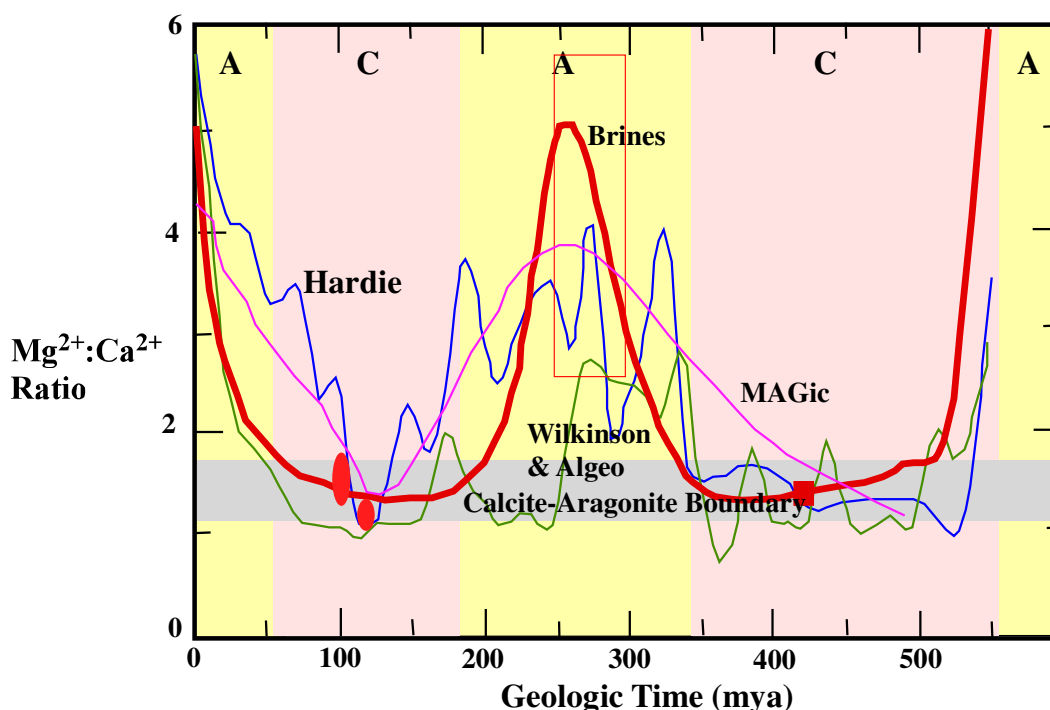


Figure 3. Estimated variations in the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater over the Phanerozoic Eon to present. The heavy red line and red symbols are based on marine evaporite fluid inclusions as discussed in Figure 2. Examples of model results from Wilkinson and Algeo (1989), Hardie (1996) and MAGic (Arvidson et al., 2006) are also shown. **A** indicates “aragonite seas” and **C** indicates “calcite seas” (Hardie, 1996). The calcite-aragonite grey horizontal boundary is based on the experimental studies for carbonate mineral nucleation from seawater between 20 °C and 30 °C of Morse et al. (1997).

The changes in seawater chemistry throughout geologic history have widely been attributed to mid-ocean ridge (MOR) hydrothermal brine fluxes driven by seafloor spreading (Horita et al., 2002; Lowenstein et al., 2001). The mid-ocean ridges serve as a fluid exchange system for Mg^{2+} , SO_4^{2-} and Ca^{2+} . Mg^{2+} and SO_4^{2-} are incorporated into the rock and Ca^{2+} is released into the water. It is believed that low spreading rates yield higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios and faster spreading rates yield lower $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios (Stanley and Hardie, 1999). Seawater-driven dolomitization and biological evolution are also

believed to contribute to the changes in the major ions in seawater, although to a much lesser extent (Horita et al., 2002; Lowenstein et al., 2001). There were also considerable sea level variations during the Phanerozoic Eon associated with plate tectonics and the changes in mid-ocean ridges (Mackenzie and Pigott, 1981). These predictions are important because aragonite dominates during low sea level stands and calcite dominates during high sea level stands (Wilkinson and Given, 1986). Changes in sea level are attributed to seafloor spreading at MORs. Rapid seafloor spreading rates are indicative of large MOR volumes and therefore high sea level stands whereas slow spreading rates are associated with smaller MOR volumes and low sea level stands (Holland, 2005).

Changes in atmospheric CO₂ levels throughout time have also been hypothesized to contribute to changes in carbonate mineralogy (Mackenzie and Pigott, 1981). For example, Wilkinson and Given (1986) suggested that elevated $p\text{CO}_2$ levels in the Phanerozoic Eon should correspond to lower carbonate (CO₃²⁻) concentrations making calcite the dominate polymorph. However, more recent models, such as MAGic (Arvidson et al., 2006), indicate that this does not occur due to elevated alkalinity in some instances. Dissolved inorganic carbon (DIC) and alkalinity are very similar; therefore DIC can be used as approximation for alkalinity in the graph of higher $p\text{CO}_2$ below (Fig. 4).

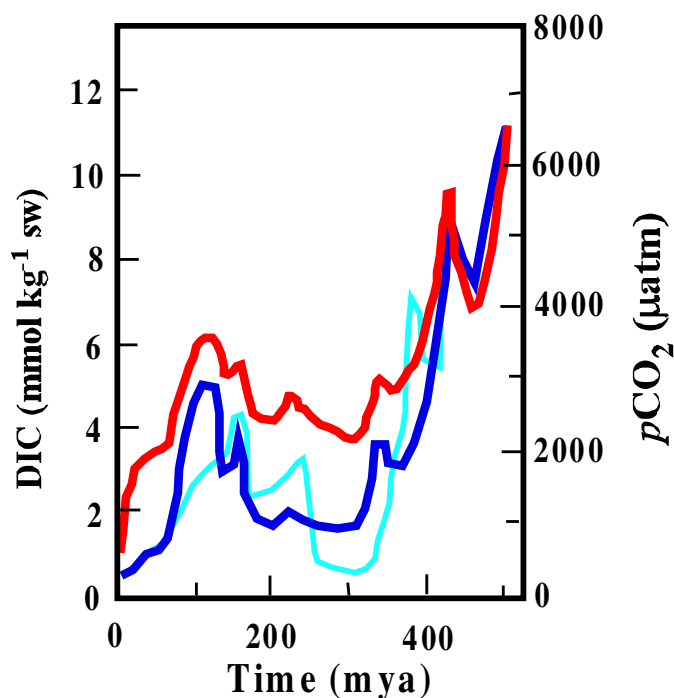


Figure 4. Changes in dissolved inorganic carbon (DIC) and $p\text{CO}_2$ during the Phanerozoic Eon. DIC is represented by the heavy red line (Arvidson et al., 2006) and MAGic model $p\text{CO}_2$ estimates by the heavy dark blue line (Arvidson et al., 2006) and the GEOCARB III model $p\text{CO}_2$ estimates by the thinner light blue line (Berner and Kothavala, 2001).

The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater is very important in determining the fate of CaCO_3 in seawater. This ratio determines the specific CaCO_3 polymorph, calcite versus aragonite, that is precipitated from seawater (Given and Wilkinson, 1985). The general scientific consensus has been that the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio for aragonite versus calcite nucleation is about 2 with aragonite precipitating above 2 and calcite precipitating below 2 (Given and Wilkinson, 1985; Hardie, 1996; Lowenstein et al., 2001; Stanley and Hardie, 1999). Though calcite is generally precipitated in seawater with low $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios at normal seawater temperatures, it was found that at low

temperatures ($< \sim 8^\circ\text{C}$) calcite can nucleate from seawater when the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio is high (Morse et al., 1997).

The supersaturation of seawater with respect to CaCO_3 plays an important role in determining whether CaCO_3 precipitates from seawater as well as what polymorph precipitates (Berner, 1975). Precipitation of carbonates in seawater occurs when the water is very supersaturated and as such requires seawater to have higher pH values and/or higher alkalinities than expected of normal seawater (Berner, 1975; Pytkowicz, 1973). Aragonite is formed in water that is favorable for rapid precipitation. Rapid degassing of CO_2 leads to high degrees of supersaturation in seawater. As the CO_2 degassing rate increases so does the CO_3^{2-} concentration and therefore aragonite precipitation. Lower CO_3^{2-} concentrations in seawater produce calcite (Given and Wilkinson, 1985).

The objective of this research was to significantly improve our understanding of CaCO_3 nucleation in synthetic seawater whose composition is representative of that found during periods of “calcite seas” in the Phanerozoic Eon. These seawaters differ significantly from the composition of present day seawater, especially the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios and SO_4^{2-} concentration, as well as having higher $p\text{CO}_2$ and alkalinity values (Arvidson et al., 2006; Horita et al., 2002; Lowenstein et al., 2001; Tyrrell and Zeebe, 2004; Zeebe, 2001). Advancing knowledge in this area is important because it provides a basis for understanding “calcite seas” versus “aragonite seas”, and the co-evolution of carbonates and seawater during the Phanerozoic Eon. This is relevant to current changes in seawater chemistry associated with ocean acidification because it improves our

understanding of how organisms may have responded to the chemical evolution of seawater through time (Morse, 2008). Additionally it is important for modeling geochemical cycles, determining the impact of changes in CO₂ over time, and may be used to reconstruct ocean chemistry and other paleorecords (Morse and Arvidson, 2002; Paytan and De La Rocha, 2005).

2. METHODS

Calcium carbonate (CaCO_3) nucleation experiments were conducted in “aragonite sea” seawater, which represents present day seawater, and synthetic “calcite sea” seawater, which represents ancient seawater. The “calcite seas” seawater was synthesized so that it was of estimated composition from the Albian stage of the Cretaceous period (99 – 112 Ma), based on the estimates of Horita et al. (2002, see Introduction, Table 1). This seawater had an estimated $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 1.2. Further experiments were conducted in altered synthetic Albian seawater that had a higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 1.7, which was achieved by increasing the Mg^{2+} concentration and decreasing the Ca^{2+} concentration. This was done to see if calcite could be nucleated at this higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio. The Na^+ concentration in the synthetic seawaters was adjusted such that they matched the ionic strength of the salinity of natural seawater, which is 35. Titrations were performed to determine the Mg^{2+} , Ca^{2+} , Cl^- , and total alkalinity (TA) for characterization of the seawater (APHA et al., 1992; Grasshoff et al., 1999; Midgley and Torrance, 1991; Millero and Sohn, 1992; Schwarzenbach and Flaschka, 1969). All pH readings were measured on the NBS scale. The saturation state of the seawaters with respect to calcite and aragonite (Ω_{cal} and Ω_{arag}) and $p\text{CO}_2$ were calculated using the Pitzer equation method of Morse and He (1993).

Table 1. Estimated composition and related parameters of “calcite seas” during the Albian stage of the Cretaceous period. Data is based on Horita et al. (2002) and Arvidson et al. (2006). pH and Ω_{arag} ($\Omega_{\text{cal}} = \Omega_{\text{arag}}/1.51$ equaling ~ 13) were calculated using the Pitzer equation program of Morse and He (1993). The ratio of $p\text{CO}_2$ values was based on the modern preindustrial value and the Albian value estimated in the MAGic model (Arvidson et al., 2006).

Parameter	Albian Value	% Mod SW S = 35
Na^+ (mM)	425	86
K^+ (mM)	11	100
Mg^{2+} (mM)	42	58
Ca^{2+} (mM)	36	214
Cl^- (mM)	565	100
SO_4^{2-} (mM)	9	39
DIC (mM)	6	132
$p\text{CO}_2$ (μatm)	2800	1000
pH	7.9	$\Delta = 0.2$
Ω_{arag}	19	5.3x
$\text{Mg}^{2+}/\text{Ca}^{2+}$	1.2	23

Nucleation experiments were conducted following the method of Morse et al. (1997) in which CO_2 is initially bubbled through the seawater to prevent nucleation while alkalinity is raised to the desired level. Subsequently, the $p\text{CO}_2$ is lowered which raises the seawater saturation state until nucleation of CaCO_3 occurs. In this study, differing initial alkalinity values were used resulting in widely differing values of $p\text{CO}_2$ and Ω_{arag} at the time of nucleation. The bubbling rate was also varied over a wide range, including no bubbling at all, to determine if the rate of change in saturation state affects the final results. Experiments were run at room temperature, approximately 23°C .

During the experiments, the pH of the seawater was constantly monitored by computer, via a specially written LabView program, in order to determine when nucleation occurred. The nucleation pH, in combination with the known initial alkalinity, made it possible to calculate the prenucleation Ω_{cal} and Ω_{arag} and $p\text{CO}_2$ values.

After nucleation, the precipitate was collected on filter paper, oven dried at approximately 80°C, and a subsample was sent for X-ray diffraction (XRD) analysis on a Bruker D-8 high resolution X-ray powder diffractometer, in the Chemistry Department at Texas A&M University. This allowed for the determination of the mineralogy and the approximate calcite to aragonite molar ratio based on relative peak heights. Standards with known percentages of calcite and aragonite were mixed and sent for XRD analysis to be used as a check on the XRD results of the subsamples. The morphology of the precipitate of selected samples was examined using a JEOL JSM-6400 scanning electron microscope (SEM) at the Microscopy and Imaging Center at Texas A&M University. Using SEM to determine the morphology of the precipitates was a way of ensuring that other forms of CaCO_3 , such as vaterite, did not precipitate when they were not expected to. The morphology of calcite and aragonite are very different and the differences are easily seen in SEM images. Calcite takes the form of blocky rhombs and aragonite takes the form of radial needles. XRD and SEM analyses were run as a check on the results that each method gave.

3. RESULTS

The results of the nucleation experiments and associated calculated parameters are summarized in Table 2.

Table 2. Seawater nucleation experiment results.

Solution	TA (mM)	pH (NBS)	Ω_{cal}	Ω_{arag}	pCO_2 (μatm)	Time (h)	% Calcite
Modern	11.1	8.38	33	22	1,117	5	0
Seawater	11.9	8.59	49	34	614	3	0
Mg:Ca = 5.1	11.8	8.64	51	35	523	3	0
Ca = 0.0104m	11.7	8.63	50	35	526	6	0
	11.7	8.60	48	33	583	3	0
	11.9	8.57	47	32	667	3	0
	12.0	8.49	42	29	864	27	0
	11.8	8.35	33	23	1,274	14	0
	11.7	8.47	40	27	887	5	0
	12.3	8.32	33	23	1,455	16	0
Ancient	10.0	8.07	51	35	2,376	1	29
Seawater	10.4	8.08	53	37	2,444	4	25
Mg:Ca = 1.2	9.8	7.85	32	22	4,135	7	0
Ca = 0.0314m	10.7	8.05	52	36	2,714	2	0
	10.2	8.17	63	43	1,849	2	38
	10.2	8.01	46	32	2,857	3	0
	49.8	7.38	59	41	67,365	2	8
	6.2	8.20	40	28	1,016	2	0
	5.5	8.38	48	33	544	5	18
	44.7	7.78	127	87	22,721	1	42
	7.8	8.01	35	24	2,187	3	4
	19.1	8.08	98	68	4,485	2	6
	44.6	7.33	47	33	67,866	4	22
	43.6	7.67	98	67	29,211	1	39
	7.7	8.31	61	42	939	3	1
Ancient	9.3	8.07	33	22	2,297	2	0
Seawater	44.6	7.56	55	36	40,174	2	4
Mg:Ca = 1.7	5.1	8.36	30	20	547	6	0
Ca = 0.0224m	10.5	8.04	35	23	2,799	4	0

Nucleation in Present Day Seawater

Before beginning nucleation experiments in the “Albian” seawater, they were first conducted in present day seawater to determine that the experimental technique was sound. The technique was found to be applicable for this study and the results were as expected. The alkalinities for these experiments were between 11 and 12 mM and all runs nucleated and produced a precipitate. Only aragonite precipitated in these experiments, as expected of seawater with higher Mg^{2+}/Ca^{2+} ratios. However, a few experiments were set up to have lower initial alkalinities and they did not nucleate. These results have been omitted from the data table for easier comparison of those runs that did nucleate. These results are in agreement with the earlier work of Morse et al. (1997). The nucleated precipitate’s morphology and mineralogy was determined using both SEM imaging and XRD analysis, respectively.

Nucleation in Albian Seawater at Constant Alkalinity and Mg^{2+}/Ca^{2+} Ratio=1.2

The first experiments were designed to study the changes in pCO_2 , particularly at the time of nucleation, and what polymorph was precipitated for a given alkalinity and a Mg^{2+}/Ca^{2+} ratio of 1.2. In this case, the alkalinity was kept constant around 10 mM, which is deemed reasonable based on, and in accordance with, the estimates from the MAGic model (Arvidson et al., 2006). Supersaturation at nucleation, time to nucleation, and the mineralogy and morphology of the $CaCO_3$ that precipitated were also factors examined to determine what effect, if any, they had on the precipitation of $CaCO_3$.

At a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 1.2 and an initial alkalinity of approximately 10 mM, it was found that the polymorph that precipitates is dependent on the $p\text{CO}_2$. The $p\text{CO}_2$ phase boundary is found to be approximately 2,500 μatm . Below the 2,500 μatm $p\text{CO}_2$ divide, calcite was found to precipitate first followed by overgrowth of aragonite. As discussed by Morse et al. (1997), the aragonite overgrowth is due to a rising $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the solution as Ca^{2+} is removed. Above the 2,500 μatm $p\text{CO}_2$ divide it was found that only aragonite precipitates (Fig. 5). Calcite nucleated at both the highest and lowest supersaturation (Table 2).

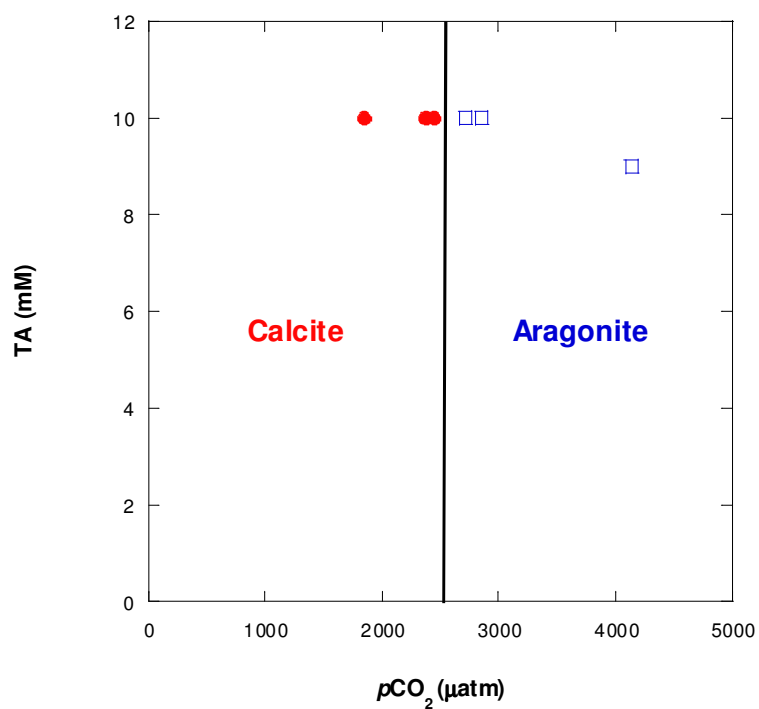


Figure 5. The $p\text{CO}_2$ phase boundary for nucleation of CaCO_3 at an alkalinity of 10 mM and a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.2 based on XRD data.

The time it took for the seawater solution to nucleate and the rate of approach to nucleation, or the bubbling rate, had no observable effect on what polymorph precipitated. However, the bubbling rate determined how fast the solution nucleated. Generally, a slower bubbling rate led to longer nucleation times and a faster bubbling rate caused more rapid nucleation. In addition, it seems the more rapid bubbling rates lead to higher and more variable Ω_{arag} (or Ω_{cal}) values.

To determine CaCO_3 polymorph morphology, precipitate subsamples were analyzed using SEM. The SEM images (Figs. 6, 7) show that the precipitates were either calcite that was overgrown with aragonite or pure aragonite. It was found that samples containing pure aragonite had precipitated at $p\text{CO}_2$ values greater than 2,500 μatm , while the samples that contained calcite overgrown by aragonite were found to have nucleated at $p\text{CO}_2$ values below 2,500 μatm .



Figure 6. SEM images showing the progression of calcite being overgrown by aragonite.

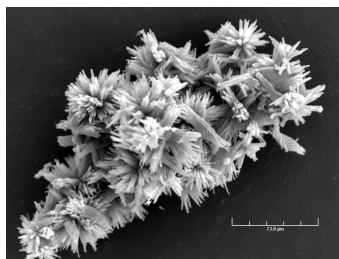


Figure 7. SEM image of pure aragonite.

Nucleation in Albian Seawater with Varied Alkalinity and Mg^{2+}/Ca^{2+} Ratio=1.2

This set of experiments in Albian seawater with a Mg^{2+}/Ca^{2+} ratio=1.2 had alkalinities that varied from approximately 5 mM to 50 mM, excluding 10 mM. There appears to be no correlation between what polymorph precipitates and pCO_2 values as found in the experiments with a constant alkalinity. When the alkalinity was above 40 mM, the pCO_2 always exceeded 20,000 μatm . In this case, calcite was always formed and typically had a higher percentage than those experiments with lower alkalinities and pCO_2 values, with one exception. At alkalinities lower than 10 mM, the pCO_2 as well as the percentage of calcite tended to be more variable. With one exception, in all the variable alkalinity experiments the polymorph that precipitated was calcite overgrown with aragonite. There seems to be no clear pattern as was seen in the constant alkalinity experiments, unless the results are grouped based on high versus low alkalinity. As with the previous experiments, SEM and XRD analyses were performed on precipitate subsamples to determine the morphology and mineralogy.

Nucleation in Albian Seawater with Varied Alkalinity and Mg^{2+}/Ca^{2+} ratio=1.7

In these experiments, the alkalinity was varied between approximately 5 mM to 45 mM. It was found that at lower alkalinities, below 11 mM, and lower pCO_2 values only aragonite precipitated (Fig 8). However, in the sample with extremely high alkalinity, about 45 mM, and a very high pCO_2 value, calcite was observed, which is consistent with the results from the $Mg^{2+}/Ca^{2+}=1.2$ ratio seawater.

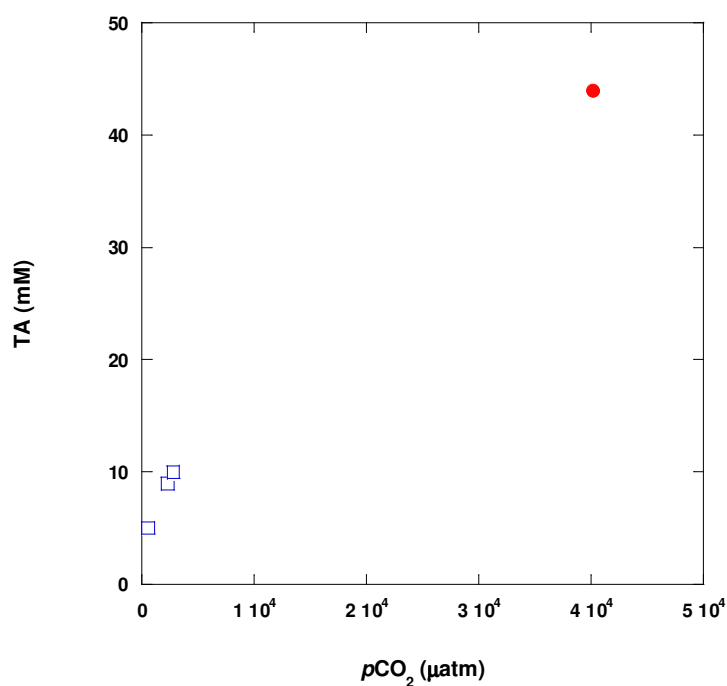


Figure 8. Results of nucleation of $CaCO_3$ at variable alkalinities for a Mg^{2+}/Ca^{2+} ratio of 1.7 based on XRD data. Aragonite is represented by the open blue boxes and calcite is represented by the solid red circle.

4. DISCUSSION

There is some disagreement on the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio for “calcite” versus “aragonite seas”. We believe this to be the result of differing experimental methods as well as how closely actual concentrations of the three major ions, Mg^{2+} , Ca^{2+} , SO_4^{2-} , were best matched to hypothesized values for Phanerozoic seawater. Additionally, how closely alkalinity and $p\text{CO}_2$ values used in previous studies matched with their best estimates for “calcite seas” versus “aragonite seas” compositions can create differing results.

As stated earlier the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio divide has been found to be about 2. Studies have been conducted to further define the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio divide and to determine what other factors affect CaCO_3 nucleation. Morse et al. (1997) varied only the Mg^{2+} concentration for present day seawater at 25°C and found that if the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio is below 1.4 ± 0.1 calcite will be the dominate polymorph precipitated. Below about 8°C Morse et al. (1997) found that even at the present $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 5, calcite could be nucleated. Consequently, the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio is temperature dependent.

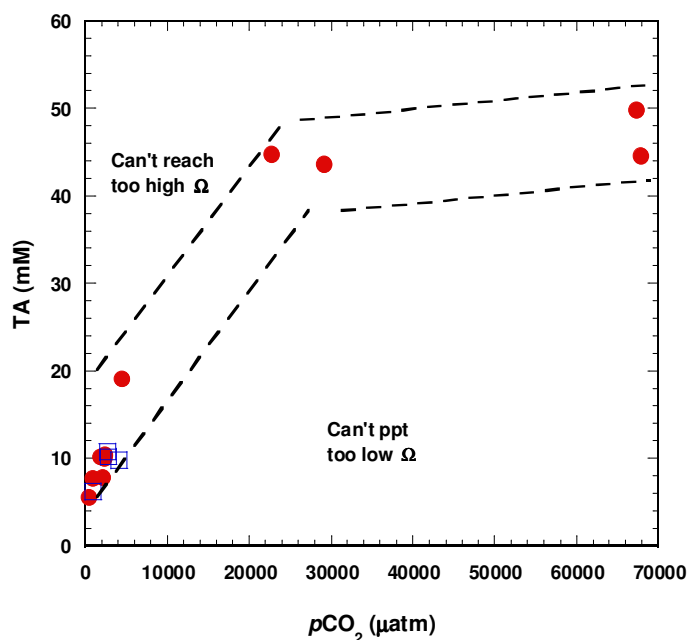
In this study, the temperature was held constant around 23°C but the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio was varied in the “critical” region of 1 to 2 along with initial alkalinity to determine what polymorph precipitates. In the $\text{Mg}^{2+}/\text{Ca}^{2+}=1.2$ seawater it was found that calcite could be precipitated in most but not all experiments. However, in the $\text{Mg}^{2+}/\text{Ca}^{2+}=1.7$ seawater it was more difficult to produce calcite. Therefore, this shows a tendency for

seawater with a lower $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio to produce more calcite than a higher $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio seawater. These results are in good general agreement with the value for the “critical” $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.4 ± 0.1 found by Morse et al. (1997).

In addition to the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio determining which polymorph precipitates from seawater, other factors have been considered in the past but not necessarily together. Morse et al. (1997) confirmed that the large change in $p\text{CO}_2$ levels that was thought to be required to change the precipitated polymorph from calcite to aragonite may be decreased if other parameters are changed, for example alkalinity. In our study, we found that the initial alkalinity and $p\text{CO}_2$ value at which nucleation occurs play significant roles in which polymorph is precipitated from seawater in conjunction with the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio. When looking at the results from both $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio seawaters studied, it is clear that varying the initial alkalinity varied the $p\text{CO}_2$ at which nucleation occurred which resulted in different polymorphs for different experiments.

In our study, the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio=1.2 produced more variable results than the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio=1.7 seawater. For the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.2 when the alkalinity was kept constant at a reasonable ~10 mM (Arvidson et al., 2006), the polymorph that precipitated was found to be dependent on $p\text{CO}_2$ (Fig. 5). However, calcite was almost always present when the alkalinity and $p\text{CO}_2$ values were varied (Fig. 9). Figure 9 clearly shows that as the alkalinity varies, the $p\text{CO}_2$ at which nucleation occurs varies as well. This creates a nucleation boundary in which all the results are confined. In addition to the nucleation boundary, it is also evident that there is a phase boundary at lower alkalinity and $p\text{CO}_2$ values. These results make it difficult to determine whether

this $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio seawater can be called a “calcite” or “aragonite sea”. Although calcite always dominated the high alkalinity experiments the alkalinities used are not believed to be a good representation of ancient seawater.



the aragonite/calcite boundary at a $p\text{CO}_2$ of about 2,200 μatm exhibits only trace (0.8%) calcite. To further define this boundary more experiments need to be run that vary ever so slightly from the trace calcite experiments.

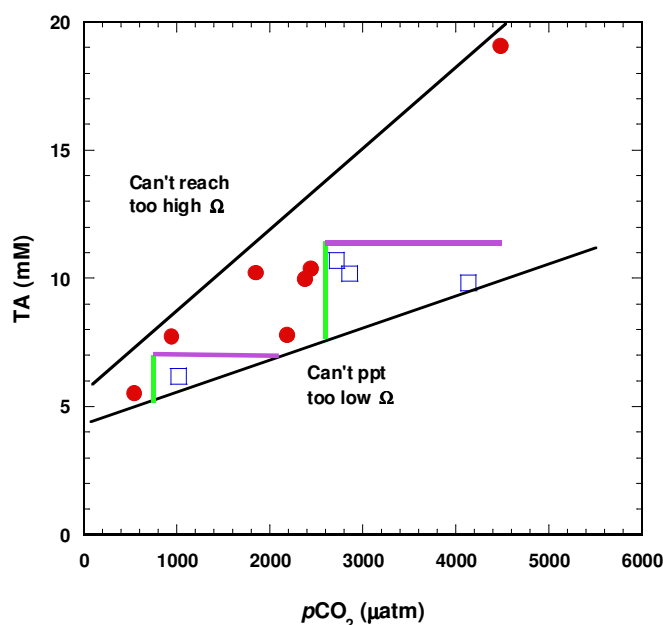


Figure 10. $p\text{CO}_2$ versus total alkalinity below 20 mM for $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.2. Calcite is represented by the solid red circles and aragonite is represented by the open blue boxes.

The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio=1.7 seawater produced only aragonite unless the alkalinity and $p\text{CO}_2$ values were extremely high. Since values of excessive alkalinity and $p\text{CO}_2$ would never be found in the real world, even during those time periods characterized with high alkalinity and $p\text{CO}_2$ values, it is safe to consider that a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio=1.7 be considered an “aragonite sea” ratio. As such this severely, limits the “window” of $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios that can be considered for “calcite seas” and seawater with a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio=2 could be typical of an “aragonite sea”.

When both $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio seawaters are compared at about 10 mM it was found that the $\text{Mg}^{2+}/\text{Ca}^{2+}=1.2$ seawater had a tendency to produced calcite and exhibited a $p\text{CO}_2$ phase boundary. The $\text{Mg}^{2+}/\text{Ca}^{2+}=1.7$ seawater does not show a $p\text{CO}_2$ phase boundary at moderate alkalinities. While there is sufficient data to make these comparisons, the database for $\text{Mg}^{2+}/\text{Ca}^{2+}=1.7$ seawater is limited and should be expanded further.

According to Mackenzie and Pigott (1981), elevated $p\text{CO}_2$ values during the Phanerozoic resulted in lower marine CO_3^{2-} concentrations and calcite being the dominate polymorph precipitated. Given and Wilkinson (1985), Mackenzie and Pigott (1981) and Pigott et al. (1980) state that lowering the $p\text{CO}_2$ levels caused the polymorph to change from calcite to aragonite. This would make seawater with low $p\text{CO}_2$ values “aragonite seas” and seawater with high $p\text{CO}_2$ levels “calcite seas”. We found the opposite to be true for seawater with an alkalinity of 10mM and $\text{Mg}^{2+}/\text{Ca}^{2+}=1.2$. This means that the $p\text{CO}_2$ could be important in determining whether seawater is a “calcite” or “aragonite sea” as it has varied by over an order of magnitude during the Phanerozoic.

When setting up these experiments it was crucial that special attention was paid to the initial alkalinity and $p\text{CO}_2$ values, particularly to whether the values are reasonable when compared to the best estimates of Phanerozoic seawater. Alkalinity and $p\text{CO}_2$ values used should be modeled after published models and experimental studies. It is particularly important to pay attention to what model previous studies have used and to what $p\text{CO}_2$ value that model gives for the Phanerozoic Eon because the variations in each model’s estimated $p\text{CO}_2$ values will determine what polymorph

precipitates for that particular study. In this study the experiments that exhibit reasonable alkalinity and $p\text{CO}_2$ values give variable results on what polymorph is precipitated whereas all experiments that exceed reasonable values produce some percentage of calcite. As discussed earlier, in order to nucleate calcite at reasonable alkalinity and $p\text{CO}_2$ values the seawater must maintain a lower $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio.

5. CONCLUSIONS

The objective of this research was to determine the effect of changes to the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater, initial alkalinity and $p\text{CO}_2$ levels on the polymorph of CaCO_3 that is nucleated from seawater. As a result of this study, we determined that the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio that divides “calcite” and “aragonite seas” is much lower than the previously thought value of approximately 2 and seems to fall somewhere between 1.2 and 1.7. In order to obtain results representative of Phanerozoic times, the initial alkalinity of the seawater was important because it caused variations in the $p\text{CO}_2$ value and thus the polymorph that was precipitated.

If reasonable alkalinities (~ 10 mM) and $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.2 are used in experiments, then the polymorph that was precipitated was dependent on $p\text{CO}_2$. The $p\text{CO}_2$ phase boundary occurred at approximately 2,500 μatm . Lower $p\text{CO}_2$ values precipitated calcite that was overgrown with aragonite whereas higher $p\text{CO}_2$ values resulted in precipitation of pure aragonite. When the alkalinity was variable in seawater with a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.2, the resulting pattern was less clear, but calcite typically was precipitated.

For seawater with a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of 1.7 aragonite was the dominant polymorph precipitated except when the alkalinity and $p\text{CO}_2$ values were unrealistically high, typically above 10 mM. For waters representing “calcite seas,” the $p\text{CO}_2$ values that produced aragonite were higher than those that produced calcite. This was the opposite of what was previously assumed and what is required for “aragonite seas”. As

such this research provides conclusive evidence that the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, initial alkalinity and $p\text{CO}_2$ level are all important in determining whether seawater can be classified as a “calcite sea” or “aragonite sea”.

REFERENCES

- APHA, AWWA, and WEF, 1992. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.
- Arvidson, R. S., Guidry, M., and Mackenzie, F. T., 2006. MAGic: a Phanerozoic model for the geochemical cycling of major rock-forming components. *American Journal of Science* **306**, 135-190.
- Berner, R. A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from seawater. *Geochimica et Cosmochimica Acta* **39**, 489-504.
- Berner, R. A. and Kothavala, Z., 2001. GEOCARB III: a revised model for atmospheric CO₂ over Phanerozoic time. *American Journal of Science* **301**, 182-204.
- Brennan, S. T. and Lowenstein, T. K., 2002. The major-ion compositions of Silurian seawater. *Geochimica et Cosmochimica Acta* **66**, 2683-2700.
- Given, R. K. and Wilkinson, B. H., 1985. Kinetic control of morphology, composition, and mineralogy of abiotic sedimentary carbonates. *Journal of Sedimentary Petrology* **55**, 0109-0119.
- Grasshoff, K., Kremling, K., and Ehrhardt, M., 1999. *Methods of Seawater Analysis*. Wiley-VCH, Weinheim, Germany.
- Hardie, L. A., 1996. Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y. *Geology* **24**, 279-283.
- Holland, H. D., 1984. *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, NJ.
- Holland, H. D., 2005. Sea level, sediments, and the composition of seawater. *American Journal of Science* **305**, 220-239.

- Horita, J., Zimmermann, H., and Holland, H. D., 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. *Geochimica et Cosmochimica Acta* **66**, 3733-3756.
- Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A., and Demicco, R. V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. *Science* **294**, 1086-1088.
- Lowenstein, T. K., Timofeeff, M. N., Kovalevych, V. M., and Horita, J., 2005. The major-ion composition of Permian seawater. *Geochimica et Cosmochimica Acta* **69**, 1701-1719.
- Mackenzie, F. T. and Lerman, A., 2006. *Carbon in the Geobiosphere-Earth's Outer Shell*. Springer, Dordrecht, Netherlands.
- Mackenzie, F. T. and Pigott, J. D., 1981. Tectonic controls of Phanerozoic sedimentary rock cycling. *Journal of Geologic Society of London* **138**, 183-196.
- Midgley, D. and Torrance, K., 1991. *Potentiometric Water Analysis*. John Wiley & Sons Ltd., Chichester, UK.
- Millero, F. J. and Sohn, M. L., 1992. *Chemical Oceanography*. CRC Press, Inc., Boca Raton, FL.
- Morse, J. W., 2008. Personal Communication.
- Morse, J. W. and Arvidson, R. S., 2002. The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Science Reviews* **58**, 51-84.
- Morse, J. W. and He, S., 1993. Influences of T, S and $p\text{CO}_2$ on the pseudo-homogeneous precipitation of CaCO_3 from seawater: implications for whiting formation. *Marine Chemistry* **41**, 291-297.
- Morse, J. W., Wang, Q., and Tsio, M. Y., 1997. Influences of temperature and Mg:Ca ratio on CaCO_3 precipitates from seawater. *Geology* **25**, 85-87.

- Palmer, T. J., Hudson, J. D., and Wilson, M. A., 1988. Palaeoecological evidence for early aragonite dissolution in ancient calcite seas. *Nature* **335**, 809-810.
- Paytan, A. and De La Rocha, C. L., 2005. Editorial: directions in the study of ocean chemistry over the Phanerozoic and its links to geologic processes. *Marine Geology* **217**, 193-197.
- Pigott, J. D., Schoonmaker, J., and Mackenzie, F. T., 1980. Phanerozoic carbonate diagenesis: a new model. *American Association of Petroleum Geologists Bulletin* **64**, 764-765.
- Pytkowicz, R. M., 1973. Calcium carbonate retention in supersaturated seawater. *American Journal of Science* **273**, 515-522.
- Sandberg, P. A., 1975. New interpretations of Great Salt Lake ooids and of ancient non-skeletal carbonate mineralogy. *Sedimentology* **22**, 497-537.
- Sandberg, P. A., 1983. An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. *Nature* **305**, 19-22.
- Schwarzenbach, G. and Flaschka, H., 1969. *Complexometric Titrations*. Methuen & Co Ltd, London.
- Stanley, S. M. and Hardie, L. A., 1999. Hypercalcification: paleontology links plate tectonics and geochemistry to sedimentology. *GSA Today* **9**, 1-7.
- Timofeeff, M. N., Lowenstein, T. K., Brennan, S. T., Demicco, R. V., Zimmermann, H., Horita, J., and Von Borstel, L. E., 2001. Evaluating seawater chemistry from fluid inclusions in halite: examples from modern marine and nonmarine environments. *Geochimica et Cosmochimica Acta* **65**, 2293-2300.
- Timofeeff, M. N., Lowenstein, T. K., da Silva, M. A. M., and Harris, N. B., 2006. Secular variation in the major-ion chemistry of seawater: evidence from fluid inclusions in Cretaceous halites. *Geochimica et Cosmochimica Acta* **70**, 1977-1944.

- Tyrrell, T. and Zeebe, R. E., 2004. History of carbonate ion concentration over the last 100 million years. *Geochimica et Cosmochimica Acta* **68**, 3521-3530.
- Wilkinson, B. H. and Algeo, T. J., 1989. Sedimentary carbonate record of calcium-magnesium cycling. *American Journal of Science* **289**, 1158-1194.
- Wilkinson, B. H. and Given, R. K., 1986. Secular variation in abiotic marine carbonates: constraints on Phanerozoic atmospheric carbon dioxide contents and oceanic Mg/Ca ratios. *Journal of Geology* **94**, 321-333.
- Zeebe, R. E., 2001. Seawater pH and isotopic paleotemperatures of Cretaceous oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology* **170**, 49-57.

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