



Life on the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers

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ABSTRACT: Future anthropogenic emissions of CO₂ and the resulting ocean acidification may have severe consequences for marine calcifying organisms and ecosystems. Marine calcifiers depositing calcitic hard parts that contain significant concentrations of magnesium, i.e. Mg-calcite, and calcifying organisms living in high latitude and/or cold-water environments are at immediate risk to ocean acidification and decreasing seawater carbonate saturation because they are currently immersed in seawater that is just slightly supersaturated with respect to the carbonate phases they secrete. Under the present rate of CO₂ emissions, model calculations show that high latitude ocean waters could reach undersaturation with respect to aragonite in just a few decades. Thus, before this happens these waters will be undersaturated with respect to Mg-calcite minerals of higher solubility than that of aragonite. Similarly, tropical surface seawater could become undersaturated with respect to Mg-calcite minerals containing ≥12 mole percent (mol%) MgCO₃ during this century. As a result of these changes in surface seawater chemistry and further penetration of anthropogenic CO₂ into the ocean interior, we suggest that (1) the magnesium content of calcitic hard parts will decrease in many ocean environments, (2) the relative proportion of calcifiers depositing stable carbonate minerals, such as calcite and low Mg-calcite, will increase and (3) the average magnesium content of carbonate sediments will decrease. Furthermore, the highest latitude and deepest depth at which cold-water corals and other calcifiers currently exist will move towards lower latitudes and shallower depth, respectively. These changes suggest that anthropogenic emissions of CO₂ may be currently pushing the oceans towards an episode characteristic of a 'calcite sea.'

KEY WORDS: Ocean acidification · Calcification · Carbonate dissolution · Mg-calcite · High latitude · Aragonite · Saturation state · Calcite sea

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INTRODUCTION

Continuous anthropogenic emissions of CO₂ to the atmosphere and uptake of part of this CO₂ by the oceans will result in a continuous decline in surface seawater calcium carbonate saturation state (Ω ; see Appendix 1) and a decrease in pH, often termed ocean acidification (e.g. Broecker et al. 1971, Bacastow & Keeling 1973, Kleypas et al. 1999a, Caldeira & Wickett 2003, Andersson et al. 2005, Orr et al. 2005). On timescales of several thousands of years, much of the

CO₂ originating from anthropogenic activities will be absorbed by the oceans and ultimately neutralized by dissolution of sedimentary calcium carbonate minerals (Broecker et al. 1971, Archer et al. 1998). However, on shorter timescales, the only way to slow down significantly or prevent future ocean acidification is to reduce the emissions of CO₂ from human activities to the atmosphere. At this time, because of the current global political and socio-economic situation, a large reduction in CO₂ emissions is highly unlikely (Clarke et al. 2007). Therefore, surface seawater pH will continue to

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decline, with all the ecological implications of such a change in a major earth surface system carbon reservoir, until emissions are reduced and the atmospheric CO₂ concentration stabilizes.

Ocean acidification has raised serious concerns about the potential effects on marine organisms and ecosystems, especially those organisms producing shells, tests or skeletons out of calcium carbonate (CaCO₃). In particular, the fates of tropical coral reefs and scleractinian corals have received most of the attention in the ongoing ocean acidification debate (e.g. Kleypas et al. 1999a, 2006, Marubini et al. 2003, Hoegh-Guldberg et al. 2007). Much less attention has been given to marine calcifiers depositing calcium carbonate minerals containing significant proportions of magnesium ions, i.e. Mg-calcite (Borowitzka 1981, Mackenzie & Agegian 1989, Gao et al. 1993, Kuffner et al. 2008), and calcifying organisms living in high latitude and/or cold-water environments (Orr et al. 2005, Guinotte et al. 2006, Roberts et al. 2006, Turley et al. 2007). In either situation, these organisms exist under conditions more corrosive to their shells and skeletons than organisms depositing less soluble mineral phases or organisms living at lower latitudes. The solubility of Mg-calcite minerals with a significant mole percent (mol%) MgCO₃ is greater than the solubility of aragonite and calcite, and the seawater saturation state with respect to carbonate minerals is lower in high latitudes than at low latitudes. The same is true for deep waters compared with shallow waters. Thus, it is likely that Mg-calcite, high latitude and cold-water calcifying organisms will be the first responders to ocean acidification and will serve as 'canaries' to the potential detrimental consequences of this process.

The objective of the present investigation is to evaluate how the surface seawater carbonate saturation state may change in different environments and with respect to Mg-calcite minerals as a result of future ocean acidification. In the second part of this study we evaluate these changes numerically under a business-as-usual (BAU) CO₂ emissions scenario and review the results in terms of the potential consequences to marine calcifiers and carbonate environments.

OVERVIEW OF MARINE CALCIFICATION AND Mg-CALCITE MINERALS

Marine calcifying organisms are an important component of almost all ecosystems, ranging from warm tropical to cold high latitude waters and also the deep sea. In fact, carbonate sediments will accumulate and reflect their presence in the sedimentary column, where they are not significantly exported, dissolved or diluted by terrigenous clastics or other sedimentary

material (Chave 1967). Most of the calcifying taxa found in tropical and subtropical regions are also found in colder environments and include corals, mollusks, coralline algae, foraminifera, bryozoans, echinoderms and crustaceans (Chave 1954). There are even high latitude and cold-water corals and coral ecosystems that produce extensive calcium carbonate structures comparable with shallow tropical reefs (e.g. Rogers 1999, Freiwald et al. 2004, Freiwald & Roberts 2005, Roberts et al. 2006). There are also both warm- and cold-water, shallow-living calcifiers including coralline algae, echinoderms and bryozoans that deposit Mg-calcite of variable composition that can contribute significantly to regional carbonate budgets (Chave 1954). Furthermore, planktonic calcifiers, such as coccolithophorids, pteropods, foraminifera and heteropods, play disproportionately important roles in temperate and high latitude marine environments relative to their role in warmer subtropical/tropical environments. Coccolithophorids and pteropods are the major pelagic producers of calcite and aragonite, respectively, and account for a significant proportion of the particulate organic and particulate inorganic carbon exported from the surface ocean to the deep ocean both regionally and globally (e.g. Iglesias-Rodríguez et al. 2002, Jin et al. 2006).

The occurrence of magnesium in marine skeletal hard parts was first documented by Silliman (1846). Almost a century later while studying mollusk shells, Bøggild (1930) recognized a relationship between magnesium content and skeletal carbonate mineralogy. Bøggild (1930) distinguished among 3 different compositional carbonate phases that occurred in nature: low Mg-aragonite, low Mg-calcite (<4% MgCO₃), and high Mg-calcite (>4% MgCO₃). At first it was commonly believed that the magnesium in high magnesian calcite skeletons was present in the form of the mineral dolomite. This assumption was disproved by Chave (1952), who demonstrated that calcium ions were replaced by magnesium ions in the calcite lattice, shrinking it, and forming a partial solid solution at low temperatures between calcite and dolomite. Mg-calcites are essentially isomorphs of calcite, but compared with pure calcite the substitution of calcium ions with the much smaller magnesium ions in a completely random fashion causes variations in the mineralogical structure, such as carbonate anion and cation positional disorder (e.g. Reeder 1983, Bischoff et al. 1987, Tribble et al. 1995). As a result, under present earth surface temperature and pressure conditions, Mg-calcite minerals are metastable relative to nearly pure calcite and dolomite, i.e. thermodynamically we would not expect their existence, but they persist owing to kinetic constraints (Goldschmidt 1983, Mackenzie et al. 1983).

A wide range of marine calcifiers produce shells, tests or skeletons containing various amounts of magnesium in calcite. The most common and probably also the most important Mg-calcite producers containing significant mol% MgCO_3 are the red coralline algae, benthic foraminifera, bryozoans and echinoderms, but other groups of organisms such as crustaceans, molluscs, annelid worms, calcareous sponges, barnacles and brachiopods also deposit Mg-calcite of varying composition (Chave 1954, Morse & Mackenzie 1990). Mg-calcite-producing marine calcifiers make up a significant proportion of the total biomass of calcifying organisms on coral reefs and in shoal water environments although aragonite-producing organisms (e.g. scleractinian corals, green algae and certain molluscs) are the most important calcifiers in these environments. However, in many coral reefs, coralline algae of high magnesian calcite compositions are the major framework and cementing taxa. Based on more than 700 sediment samples from different tropical and subtropical neritic environments, the relative proportions of aragonite, Mg-calcite and calcite (including low Mg-calcite) were found to be 63, 24 and 13%, respectively (Land 1967). The average Mg-calcite composition of carbonate sediments in the same environments contains about 13 to 15 mol% MgCO_3 (Morse & Mackenzie 1990).

The mechanisms controlling the magnesium content of marine calcitic skeletons are poorly understood and exert different influences on different organisms. Marine calcifiers depositing aragonite contain almost none or very little magnesium (<1 mol%) and the same is true for calcite producers, which are mostly represented by pelagic calcifiers, such as certain species of coccolithophorids and foraminifera. Among organisms depositing Mg-calcite of various compositions, ranging from a few mol% to as much as 30 mol%, there are distinct differences between different species. Clearly, there is a strong taxonomic control on the magnesium content of calcitic skeletons (Chave 1954). Also, the magnesium content of marine calcifiers depositing Mg-calcite is seen to decrease as a function of increasing latitude (Fig. 1). Thus, the Mg content of skeletal hard parts covaries with changes in environmental variables such as temperature, light and seawater carbonate saturation state, all of which decrease with increasing latitude (Chave 1954, Mackenzie et al. 1983). This variation in magnesium content has been attributed to variation in growth rate (Moberly 1968), which is not only a function of temperature and seawater carbonate saturation state, but also energy availability (i.e. food), and in phototrophic organisms (or organisms dependent on phototrophic symbionts) it is also a function of photosynthetic activity and consequently light and nutrient concentration (Mackenzie et al. 1983). The magnesium content of shallow water

Mg-calcite cements follows a similar latitudinal trend as biogenic phases, and a similar trend has also been observed as a function of depth and consequently decreasing seawater carbonate ion concentration and temperature (Schlager & James 1978, Mackenzie et al. 1983, Videtich 1985).

Experimental results have clearly demonstrated that the rate of calcification in marine calcifiers is directly related to the seawater carbonate saturation state (e.g. Gattuso et al. 1999, Langdon et al. 2000, Marubini et al. 2003). Furthermore, Mackenzie & Agegian (1989) showed that the growth rate of *Porolithon gardineri*, measured as linear extension and the magnesium content were directly correlated to seawater carbonate saturation state and temperature. Other studies have demonstrated that the magnesium content of calcitic skeletons varies as a result of changes in the Mg to Ca ratio in seawater (Stanley et al. 2002, Ries 2006, see also Mackenzie et al. 1983 for a synthesis of data on Mg to Ca ratio of solution versus precipitate Mg-calcite composition), but this is only important on timescales of millions of years when significant changes of this ratio in seawater occurred (Guidry et al. 2007). However, a change in Ca and Mg concentrations and the ratio of these ions essentially implies a change in the seawater saturation state with respect to Mg-calcite phases, which also could be accomplished by a change in the carbonate ion concentration (Appendix 1). Lower CO_3^{2-} concentration and consequently lower carbonate saturation state favour Mg-calcite deposits of lower magnesium content both kinetically and thermodynamically (Mackenzie et al. 1983). Lower seawater carbonate saturation states also result in increas-

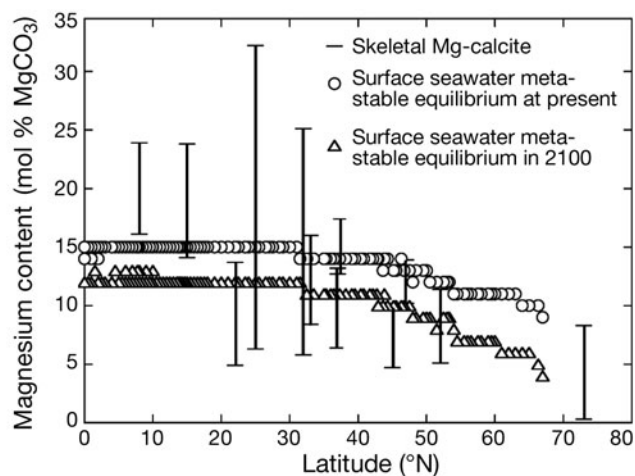


Fig. 1. Range of magnesium content of calcitic skeletons as a function of latitude (Chave 1954). The Mg-calcite phase in metastable equilibrium with the surface seawater according to the 'minimally prepared' solubility curve (see text) is also shown at present time and in the year 2100 under a business-as-usual (BAU) CO_2 emissions scenario (IS92a)

ing dissolution rates of metastable carbonate mineral phases subjected to undersaturated conditions.

One of the most controversial and highly debated problems related to the Mg-calcite minerals is that of their solubility (see Morse et al. 2006 for a detailed discussion and references therein). In general, biogenic Mg-calcites with a significant mol% MgCO₃ are more soluble than both calcite and aragonite, and the approximate Mg-calcite composition with the same solubility as aragonite ranges from 8 to 12 mol% MgCO₃ depending on the experimental solubility curve adopted. There are essentially 2 different experimental solubility curves for biogenic Mg-calcites that are referred to as either the biogenic 'minimally prepared' (Plummer & Mackenzie 1974) or the biogenic 'cleaned' solubility curve (e.g. Bischoff et al. 1987), and each is differentiated by the extent of preparation of the experimental materials. At this time, it is not fully understood which solubility curve most accurately reflects the behaviour of biogenic Mg-calcite minerals in the natural environment (Morse et al. 2006), although suggestions in favour of the use of the 'minimally prepared' solubility curve have been made in the literature (Bischoff et al. 1993, Tribble et al. 1995). One of the problems in determining the solubility of biogenic Mg-calcites arises from their heterogeneous nature and inclusion of impurities other than Mg, such as H₂O, OH⁻, HCO₃⁻, SO₄²⁻ and other ions, which commonly are found in biogenic skeletons. Furthermore, another problem arises from the fact that a true equilibrium cannot be established between a given Mg-calcite and a solution (Garrels & Wollast 1978). In the initial stages of experimental dissolution studies, the dissolution process occurs congruently, but becomes incongruent as the solution becomes supersaturated with respect to a Mg-calcite phase of lower magnesium content, which then starts to precipitate. To overcome this problem, experimentalists have extrapolated data from the congruent step to infinite time, making the assumption that this represents equilibrium at a condition referred to as stoichiometric saturation for the solid solution.

FUTURE CHANGES IN SEAWATER CARBONATE SATURATION STATE AND EFFECTS ON CALCIFIERS

Methodology

In the present calculations, surface seawater saturation states with respect to calcite, aragonite, and 18, 15 and 12 mol% Mg-calcite were calculated as follows. Average salinity (S) and total alkalinity (TA) were extracted for the chosen temperature regimes from a

global model developed by M. Jeffries at the Bermuda Institute of Ocean Sciences (BIOS) based on data from the World Ocean Circulation Experiment (WOCE) and the Global Ocean Data Analysis Project (GLODAP) (M. Jeffries & N. Bates unpubl. data). The following conditions for 3 typical environments were determined: tropical/subtropical (temperature = 25 ± 1°C, S = 35.53 ± 0.87, TA = 2333.8 ± 51.5 μmol kg⁻¹), temperate (temperature = 13 ± 1°C, S = 34.51 ± 0.88, TA = 2284.1 ± 50.0 μmol kg⁻¹) and high latitude (temperature = 4 ± 1°C, S = 33.82 ± 0.45, TA = 2271.0 ± 28.3 μmol kg⁻¹). Saturation state with respect to Mg-calcite mineral compositions were calculated based on both the biogenic 'minimally prepared' and biogenic 'cleaned' solubility curves using total ion activity coefficients defined by Millero & Pierrot (1998) (Appendix 1). Assuming equilibrium between the atmosphere and the surface ocean with respect to the partial pressure of CO₂ (pCO₂), dissolved inorganic carbon parameters were calculated using CO2SYS (Lewis & Wallace 1998) and stoichiometric carbonic acid system constants defined by Mehrbach et al. (1973) and refit by Dickson & Millero (1987). Future projections until the year 2100 were based on the Intergovernmental Panel on Climate Change IS92a CO₂ emissions scenario (IPCC 2001). Since increasing temperature counteracts the effect of rising pCO₂ on seawater carbonate saturation state, the effect of increasing surface seawater temperature (SST) on this parameter was also evaluated. The fossil fuel intensive emissions scenario A1FI was adopted in this simulation to evaluate the maximum effect of increasing temperature during the present century.

Results

At present, surface seawater saturation state with respect to carbonate minerals decreases with increasing latitude owing to decreasing CO₃²⁻ concentration and temperature (Figs. 1 & 2). Typical tropical/ subtropical surface seawater is currently supersaturated with respect to calcite and aragonite by 550 and 360%, respectively (Fig. 2). Temperate surface seawater is supersaturated with respect to these mineral phases by 370 and 230%, respectively, and typical high latitude surface seawater is supersaturated by 260 and 160%, respectively (Fig. 2). Based on the biogenic 'minimally prepared' solubility curve (Plummer & Mackenzie 1974), saturation state calculations show that average tropical/subtropical surface seawater is close to a metastable equilibrium state with 15 mol% Mg-calcite and, consequently, undersaturated with respect to Mg-calcite phases with higher magnesium content. The same calculations show that average high latitude and temperate surface seawater is currently undersaturated

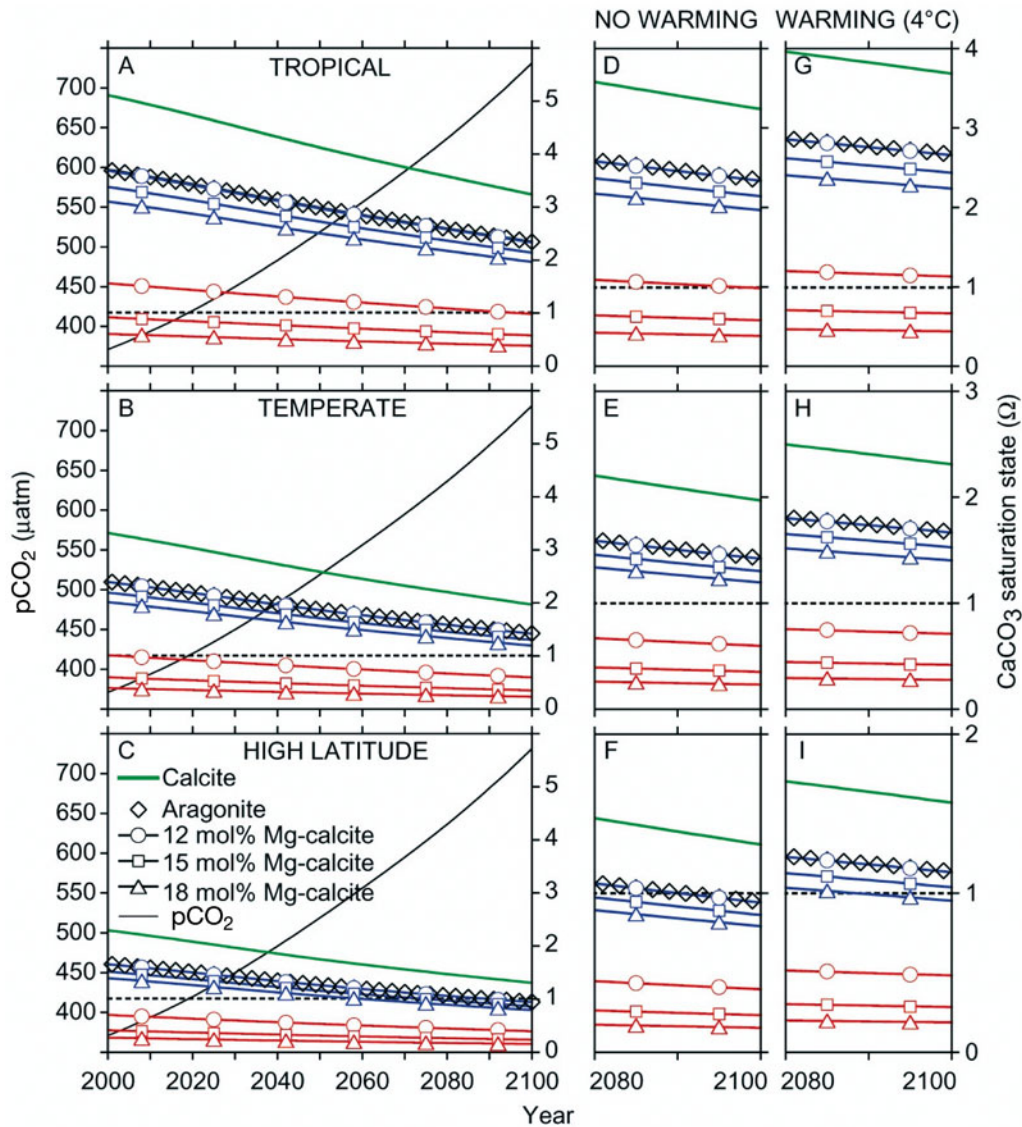


Fig. 2. Surface seawater pCO₂ (partial pressure of CO₂) and carbonate saturation state with respect to calcite, aragonite, and 12, 15 and 18 mol% Mg-calcite for a typical tropical/subtropical (temperature = 25 ± 1°C, salinity [S] = 35.53 ± 0.87, total alkalinity [TA] = 2333.8 ± 51.5), temperate (temperature = 13 ± 1°C, S = 34.51 ± 0.88, TA = 2284.1 ± 50.0) and high latitude (temperature = 4 ± 1°C, S = 33.82 ± 0.45, TA = 2271.0 ± 28.3) ocean environment during the 21st century. The calculations were forced by an increase in pCO₂ following the IS92a CO₂ emissions scenario (IPCC 2001) and assuming instantaneous equilibrium between the atmosphere and the surface ocean. TA, S and temperature were assumed constant in panels (A) through (F). In panels (G) through (I), the calculations were forced by an increase in global mean temperature following the A1FI CO₂ emissions scenario, resulting in an increase in temperature of ~4°C from the year 2000 to 2100 (IPCC 2001). Years 2080 to 2100 are highlighted in panels (D) through (I) to demonstrate the effect of warming on the seawater carbonate saturation state. The seawater saturation state with respect to biogenic Mg-calcite minerals was calculated based on the solubility curve of both the 'minimally prepared' (red lines; Plummer & Mackenzie 1974) and the 'cleaned' (blue lines) biogenic carbonate material (Bischoff et al. 1987, 1993)

with respect to 12, 15, and 18 mol% Mg-calcite (Fig. 2). In contrast, calculations based on the biogenic 'cleaned' solubility curve (e.g. Bischoff et al. 1987, 1993) suggest that surface seawater in all climatic regions is currently well supersaturated with respect to these Mg-calcite compositions (Fig. 2).

In the present model scenario, the surface seawater saturation state with respect to carbonate minerals will

decrease in all environments owing to uptake of anthropogenic CO₂. Numerical simulations show that tropical/subtropical and temperate surface seawater will remain supersaturated with respect to calcite and aragonite by the year 2100. However, average high latitude surface seawater could become undersaturated in the second half of this century with respect to aragonite and, thus, become undersaturated with respect to

Mg-calcite phases that are more soluble than aragonite prior to this (see Orr et al. 2005 for a detailed evaluation on the effects of anthropogenic CO₂ on surface seawater aragonite saturation). According to the biogenic 'minimally prepared' solubility curve (Plummer & Mackenzie 1974), surface seawater in all climatic regions will be undersaturated or at metastable equilibrium with respect to a 12 mol% Mg-calcite and phases of greater magnesium content by the year 2100 (Fig. 2). High latitude surface seawater could be in metastable equilibrium with a Mg-calcite phase containing as little as 4 to 5 mol% MgCO₃ by 2100 (Fig. 1). In contrast, calculations based on the biogenic 'cleaned' solubility curve (e.g. Bischoff et al. 1987, 1993) show that only high latitude surface seawater will become undersaturated with respect to Mg-calcite phases containing 12 mol% and higher MgCO₃ during the 21st century (Fig. 2). A potential increase in SST of approximately 4°C during the 21st century will affect the final saturation state index with respect to aragonite in year 2100 by 0.32 Ω units in tropical/subtropical environments, 0.25 Ω units in temperate environments and 0.19 Ω units in high latitude environments. Thus, the effect of warming on the seawater aragonite saturation state (and other carbonate mineral phases) is small compared with the decrease in this variable owing to uptake of anthropogenic CO₂ and ocean acidification (Fig. 2).

Discussion

Clearly, to predict accurately the timing of when seawater becomes undersaturated with respect to a particular Mg-calcite phase owing to ocean acidification, it is necessary to determine more accurately the solubility and kinetic behaviour of these mineral phases in the natural environment and under conditions of increasing CO₂. Nevertheless, the seawater saturation level for many of these mineral phases is lower than that of aragonite and the degree of saturation is decreasing in most marine environments owing to rising atmospheric CO₂ and ocean acidification. Surface seawater is likely to become undersaturated with respect to aragonite (its solubility is well characterised) at high latitudes in a matter of decades (Fig. 2; Orr et al. 2005); thus, seawater will be undersaturated with respect to many Mg-calcite phases prior to this time.

The observed trend of decreasing Mg content in calcitic skeletons as a function of increasing latitude is in all probability partly a direct reflection of the slower growth rate of these organisms due to decreasing seawater carbonate saturation state and colder temperatures. Although the Mg content is highly variable and affected by additional factors (see previous discussion),

changes in seawater chemistry owing to uptake of anthropogenic CO₂ will most probably result in a decrease in the average Mg composition of Mg-calcite-producing organisms in all environments, despite the warmer SSTs of the future. The same could be true for inorganic precipitates, such as carbonate cements. As a result, the average magnesium content of contemporary carbonate sediments will decrease because of the lower magnesium content in the source material, i.e. marine calcifiers and inorganic precipitates, but also owing to the selective dissolution of highly soluble Mg-calcite phases (Andersson et al. 2005, 2007, Morse et al. 2006).

Despite uncertainties in terms of the Mg-calcite solubility curve as a function of MgCO₃ content, it is probable that many Mg-calcite-secreting organisms and contemporary carbonate sediments currently exist or soon may exist close to a metastable equilibrium with the seawater in which they are immersed (Fig. 1). Thus, a small alteration of the seawater carbonate saturation state owing to CO₂ uptake will result in these organisms and sediments being immersed in seawater undersaturated with respect to these mineral phases. The same is true for organisms depositing aragonite and living in high latitude or cold-water environments, such as pteropods and cold-water corals, which soon could also be immersed in seawater undersaturated with respect to this mineral phase (Orr et al. 2005, Guinotte et al. 2006, Turley et al. 2007; Fig. 2). Undersaturated seawater conditions certainly imply that unprecedented challenges and alterations to the function, structure and distribution of calcifying organisms and carbonate ecosystems exposed to these conditions will occur. It is improbable that, under such conditions, marine calcifiers could sustain themselves as they do today. Hence, as high latitude environments progressively become increasingly acidic and undersaturated with respect to aragonite, the highest latitude at which cold-water corals and other calcifiers are found is likely to move progressively towards lower latitudes. A similar situation has been proposed with respect to tropical aragonitic corals as the aragonite saturation state reaches a 'critical' threshold, below which these organisms cannot thrive (Kleypas et al. 1999b, Guinotte et al. 2003). Furthermore, as anthropogenic CO₂ penetrates deeper into the oceans, the seawater saturation horizons (the depth at which Ω = 1; Appendix 1) with respect to various carbonate mineral phases will become shallower (Feely et al. 2004). Consequently, the maximum depth at which deep water corals and other calcifying organism are found will shoal (Guinotte et al. 2006, Turley et al. 2007). If significant dissolution takes place above the chemical lysoclines of the biogenic carbonate minerals (Milliman et al. 1999), anthropogenic CO₂ may not have to penetrate

as deep into the ocean as currently thought to begin to dissolve carbonate phases at depth. The timing of these changes depends on the rate at which anthropogenic CO₂ is transported into the interior of the oceans, but this may already occur in certain environments.

Lower seawater carbonate saturation state most certainly implies slower rates of calcification for most marine calcifiers and possibly a lessened ability to compete for space and other important resources (e.g. Kleypas et al. 1999a, 2006, Andersson et al. 2005, Kuffner et al. 2008). As a result, the relative proportion of non-calcifying organisms to calcifying organisms may become increasingly larger in the near future than is seen today. Lower carbonate saturation state also favours deposition of less soluble mineral phases (Mackenzie et al. 1983). Thus, organisms depositing stable carbonate minerals, such as calcite and low Mg-calcite could become increasingly dominant under future increasingly acidic seawater conditions. Some organisms currently depositing metastable carbonate phases such as aragonite and high Mg-calcite may not be able to sustain themselves under such conditions (Kuffner et al. 2008), but others could possibly persist through deposition of carbonate minerals of greater stability. For example, Stolarski et al. (2007) discovered that corals known to deposit aragonite actually secreted calcite during an episode of the Cretaceous Period, but the controlling mechanisms are unknown. Ries et al. (2006) observed similar results for corals growing in artificial seawater of variable magnesium to calcium ratio, thus, changing the composition of the mineral phase favoured to precipitate based on thermodynamic and kinetic principles. Other evidence suggests that some corals could survive detrimental acidic seawater conditions in a non-calcifying state (Fine & Tchernov 2007).

It is noteworthy that the ecological and compositional changes for marine calcifiers and ecosystems discussed here (as a result of ocean acidification and decreasing carbonate saturation state) are similar to those changes inferred from the carbonate sedimentary record, which showed that the transitions from aragonite to calcite seas favoured the deposition of carbonate minerals of increasing stability in both skeletal and non-skeletal precipitates (e.g. Mackenzie & Pigott 1981, Sandberg 1983, Stanley & Hardie 1998, Stanley et al. 2002). Mackenzie & Pigott (1981) and Sandberg (1983) first noted oscillations in the primary mineralogy of ooids and marine cements between calcite and aragonite during the Phanerozoic Eon. Sandberg (1983) referred to these oscillations as aragonite-inhibiting or aragonite-facilitating episodes and Mackenzie & Pigott (1981) referred to them as oscillatory and submergent tectonic modes. Later these

episodes have been referred to as aragonite or calcite seas. Stanley & Hardie (1998) subsequently demonstrated that the dominant mineralogy of biogenic skeletal carbonate deposits also varied between calcite (and low Mg-calcite) and aragonite mineralogy (and high Mg-calcite) during this time period, which correlated well with Sandberg's (1983) and Mackenzie & Pigott's (1981) episodes. These oscillations are commonly associated with climatic episodes, sea level fluctuations, plate tectonic modes and carbonate-silicate weathering cycles, involving changes in seawater Mg to Ca ratio, atmospheric and seawater CO₂ concentrations and, consequently, seawater carbonate saturation state (Sandberg 1983, Morse & Mackenzie 1990, Stanley & Hardie 1998, Guidry et al. 2007). Although seawater composition and chemistry were significantly different during these episodes relative to the present (Guidry et al. 2007), decadal to centennial scale ocean acidification owing to the absorption of CO₂ in the oceans from the burning of fossil fuels and land use changes and consequent changes in the seawater carbonate saturation state could push the Earth towards an episode with carbonate environments similar to that of a calcite sea. Mg-calcite, high latitude and cold-water marine calcifiers, which already exist on the margin in terms of seawater carbonate saturation state, will be the first responders to this major transition. The consequences to Mg-calcite-producing organisms and sediments are most certainly drastic, but the timing is uncertain because we do not fully understand the solubilities and kinetic behaviour of these mineral phases in the natural environment. This lack of knowledge of these phenomena warrants further study.

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LITERATURE CITED

- Andersson AJ, Mackenzie FT, Lerman A (2005) Coastal ocean and carbonate systems in the high CO₂ world of the Anthropocene. *Am J Sci* 305:875–918
- Andersson AJ, Bates NR, Mackenzie FT (2007) Dissolution of carbonate sediments under rising pCO₂ and ocean acidification: observations from Devil's Hole, Bermuda. *Aquat Geochem* 13:237–264
- Archer D, Kheshgi H, Maier-Reimer E (1998) Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃. *Global Biogeochem Cycles* 12:259–276
- Bacastow RD, Keeling CD (1973) Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: II. Changes

- from A.D. 1700 to 2070 as deduced from a geochemical model. In: Woodwell GM, Pecan EV (eds) Carbon and the biosphere. US Atomic Energy Commission, Washington, DC, p 86–135
- Bischoff WD, Mackenzie FT, Bishop FC (1987) Stabilities of synthetic Mg-calcites in aqueous solution: comparison with biogenic materials. *Geochim Cosmochim Acta* 51: 1413–1423
- Bischoff WD, Bertram MA, Mackenzie FT, Bishop FC (1993) Diagenetic stabilization pathways of magnesian calcites. *Carb Evap* 8:82–89
- Bøggild OB (1930) The shell structure of the mollusk. *Danske Vidensk Selsk Skr* 9:235–326
- Borowitzka MA (1981) Photosynthesis and calcification in the articulated coralline red algae *Amphiroa anceps* and *A. foliacea*. *Mar Biol* 62:17–23
- Broecker WS, Li YH, Peng TH (1971) Carbon dioxide—man's unseen artifact. In: Hood DW (ed) Impingement of man on the oceans. John Wiley & Sons, New York, p 287–324
- Caldeira K, Wickett ME (2003) Anthropogenic carbon and ocean pH. *Nature* 425:365
- Chave KE (1952) A solid solution between calcite and dolomite. *J Geol* 60:190–192
- Chave KE (1954) Aspects of biogeochemistry of magnesium 1. Calcareous marine organisms. *J Geol* 62:266–283
- Chave KE (1967) Recent carbonate sediments: an unconventional view. *J Geol Educ* 15:200–204
- Clarke LE, Edmonds JA, Jacoby HD, Pitcher HM, Reilly JM, Richels RG (2007) Scenarios of greenhouse gas emissions and atmospheric concentrations. Sub-report 2.1A Synthesis and Assessment Product 2.1 by the US Climate Change Science Program and the Subcommittee on Global Change Research. Department of Energy, Office of Biological & Environmental Research, Washington, DC
- Dickson A, Millero FJ (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res* 34:1733–1743
- Feely RA, Sabine CL, Lee K, Berelson W, Kleypas J, Fabry VJ, Millero FJ (2004) Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. *Science* 305:362–366
- Fine M, Tchernov D (2007) Scleractinian coral species survive and recover from decalcification. *Science* 315:1811
- Freiwald A, Roberts JM (eds) (2005) Cold-water corals and ecosystems. Springer Verlag, Heidelberg
- Freiwald A, Fosså JH, Grehan A, Koslow T, Roberts JM (2004) Cold-water coral reefs. UNEP-WCMC, Cambridge
- Gao K, Aruga Y, Asada K, Ishihara T, Akano T, Kiyohara M (1993) Calcification in the articulated coralline alga *Coralline pilulifera*, with special reference to the effect of elevated CO₂ concentration. *Mar Biol* 117:129–132
- Garrels R, Wollast R (1978) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—example: the magnesian calcite discussion. *Am J Sci* 278:1469–1474
- Gattuso JP, Allemand PD, Frankignoulle M (1999) Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. *Am Zool* 39:160–183
- Goldschmidt JR (1983) Phase relations of rhombohedral carbonates. In: Reeder RJ (ed) Carbonates: mineralogy and chemistry. Reviews in mineralogy, Vol 11. Mineralogical Society of America, Washington, DC, p 49–76
- Guidry MW, Arvidson RS, Mackenzie FT (2007) Biological and geochemical forcings to Phanerozoic change in seawater, atmosphere, and carbonate precipitate composition. In: Falkowski PG, Knoll AH (eds) Evolution of aquatic photoautotrophs. Academic Press, New York, p 377–403
- Guinotte JM, Buddemeier RW, Kleypas JA (2003) Future coral reef marginality: temporal and spatial effects of climate change in the Pacific basin. *Coral Reefs* 22:551–558
- Guinotte JM, Orr J, Cairns S, Freiwald A, Morgan L, George R (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? *Front Ecol Environ* 4:141–146
- Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS and others (2007) Coral reefs under rapid climate change and ocean acidification. *Science* 318:1737–1742
- Iglesias-Rodríguez MD, Armstrong R, Feely R, Hood R and others (2002) Progress made in study of ocean's calcium carbonate budget. *Eos Trans AGU* 83(34):365
- IPCC (Intergovernmental Panel on Climate Change) (2001) Climate change 2001: the scientific basis In: Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Dai X, Maskell K, Johnson CA (eds) Contribution of Working Group I to the third assessment report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge
- Jin X, Gruber N, Dunne JP, Sarmiento JL, Armstrong RA (2006) Diagnosing the contribution of phytoplankton functional groups to the production and export of particulate organic carbon, CaCO₃, and opal from global nutrient and alkalinity distributions. *Global Biogeochem Cycles* 20: GB2015, doi:10.1029/2005GB002532
- Kleypas JA, Buddemeier RW, Archer D, Gattuso JP, Langdon C, Opdyke BN (1999a) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* 284:118–120
- Kleypas JA, McManus J, Menez LB (1999b) Environmental limits to coral reef development: Where do we draw the line? *Am Zool* 39:146–159
- Kleypas JA, Feely RA, Fabry VJ, Langdon C, Sabine CL, Robbins LL (2006) Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research. Report of a workshop held 18–20 April 2005, sponsored by NSF, NOAA, and the US Geological Survey, St. Petersburg, FL
- Kuffner IB, Andersson AJ, Jokiel P, Rodgers KS, Mackenzie FT (2007) Decreases in recruitment of crustose coralline algae due to ocean acidification. *Nat Geosci* 1:114–117
- Land LS (1967) Diagenesis of skeletal carbonates. *J Sediment Petrol* 37:914–930
- Langdon C, Takahashi T, Sweeney C, Chipman D and others (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem Cycles* 14:639–654
- Lewis E, Wallace DWR (1998) Program developed for CO₂ system calculations. ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN
- Mackenzie FT, Agegian CR (1989) Biomineralization and tentative links to plate tectonics. In: Crick RE (ed) Origin, evolution, and modern aspects of biomineralization in plants and animals. Plenum Press, New York, p 11–27
- Mackenzie FT, Pigott JP (1981) Tectonic controls of Phanerozoic sedimentary rock cycling. *J Geol Soc Lond* 138: 183–196
- Mackenzie FT, Bischoff WD, Bishop FC, Loijens M, Schoonmaker J, Wollast R (1983) Magnesian calcites: low temperature occurrence, solubility and solid-solution behavior. In: Reeder RJ (ed) Carbonates: mineralogy and chemistry. Reviews in Mineralogy, Vol 11. Mineralogical Society of America, Washington, DC, p 97–143
- Marubini F, Ferrier-Pagés C, Cuif JP (2003) Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. *Proc R Soc Lond B Biol Sci* 270:179–184

- Mehrbach C, Culbertson CH, Hawley JE, Pytkowicz RM (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol Oceanogr* 18:897–907
- Millero FJ, Pierrot D (1998) A chemical equilibrium model for natural waters. *Aquat Geochem* 4:153–199
- Milliman JD, Troy PJ, Balch WM, Adams AK, Li YH, Mackenzie FT (1999) Biologically mediated dissolution of calcium carbonate above the chemical lysocline? *Deep-Sea Res I* 46:1653–1669
- Moberly R (1968) Composition of magnesian calcites of algae and pelecypods by electron microprobe analysis. *Sedimentology* 11:61–82
- Morse JW, Mackenzie FT (1990) *Geochemistry of sedimentary carbonates*. Elsevier Science, Amsterdam
- Morse JW, Andersson AJ, Mackenzie FT (2006) Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO₂ and ocean acidification: role of high Mg-calcites. *Geochim Cosmochim Acta* 70:5814–5830
- Orr JC, Fabry VJ, Aumont O, Bopp L and others (2005) Anthropogenic ocean acidification over the twenty-first century and its impacts on calcifying organisms. *Nature* 437:681–686
- Plummer LN, Mackenzie FT (1974) Predicting mineral solubility from rate data: application to the dissolution of Mg-calcites. *Am J Sci* 274:61–83
- Reeder RJ (1983) Crystal chemistry of the rhombohedral carbonates. In: Reeder RJ (ed) *Carbonates: mineralogy and chemistry*. Reviews in Mineralogy, Vol 11. Mineralogical Society of America, Washington, DC, p 1–47
- Ries J (2006) Mg fractionation in crustose coralline algae: geochemical, biological, and sedimentological implications of secular variation in the Mg/Ca ratio of seawater. *Geochim Cosmochim Acta* 70:891–900
- Ries J, Stanley S, Hardie LA (2006) Scleractinian corals produce calcite, and grow more slowly, in artificial Cretaceous seawater. *Geology* 34:525–528
- Roberts JM, Wheeler AJ, Freiwald A (2006) Reefs of the deep: the biology and geology of cold-water coral ecosystems. *Science* 312:543–547
- Rogers AD (1999) The biology of *Lophelia pertusa* (Linnaeus 1758) and other deep-water reef-forming corals and impacts from human activities. *Int Rev Hydrobiol* 84: 315–406
- Sandberg PA (1983) An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. *Nature* 305:19–22
- Schlager W, James NP (1978) Low-magnesian calcite limestones forming at the deep-seafloor, Tongue of the Ocean, Bahamas. *Sedimentology* 25:675–702
- Silliman B (1846) On the chemical composition of the calcareous corals. *Am J Sci* 1:189–199
- Stanley SM, Hardie LA (1998) Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeogr Palaeoclimatol Palaeoecol* 144:3–19
- Stanley SM, Ries JB, Hardie LA (2002) Low-magnesium calcite produced by coralline algae in seawater of late Cretaceous composition. *Proc Natl Acad Sci USA* 99: 15323–15326
- Stolarski J, Meibom A, Przeniostko R, Mazur M (2007) A Cretaceous scleractinian coral with a calcitic skeleton. *Science* 318:92–94
- Thorstenson DC, Plummer LN (1977) Equilibrium criteria for two component solids reacting with fixed composition in an aqueous phase; example: the magnesian calcites. *Am J Sci* 277:1203–1223
- Tribble JS, Arvidson RS, Lane M III, Mackenzie FT (1995) Crystal chemistry and thermodynamic and kinetic properties of calcite, dolomite, apatite, and biogenic silica: application to petrologic problems. *Sediment Geol* 95:11–37
- Turley CM, Roberts JM, Guinotte JM (2007) Corals in deep-water: Will the unseen hand of ocean acidification destroy cold-water ecosystems? *Coral Reefs* 26:445–448
- Vidulich PE (1985) Electron microprobe study of Mg distribution in recent Mg calcites and recrystallized equivalents from the Pleistocene and Tertiary. *J Sediment Petrol* 55: 421–429

Appendix 1. Calculating seawater carbonate saturation state (Ω)

A general expression for the calculation of seawater saturation state with respect to carbonate minerals is: $\Omega = \frac{[Mg^{2+}]^x [Ca^{2+}]^{(1-x)} [CO_3^{2-}]}{K_x}$, where brackets {} represent ion activities, x is the mol fraction magnesium ions, and K_x is the equilibrium constant with respect to the particular carbonate phase ($K_x = IAP$, ion activity product at equilibrium).

Ion activities are not easily measured and most commonly seawater saturation state with respect to calcite and aragonite are calculated using ion concentrations (denoted by square brackets []) and stoichiometric solubility products ($K_{sp}^* = ICP$, ion concentration product at equilibrium): $\Omega = \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}^*}$.

In contrast, stoichiometric solubility products with respect to Mg-calcite minerals have not been determined and the saturation state with respect to these mineral phases has to be calculated based on ion activities. The ion activity (a) is calculated based on the observed ion concentrations (C) multiplied by the total ion activity coefficient (γ_T), which has been determined experimentally or from theory (e.g.

Millero & Pierrot 1998): $a = \gamma_T \times C$. Since a true equilibrium cannot be achieved with respect to Mg-calcite minerals, K_x represents a metastable equilibrium state obtained from what has been referred to as stoichiometric saturation (Thorstenson & Plummer 1977; a term not equivalent to the definition of the stoichiometric solubility product, see for example Morse et al. 2006 and references therein).

If $\Omega > 1$ with respect to a particular mineral phase, the seawater is supersaturated with respect to that phase, and if $\Omega < 1$, the seawater is undersaturated. When $\Omega = 1$ this implies that the seawater is in thermodynamic equilibrium with respect to that mineral phase, i.e. the forward and backward reaction (dissolution and precipitation) are equal to one another. Thermodynamically, one would expect net dissolution if a mineral phase were immersed in a solution undersaturated with respect to that mineral phase, and the opposite, i.e. net precipitation, if the solution were supersaturated. This is strictly not the case because of kinetic constraints and inhibition by various components present in seawater.