

# Initial responses of carbonate-rich shelf sediments to rising atmospheric $p\text{CO}_2$ and “ocean acidification”: Role of high Mg-calcites

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## Abstract

Carbonate-rich sediments at shoal to shelf depths (<200 m) represent a major  $\text{CaCO}_3$  reservoir that can rapidly react to the decreasing saturation state of seawater with respect to carbonate minerals, produced by the increasing partial pressure of atmospheric carbon dioxide ( $p\text{CO}_2$ ) and “acidification” of ocean waters. Aragonite is usually the most abundant carbonate mineral in these sediments. However, the second most abundant (typically ~24 wt%) carbonate mineral is high Mg-calcite (Mg-calcite) whose solubility can exceed that of aragonite making it the “first responder” to the decreasing saturation state of seawater. For the naturally occurring biogenic Mg-calcites, dissolution experiments have been used to predict their “stoichiometric solubilities” as a function of mol%  $\text{MgCO}_3$ . The only valid relationship that one can provisionally use for the metastable stabilities for Mg-calcite based on composition is that for the synthetically produced phases where metastable equilibrium has been achieved from both under- and over-saturation. Biogenic Mg-calcites exhibit a large offset in solubility from that of abiotic Mg-calcite and can also exhibit a wide range of solubilities for biogenic Mg-calcites of similar Mg content. This indicates that factors other than the Mg content can influence the solubility of these mineral phases. Thus, it is necessary to turn to observations of natural sediments where changes in the saturation state of surrounding waters occur in order to determine their likely responses to the changing saturation state in upper oceanic waters brought on by increasing  $p\text{CO}_2$ . In the present study, we investigate the responses of Mg-calcites to rising  $p\text{CO}_2$  and “ocean acidification” by means of a simple numerical model based on the experimental range of biogenic Mg-calcite solubilities as a function of Mg content in order to bracket the behavior of the most abundant Mg-calcite phases in the natural environment. In addition, observational data from Bermuda and the Great Bahama Bank are also presented in order to project future responses of these minerals. The numerical simulations suggest that Mg-calcite minerals will respond to rising  $p\text{CO}_2$  by sequential dissolution according to mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain. These results are confirmed by laboratory experiments and observations from Bermuda. As a consequence of continuous increases in atmospheric  $\text{CO}_2$  from burning of fossil fuels, the average composition of contemporary carbonate sediments could change, i.e., the average Mg content in the sediments may slowly decrease. Furthermore, evidence from the Great Bahama Bank indicates that the amount of abiotic carbonate production is likely to decline as  $p\text{CO}_2$  continues to rise.

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## 1. Introduction

The partial pressure of carbon dioxide ( $p\text{CO}_2$ ) in the atmosphere is rising at an increasing rate due to human activities such as burning of fossil fuels. This increase in

atmospheric  $\text{CO}_2$  would be even more rapid if the global ocean were not capable of relatively rapidly acting as a sink for currently about half the “excess”  $\text{CO}_2$  that has been produced by fossil fuel combustion. As the rate of  $\text{CO}_2$  emissions continues to rise, and in turn the oceans take up larger amounts of  $\text{CO}_2$ , there also will be increasing impacts on the chemistry of the oceans and marine life. Among the most important of these impacts on seawater chemistry will be the lowering of the pH and saturation

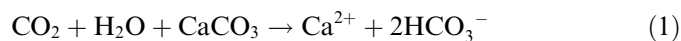
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state of seawater with respect to calcium carbonate minerals, generally referred to as the process of “acidification” of ocean waters (e.g., Kleypas et al., 1999, 2006; Andersson et al., 2005; Orr et al., 2005).

Consequently, considerable attention has been focused on the problem of declining surface seawater carbonate mineral saturation state due to past and future rising atmospheric CO<sub>2</sub> concentrations and the effects on marine calcifying organisms. It has been shown in experimental situations for both single calcifying species of corals, foraminifera, coccolithophores, and coralline algae and carbonate communities that as seawater carbonate saturation decreases, the rate of calcification decreases (see for example Gattuso et al., 1999; Riebesell et al., 2000; Langdon et al., 2000; Orr et al., 2005). These results, along with the predicted rising temperatures of the future and other stresses, suggest the potential of devastating effects on coral reef and other carbonate ecosystems (Kleypas et al., 2006), including those currently exposed to cold waters – the “cold-water” carbonates (e.g., Alexandersson, 1979; James and Clarke, 1997). Our knowledge of the effects of ocean acidification on the Mg-calcite calcifiers is limited because of the problems involving the basic thermodynamic and kinetic properties of these phases. For the naturally occurring biogenic phases, only a kinetic “equilibrium”, expressed as an ion activity product (IAP) mainly obtained from the extrapolation of data acquired in dissolution experiments, has formed the foundation for the “solubilities” of these phases.

In addition to reducing biogenic marine carbonate mineral production, the lowered saturation state of seawater will lead to an increase in carbonate mineral dissolution. In fact, the dissolution of carbonate minerals will play an increasing important role in the future in modifying changes to ocean chemistry and the ability of the oceans to take up atmospheric CO<sub>2</sub> (e.g., Garrels and Mackenzie, 1980; Andersson et al., 2003, 2005). Simply put, biogenic carbonate minerals may act as the ocean’s “anti-acid tablet” via the schematic reaction that increases the total alkalinity of seawater:



In considering this reaction, it is important to note that, rather counter intuitively, precipitation of calcium carbonate raises *p*CO<sub>2</sub>, whereas its dissolution lowers it (e.g., Smith, 1985; Frankignoulle et al., 1994; Lerman and Mackenzie, 2005).

Biogenic high (generally taken as >3–4 mol% MgCO<sub>3</sub>; Reeder, 1983; Mackenzie et al., 1983) Mg-calcites have been found to exceed the solubility of aragonite at approximately 12 mol% MgCO<sub>3</sub> (e.g., Bischoff et al., 1983, 1987; Walter and Morse, 1984). In tropical and subtropical shoal and shelf carbonate-rich sediments, most Mg-calcites have >12 mol% MgCO<sub>3</sub> (Chave, 1954), and thus are presumably the most soluble metastable carbonate minerals in contact with relatively shallow ocean water. They have consequently been widely considered to likely be the ocean’s “first

responders” to a falling saturation state associated with increasing atmospheric *p*CO<sub>2</sub>.

This paper examines the several major issues that contribute to the complexity, controversy, and mysteries still surrounding the solubility of Mg-calcites and if indeed the concept of thermodynamic solubility is even meaningful for this group of carbonate minerals. In doing so, we caution that this examination is definitely not intended as a comprehensive review of the large number of papers that have been written regarding Mg-calcites (see e.g., Mackenzie et al., 1983; Morse and Mackenzie, 1990). We then use the Mg-calcite solubility discussion to form the foundation for discussion of the chemistry of the shoal-water CO<sub>2</sub>–carbonic acid–carbonate system and ocean acidification in the past and future, using a simple numerical model, laboratory experiments, and observations from what are reasonably representative carbonate-rich sedimentary environments on the Great Bahama Bank and the Bermuda Platform, where we and our associates have been carrying out research on the interactions between sedimentary carbonates and the waters of these areas for decades.

## 2. Mg-calcite solubility and related chemistry

### 2.1. General considerations

Calcite occurs in the marine environment with a wide variety of coprecipitated cationic and anionic components. Most of these components are generally found only at minor-to-trace concentrations (<1 mol%) in calcite and generally exert minor influences on the chemical behavior of the bulk mineral, such as its solubility, reaction kinetics, and surface chemistry. An important exception is Mg<sup>2+</sup> which is found to occur in both biogenic and abiotic marine calcites over a wide range of concentrations, typically up to about 20 mol% MgCO<sub>3</sub> (Fig. 1). Pelagic biogenic calcite, from organisms such as coccolithophores and foraminifera, has <1 mol% MgCO<sub>3</sub>, whereas the calcite in tropical and subtropical carbonate-rich sediments typically averages about 13–15 mol% MgCO<sub>3</sub> (Garrels and Wollast, 1978; Agegian and Mackenzie, 1989), with the magnesium content of specific taxa contributing to the sediments generally decreasing with decreasing sea surface temperature polewards (Chave, 1954). It has become customary to divide marine calcites into low and high Mg-calcites based on a boundary of a few mol% MgCO<sub>3</sub> (~3–4 mol% MgCO<sub>3</sub>), which is representative of the least soluble Mg-calcite phase (e.g., Reeder, 1983; Mackenzie et al., 1983). High Mg-calcites are often denoted simply as Mg-calcite.

It is the general practice, as was done in the preceding paragraph, to consider the Mg(II) in Mg-calcites to be present as MgCO<sub>3</sub>. However, the mineral magnesite (MgCO<sub>3</sub>) does not form at near Earth surface temperatures from aqueous solutions except in highly saline solutions (e.g., Lippmann, 1973). Hydrated forms of MgCO<sub>3</sub>

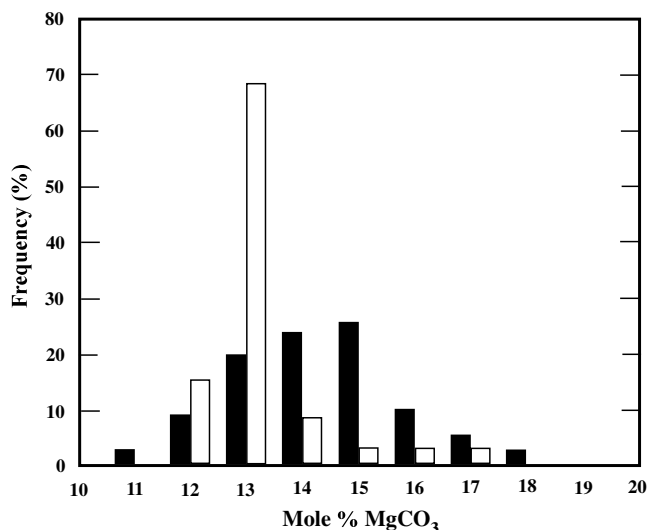


Fig. 1. The relative frequencies of occurrence of calcites containing different mol% MgCO<sub>3</sub> for marine cements (open bars; Morse and Mackenzie, 1990) and mid-depth bank carbonate sands (solid bars; Agegian and Mackenzie, 1989).

precipitate from solution, such as nesquehonite (MgCO<sub>3</sub> · 3H<sub>2</sub>O), hydromagnesite (Mg<sub>4</sub>(CO<sub>3</sub>)<sub>3</sub>(OH)<sub>2</sub> · 3H<sub>2</sub>O), and artinite (Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> · 3H<sub>2</sub>O). The many possible end members for the Mg-calcite solid solutions, in addition to the above minerals, include ordered phases, such as dolomite, proto-dolomite, and huntite (CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub>). This lack of a critical end member has led to extensive theoretical controversy (e.g., Busenberg and Plummer, 1989; Lippmann, 1991; Glynn and Reardon, 1992a,b; Königsberger and Gamsjäger, 1992; Arvidson and Mackenzie, 1999).

The studies of Bischoff et al. (1983, 1985, 1987) and Gaffey (1988) indicated that biogenic calcites, even with low Mg(II) content, contain variable amounts of water and it is possible that H<sub>2</sub>O, and perhaps OH<sup>-</sup>, should be considered additional solid-phase components in biogenic calcites. Raman spectra studies (Bischoff et al., 1985) and dissolution enthalpy measurements (Bischoff, 1998) of Mg-calcites indicate that biogenic Mg-calcites have more carbonate and cation disordering than synthetic Mg-calcites. A further complication is that Mg-calcites derived from at least some organisms, such as red algae (e.g., *Goniolithon*), contain brucite (Mg(OH)<sub>2</sub>) (Moberly, 1968) and, consequently, their Mg content determined by X-ray diffraction can indicate a substantially lower mol% MgCO<sub>3</sub> than that measured by direct chemical analysis (see Walter and Morse, 1984, for discussion). In their extensive review of Mg-calcite chemistry, Morse and Mackenzie (1990; also see Mackenzie et al., 1983; Busenberg and Plummer, 1989), came to the general conclusion that the physical and chemical heterogeneities found in biogenic Mg-calcites *a priori* exclude them from being good materials for the study of the thermochemical properties of Mg-calcite.

## 2.2. Mg-calcite solubility

### 2.2.1. The kinetic experimental method and the stoichiometric solubility product

With the exception of the precipitation experiments of Mucci and Morse (1984), Mg-calcite solubility has been measured by a rather unconventional technique. This technique is not based on obtaining a true equilibration between a given Mg-calcite and a solution, which is rarely or probably never attained in the natural environment or under laboratory conditions. It is based on an extrapolation of the concentrations of dissolved components of the dissolution to an ion activity product (IAP) calculated at infinite time at which the rate of change of the concentrations of the components approaches zero (see Garrels et al., 1960; Plummer and Mackenzie, 1974 for methodology). A particularly vexing problem for Mg-calcite solubility studies in dilute solutions is that the solution will become supersaturated with respect to a calcite phase with low Mg-content, which will start to precipitate, while the high Mg-calcite continues to dissolve (Plummer and Mackenzie, 1974; Fig. 2). To overcome this problem, data from the congruent step of the reaction is extrapolated to infinite time, making the assumption that this represents equilibrium for the solid solution. The validity of the method has been intensely debated because it considers congruent dissolution of Mg-calcite as a one-component phase or a phase of constant composition while in fact it is at least a two-component phase forming a partial solid solution series (Thorstenson and Plummer, 1977; Lafon, 1978; Garrels and Wollast, 1978; Morse and Mackenzie, 1990). The extrapolation of experimental data contains many other potential theoretical and practical pitfalls that increase with the distance between the experimental solution compositions reached and the extrapolated equilibrium solution compositions (e.g., Lafon, 1978; Garrels and Wollast, 1978; also see recent discussion of “kinetic solubility” by Gledhill and Morse, in press).

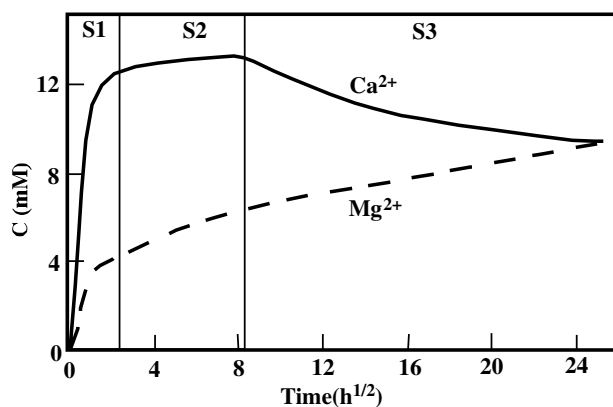


Fig. 2. The evolution of Ca<sup>2+</sup> and Mg<sup>2+</sup> during the dissolution of *Amphiroa rigida* in pure water. S1, congruent dissolution; S2, incongruent dissolution; S3, less Mg-rich calcite starts to precipitate while *Amphiroa rigida* continues to dissolve. (After Plummer and Mackenzie, 1974.)

Although other formulations have been proposed, the generally used convention for expressing the solubility of Mg-calcites containing a mole fraction  $x$  of Mg-carbonate ( $\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$ ) is to use a *stoichiometric solubility product*  $K_{\text{Mg-cal}}$  that is defined (Thorstenson and Plummer, 1977) as ( $a_i$  is activity of species  $i$ ; note the more common usage of the term *stoichiometric solubility product* uses concentrations not activities and unfortunately some authors compare these with the IAP values):

$$K_{\text{Mg-cal}} = a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} a_{\text{CO}_3^{2-}} \quad (2)$$

A major problem is that although this approach fixes the cation activity product ( $P_x$ ; Eq. (3)) to a constant value that depends directly on the solubility product to carbonate ion activity ratio, the cation activity ratio ( $R_{\text{cat}}$ , Eq. (4)) is not fixed for a given value of  $P_x$ , but will vary as a function of either calcium activity (Eq. (4)) or magnesium activity.

$$P_x = a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} = \frac{K_{\text{Mg-cal}}}{a_{\text{CO}_3^{2-}}} \quad (3)$$

$$R_{\text{cat}} = \frac{a_{\text{Mg}^{2+}}}{a_{\text{Ca}^{2+}}} \neq \text{constant} = \left( \frac{P_x}{a_{\text{Ca}^{2+}}} \right)^{1/x} \quad (4)$$

This leads to the impossible situation where a solid, with a fixed cation ratio  $x$ , can be in equilibrium with solutions with widely ranging values of  $R_{\text{cat}}$  that depend on the calcium, or magnesium, and carbonate ion activities. This clearly violates the concept of microscopic reversibility and is a fundamental problem with the use of stoichiometric solubility products to estimate the saturation state of waters with respect to Mg-calcites, which cannot be in exchange equilibrium with the solution (see Morse and Mackenzie, 1990, for discussion). To put this another way, for a given set of temperature, pressure, and solution composition conditions, only a single value of the  $\text{MgCO}_3$  content of calcite can be in equilibrium with a solution of a given magnesium to calcium ion activity ratio. Based on numerous precipitation experiments, in seawater where the magnesium to calcium activity ratio is  $\sim 5$ , the equilibrium mol%  $\text{MgCO}_3$  in calcite is about  $8 \pm 1$  (e.g., Berner, 1978; Mucci and Morse, 1984; Morse and Mucci, 1984; Mucci et al., 1985; Zhong and Mucci, 1989; Hartley and Mucci, 1996; Ohde et al., 2005). Despite the fact that seawater carbonate cements form generally in compositionally modified seawater, this clearly contrasts with the dominant Mg-calcite cement composition of  $\sim 12$ – $13$  mol%  $\text{MgCO}_3$  (Garrels and Wollast, 1978; Videtich, 1985; Fig. 1), which raises a serious question whether or not they are formed by completely abiotic processes, as is generally presumed.

### 2.2.2. Observed apparent Mg-calcite solubilities

Morse and Mackenzie (1990, see their Fig. 3.7) summarized the studies of Mg-calcite solubility. They divided the results into three major categories: (1) the early results of Plummer and Mackenzie (1974), as revised by Thorstenson and Plummer (1977), for a variety of biogenic Mg-calcites which gave by far the highest values for Mg-calcite solubility

and are probably the most often quoted values in the literature; (2) the “best fit” biogenic Mg-calcite solubilities, of which here we will use the results of Bischoff et al. (1987) and Walter and Morse (1984); and (3) synthetic Mg-calcites which were based on the results of Bischoff et al. (1987) and Mucci and Morse (1984). Since the summary by Morse and Mackenzie (1990), Busenberg and Plummer (1989) reexamined the stability of a wide range of natural inorganic, biogenic, and synthetic Mg-calcite minerals. Based on their results, magnesian calcite solid-solutions were separated into two groups according to their stoichiometric solubilities. These conform to categories (2) and (3) mentioned above and confirm the previous stoichiometric solubility results of Bischoff et al. (1987), Walter and Morse (1984), and Mucci and Morse (1984). In this part of the paper dealing with Mg-calcite solubility, we will use the data for these two categories of Mg-calcite solubilities (Fig. 3), which Bischoff et al. (1987) felt were the best Mg-calcite solubility data.

The linear least squares fit for the abiotic Mg-calcite solubility as a function of mol fraction  $\text{MgCO}_3$  ( $x$ ) is given in Eq. (5). This relationship for biotic Mg-calcites is given in Eq. (6) for all data, and in Eq. (7), the data point that falls far off the linear least squares line with the arrow next to it (Fig. 3) has been excluded. Excluding this data point increases the slope from  $7.1 \times 10^{-3}$  to  $8.9 \times 10^{-3}$ , making the solubility more  $\text{MgCO}_3$  concentration dependent. It also significantly increases  $r^2$  from 0.31 to 0.71. The slope of the abiotic line (Fig. 3) is similar with a value of  $8.6 \times 10^{-3}$  and has an  $r^2$  value of 0.87. However, the extrapolated values of  $-\log \text{IAP}$  for pure calcite (0 mol%  $\text{MgCO}_3$ ) are quite different for biotic and abiotic Mg-calcites at 8.35 and 8.52, respectively. The extrapolated abiotic value is very close to

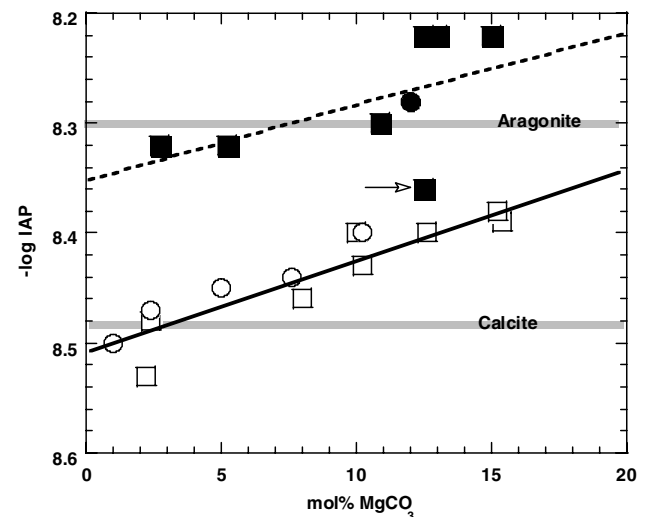


Fig. 3. Solubilities of biogenic (solid symbols) and synthetic (open symbols) Mg-calcites versus mol%  $\text{MgCO}_3$ . Lines are linear least square fits through the data sets. The data point with the arrow next to it was excluded in making the biogenic fit. Grey lines are for the solubilities of calcite and aragonite. Squares are from Bischoff et al. (1987); solid circle from Walter and Morse (1984); and open circles from Mucci and Morse (1984).



the accepted value for the solubility of pure calcite (8.48), and thus to some extent confirms the validity of the abiotic IAP versus Mg content curve. It should be noted that we did not include the solubility of [Walter and Morse \(1984\)](#) for the red algae *Goniolithon* that, as previously discussed, contains brucite. If the X-ray-based value of 18 mol% MgCO<sub>3</sub> were used, its solubility would plot about 0.25 – log IAP units (7.95) above the line for biogenic calcites.

$$-\log \text{IAP} = 8.52 - (8.6 \times 10^{-3})x \quad (5)$$

$$-\log \text{IAP} = 8.35 - (7.1 \times 10^{-3})x \quad (6)$$

$$-\log \text{IAP} = 8.35 - (8.9 \times 10^{-3})x \quad (7)$$

There are several noteworthy observations to be made from this treatment of Mg-calcite solubility. The first is that the results for the abiotic calcite solubility variation with mol% MgCO<sub>3</sub> are in excellent agreement. This is true even though the solubilities were obtained both from supersaturation and undersaturation. The observation that the hydrothermally prepared material was in good agreement with the Mg-calcite precipitates, from room temperature solutions, indicates that possible hydration of MgCO<sub>3</sub> and coprecipitation of ions such as sulfate and sodium did not produce measurable influences on solubility (see also [Bischoff et al., 1987](#); [Busenberg and Plummer, 1989](#)) and, as noted above, the intercept for pure calcite solubility was also in close agreement with the thermodynamic solubility of calcite. The projected change in solubility with increasing MgCO<sub>3</sub> content is modest, as recognized by [Bischoff et al. \(1987\)](#), and results in even a 20 mol% MgCO<sub>3</sub> synthetic Mg-calcite being less soluble than aragonite ([Fig. 3](#)). Consequently, if common marine high Mg-calcite cements of ~12–13 mol% MgCO<sub>3</sub> were indeed compositionally pure and structurally well ordered abiotic precipitates, they should be less soluble than aragonite.

The results for the biogenic Mg-calcites are considerably more perplexing. Although the change in solubility with increasing MgCO<sub>3</sub> content is modest and similar to that for abiotic Mg-calcites, there is a substantial offset between the solubilities that is reflected in the intercept for pure calcite being relatively close to that for aragonite solubility rather than that of calcite and about equal to the value for a 20 mol% MgCO<sub>3</sub> abiotic Mg-calcite. Consequently, it appears that the influences on the solubility of biogenic calcites with little-to-no MgCO<sub>3</sub> of carbonate anion and cation disorder and containing H<sub>2</sub>O, OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and perhaps other ions are similar to the influence of major concentrations of MgCO<sub>3</sub> on abiotic calcite solubility ([Busenberg and Plummer, 1989](#)).

A further concern is that the range of biogenic calcite solubilities, at about 12–15 mol% MgCO<sub>3</sub>, is larger than the whole predicted influence of MgCO<sub>3</sub> from 0 to 20 mol% MgCO<sub>3</sub>. The situation is even much worse if the solubility for the red algae *Goniolithon* were to be included. These results clearly illustrate that, for biogenic high and low Mg-calcites, MgCO<sub>3</sub> content could be a very poor predictor of solubility, which instead may be dominated by organism-

specific factors that are not readily quantified ([Busenberg and Plummer, 1989](#)). Based on the biogenic solubility data included in the current evaluation, it appears that about the best we can say for the solubility of biogenic high Mg-calcites, in the dominant composition range of about 12–16 mol% MgCO<sub>3</sub>, is that most are only slightly (~20%) more soluble than aragonite. This is considerably different from the widely used high Mg-calcite solubility value from the early work of [Plummer and Mackenzie \(1974\)](#) who obtained a solubility of about five times (500%) that of aragonite for Mg-calcites in this compositional range. According to [Bischoff et al. \(1993\)](#), the Plummer and Mackenzie solubilities are most representative of the behavior of Mg-calcites in natural environments because the materials used in these authors' experiments received minimal treatment and preparation prior to evaluating their stabilities. In contrast, the biogenic materials used in the experiments represented by the biogenic "best fit" solubilities were cleaned and annealed before evaluating their stabilities, yielding lower solubilities relative to their untreated counterparts ([Walter and Morse, 1984](#); [Bischoff et al., 1987, 1993](#)). It is not certain which one of these solubilities most accurately conform to Mg-calcite solid solutions in the natural environment. It is likely that the solubility of biogenic Mg-calcite phases viewed only as a function of MgCO<sub>3</sub> content is an insufficient parameter to describe their behavior in natural aqueous solutions, as follows from our previous discussion. However, this does not preclude the use of present biogenic Mg-calcite solubility data to obtain some insights into the behavior and reaction pathways of these phases in nature. Thus in the subsequent section, the behavior of Mg-calcites under rising atmospheric CO<sub>2</sub> conditions and "ocean acidification" based on the solubilities of [Plummer and Mackenzie \(1974\)](#) and the biogenic "best fit" is evaluated by means of a numerical model and compared to observations from the natural environment. Using both solubility trends provides the reader with an idea of how solubility affects model output and the conclusions we draw from the modeling and field observations.

### 3. Response of carbonate minerals to rising pCO<sub>2</sub>

#### 3.1. Modeling the response of Mg-calcite minerals

Despite the uncertainties associated with Mg-calcite solubility previously described, a simple numerical model was constructed in order to predict the response of Mg-calcite minerals to rising pCO<sub>2</sub> based on solubility as a function of the mineral MgCO<sub>3</sub> content. The model environment represents the shoal-water ocean region of shelves, banks, atolls, estuaries, and reefs containing a variety of carbonate minerals, including a range of Mg-calcite compositions. Two different model scenarios were employed adopting two different solubility simulations in each model scenario. The two solubility simulations were based on the "best fit" biogenic Mg-calcite solubilities (e.g., [Bischoff et al., 1987](#);

Walter and Morse, 1984; see previous discussion in Section 2.2.2), or those solubilities corresponding to the results obtained by Plummer and Mackenzie (1974). These two solubility simulations probably reasonably bracket the behavior of the dissolution of the more abundant biogenic Mg-calcites in the natural environment. In the first model scenario, the shoal water ocean region was assumed to be a closed system and no mixing or exchange of water with the open ocean were taken into account. Simply the response of carbonate minerals to rising  $p\text{CO}_2$  was investigated in this scenario. In the second model scenario, mixing with an open ocean surface seawater reservoir was considered and the combined effect of mixing and rising  $p\text{CO}_2$  on carbonate mineral dissolution was investigated. It is emphasized that the objectives of the model scenarios were not to determine the inclusive effects of increasing  $p\text{CO}_2$  arising from human activities on the carbonate geochemistry of the global shoal-water ocean region (e.g., Andersson et al., 2003, 2005, 2006), but simply to investigate the behavior and dissolution response, as a function of solubility and water residence time, of high Mg-calcite minerals to rising  $p\text{CO}_2$  in a system constrained by the physical properties of the shoal water ocean region. Consequently, processes that are important in order to determine the integrated response of the natural system to rising  $p\text{CO}_2$  including temperature, carbonate mineral precipitation, biological production and decomposition, etc., have not been included in the present model but are discussed in the aforementioned Andersson et al. papers.

### 3.1.1. Model methodology

A simple box model was constructed containing a seawater reservoir and 10 carbonate reservoirs representing calcite, aragonite, and individual Mg-calcite phases

containing 11–18 mol%  $\text{MgCO}_3$  (Fig. 4). The seawater reservoir was set equal to the global shoal-water ocean volume of  $3.7 \times 10^{18}$  L, having an initial  $p\text{CO}_2$  of 280  $\mu\text{atm}$ , dissolved inorganic carbon,  $\text{DIC} = 1846 \mu\text{mol kg}^{-1}$ , and total alkalinity,  $\text{TA} = 2200 \mu\text{mol kg}^{-1}$ , corresponding to typical surface seawater conditions in the year 1700 when the model was initiated (Andersson et al., 2006). In the second model scenario, an open ocean surface seawater reservoir ( $V = 9.98 \times 10^{19}$  L) with the same prescribed seawater conditions as the shoal-water reservoir was included in the model in order to allow for mixing between these two reservoirs. Sensitivity analyses on the effect of different shoal-water residence times ( $\tau$ ) were conducted for this model scenario. Water input via rivers and runoff were not included in any of the model scenarios. Only dissolution of carbonate minerals was investigated and no precipitation reactions were taken into account (see Andersson et al., 2005 for discussion of the precipitation issue and section 4.2). The total masses of reactive carbonate minerals were based on the estimate by Andersson (2003) of  $43.1 \times 10^{15}$  mol  $\text{CaCO}_3$ . The proportions of calcite:aragonite:Mg-calcite (13%:63%:24%) were based on the relative abundance of these phases observed in neritic carbonate sediments (Land, 1967). Relative proportions of Mg-calcite minerals with different mol%  $\text{MgCO}_3$  were obtained from the mineral distributions observed for mid-depth bank carbonate sands (Fig. 1; Agegian and Mackenzie, 1989). In both model scenarios, Mg-calcite saturation state was calculated using *stoichiometric solubility products* ( $K_{\text{Mg-cal}(x)}$ ; Eq. (2)) based on the biogenic “best fit” solubilities or the Plummer and Mackenzie (1974) solubilities, according to the general equation:

$$\Omega_x = \frac{a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} a_{\text{CO}_3^{2-}}}{K_{\text{Mg-cal}(x)}}, \quad (8)$$

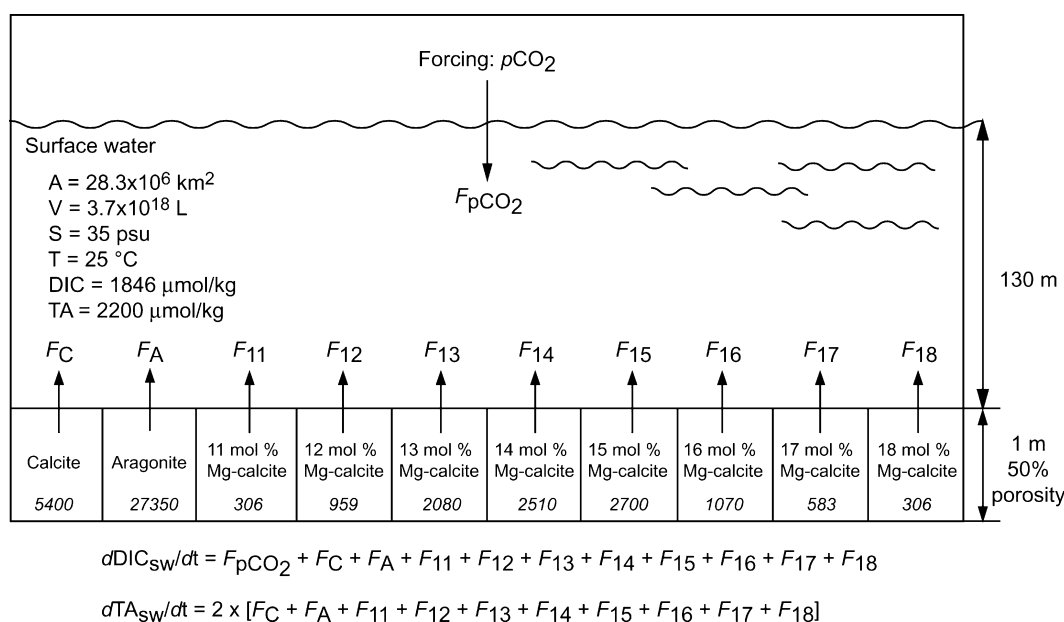


Fig. 4. Model schematic of simple dissolution model representing the global shoal-water ocean environment. Arrows denote fluxes. The masses of carbonate phases are shown at the bottom of each carbonate mineral reservoir in  $10^{12}$  mol.

where  $\Omega_x$  denotes the saturation state with respect to a Mg-calcite phase with  $x$  mol%  $\text{MgCO}_3$  and  $a$  is the total ion activity of the dissolved components in solution. Thermodynamically, net dissolution of a particular phase may occur if  $\Omega < 1$ . Once the saturation state with respect to a particular Mg-calcite phase was less than 1 in the model calculations, the kinetic rate of dissolution ( $R_d$ ) of that phase was calculated according to the empirically derived relationship:

$$R_d = k(1 - \Omega)^n, \quad (9)$$

where  $k$  is the rate constant and  $n$  the reaction order. In either solubility scenario, the constants were based on the experimental results of Walter and Morse (1985) who investigated the dissolution kinetics of shallow marine carbonates in seawater as a function of reactive surface area, ion molal product (IMP), mineral stability, and microstructure. Because data were only available for Mg-calcite phases of 12, 15, and 18 mol%  $\text{MgCO}_3$ , and no direct trend with Mg content was apparent, the dissolution rates for the remaining Mg-calcite phases were obtained from the mean kinetic dissolution rate observed for these phases. In reality, factors controlling dissolution kinetics are specific for each mineral grain and the rate of reaction may also be inhibited by additional factors such as dissolved phosphate and dissolved organic matter, as well as the freshness of the material (Morse and MacKenzie, 1990).

Both model scenarios were forced by observed atmospheric  $\text{CO}_2$  concentrations between year 1700 and present followed by IPCC IS92a atmospheric  $\text{CO}_2$  projections until year 2100 (Enting et al., 1995) and then a linear extrapolation until year 2300 assuming that equilibrium between the surface water and the atmosphere was established instantaneously i.e., the  $p\text{CO}_2$  of the surface water was equal to the  $p\text{CO}_2$  of the atmosphere. At this time, the global reservoirs of conventional fossil fuels will most likely be very close to exhaustion and the atmospheric  $\text{CO}_2$  concentration is not likely to continue to rise considerably beyond the level observed at this time owing to burning of fossil fuels (Archer et al., 1998; Caldeira and Wickett, 2003; Andersson et al., 2005). However, in order to investigate the extended response of Mg-calcite minerals to elevated  $\text{CO}_2$  concentrations, the surface water  $p\text{CO}_2$  of the closed system model scenario was allowed to continue to rise linearly to a level of 20,000  $\mu\text{atm}$  compared to  $\sim 380$   $\mu\text{atm}$  in the atmosphere in 2005 (at sea level) and perhaps as high as  $\sim 7000$ – $9000$   $\mu\text{atm}$  in the early Phanerozoic (Berner and Kothavala, 2001; Arvidson et al., 2006). In addition, presently, interstitial sediment pore waters may reach  $p\text{CO}_2$  levels of more than several thousand  $\mu\text{atm}$  (e.g., Morse et al. (1985) observed  $p\text{CO}_2$ s as high as  $10^{-1.5}$  atm in carbonate rich sediments in Bahamas) owing to microbial decay and remineralization of organic matter deposited in the sediments, resulting in production and release of  $\text{CO}_2$ . Consequently, the high  $p\text{CO}_2$  forcing of the closed system model scenario is warranted to explore fully the behavior of Mg-

Table 1

Seawater equilibrium constants for the solubility of  $\text{CO}_2$  ( $K_0$ ), dissociation of carbonic acid ( $K_1^*$ ,  $K_2^*$ ), ion product of water ( $K_w^*$ ), and dissociation of boric acid ( $K_B^*$ ;  $p$  denotes  $-\log K$ ) used in the current model to calculate the dissolved inorganic carbon system at 25 °C and a salinity of 35 (Zeebe and Wolf-Gladrow, 2002)

$pK_0$	1.5468	Weiss (1974)
$pK_1^*$	5.8472	Mehrbach et al. (1973) given on $\text{pH}_T$ by Lueker et al. (2000)
$pK_2^*$	8.9660	Mehrbach et al. (1973) given on $\text{pH}_T$ by Lueker et al. (2000)
$pK_w^*$	13.2173	DOE (1994)
$pK_B^*$	8.5975	DOE (1994), based on Dickson (1990)

calcite minerals under elevated  $p\text{CO}_2$ . Dissolved inorganic carbon chemistry was calculated based on  $p\text{CO}_2$  and TA at 25 °C and a salinity of 35 using the equilibrium constants given in Table 1 (Zeebe and Wolf-Gladrow, 2002). In order to calculate the saturation state with respect to Mg-calcite minerals, seawater concentrations of calcium, magnesium, and carbonate ions were converted to ion activities using total activity coefficients (Millero and Pierrot, 1998), so that the IAPs could be compared directly with the values of the stoichiometric solubility products. Numerical integration was conducted with Matlab (The MathWorks, Inc.) using an ordinary differential equation solver based on an explicit Runge–Kutta (4) and (5) formula.

### 3.1.2. Model results

As  $p\text{CO}_2$  rises, the saturation state with respect to carbonate minerals rapidly decreases as carbonate ions are titrated by  $\text{CO}_2(\text{aq})$  to form bicarbonate:



In the closed system model scenario adopting the biogenic “best fit” solubilities, seawater became undersaturated with respect to 18 mol% Mg-calcite once the surface seawater  $p\text{CO}_2$  reached a level of 1414  $\mu\text{atm}$ . Subsequently, this mineral phase became subject to dissolution (Fig. 5). The dissolution of this mineral phase was observed as a buffer effect in the seawater reservoir, i.e., the increase in alkalinity owing to carbonate dissolution strengthened the capacity of seawater to absorb  $\text{CO}_2$  without a significant further change in pH and carbonate saturation state (Eq. (1)). By adding alkalinity to the system, a metastable equilibrium was established between the seawater and 18 mol% Mg-calcite, the most soluble carbonate phase present in the model sediments. The metastable equilibrium and the buffer effect persisted until the entire reservoir of 18 mol% Mg-calcite had dissolved and was completely exhausted. Because the 18 mol% Mg-calcite reservoir was relatively small and rapidly dissolved, the buffer effect was quite short in duration under the present  $\text{CO}_2$  forcing. Following the exhaustion of this phase, the pH and saturation state rapidly dropped until the seawater became undersaturated with the next most soluble phase, 17 mol% Mg-calcite, which consequently started to dissolve and a new metastable equilibrium was established. The same trend then repeated itself for each

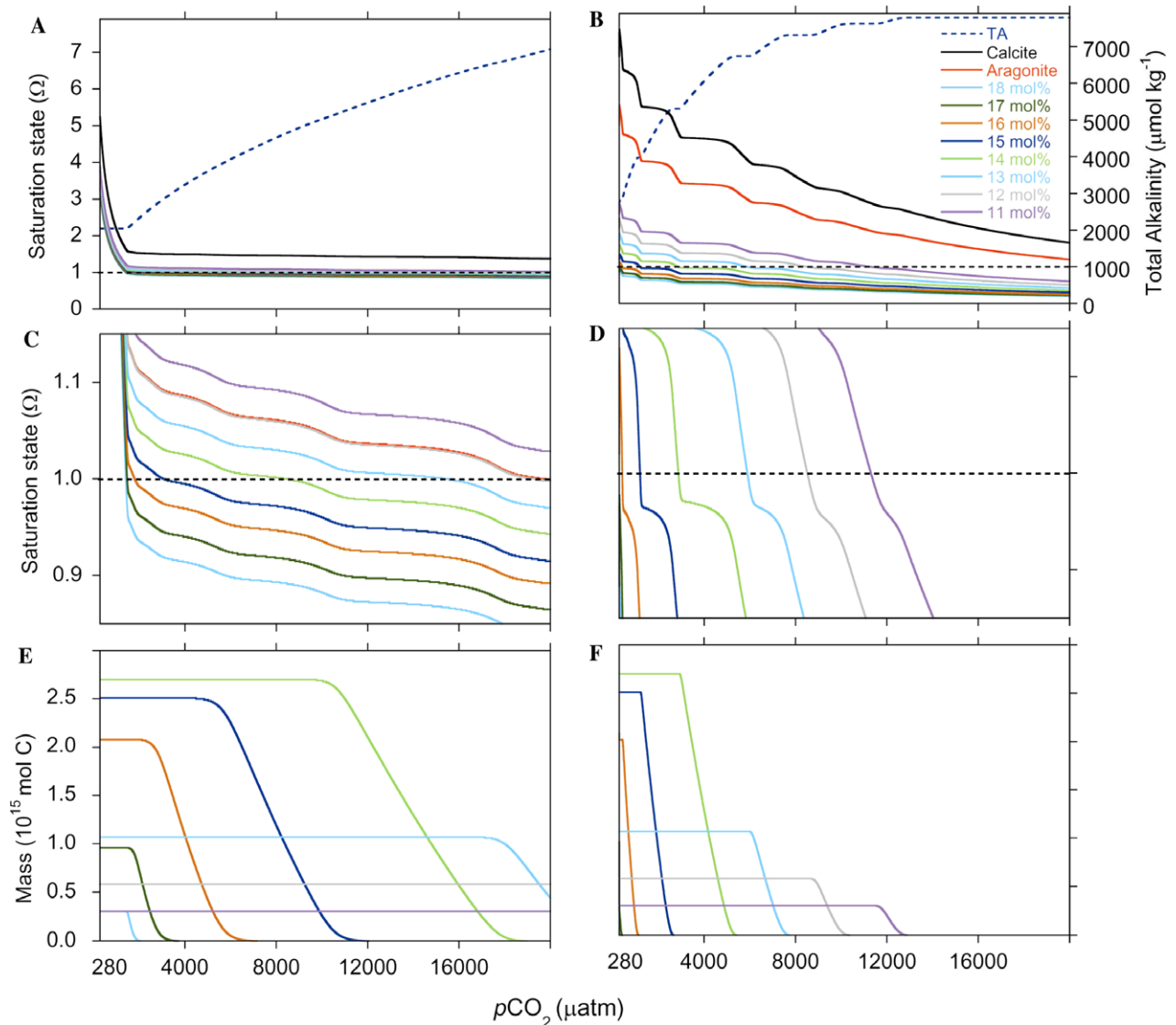


Fig. 5. Mg-calcite reservoir masses and calculated surface seawater saturation state with respect to calcite, aragonite and 11–18 mol% Mg-calcite based on the biogenic “best fit” solubility data (A, C, E) and the [Plummer and Mackenzie \(1974\)](#) solubility data (B, D, F) as a function of  $p\text{CO}_2$  in the closed system model scenario. Seawater total alkalinity is also shown. The same saturation state data are shown in panel A and C, B and D, but on different scales in order to highlight the sequential dissolution of the most soluble carbonate phase present in the model simulation as well as the establishment of a metastable equilibrium between the seawater and this phase.

consecutive mineral phase following this sequence of events:

1. Seawater pH and carbonate saturation state decrease owing to increasing  $\text{CO}_2$ .
2. Seawater becomes undersaturated with respect to the most soluble carbonate phase present in the sediments, and undergoes dissolution.
3. The dissolving phase maintains a metastable equilibrium with seawater and produces a buffer effect that maintains pH and saturation state relatively constant. The metastable equilibrium persists until the dissolving phase has completely dissolved. The stage at which the phase completely dissolves depends on the  $\text{CO}_2$  forcing, the rate of dissolution, and the total mass of the dissolving mineral phase.

4. Once the dissolving phase has completely dissolved, seawater pH and carbonate saturation state will decline until a new metastable equilibrium has been established with the next most soluble carbonate phase present in the sediments, and so on.

In the closed system model scenario adopting those solubilities determined by [Plummer and Mackenzie \(1974\)](#), the seawater was initially significantly undersaturated with both 17 and 18 mol% Mg-calcite. Consequently, these reservoirs rapidly dissolved and immediately raised the total alkalinity, pH, and carbonate saturation state of the seawater in the first year of the simulation (Fig. 5). Eventually, the seawater became undersaturated with respect to 16 mol% Mg-calcite, which then became subject to dissolution. A metastable equilibrium was established between the



seawater and the 16 mol% Mg-calcite, which persisted until this phase had completely dissolved. From then on, not unexpectedly, the same sequential dissolution trend observed in the first solubility simulation was also observed in the second solubility simulation. It should be noted that although the two solubility simulations predict sequential dissolution of distinct Mg-calcite phases, in reality the dissolution pathway would more likely follow a continuum since the distribution of Mg-calcite compositions in nature may be more of a continuum.

In the open system model scenario, the initial responses and the overall trends of the two solubility simulations were similar to the results observed for the closed system solubility simulations. However, any buffer effect produced from carbonate dissolution and resulting accumulation of alkalinity in the surface seawater was rapidly diluted by mixing with the much larger open ocean reservoir. In the

biogenic “best fit” solubility simulation, the effect of mixing on the surface seawater carbonate chemistry was negligible independent of the residence time because the surface water remained supersaturated with respect to the most soluble carbonate mineral phase present in the model until year 2236. No dissolution took place prior to this year. Consequently, the surface seawater pH decreased almost as much in a scenario of infinite residence time and taking carbonate dissolution into account, as the pH decreased in a scenario assuming  $\text{CO}_2$  solution in seawater to be a simple homogenous reaction (Fig. 6). The latter represents the maximum change in pH projected from the present  $\text{CO}_2$  forcing. Adopting the Plummer and Mackenzie solubilities, the results were significantly different (Fig. 6). Because dissolution of carbonate minerals was ongoing at the onset of this solubility scenario, an infinite residence time and subsequent accumulation of alkalinity within the shoal-water

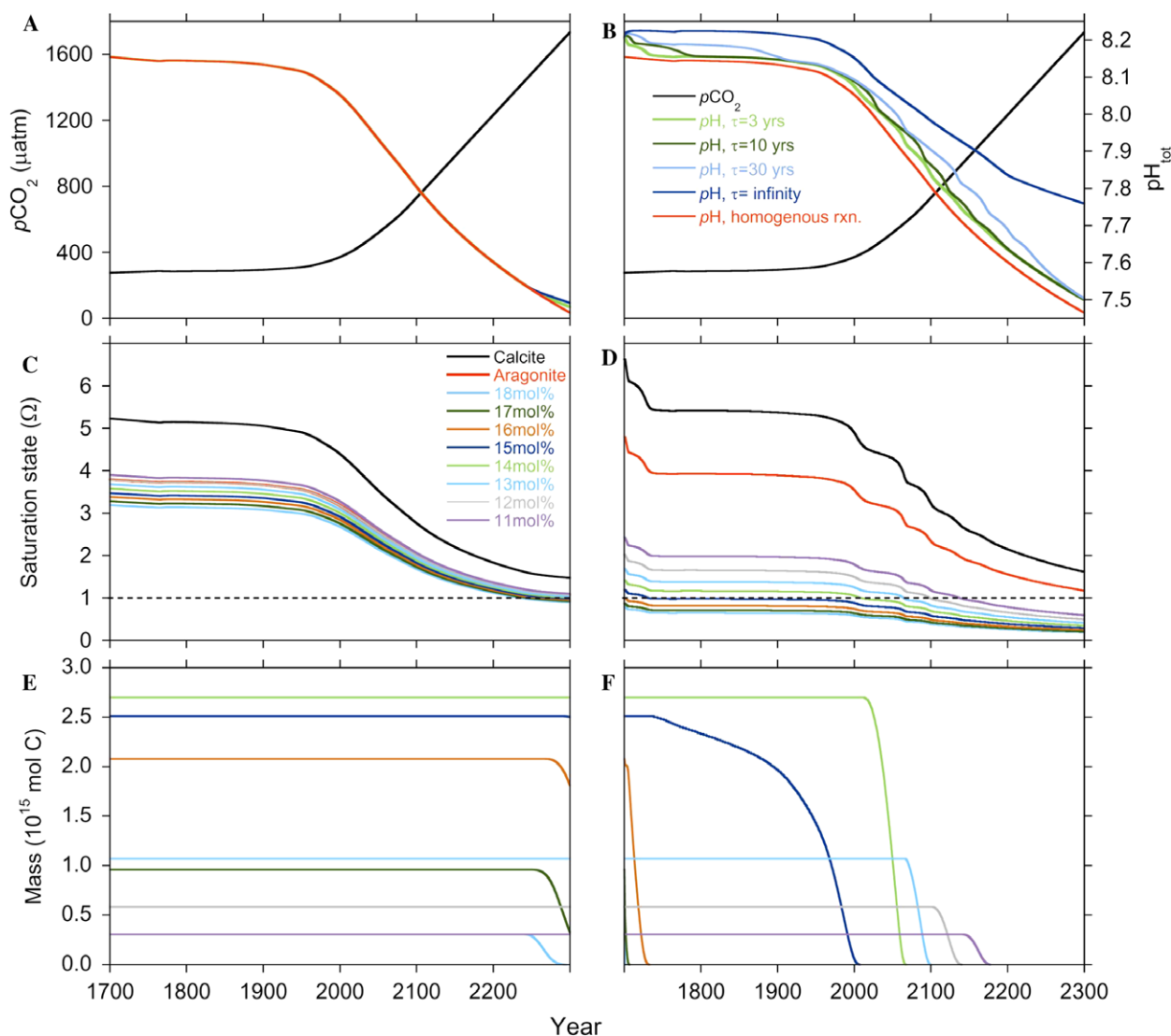


Fig. 6. Open system model results between years 1700 and 2300 for the biogenic “best fit” solubility (A, C, E) and the Plummer and Mackenzie (B, D, F) solubility simulations. (A, B)  $p\text{CO}_2$  forcing and resulting surface seawater pH in multiple scenarios adopting different shoal-water residence times ( $\tau$ ). The results of panels C–F are based on the scenario of a 3 year residence time showing, (C, D) surface seawater carbonate saturation state ( $\Omega$ ), and (E, F), Mg-calcite reservoir masses.

ocean reservoir produced a strong buffer effect and a significantly higher surface seawater pH than if solution of CO<sub>2</sub> in seawater were simply homogeneous (Fig. 6). However, the buffer effect was rapidly diluted if the shoal-water ocean residence times were considered to be a few years or even several decades. In this model scenario, the entire Mg-calcite reservoir was exhausted by the year 2200 adopting a water residence time of 3 years (Chavez and Toggweiler, 1995).

### 3.1.3. Model discussion

Although the results of the different modeling scenarios show differences in trends and timing of events, they indicate that once dissolution is initiated, a metastable equilibrium could be established between the seawater and the dissolving mineral phase, provided that the rate of carbonate dissolution is fast enough relative to the rate of increase in pCO<sub>2</sub> and the rate of water mixing. The establishment of a metastable equilibrium was suggested decades ago by Chave (1962; Schmalz and Chave, 1963) based on observational data from Bermuda. If an existing metastable equilibrium between seawater and the most soluble carbonate phase present in the sediments were able to keep up with the current rise in pCO<sub>2</sub>, surface seawater pH and carbonate saturation state would remain relatively constant and the seawater would be buffered owing to carbonate mineral dissolution. Consequently, the rate at which marine calcifying organisms produce their shells, tests, and skeletons would probably not be negatively affected owing to a decrease in surface water carbonate saturation state arising from increasing pCO<sub>2</sub> (Halley and Yates, 2000; Barnes and Cuff, 2000; Andersson et al., 2003).

The results of the biogenic “best fit” solubility simulations of the current model scenarios suggest that a buffer effect owing to carbonate dissolution will not be in effect until year 2236 or when the pCO<sub>2</sub> is equal to 1414 μatm. At this time, the saturation state with respect to aragonite and calcite will already be low enough to decrease the rate of calcification of marine calcareous organisms based on current experimental results (e.g., Gattuso et al., 1999; Langdon et al., 2000; Orr et al., 2005). In contrast, the results of the Plummer and Mackenzie solubility simulations indicate that the shoal-water surface seawater reservoir is currently close to or in metastable equilibrium with a Mg-calcite phase of 15 mol% MgCO<sub>3</sub> that consequently is subject to dissolution and acts to buffer the carbonate chemistry of the seawater reservoir. However, under the present CO<sub>2</sub> forcing, the apparent buffer effect is only significant if one assumes an infinite residence time and allows alkalinity to accumulate within the shoal-water reservoir (Fig. 6). The buffer effect becomes rapidly insignificant if water exchange with the open ocean is taken into account. Even at unrealistic long residence times, the buffer effect is insignificant despite substantial carbonate dissolution. As a result, it is not likely that marine calcifying organisms will be significantly protected from rising atmospheric pCO<sub>2</sub> owing to dissolution of high Mg-calcite minerals. This con-

firms the results of Andersson et al. (2003, 2005, 2006); they investigated the integrated effect of both rising pCO<sub>2</sub> and temperature on the global coastal ocean and concluded that metastable carbonate minerals will not dissolve rapidly enough to provide sufficient alkalinity to buffer the global coastal surface ocean against changes in seawater chemistry arising from increasing atmospheric CO<sub>2</sub> on the time scale of hundreds of years. A minor buffer effect could be observed in certain regions of restricted circulation such as atolls and lagoons once dissolution of carbonate minerals exceeds precipitation (Andersson et al., 2003, 2005, 2006). However, it is important to realize that even if the entire reactive Mg-calcite reservoir dissolved, and the rate of dissolution were equal to the rate of CO<sub>2</sub> invasion into the surface ocean, the buffer effect would only last for a few decades. Assuming an oceanic uptake of anthropogenic CO<sub>2</sub> of about 2 Gt C yr<sup>-1</sup> (167 × 10<sup>12</sup> mol C yr<sup>-1</sup>; e.g., Sarmiento and Gruber, 2002) and a rate of dissolution of high Mg-calcite minerals equal to the uptake rate, our estimate of 10.3 × 10<sup>15</sup> mol of readily accessible reactive high Mg-calcite (24% of 43.1 × 10<sup>15</sup>) present in the sediments of the global coastal ocean would be exhausted in only 62 years.

Even though no significant buffer effect may be observed from carbonate dissolution induced by rising pCO<sub>2</sub>, the results of the open system model scenario adopting the Plummer and Mackenzie solubilities, and a shoal-water ocean residence time of 3 years, suggest that the average shoal water carbonate content and composition could change dramatically. By year 2200, the entire reservoir of readily available reactive Mg-calcite had dissolved and the sediments were solely comprised of calcite and aragonite in this model simulation. In contrast, the sediment Mg-calcite content and composition were little affected in the biogenic “best fit” solubility simulation. As previously discussed, it is far from certain what solubility scenario most accurately reflects the behavior of Mg-calcite minerals in the natural environment. Observations from tropical and subtropical surface seawater suggest that these waters are in metastable equilibrium with a Mg-calcite phase of 13–16 mol% MgCO<sub>3</sub> based on the solubilities of Plummer and Mackenzie. This is very close to the average composition of Mg-calcite phases (13–15 mol%; Fig. 1) found in neritic sediments of these ocean regions. In comparison, the same waters are supersaturated by 200–360% with respect to 20 mol% Mg-calcite based on the biogenic “best fit” solubilities. Furthermore, the modal magnesium content in skeletons and shells of calcareous organisms producing Mg-calcite (Chave, 1954; Mackenzie et al., 1983) appears to correlate well with the Mg-calcite phase in metastable equilibrium with surface seawater according to the Plummer and Mackenzie solubilities based on ion activity products calculated as a function of latitude using the WOCE P15 leg surface water dissolved inorganic carbon hydrographic data for the Pacific Ocean (<http://whpo.ucsd.edu/index.htm>; Fig. 7). However, the range of Mg content in biogenic hard parts is large (Fig. 7), and factors other than

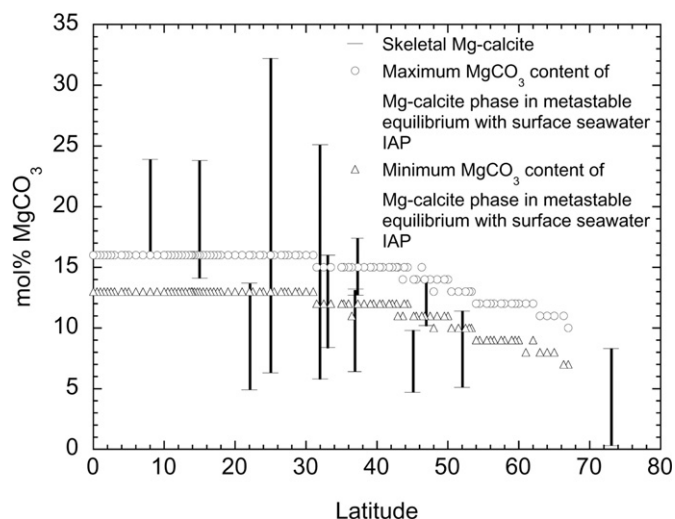


Fig. 7. Latitudinal distribution of the  $\text{MgCO}_3$  content of skeletal Mg-calcite (Chave, 1954; Mackenzie et al., 1983) and the Mg-calcite phase in metastable equilibrium with surface seawater based on the Plummer and Mackenzie (1974) solubility curve and ion activity products (IAPs) in the Pacific Ocean calculated from WOCE section P15 (CLIVAR and Carbon Hydrographic Data Office; <http://whpo.ucsd.edu/index.htm>). In calculating surface seawater ion activities of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{CO}_3^{2-}$  from ion concentrations, a range of total ion activity coefficients given in the literature (Millero and Pierrot, 1998), was used in order to calculate the full range of Mg-calcite phases potentially in metastable equilibrium with the surface seawater.

seawater saturation state, such as temperature and growth rate, could be more important in controlling the Mg content of these calcareous hard parts (Chave, 1954; Mackenzie et al., 1983). In addition, if one were to apply the solubilities of Plummer and Mackenzie to interstitial pore waters, which have significantly different dissolved inorganic carbon chemistry than surface seawater owing to microbial decomposition of organic matter in the sediments, these waters would be significantly undersaturated with respect to the average Mg-calcite composition found in shoal water sediments. In contrast, the biogenic “best fit” solubilities projects that these porewaters are close to a metastable equilibrium with the average Mg-calcite sediment composition. Thus, observations from the natural environment do not unequivocally agree on which one of the evaluated solubilities is most realistic. Furthermore, they raise the question: is it the surface seawater chemistry or the interstitial porewater chemistry that controls the bulk carbonate composition in sediments?

Porewater chemistry is strongly controlled by the various microbial processes taking place in the sediments, the delivery rate and amount and reactivity of organic matter deposited, and the rate of water exchange with the overlying seawater. The extensive decay of organic matter that takes place within sediments produces  $\text{CO}_2$  and consequently consumes carbonate ions according to Eq. (10), resulting in a lower saturation state with respect to carbonate minerals and dissolution of mineral phases with which the water is undersaturated. In fact, the extent of carbonate

dissolution could be controlled by the amount and the rate at which organic matter is being remineralized (Moulin et al., 1985; Morse and Mackenzie, 1990; Andersson et al., 2005). However, it should be pointed out that as the interstitial waters of sediments become anoxic with sediment depth and microbial sulfate reduction becomes important, alkalinity is produced from this process, increasing the saturation state with respect to carbonate minerals and potentially leading to carbonate precipitation rather than dissolution (Ben-Yaakov, 1973; Morse and Mackenzie, 1990). If  $28 \text{ mmol kg}^{-1}$  of  $\text{SO}_4^{2-}$  in sediment pore waters are reduced, this can potentially lead to production of  $56 \text{ meq kg}^{-1}$  of total alkalinity and oversaturation of the pore waters with respect to carbonate mineral phases.

### 3.2. Laboratory experiments

We recognize that the modeling scenarios presented previously are purely hypothetical and unrealistic in several different ways, but they still represent important results regarding the responses of Mg-calcite minerals to increasing  $p\text{CO}_2$  because they conform to laboratory experiments and observations from the natural environment, as well as to theoretical considerations, and provide boundaries on the pathways of dissolution of the Mg-calcites under rising atmospheric  $\text{CO}_2$  conditions and “ocean acidification”.

Fig. 8 illustrates the results from saturation experiments with seawater containing equal amounts of high Mg-calcite (15–18 mol%  $\text{MgCO}_3$ ) derived from the coralline algae *Porolithon gardineri* or Iceland spar calcite of similar grain size. An instant addition of a constant volume of acid (0.1 N HCl) was added to solutions of pure seawater, seawater containing calcite, and seawater containing Mg-calcite, and the changes in pH were recorded. A decrease in pH owing to a small acid addition shifts the equilibrium of the dissolved inorganic carbon species resulting in an increase in  $\text{CO}_2$  and  $\text{HCO}_3^-$  and a decrease in  $\text{CO}_3^{2-}$  concentration, and consequently, the saturation state with respect to carbonate minerals. As was expected, a significantly larger buffer effect owing to carbonate dissolution was observed in the experiment containing the high Mg-calcite phase compared to the experiment with Iceland spar calcite because of the former mineral’s higher solubility (Fig. 8A). In a second experiment, a constant volume of acid was added at regular intervals to a solution containing equal amounts of either seawater and calcite or seawater and Mg-calcite while the pH was continuously monitored. In both experiments, after each acid addition and an initial decrease in pH, the pH slowly increased owing to mineral dissolution until the pH approached a steady state value (Fig. 8B). After each acid addition, the pH returned close to this steady state value, probably reflecting a metastable equilibrium between the solution and the most soluble carbonate phase present in the solution, analogous to the trend previously shown in the numerical simulations.

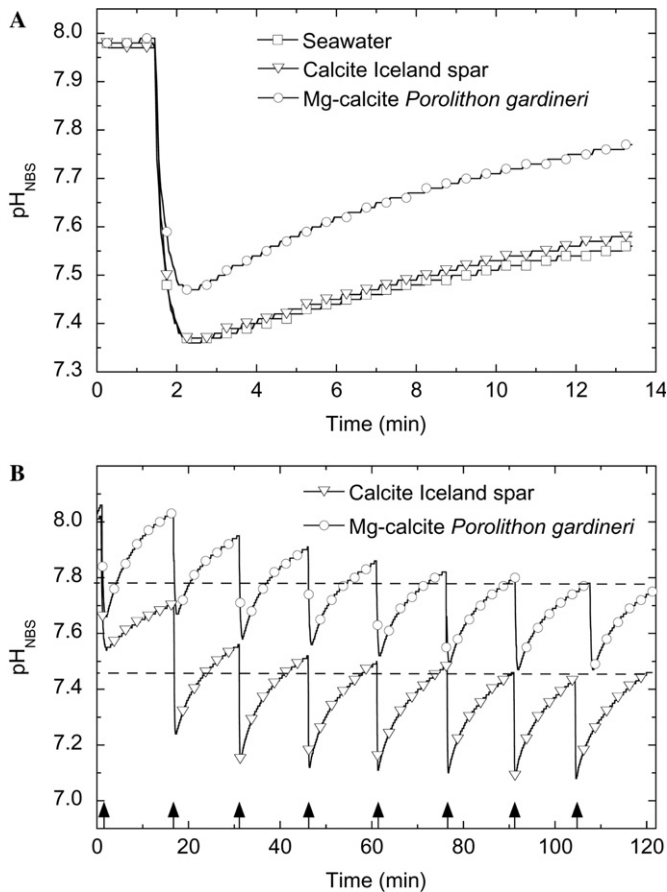


Fig. 8. (A) Responses of seawater, seawater containing Iceland spar calcite, and seawater containing Mg-calcite from the coralline red algae *Porolithon gardineri* to a single addition of an equal volume of HCl. Adding HCl to seawater changes the carbonate equilibrium resulting in an increase in  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and a decrease in  $\text{CO}_3^{2-}$  and consequently the saturation state with respect to carbonate minerals. Note the difference between Mg-calcite and calcite in their ability to restore the pH after the acid addition, reflecting the higher solubility of Mg-calcite. This difference is also clearly demonstrated in (B), illustrating the response of seawater containing an equal amount of Mg-calcite or calcite to multiple additions of a constant volume of HCl. For each acid addition, the pH decreases until it approaches an equilibrium value (dashed lines). If the two scenarios were combined, one would expect the pH to decrease until a metastable equilibrium was established between the seawater and the Mg-calcite phase. This metastable equilibrium would persist until the Mg-calcite has completely dissolved, followed by a drop in pH until a new equilibrium was established with the calcite phase.

In a different experiment, reagent-grade calcite seeds were submerged in seawater collected from the Sargasso Sea offshore of Bermuda. The seawater was initially equilibrated with an air mixture of 330 ppm  $\text{CO}_2$  and nitrogen gas, and then followed by equilibration of the seawater with 605 ppm  $\text{CO}_2$  in  $\text{N}_2$  (Tribble and Mackenzie, 1998). Initially during the first stage of the experiment, a drop in pH and total alkalinity was interpreted by the authors to represent precipitation of carbonate coatings on the pure calcite seeds. The initial pH drop was then followed by an additional drop in pH, but an increase in total alkalinity during the second stage of the experiment, indicating

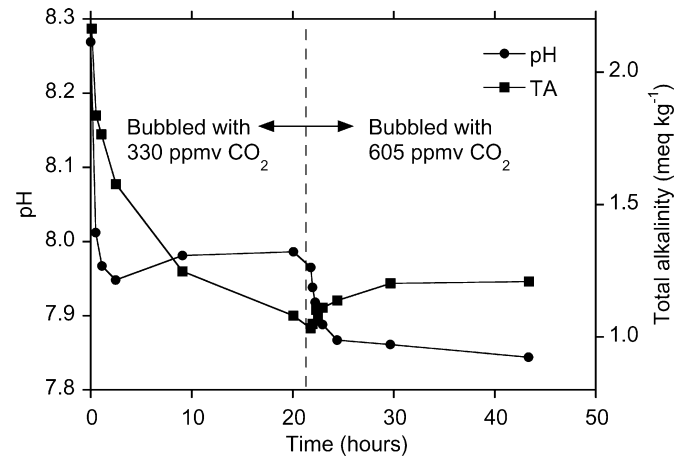


Fig. 9. Trends of Sargasso seawater pH and total alkalinity during reaction of calcite seeds in an open system equilibrated first with 330 ppm  $\text{CO}_2$ , then with 605 ppm  $\text{CO}_2$ , adopted from Tribble and Mackenzie (1998). The initial decrease in pH and total alkalinity reflects precipitation and coatings on the calcite seeds. The observed decrease in pH and increase in total alkalinity after equilibration with 605 ppm  $\text{CO}_2$  reflects dissolution of a carbonate phase. Because the seawater was still supersaturated with respect to calcite and aragonite the dissolving phase was concluded to be Mg-calcite.

dissolution as the system equilibrated with the gas containing 605 ppm  $\text{CO}_2$  (Fig. 9). Because the seawater was supersaturated with respect to aragonite and calcite, the dissolving material was thought to be a Mg-calcite phase that probably was precipitated on the calcite seeds during the first stage of the experiment.

The results of the numerical model and the laboratory experiments all agree, and suggest that Mg-calcite minerals will respond to increasing  $p\text{CO}_2$  and subsequent decreasing saturation state by sequential dissolution based on mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain. Such selective dissolution of metastable carbonate minerals has been observed in both experiments and natural environments (Chave, 1962; Schmalz and Chave, 1963; Neumann, 1965; Wollast et al., 1980; Balzer and Wefer, 1981; Morse and Mackenzie, 1990). Observations from carbonate sediments in Bermuda follow a trend of increasing carbonate mineral stability with decreasing grain size, which most likely indicates selective dissolution of highly soluble Mg-calcite phases (Chave, 1962; Schmalz and Chave, 1963; Neumann, 1965).

#### 4. Observations from carbonate-dominated regions

##### 4.1. Bermuda

During spring and summer, a strong thermocline is developed in the water column in Devil's Hole, located within Harrington Sound, Bermuda. As organic matter produced in the surface waters sinks, it is remineralized by microbial activity below the thermocline, releasing  $\text{CO}_2$  and driving the  $p\text{CO}_2$  to very high levels and the



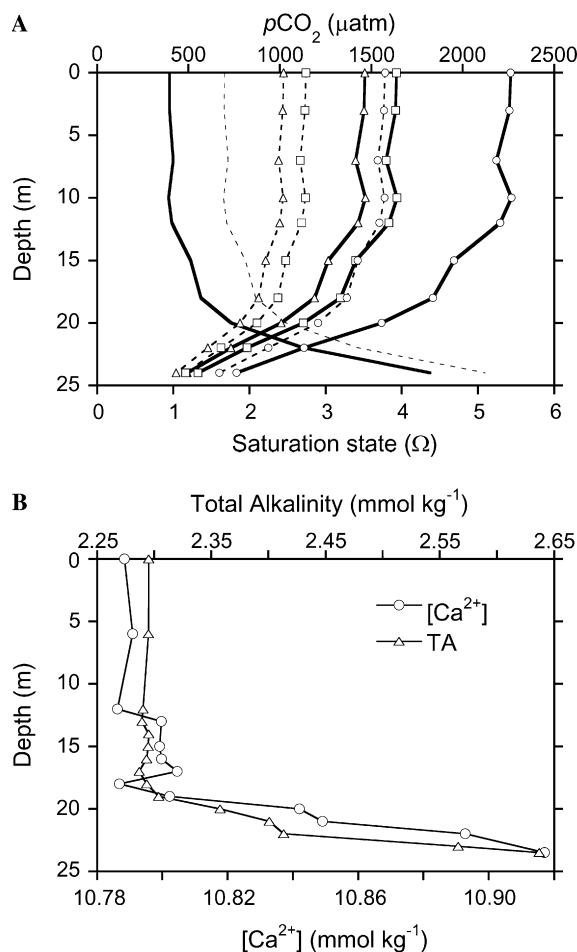


Fig. 10. (A) Vertical profiles from Devil's Hole, Harrington Sound, Bermuda, during summer showing saturation state with respect to calcite (circles), aragonite (squares) 15 mol% Mg-calcite (triangles) and  $p\text{CO}_2$  (no symbol). Due to the development of a seasonal thermocline during summer, decay of organic matter below this boundary produces very high  $p\text{CO}_2$  and consequently low saturation state with respect to carbonate minerals, which may become subject to dissolution. Solid lines indicate present summer conditions observed in August 2004 and dashed lines the conditions projected for the year 2100. The saturation state with respect to 15 mol% Mg-calcite was calculated from the solubility of the "biogenic best fit" data (see discussion in Section 2.2.2). (B) Changes in total alkalinity and calcium concentration with depth confirming dissolution of calcium carbonate minerals.

saturation state with respect to carbonate minerals down (Fig. 10). As summer progresses and the stratification of the water column usually becomes stronger, DIC builds up owing to organic matter decay and dissolution of carbonate minerals, and the  $p\text{CO}_2$  may reach levels of several thousand  $\mu\text{atm}$ . The bottom water overlying the sediments is significantly undersaturated with respect to high Mg-calcite minerals and sometimes even aragonite, leading to dissolution of these phases. This is clearly demonstrated by a change in total alkalinity and calcium concentrations with depth (Fig. 10). Investigations of the mineral composition of subthermocline sediments in Harrington Sound have shown that these sediments are depleted in high Mg-calcite minerals despite significant biogenic production of these

phases by coralline algae, echinoids, and other Mg-calcite calcifiers in the shallow waters of the sound (Neumann, 1965). This confirms that the chemical changes observed in the water column most likely arise from mineral dissolution and consequently confirm what is predicted from thermodynamic and laboratory considerations.

As the atmospheric  $\text{CO}_2$  concentration continues to rise, the surface water carbonate saturation state within Harrington Sound will decrease. Consequently, in future years from today, the initial carbonate saturation state likely will be lower during the onset of the development of the thermocline in the spring or early summer. Assuming that the transport of organic matter to the sediments and the extent of remineralization remain constant, the carbonate saturation state of the bottom water in Devil's Hole will be even lower than what is observed today, shifting the saturation state trend throughout the water column towards the left as shown in Fig. 10a. Consequently, dissolution will follow the sequence of events previously described and supported by modeling and laboratory experiments. A similar effect to that taking place in the water column of Devil's Hole owing to increasing atmospheric  $\text{CO}_2$  will also apply to sediment interstitial waters, because the surface seawater will have an initial higher  $p\text{CO}_2$  and lower carbonate saturation state upon entry into the porewater-sediment system in the future relative to today. However, the projected changes in surface seawater  $p\text{CO}_2$  are relatively small compared to the  $\text{CO}_2$  levels observed in porewaters owing to remineralization of organic material. Consequently, changes in organic matter deposition and remineralization may have a much larger effect on the interstitial porewater chemistry, carbonate composition, and dissolution than the projected changes in atmospheric  $\text{CO}_2$  (Andersson et al., 2005).

#### 4.2. The Great Bahama Bank

The waters and sediments of the Great Bahama Bank have been intensely studied for more than 40 years (see for example Morse et al., 2003, and the many references given therein). This is in large part because of the carbonate "whittings" that occur on the northern part of the bank, whose abiotic versus biotic origins have been widely disputed, and the long residence time ( $\sim 240$  days) of the shallow inner bank waters where about a third of the specific alkalinity has been lost. These conditions make this area a "natural laboratory" where, although the decreased saturation state of the waters is largely due to a loss of alkalinity rather than an increase in  $p\text{CO}_2$ , potential insights on the behavior of shallow water carbonate sediments under reduced saturation conditions may be obtained.

Fig. 11 presents the change in the  $\text{CaCO}_3$  ion concentration product (ICP) for seawater at constant salinity, temperature, and TA as a function of  $p\text{CO}_2$ . The current ICP and that calculated for inner Bank waters also appear on the curve. The ICP of the inner bank waters is the ICP that would be obtained for a  $p\text{CO}_2$  of  $\sim 880$   $\mu\text{atm}$  when the

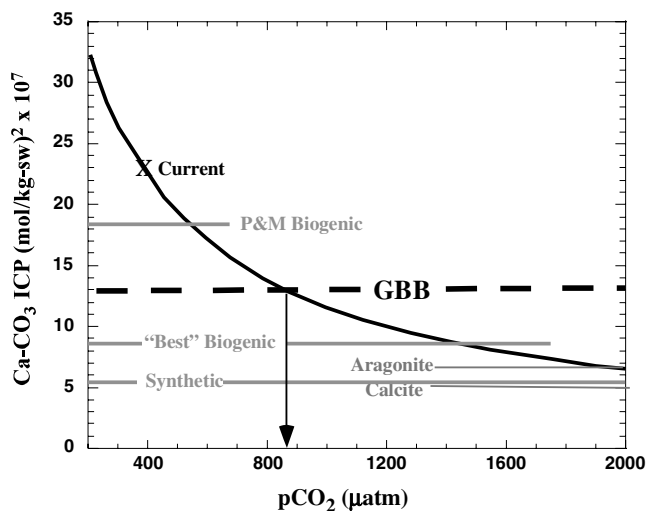


Fig. 11. The  $\text{CaCO}_3$  ion concentration product (ICP) versus  $p\text{CO}_2$  for seawater of  $S = 35$ ,  $t = 25^\circ\text{C}$ ,  $TA = 2300 \mu\text{mol kg}_{\text{sw}}^{-1}$  (solid curve where X marks current  $p\text{CO}_2$ ). Shown in grey are the equilibrium ICP values for calcite, aragonite, and 15 mol% Mg- $\text{CO}_3$  Mg-calcite from synthetic, best biogenic, and Plummer and Mackenzie (1974). The dashed line is the ICP of inner Great Bahama Bank waters.

alkalinity change is converted to a change in  $p\text{CO}_2$ . For 15 mol% Mg-calcite, this ICP value is intermediate between that for our “best biogenic” and Plummer and Mackenzie (1974) values, and not surprisingly well above that for synthetic Mg-calcite of this composition.

Morse et al. (2003) determined the “kinetic solubility” of suspended whiting material to be about 1.9 times that of aragonite. These experiments were conducted in a manner similar to the experiments of Mucci and Morse (1984) on calcite where a much lower equilibrium ICP value (about 1/3) was obtained using synthetic calcite as a substrate in seawater. Morse et al. (2003) compared their kinetic solubility value with ICPs of Great Bahama Bank waters (Fig. 12), where it can be seen that the inner Bank waters are close to metastable equilibrium with the phase that gives this kinetic solubility. Consequently, if this equilibrium ICP value were to be maintained in the future, a smaller decline in TA will occur as  $p\text{CO}_2$  rises. This means that the amount of abiotic carbonate production on the Great Bahama Bank will decline as  $p\text{CO}_2$  rises adding to the impact of declining biotic calcification rates.

Although there is some scatter, it is interesting that similar values of ICP were observed for many porewaters from many carbonate-rich sediments in this region (Fig. 13; Morse et al., 1985) to the kinetically measured value. Bernstein and Morse (1985) conducted closed system solubility experiments on carbonate-rich sediments from the Bahamas. Measurements from initially under- and super-saturated seawater, with and without biocide and destruction of organic matter, and ranging from 8 to 50 days of reaction, gave similar results. Fine-grained aragonitic muds yielded steady-state IAP values close to that for the solubility of aragonite, whereas coarser sediments yielded steady-

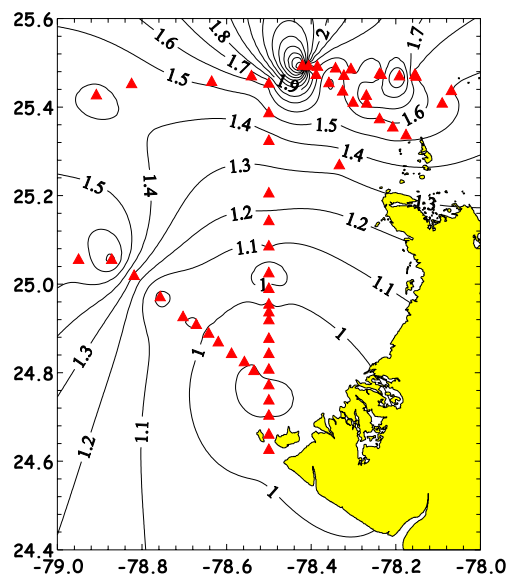


Fig. 12. Contours of the saturation state of Great Bahama Bank waters with respect to the experimentally determined “kinetic” solubility of suspended whiting carbonates of Morse et al. (2003). Note that the inner Bank waters are very close to being in equilibrium with this solubility which is  $\sim 1.9$  times that of aragonite. Solid triangles are sampling stations (Figure published with the kind permission of Elsevier.)

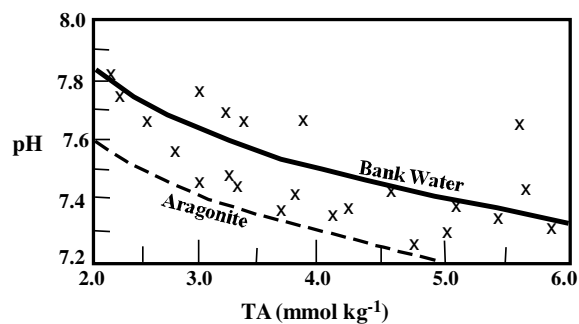


Fig. 13. Data for aragonitic muds in the Bahamas derived from Morse et al. (1985). Sixty percent of the data fall within the uncertainty of about  $\pm 0.1$  pH units for “punch-in” electrode measurements of the line for the “kinetic solubility product”. Five points fall above the uncertainty and six below. Three points were excluded from the plot at extremely high and low pH, and high alkalinity, respectively. The dashed line is for the stoichiometric solubility product of aragonite. Note that in this figure only the pH values are on the NBS scale as reported by Morse et al. (1985).

state IAP values up to about 2.8 times that of aragonite solubility. It is also interesting to note that the kinetic solubility value obtained for the dominantly aragonitic suspended sediment from the Bahamas is very similar to that obtained by Tribble and Mackenzie (1998) for thin overgrowths on calcite (see Morse et al., 2003, for discussion).

The studies from the Bahamas yield a considerable body of evidence that some carbonate phase with a solubility on the order of two times that of aragonite is what current Bahamas Bank seawater will come to equilibrium with given either enough time or a high enough solid to seawater ratio. The presumption of most investigators in these studies has been that this is a high Mg-calcite, the composition

of which depends on whose solubility values are chosen. However, as discussed previously in this paper, the Mg content is not necessarily the only component controlling the solubility of the Mg-calcites. It is possible, and even likely, that a surface phase is formed that may be highly hydrated, disordered, or compositionally impure. The practical consequence of this is that for seawater with a TA typical of that found today, this solubility-controlling phase will probably not be able to form from seawater with a  $p\text{CO}_2$  greater than about 900  $\mu\text{atm}$ .

## 5. Summary

Shallow water Mg-calcite minerals represent a major reservoir that could rapidly react to increasing  $p\text{CO}_2$  and “ocean acidification”, being the “first responder” to decreasing carbonate saturation state because of their higher solubility than aragonite, and acting as a potential sink for anthropogenic  $\text{CO}_2$ . If the total reservoir of reactive high Mg-calcite were completely dissolved in proportional amounts to the present annual oceanic uptake of anthropogenic  $\text{CO}_2$ , surface ocean pH and aragonite saturation state would remain unchanged for about 60 years. In order to predict the response of Mg-calcite minerals to increasing  $p\text{CO}_2$ , it is critical to understand their solubilities as a function of seawater chemistry. At present, it is only the solubilities of the synthetic Mg-calcite minerals that can be considered valid as a function of mol%  $\text{MgCO}_3$  because these solubilities have been achieved from both over- and under-saturation. Current solubility estimates of biogenic Mg-calcites show a wide degree of scatter between different studies and even between Mg-calcite phases of similar  $\text{MgCO}_3$  content making it difficult to predict the behavior of these mineral phases in the *natural environment*. The wide scatter also indicates that factors other than Mg content such as structural disorder and impurities can significantly influence solubility. Nevertheless, because the Mg content of skeletal Mg-calcite appears to correlate with the trend of Mg-calcite phases in metastable equilibrium with surface seawater ion activity products (IAPs) as a function of latitude (Fig. 7), solubilities as a function of  $\text{MgCO}_3$  content may have merit to some extent.

Numerical simulations show that once the surface seawater is undersaturated with respect to a particular Mg-calcite phase, this phase may undergo dissolution. Depending on the solid to solution ratio, rate of dissolution, and the rate of physical mixing of the water mass, a metastable equilibrium may be established between the dissolving phase and the seawater. This metastable equilibrium will persist until the dissolving phase has completely dissolved and a new metastable equilibrium can be established with the next most soluble solid carbonate present in the sediments. The trend of sequential dissolution based on mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain, is confirmed by laboratory experiments and by observations from Bermuda. As the atmospheric  $\text{CO}_2$  concentration continues to increase

owing to burning of fossil fuels, the average composition of contemporary carbonate sediments may change in favor of minerals with lower magnesium content and consequently higher stability. Furthermore, considerable evidence from the Bahamas suggests that the amount of abiotic carbonate production on the Great Bahama Bank will decline as  $p\text{CO}_2$  rises, in accord with model predictions for the global coastal ocean in the future (Andersson et al., 2005).

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