

SEAWATER CHEMISTRY CONTROL OF MARINE LIMESTONE ACCUMULATION OVER THE PAST 550 MILLION YEARS

R. RIDING¹ AND L. LIANG^{2,3}

¹ School of Earth, Ocean and Planetary Sciences, Cardiff University, Cardiff CF10 3YE, United Kingdom
E-mail: riding@cardiff.ac.uk

² School of Engineering, Cardiff University, Cardiff CF24 0YF, United Kingdom
E-mail: liang@cardiff.ac.uk

³ Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
E-mail: liangl@ornl.gov

Abstract

Using estimates of past seawater ionic composition and atmospheric CO₂ levels, and assuming constant temperature of 15 °C, we calculated seawater saturation state with respect to CaCO₃ minerals (aragonite and calcite) and dolomite for the past ~550 million years. Comparison shows that measured rates of shallow marine limestone accumulation for this period broadly conform to fluctuations in calculated aragonite and calcite saturation ratios. This relationship suggests a primary control by seawater chemistry on limestone formation, and therefore also on the biomineralization processes of many algae and invertebrates whose shells are common limestone components. This inference is supported by increased abundance of microbial and nonskeletal carbonates during periods of elevated seawater saturation state. Higher values of saturation state and limestone accumulation during times of ‘calcite seas’, and lower values during ‘aragonite seas’, suggest an integrated pattern of variation in marine CaCO₃ precipitation, and consequently in CO₂ sequestration, reflecting global geochemical cycles.

Key words: Biomineralization, Carbonate, Phanerozoic, Precipitation, Saturation.

Resumen

Usando las estimaciones de la composición iónica del agua del mar en el pasado y de los niveles de CO₂ atmosférico, y asumiendo una temperatura constante de 15 °C, hemos calculado el estado de saturación del agua del mar con respecto a los minerales de CO₃Ca (aragonito y calcita) y a la dolomita para los últimos ~550 millones de años. La comparación muestra que las variaciones en la tasa de acumulación de calizas en aguas marinas someras para este intervalo se ajustan a las fluctuaciones en las tasas de saturación calculadas para la calcita y el aragonito. Esta relación sugiere un control primario de la química del agua marina sobre la formación de calizas y, por tanto, también sobre los procesos de biomineralización de algunas algas e invertebrados cuyas conchas son componentes comunes en las calizas. Esta inferencia está apoyada por un incremento en la abundancia de calizas microbianas y de carbonatos no esqueléticos durante períodos de elevada saturación del agua marina. Valores más altos del estado de saturación y de acumulación de calizas durante los intervalos de “mares calcíticos”, y bajos valores durante los intervalos de “mares aragoníticos” sugieren una pauta integrada de variación en la precipitación de CO₃Ca y, consecuentemente, en el secuestro de CO₂, reflejando ciclos geoquímicos globales.

Palabras clave: Biomineralización, carbonatos, Fanerozoico, precipitación, nivel de saturación.

INTRODUCTION

One of the environmental consequences of the presence of long-lived oceans on Earth has been the continuing extensive sequestration of atmospheric CO₂ in the form of sedimentary calcium carbonate minerals such as aragonite and calcite. This inorganic carbon reservoir, preserved as limestones in crustal rocks, far exceeds the organic carbon in modern biomass and fossil fuels combined (Holland, 1978; Stumm and Morgan, 1996). Without such CO₂ sequestration, Earth's habitability may have been jeopardized by a runaway greenhouse climate similar to Venus (Walker *et al.*, 1981).

Significant questions concerning long-term controls on marine CaCO₃ precipitation are still unresolved (Leeder, 1999). Both organic and inorganic processes can result in CaCO₃ precipitation (Leeder, 1999). The relative importance of these processes over geological time (Opdyke and Wilkinson, 1990; Bosscher and Schlager, 1993) together with the effects of secular variations in seawater composition (Hardie, 1996, 2003; Stanley and Hardie, 1998; Horita *et al.*, 2002; Lowenstein *et al.*, 2001) are uncertain. Many algae and invertebrates have exploited the availability of calcium (Ca²⁺) and carbonate (CO₃²⁻) ions in the oceans to precipitate CaCO₃ shells. These skeletons, in addition to non-skeletal precipitates, are often major components of limestone throughout much of the Phanerozoic (Leeder, 1999). Such biomineralization could therefore constitute a significant control on limestone formation over time. However, lack of close correspondence between the evolutionary history of skeletal organisms and variation in the measured accumulation rate of shallow marine limestones during the Phanerozoic, suggests that other factors are involved in determining limestone accumulation (Bosscher and Schlager, 1993). In contrast to biological control, assumption of a long-term balance between Ca²⁺ input to the oceans, from volcanic and weathering fluxes, and output as CaCO₃ precipitation from seawater (Holland, 1978; Berner *et al.*, 1983), would imply an essentially inorganic chemical control of limestone formation. In this case, the biomineralization processes in many of the organisms whose shells dominate marine limestones, rather than controlling precipitation would instead have been dependent on seawater chemistry.

Knowledge of long-term variation in the saturation state of seawater with respect to CaCO₃ minerals would aid assessment of the relative importance of biological and inorganic chemical processes for limes-

tone formation (Webb, 2001). In particular, such knowledge would allow comparison of secular variation in marine limestone accumulation rate (Bosscher and Schlager, 1993) and seawater saturation state with respect to CaCO₃ minerals. Positive correlation between these trends would support a primary inorganic chemical control on limestone precipitation, and therefore on CO₂ sequestration, over geological time scales. This in turn would have significant implications for the role of biomineralization processes in carbonate precipitation. Accordingly, we set out to calculate the saturation state of seawater with respect to CaCO₃ minerals for the Phanerozoic and to compare this trend with that of measured marine limestone accumulation rate (Bosscher and Schlager, 1993) for the same interval (Riding and Liang 2003; Riding and Liang 2004). Here we explain our methodology and initial results.

CALCULATION OF SATURATION STATE

Under chemical equilibrium conditions, saturation state (Ω) for CaCO₃ minerals is determined by activity product over solubility constant: $\Omega = (\text{Ca}^{2+}) (\text{CO}_3^{2-}) / K_{\text{CaCO}_3}$, where K_{CaCO_3} differs for aragonite and calcite (Stumm and Morgan, 1996). To calculate seawater carbonate concentration, two of the following values are required: alkalinity, partial pressure of carbon dioxide (p_{CO_2}), dissolved inorganic carbon (DIC), or pH. Ω_{calcite} has been calculated for the past 100 Myr (Arvidson *et al.*, 2000) from estimates of p_{CO_2} , Ca²⁺, pH, and DIC (Berner *et al.*, 1983; Lasaga *et al.*, 1985). To calculate $\Omega_{\text{aragonite}}$ and Ω_{calcite} for the past 550 Myr we used estimated values for Ca and Mg (Stanley and Hardie, 1998), and K and SO₄²⁻ (Hardie, 1996); and we assumed present-day values for other major ions (e. g., Na⁺, Cl⁻). In our calculations we held temperature constant at 15 °C and used p_{CO_2} values from the GEOCARB III model (Berner and Kothavala, 2001). Because of the lack of specific information regarding changes in pH, alkalinity and DIC over geological time, as a first approximation we estimated DIC using the correlation established for p_{CO_2} and HCO₃⁻ for the last 100 Myr (Lasaga *et al.*, 1985). DIC prior to 100 Myr was extrapolated from this correlation using GEOCARB III p_{CO_2} data.

With this input, we calculated $\Omega_{\text{aragonite}}$, Ω_{calcite} and pH for the past ~550 Myr (Fig. 1a,b) using a stoichiometric equilibrium approach (PHREEQC code, version 2, Parkhurst and Appelo, 1999). Equilibrium constants for aqueous species were taken from the PHREEQC database. Activity coefficients were esti-

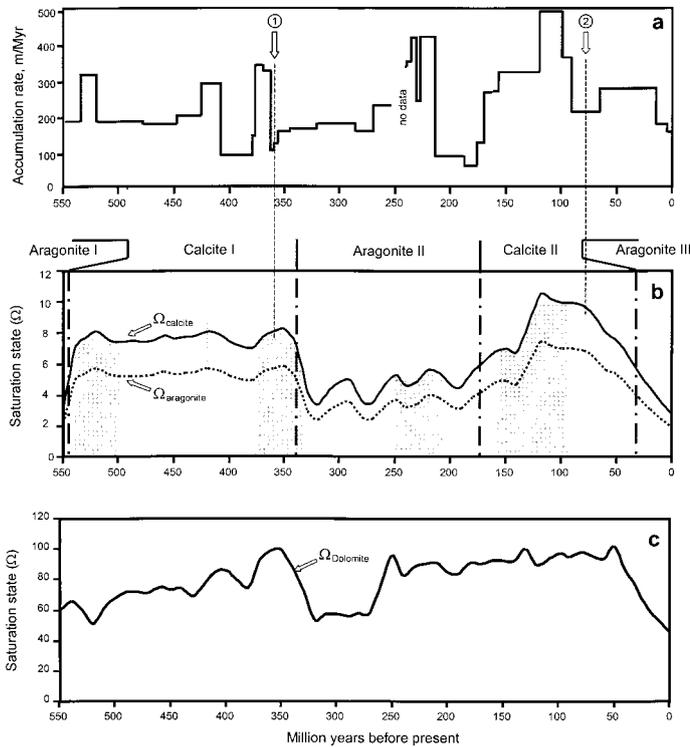


FIGURE 1—*a.* Normalized limestone accumulation rate (NLAR, (Bosscher and Schlager, 1993) in metres per million years for the past ~550 Myr (no data for the interval 239-250 Myr). Arrows 1 and 2 indicate divergence between NLAR and calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} ~360 and ~100-65 Myr ago, respectively.

b. Calculated saturation state for calcite and aragonite, for the past ~550 Myr. Periods of abundance of non-skeletal and/or microbial carbonates (stippled) coincide with calculated saturation state maxima: mid-Early Cambrian to end-Cambrian (540-500 Myr) (Arp *et al.*, 2001; Riding, 1992; Wilkinson *et al.*, 1985), Mid-Silurian (420 Myr) (Arp *et al.*, 2001), Late Devonian to mid-Early Carboniferous (377-333 Myr) (Arp *et al.*, 2001; Riding, 1992), mid-Late Permian to end-Triassic (252-208 Myr) (Arp *et al.*, 2001), and Late Jurassic to Early Cretaceous (157-97 Myr) (Arp *et al.*, 2001; Wilkinson *et al.*, 1985). Aragonite I-III and Calcite I-II indicate variation in primary mineralogy of marine skeletal and non-skeletal precipitates (Stanley and Hardie, 1998). Limestone accumulation and calculated saturation states are, in general, elevated during times of ‘calcite seas’, and reduced during ‘aragonite seas’. Time scale according to (Harland *et al.*, 1990), except for base of the Cambrian Period taken at 550 Myr.

c. Calculated saturation state for dolomite for the past ~550 Myr.

mated using the extended Debye Hückel expressions incorporated in the code. To compare activity estimates based on the Debye Hückel approximation with those derived from Pitzer equations, we used PHRQ-

PITZ (Plummer *et al.*, 1988) to derive saturation state values for a selected range of our data. The saturation state results obtained with PHRQPITZ are within 5% of those derived from PHREEQC. Thus, the extended Debye Hückel expressions are a reasonable approximation to the Pitzer approach for estimating activity coefficients of seawater. Calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} curves (Fig. 1b) are similar in shape, Ω_{calcite} being 1.4 times $\Omega_{\text{aragonite}}$. Using the same input and methodology we also calculated Ω_{dolomite} for the past ~550 Myr (Fig. 1c).

LIMESTONE ACCUMULATION RATE

Accumulation rates compiled from 119 published examples of shallow marine carbonate platforms for the past 550 Myr (excluding apparently higher rates during poorly constrained periods) range 17-239 m/Myr (Bosscher and Schlager, 1993). Whereas total preserved limestone thickness reflects intra-sequence breaks (Opdyke and Wilkinson, 1993) and the effects of subsequent erosion (Hay, 1985), limestone accumulation rate (Bosscher and Schlager, 1993) represents secular variation in carbonate precipitation rate. Since carbonate accumulation rates are optimal only when equalled by sea level rise, and sediment compaction is not corrected for in these data (Bosscher and Schlager, 1993), accumulation rate can be regarded as a minimum estimate of net precipitation rate. Inverse correlation between accumulation rate and duration of sampling interval was corrected for by normalizing all rates to a 1-Myr interval (Bosscher and Schlager, 1993). Normalized rates are greater than those of the uncorrected dataset but show similar overall pattern of secular variation, with maxima ~225 and ~110 Myr ago (Bosscher and Schlager, 1993).

COMPARISONS

Calculated saturation state ($\Omega_{\text{aragonite}}$ and Ω_{calcite}) and measured normalized limestone accumulation rate (NLAR) (Bosscher and Schlager, 1993) for the past 550 Myr are compared in Fig. 1a and b. At first sight, resemblances between the trends of NLAR (Fig. 1a) and calcite and aragonite saturation (Fig. 1b) are not striking. However, examination reveals broad correspondence in the positions of the peaks (e. g., 520, 420, 365, 290, 220, 115 Myr), and overall similarity in the timing and direction of fluctuations of the trends. Correlation between saturation state and NLAR is best

in the younger part of the range, e. g., 200-0 Myr ago (correlation coefficient = 0.69, Fig. 2). Marked divergence between NLAR and calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} , which reduces the correlation, occurs ~360 and 100-65 Myr ago (arrows 1 and 2, Fig. 1a). In addition, NLAR is noticeably elevated in comparison to saturation state ~245-220 Myr ago. If these discrepancies are disregarded, then saturation states and NLAR both tend to be relatively high ~545-340 and ~170-35 Myr ago, and relatively low between ~340-170 and 35-0 Myr ago. These time segments variously correspond to 'calcite sea' and 'aragonite sea' episodes (see Sandberg, 1975; Wilkinson, 1979; Stanley and Hardie, 1998) (Fig. 1b). Very broadly, calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} and NLAR values tend to be lower during 'aragonite seas' than during 'calcite seas'.

DISCUSSION

Saturation Ratio

Calculated saturation state is based on modelled estimates of past seawater and atmospheric CO_2 composition, derived from global geochemical budgets that are subject to revision (Berner *et al.*, 1983; Lasaga *et al.*, 1985; Spencer and Hardie, 1990; Hardie, 1996; Alt and Teagle, 1999; Berner and Kothavala, 2001; Rowley, 2002; Demicco, 2004). The ionic values (Hardie, 1996; Stanley and Hardie, 1998) are based on estimated changes in mid-ocean ridge hydrothermal brine, riverine inputs to seawater, and evaporative precipitation (Spencer and Hardie, 1990). Predicted Ca and Mg values for the past 545 Myr (Hardie, 1996; Stanley and Hardie, 1998) are generally consistent with analyses of fluid inclusions preserved in marine halite (Lowenstein *et al.*, 2001; Horita *et al.*, 2002), although the latter exhibit a considerable range. Modelled p_{CO_2} values also show a large range (Berner and Kothavala, 2001). Although p_{CO_2} proxy data, such as $\delta^{13}\text{C}$ values of palaeosol carbonates (Eckart *et al.*, 1999) and densities of stomata in fossil land plants (Royer *et al.*, 2001), offer broad support for the modelled p_{CO_2} values, such evidence is scarce particularly for older periods (Crowley and Berner, 2001). For our calculations, the average values of Berner and Kothavala's (2001) p_{CO_2} data were used.

The input data are model-dependent and contain considerable noise. In addition, estimation of the seawater carbonate system prior to 100 Myr is a particular problem. CO_3^{2-} can be computed from any of the following pairs of variables: DIC and alkalinity, alkalinity and p_{CO_2} , DIC and pH, etc. In our approach, p_{CO_2}

is used in combination with DIC. As stated earlier, we took Phanerozoic p_{CO_2} values provided by the latest GEOCARB model (Berner and Kothavala 2001), and estimated DIC using the correlation between for p_{CO_2} and HCO_3^- for the last 100 Myr (Lasaga *et al.*, 1985). This is unsatisfactory because the correlation for the past 100 Myr may not hold for the earlier periods. Additionally the modelling approach used by Lasaga *et al.* (1985) to derive ionic composition differs from that of Hardie (1996) and Stanley and Hardie (1998), which may result in significant uncertainty in HCO_3^- estimates.

Despite these difficulties, we observe that the range of calculated pH values (7.5–8.2, Fig. 3a), which are dependent upon p_{CO_2} and HCO_3^- , is broadly comparable with other estimates of Phanerozoic seawater pH (Pearson and Palmer, 2000; Zeebe, 2001; Caldeira and Wickett, 2003). The relatively modest size of this range of fluctuations supports the view that pH may not have varied to any great extent over the past 550 Myr. In the short term, doubling atmospheric CO_2 would result in lowering of seawater pH by 0.28 units (Stumm and Morgan, 1996), assuming that alkalinity remains unchanged. However, with increased alkalinity through carbonate and silicate weathering (in response to increased CO_2) (Berner *et al.*, 1983), oceanic pH need not vary significantly over geological timescales (Grotzinger and Kasting, 1993).

We also note that our calculated Ω_{calcite} values (2.9–12.8) for the past 550 Myr as a whole (Fig. 1b) are comparable in their lower range with those of present-day Bahama Bank waters (Morse *et al.*, 1984), and their upper range would not be unreasonable for pre-

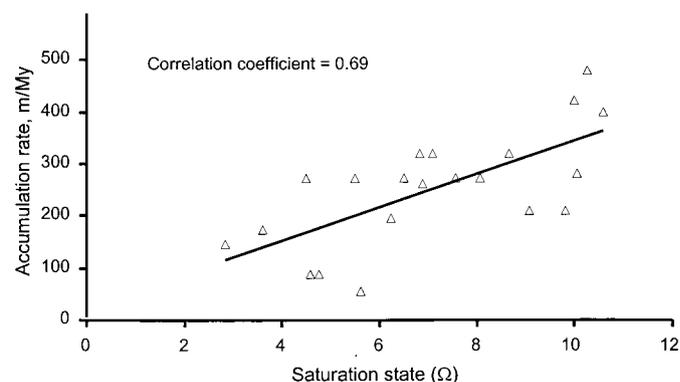


FIGURE 2—Correlation between normalized limestone accumulation rate (NLAR) and calculated saturation state of calcite for the past 200 Myr.

sent-day Persian Gulf waters in which homogeneous precipitation might occur (Morse and He, 1993). Calculated saturation ratio values do not take account of either latitudinal or secular temperature fluctuations that may have been significant over the past 550 Myr. However, incorporating temperature variations based on detrended oxygen isotope analyses derived from $d^{18}O$ values (Veizer *et al.*, 2000) is expected to amplify rather than transform the calculated saturation trend. In addition, our procedure reproduces the trend of seawater saturation with respect to calcite for the past 100 Myr calculated by Arvidson *et al.* (2000) from the chemical data given in Lasaga *et al.* (1985).

We conclude that although our calculated saturation states may not be absolute values, they merit discussion as relative estimates. Below we draw particular attention to implications arising from comparison of these trends of calculated aragonite and calcite saturation state with the geological record of $CaCO_3$ precipitates.

Limestone Accumulation

Broad correspondence between measured accumulation rate of shallow marine limestones (Bosscher and Schlager, 1993) and calculated saturation state over the past 550 Myr (Fig. 1a, b), supports the view that seawater saturation has been a primary long-term control on marine carbonate precipitation (Kempe and Kazmierczak, 1990; Opdyke and Wilkinson, 1990). Saturation state indicates the general tendency of precipitation (Stumm and Morgan, 1996). Nonetheless, $CaCO_3$ precipitation rate follows an empirical power law of seawater saturation (Zhong and Mucci, 1989) consistent with correlation between calculated saturation state and the measured net precipitation rate reflected in NLAR. Such a determining role for seawater chemistry in carbonate precipitation over geological time scales is consistent with both Holocene (Broecker and Takahashi, 1966; Opdyke and Wilkinson, 1993) and older (Opdyke and Wilkinson, 1990) tropical carbonates whose distributions have been suggested to reflect the saturation state of seawater. In addition, for as long as it has been traced (the past 140 Myr), the oceanic calcite compensation depth (CCD) (van Andel, 1975) broadly tracks calculated saturation state and NLAR, being at shallower depths during periods when saturation state and NLAR have higher values. At first sight, deepening of the CCD might suggest increase in saturation state since the Cretaceous. Alternatively, such long-term fluctuation in the CCD could primarily reflect partitioning of carbonate deposition between shallow and deep seas (van

Andel, 1975), in response to sealevel fall (Edmond and Huh, 2003). Consequently, reduction in shallow water carbonate precipitation could permit deepening of the CCD without overall increase in saturation state. Correspondence between saturation state and NLAR (Fig 1a,b) tends to support the view that marine $CaCO_3$ precipitation has balanced input of Ca^{2+} and CO_3^{2-} to the oceans over geological time scales (Holland, 1978; Berner *et al.*, 1983).

However, since NLAR only describes shallow water carbonate accumulation (Bosscher and Schlager, 1993), divergence between saturation state and NLAR is to be expected at times of increased deposition of deep-sea carbonates in response to pelagic biomineralization. Comparisons made above draw attention to divergences between NLAR and calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} , ~360 and 100-65 Myr ago (arrows 1 and 2, Fig. 1a). Low values of NLAR relative to saturation state 100-65 Myr ago (Fig. 1a, arrowed) coincide with diversification of coccolithophore algae and globigerine foraminifers (Tappan and Loeblich, 1973). These calcified plankton substantially increased deep-water carbonate accumulation (Hay, 1985; Opdyke and Wilkinson, 1988) at the expense of shelf carbonates (Wilkinson and Walker, 1989). The scant deep ocean record prior to ~180 Myr ago (Hay, 1985; Wilkinson, and Walker, 1989) hinders assessment of the relative decline in NLAR ~360 Myr ago. Nonetheless, widespread intercalations of pelagic limestones in shelf sequences near the Devonian-Carboniferous boundary (362 Myr ago) (Wendt and Aigner, 1985) coincide with diversification of calcareous plankton (Benton, 1993), suggesting parallels with the 100-65 Myr interval.

Fluctuations in NLAR ~520-370 Myr ago are much greater than those of calculated saturation state, although peaks and troughs broadly correspond. At present we have no explanation for this difference. It may indicate that NLAR values were less variable, or that the input data on which saturation ratio is based was more varied, than shown.

NLAR was very high ~245-220 Myr ago. This period relates to peaks in saturation state that are relatively high for the 340-170 Myr interval (Aragonite II), but that are low for the Phanerozoic as a whole (Fig. 1b). During 'aragonite seas' saturation state appears to have been generally lower than during 'calcite seas' (see Secular Patterns, below). The explanation for the unusually high NLAR values ~245-220 Myr ago is unclear. Assuming they are correct, a factor that conceivably would account for anomalously high NLAR relative to saturation state is exceptional rates of pro-

duction of biologically controlled calcifiers. However, common skeletal components of tropical limestones at this time were sponges and corals (Flügel, 2002), i. e., biologically induced calcifiers, together with microbial and nonskeletal carbonates that are also dependent on elevated saturation state (Riding and Liang, 2004). Another possibility is that oceanic conditions during the Early-Mid Triassic promoted saturation states higher than those calculated. Early Triassic seafloor cements have been interpreted (Woods *et al.*, 1999) as an example of increased shallow water saturation state resulting from mixing of deep anoxic water (Kempe, 1990). Such an effect would increase our calculated saturation values. These and other possibilities accounting for high limestone accumulation rates ~245-220 Myr ago deserve further consideration.

Biomineralization

It has long been recognized that non-skeletal and microbial carbonates, including ooids, marine cements, and calcified cyanobacteria, require elevated saturation state for their formation (Kempe and Kazmierczak, 1990; Opdyke and Wilkinson, 1990; Webb, 2001) and exhibit a markedly episodic secular distribution during the past 550 Myr (Riding, 1992). It follows that these limestone components should therefore have been abundant at times in the past when saturation state was elevated. This is borne out by the comparison shown in Figure 1, where peaks of calcite and aragonite saturation ratio broadly correspond with periods of increased abundance of non-skeletal and microbial carbonates (Fig. 1a,b) (Riding and Liang, 2004). For example, enhanced abundances of one or more of ooids (Wilkinson *et al.*, 1985), marine cements (Grotzinger and Knoll, 1995; Riding, 1992), and calcified cyanobacteria (Arp *et al.*, 2001; Riding, 1992) coincide with maximum calculated saturation values at 540-500 Myr, 420 Myr, 377-333 Myr, 252-208 Myr, and 155-97 Myr (Fig. 1b). Consequently, the episodic secular distribution of non-skeletal and microbial carbonates (Riding, 1992) can be linked to fluctuations in seawater chemistry, specifically saturation state.

However, similarities in the trends of NLAR and saturation state have even wider implications for organic carbonates. In aquatic organisms, skeletal biomineralization ranges from biologically controlled, where organisms closely regulate calcification, to biologically induced, where calcification is metabolically mediated but dependent on ambient water chemistry (Mann, 2001). It is proposed here that the simplest explanation for broad long-term correspondence bet-

ween NLAR and saturation state is that the majority of shells constituting Phanerozoic marine limestones were biologically induced. As a result they would have been subject, along with non-skeletal and microbial components, to the influence of saturation state. This is consistent with the view that biomineralization processes in many sediment producing marine organisms over the past 550 Myr have been (Kempe and Kazmierczak, 1990; Stanley and Hardie, 1998), and remain (Opdyke and Wilkinson, 1990; Kleypas *et al.*, 1999), strongly influenced by the saturation state of seawater. Furthermore, calculated values support the view that decline in saturation state has favoured biologically controlled over biologically induced biomineralization during the past 100 Myr (Wilkinson and Walker, 1989; Kempe and Kazmierczak, 1990; Webb, 2001). Thus, it seems likely that, in addition to non-skeletal and microbial carbonates, biomineralization processes in many of the algae and invertebrates whose skeletons are important limestone-building components have also been dependent on seawater saturation state. Such subordination of biomineralization processes to seawater chemistry in many sediment-producing organisms (Stanley and Hardie, 1998) would explain difficulty in accounting for secular variation in NLAR solely by reference to biotic factors (Bosscher and Schlager, 1993).

Secular Patterns

In addition to the thermodynamic driving force reflected by saturation state, kinetic factors strongly influence carbonate precipitation (Morse and Mackenzie, 1990; Stumm and Morgan, 1996; Leeder, 1999). During the past 550 Myr long-term oscillation between 'calcite seas' and 'aragonite seas' has been recognized from variation in primary mineralogy of marine skeletal and non-skeletal precipitates (Sandberg, 1975). This oscillation has been attributed to changes in seawater Mg^{2+}/Ca^{2+} ratio (Sandberg, 1975; Wilkinson, 1979), with $Mg^{2+}/Ca^{2+} = 2$ delimiting the aragonite-calcite fields (Stanley and Hardie, 1998). Broad comparison of saturation state, limestone accumulation rate and carbonate mineralogy reveals an integrated pattern of variation in marine $CaCO_3$ precipitation, with higher values of saturation state and limestone accumulation during 'calcite seas' and lower values during 'aragonite seas' (Riding and Liang, 2004) (Fig. 1). This indication that higher values of saturation state correspond with 'calcite seas', and therefore with times of global high sea level, is contrary to the suggestion by Mackenzie and Morse (1992, p. 3287).

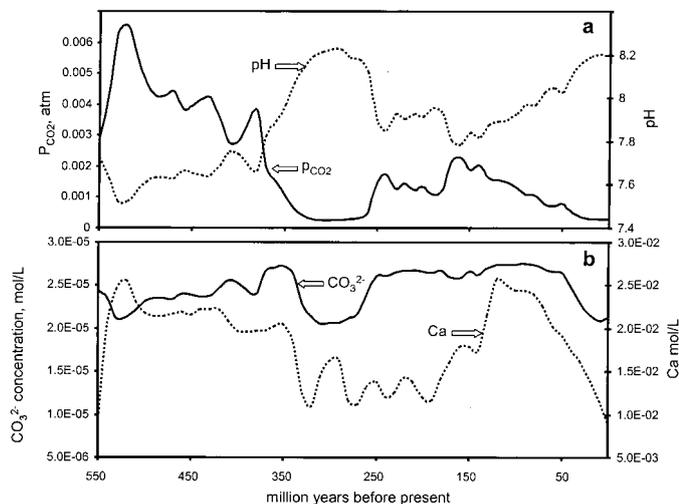


FIGURE 3—a. p_{CO_2} average values from the GEOCARB III model (Berner and Kothavala, 2001) plotted with calculated pH. Values of pH peaked when p_{CO_2} levels were lowest ~290 Myr ago.

b. Calculated CO_3^{2-} and Ca concentrations in seawater for the past 550 Myr. Ca concentration is 2 orders of magnitude higher than CO_3^{2-} . Variation in CO_3^{2-} is relatively small within a range of 20.5–27.5 micromole/L, with the lowest levels of CO_3^{2-} occurring ~310 Myr ago. Ca variation is relatively large, with a range of 8.9–25.8 millimole/L.

The saturation states of seawater with respect to aragonite and calcite reflect the rates of ionic input and removal via hydrothermal processes, riverine input following weathering on land, and mineral precipitation in seawater. Although high saturation state thermodynamically favours precipitation, it cannot be maintained together with high precipitation rate (thus accumulation rate of the precipitate), unless accompanied by large ionic flux input. The saturation states of calcite and aragonite during the past 545 Myr shows four intervals that can be related to ‘aragonite seas’ and ‘calcite seas’ (Fig. 1b). From ~545–340 Myr (Calcite I) elevated saturation state reflects high levels of both Ca and p_{CO_2} (Fig. 3b). Due to the acidification effect of CO_2 on seawater pH (Fig. 3a) a moderate level of CO_3^{2-} is observed during this period of high p_{CO_2} . Elevated saturation state presumably was maintained by high Ca flux (Fig. 3b). During the interval 340–170 Myr ago (Aragonite II), p_{CO_2} was relatively low (Fig. 3a). Between 340–255 Myr ago, especially, it was close to present-day values. Accordingly, pH was relatively high (Fig. 3a), leading to the lowest CO_3^{2-} levels of the entire Phanerozoic (Fig. 3b). The relatively low values of saturation state during this interval resulted

mainly from low Ca flux, combined with relatively low CO_3^{2-} . During the period 170–35 Myr ago (Calcite II), initially both p_{CO_2} and Ca increased (Fig. 3), peaking 170 and 120 Myr ago respectively, before declining. CO_3^{2-} levels were at their highest for the Phanerozoic, and relatively unchanged throughout this interval. From 35–0 Myr ago (Aragonite III) conditions were similar to those during Aragonite II and calculated saturation state mainly reflects Ca levels.

Overall, since Phanerozoic Ca values are at least 2 orders of magnitude higher than CO_3^{2-} (Fig. 3b), saturation state generally follows the Ca trend. Saturation state tends to be lower during ‘aragonite seas’ due to low Ca flux and relatively low CO_3^{2-} . Low Ca flux contributes to the increased $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio that favours aragonite precipitation over calcite. Conversely, high Ca flux and high CO_3^{2-} result in high saturation states during ‘calcite sea’ intervals. These elevated saturation states favoured enhanced precipitation of both aragonite and calcite during ‘calcite seas’. This is likely to have resulted in increased carbonate production by biologically induced calcifiers and increased early lithification, accounting for higher NLAR values generally observed during ‘calcite seas’ in comparison to ‘aragonite seas’ (Fig. 1a,b). Thus, the factors determining saturation state, together with rate of accumulation of the resulting precipitate, and the mineralogy of the precipitate, are fundamentally linked. Underlying controls for these fluctuations in marine carbonate precipitation can be sought in the global cycles (Sandberg, 1975; Holland, 1978, 2004; Berner *et al.*, 1983; Sandberg, 1983; Lasaga *et al.*, 1985; Wilkinson and Walker, 1989; Spencer and Hardie, 1990; Mackenzie and Morse, 1992; Hardie, 1996; Berner and Kothavala, 2001) that influence seawater chemistry.

Dolomite

Apart from markedly low values ~320–270 Myr ago, calculated Ω_{dolomite} (Fig. 1c), shows overall rise from 550–50 Myr ago followed by steep decline to the present-day. This trend has both similarities and differences to those of $\Omega_{\text{aragonite}}$ and Ω_{calcite} (Fig. 1). Our Ω_{dolomite} trend differs from that calculated for the past 100 Myr by Arvidson *et al.* (2000), who used data from Lasaga *et al.* (1985), in showing elevated Ω_{dolomite} values until ~50 Myr ago, but is in agreement in showing decline during the past 50 Myr. Comparisons of dolomite abundance with changes in seawater chemistry over geological timescales do not offer straightforward interpretations (Burns *et al.*, 2000). Nonetheless, dolomite abundance for the

Phanerozoic as a whole (Given and Wilkinson, 1987) show broad resemblances to our calculated Ω_{dolomite} trend, and it has been suggested that secular variation in Ω_{dolomite} may have significantly influenced dolomite formation in the past (Arvidson *et al.*, 2000). However, since many ancient dolostones formed by late replacement of limestone (Given and Wilkinson, 1987), data concerning the abundance of primary dolostones are required to evaluate the relationship between these and secular variation in Ω_{dolomite} .

SUMMARY AND CONCLUSIONS

We calculated Phanerozoic variation in surface seawater saturation ratio (Ω) for aragonite, calcite and dolomite using estimates of past seawater ionic composition (Hardie, 1996; Stanley and Hardie, 1998) and atmospheric CO_2 levels (Bernier and Kothavala, 2001), and assuming constant temperature of 15 °C. Fluctuation in the accumulation rate of shallow marine limestones (Bosscher and Schlager, 1993) show broad similarities to that of calculated $\Omega_{\text{aragonite}}$ and Ω_{calcite} , and episodes of increased abundance of microbial and nonskeletal carbonates (Wilkinson *et al.*, 1985, Riding, 1992; Arp *et al.*, 2001) correlate with elevated saturation ratios. Abundance of microbial and nonskeletal carbonates also broadly correlates with elevated estimated sea surface temperature (Veizer *et al.*, 2000). Incorporating temperature variations based on detrended oxygen isotope analyses (Veizer *et al.*, 2000) into our calculations would enhance calculated saturation ratio peaks.

These relationships with calculated seawater mineral saturation ratio have significance for understanding the long-term development of (i) marine carbonates in general, and (ii) microbial carbonates in particular.

(i) With regard to marine carbonates, correlation of measured limestone accumulation rate with calculated saturation ratio suggests that, despite widespread biological mediation of carbonate precipitation, the saturation state of seawater has generally exerted a primary control on the formation of shallow marine limestones during the Phanerozoic. This role of seawater saturation state in determining carbonate precipitation over geological timescales is consistent with observations of Holocene tropical carbonates (Broecker and Takahashi, 1966; Opdyke and Wilkinson, 1993), and has been inferred from palaeolatitudinal distributions of ooids and marine cements and associated skeletal carbonates (Opdyke and Wilkinson, 1990). Subordination of biomineralization processes to sea-

water chemistry in many sediment producing organisms (Stanley and Hardie, 1998), not only in microbial carbonates, explains difficulty in accounting for secular variation in limestone accumulation rate solely by reference to biotic factors (Bosscher and Schlager, 1993).

(ii) Secular correspondence between Ω maxima and episodes of Phanerozoic abundance of microbial carbonates supports the inference that seawater chemistry in general (Riding, 1982, Arp *et al.*, 2001) and saturation state in particular (Kempe and Kazmierczak, 1990; Merz-Preiß, and Riding 1999, Webb, 2001) has had a major role in determining microbial calcification, and it underscores the importance of early calcification and lithification in the formation of microbial carbonates (Riding, 2000). Therefore, this underlying inorganic chemical control must, in addition to ecological and evolutionary factors, be taken into account in assessing secular variations in microbial carbonates.

Calcification in many other sediment-producing organisms apart from bacteria is also dependent on ambient water chemistry (Leadbeater and Riding, 1986; Stanley and Hardie, 1998). It can therefore be expected that secular variation in seawater saturation state for CaCO_3 minerals should have influenced the long-term history of organisms that biologically induce, rather than closely control, their calcification. Comparison of calculated seawater saturation state with patterns of marine calcified organisms during the Phanerozoic Eon suggests that the diversity of organisms with biologically induced calcification, such as chlorophytes, corals and sponges, increased during periods of elevated saturation state and declined when saturation state was reduced. This is consistent with biomineralization processes of most shallow marine skeletal carbonates being biologically induced rather than biologically controlled (Kempe and Kazmierczak, 1990; Stanley and Hardie, 1998). In contrast, organisms with relatively controlled calcification, such as molluscs, brachiopods, bryozoans, and echinoderms, appear to have been relatively unaffected by saturation state (Riding, 2004). This indicates that CaCO_3 availability – governed by saturation state – has significantly influenced the diversity of organisms with biologically induced calcification. This effect involves many tropical marine algae and invertebrates, especially those that are most involved in reef building. Thus, despite its apparent abundance, CaCO_3 has been so widely employed in biomineralization by aquatic organisms during the past ~550 million years that it may have constituted a limiting resource, partitioned between organisms that biologically control and biologically

induce their calcification, with the surplus being inorganically precipitated. We conclude that the mineral saturation state of seawater has been the principal factor determining accumulation of shallow marine limestones. In addition, the primary control of seawater chemistry has imposed a long-term pattern of secular variation on marine limestones that is reflected by fluctuation in their accumulation rate (Bosscher and Schlager, 1993) as well as in their mineralogy (Sandberg, 1983).

Apart from the anomalous interval ~245-220 Myr ago, comparison of Sandberg's curve of mineralogical oscillation with Ω and NLAR suggests that saturation ratio and carbonate sediment accumulation rate have been elevated during times of 'calcite seas', and reduced during 'aragonite seas' (Fig. 1a,b). The controls on this integrated pattern of secular variation in marine carbonate precipitation, and thus CO_2 sequestration, over geological timescales presumably lie in processes such as the influence of oceanic crust formation on hydrothermal exchange of magnesium for calcium in seawater, CO_2 degassing, and sealevel rise that affect extent of both marine shelf and continental crust exposed to atmospheric weathering (e. g., Holland, 1978; Berner *et al.*, 1983; Wilkinson *et al.*, 1985; Wilkinson and Walker, 1989; Spencer and Hardie, 1990; Mackenzie and Morse, 1992; Berner and Kothavala, 2001). Prior to widespread appearance of skeletal carbonates in the Early Palaeozoic, this primary inorganic chemical control of marine CaCO_3 precipitation is likely to have operated even more rigorously. Further insights into secular variation in limestone formation require improved knowledge of past seawater and atmospheric compositions, especially from proxy data, and of the controls on skeletal and non-skeletal CaCO_3 precipitation.

ACKNOWLEDGEMENTS

We thank Julian Andrews, Rolf S. Arvidson, Jim Morgan and John W. Morse for advice and discussion. Thoughtful critical comments by Revista reviewers Sean T. Brennan and Bruce H. Wilkinson were very helpful.

REFERENCES

Alt, J. C., and Teagle, D. A. H. 1999. The uptake of carbon during alteration of ocean crust. *Geochimica et Cosmochimica Acta*, 63 (10), 1527-1535.

- Arp, G.; Reimer, A., and Reitner, J. 2001. Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. *Science*, 292 (5522), 1701-1704.
- Arvidson, R. S.; Mackenzie, F. T., and Guidry, M. W. 2000. Ocean/atmosphere history and carbonate precipitation rates: a solution to the "dolomite problem". In: *Marine authigenesis: from global to microbial* (Eds. C. R. Glenn, L. Prévôt-Lucas, and J. Lucas). Special Publication, Society for Sedimentary Geology, Tulsa, 1-5.
- Benton, M. J. (Ed.). 1993. *The fossil record* 2. Chapman and Hall, London, 845 pp.
- Berner, R. A., and Kothavala, Z. 2001. GEOCARB III: A revised model of atmospheric CO_2 over Phanerozoic time. *American Journal of Science*, 301 (2), 182-204.
- Berner, R. A.; Lasaga, A. C., and Garrels, R. M. 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon-dioxide over the past 100 million years. *American Journal of Science*, 283 (7), 641-683.
- Bosscher, H., and Schlager, W. 1993. Accumulation rates of carbonate platforms. *Journal of Geology*, 101 (3), 345-355.
- Broecker, W. S., and Takahashi, T. 1966. Calcium carbonate precipitation on the Bahama Banks. *Journal of Geophysical Research*, 71, 1575-1602.
- Burns, S. J., McKenzie, J. A., and Vasconcelos, C. 2000. Dolomite formation and biogeochemical cycles in the Phanerozoic. *Sedimentology*, 47, (Supplement 1), 49-61.
- Caldeira, K., and Wickett, M. E. 2003. Anthropogenic carbon and ocean pH. *Nature*, 425 (6956), 365-365.
- Crowley, T. J., and Berner, R. A. 2001. Paleoclimate - CO_2 and climate change. *Science*, 292 (5518), 870-872.
- Demico, R. V. 2004. Modeling seafloor-spreading rates through time. *Geology*, 32, 485-488.
- Edmond, J. M., and Huh, Y. 2003. Non-steady state carbonate recycling and implications for the evolution of atmospheric P_{CO_2} . *Earth and Planetary Science Letters*, 216, 125-139.
- Ekart, D. D., Cerling, T. E., Montanez, I. P., and Tabor, N. J. 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *American Journal of Science*, 299 (10), 805-827.
- Flügel, E. 2002. Triassic reef patterns. In: *Phanerozoic reef patterns* (Eds. W. Kiessling, E. Flügel and J. Golonka). SEPM Special Publication, 72, 391-463.
- Given, R. K., and Wilkinson, B. H. 1987. Dolomite abundance and stratigraphic age: constraints on rates and mechanisms of Phanerozoic dolostone formation. *Journal of Sedimentary Petrology*, 57, 457-469.
- Grotzinger, J. P., and Kasting, J. F. 1993. New constraints on Precambrian ocean composition. *Journal of Geology*, 101 (2), 235-243.

- Grotzinger, J. P., and Knoll, A. H. 1995. Anomalous carbonate precipitates: Is the Precambrian the key to the Permian? *Palaios*, 10 (6), 578-596.
- Hardie, L. A. 1996. Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 my. *Geology*, 24 (3), 279-283.
- . 2003. Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas. *Geology*, 31 (9), 785-788.
- Harland, W. B.; Armstrong, R. L.; Cox, A. V.; Craig, L. E.; Smith, A. G., and Smith, D. G. 1990. *A geologic time scale 1989*. Cambridge University Press, Cambridge, 263 pp.
- Hay, W. W. 1985. Potential errors in estimates of carbonate rock accumulating through geologic time. In: *The carbon cycle and atmospheric CO₂: natural variations Archean to present* (Eds. E. T. Sundquist and W. S. Broecker). Geophysical Monograph 32, American Geophysical Union, Washington, DC, 573-563.
- Holland, H. D. 1978. *The chemistry of the atmosphere and oceans*. Wiley, New York, 351 pp.
- . 2004. The geologic history of seawater. In: *The oceans and marine geochemistry* (Ed. H. Elderfield), pp. 583-625. Volume 6, Treatise on Geochemistry (Eds. H. D. Holland, K. K. Turekian), Elsevier-Pergamon, Oxford, 646 pp.
- Horita, J.; Zimmermann, H., and Holland, H. D. 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporates. *Geochimica et Cosmochimica Acta*, 66 (21), 3733-3756.
- Kempe, S. 1990. Alkalinity: the link between anaerobic basins and shallow water carbonates? *Naturwissenschaften*, 77, 426-427.
- Kempe, S., and Kazmierczak, J. 1990. Calcium carbonate supersaturation and the formation of in situ calcified stromatolites. In: *Facets of modern biogeochemistry* (Eds. V. Ittekkot, S. Kempe, W. Michaelis and A. Spitz). Springer, Berlin, 255-278.
- Kleypas, J. A.; Buddemeier, R. W.; Archer, D.; Gattuso, J. P.; Langdon, C., and Opdyke, B. N. 1999. Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science*, 284 (5411), 118-120.
- Lasaga, A. C.; Berner, R. A., and Garrels, R. M. 1985. An improved geochemical model of atmospheric CO₂ fluctuations over the past 100 million years. In: *The carbon cycle and atmospheric CO₂: natural variations Archean to present* (Eds. E. T. Sundquist and W. S. Broecker). Geophysical Monograph 32, American Geophysical Union, Washington, DC, 397-411.
- Leadbeater, B. S. C., and Riding, R. (Eds). 1986. *Biom mineralization in lower plants and animals*. Special Volume 30, Systematics Association, Clarendon, Oxford, 401 pp.
- Leeder, M. 1999. *Sedimentology and sedimentary basins: from turbulence to tectonics*. Blackwell, Oxford, 592 pp.
- Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A., and Demicco, R. V. 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. *Science*, 294 (5544), 1086-1088.
- Mackenzie, F. T., and Morse, J. W. 1992. Sedimentary carbonates through Phanerozoic time. *Geochimica et Cosmochimica Acta*, 56, 3281-3295.
- Mann, S. 2001. *Biom mineralization: principles and concepts in bioinorganic materials chemistry*. Oxford University Press, Oxford, 198 pp.
- Merz-Preiß, M. and Riding, R. 1999. Cyanobacterial tufa calcification in two freshwater streams: ambient environment, chemical thresholds and biological processes. *Sedimentary Geology*, 126, 103-124.
- Morse, J. W., and He, S. L. 1993. Influences of T, S and P(CO₂) on the pseudo-homogeneous precipitation of CaCO₃ from seawater - implications for whiting formation. *Marine Chemistry*, 41 (4), 291-297.
- Morse, J. W., and F. T. Mackenzie. 1990. *Geochemistry of sedimentary carbonates*. Developments in Sedimentology, Elsevier, Amsterdam, 707 pp.
- Morse, J. W.; Millero, F. J.; Thurmond, V.; Brown, E., and Ostlund, H. G. 1984. The carbonate chemistry of Grand Bahama Bank waters - after 18 years another look. *Journal of Geophysical Research - Oceans*, 89 (NC3), 3604-3614.
- Opdyke, B. N. and Wilkinson, B. H. 1988. Surface area control of shallow cratonic to deep marine carbonate accumulation. *Paleoceanography*, 3, 685-703.
- . 1990. Paleolatitude distribution of Phanerozoic marine ooids and cements. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 78 (1-2), 135-148.
- . 1993. Carbonate mineral saturation state and cratonic limestone accumulation. *American Journal of Science*, 93, 217-234.
- Parkhurst, D. L., and Appelo, C. A. J. 1999. *User's guide to PHREEQC (version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. Water-Resources Investigations Report 99-4259, US Geological Survey, Denver, Colorado, 326 pp.
- Pearson, P. N., and Palmer, M. R. 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*, 406 (6797), 695-699.
- Plummer, L. N.; Parkhurst, D. L.; Fleming, G. W., and Dunkle, S. A. 1988. *A computer program incorporating Pitzer's equations for calculations of geochemical reactions in brines*. Water-Resource Investigations Report 88-4153, US Geological Survey, Denver, Colorado, 310 pp.
- Riding, R. 1982. Cyanophyte calcification and changes in ocean chemistry. *Nature*, 299, 814-815.
- . 1992. Temporal variation in calcification in marine cyanobacteria. *Journal of the Geological Society*, 149, 979-989.

- . 2000. Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. *Sedimentology*, 47, (Supplement 1), 179-214.
- . 2004. Influence of seawater saturation state on the Phanerozoic diversity of calcified marine algae and invertebrates. 48th Palaeontological Association Annual Meeting, Lille, France, 17-20 December 2004. Abstracts with Programme, *The Palaeontological Association Newsletter*, 57, 130-131.
- Riding, R., and Liang, L. 2003. Seawater saturation state and the Phanerozoic secular distribution of microbial carbonates. 8th International Symposium on Fossil Algae, Granada, Spain, 18-20 September 2003. Abstracts: 63-64.
- . 2004. Marine limestone accumulation over the past 550 million years—control by seawater chemistry. Goldschmidt Conference 2004, Copenhagen, Conference Supplement, *Geochimica Cosmochimica Acta*, p. A354.
- Rowley, D. B. 2002. Rate of plate creation and destruction: 180 Ma to present. *Geological Society of America Bulletin*, 114 (8), 927-933.
- Royer, D. L.; Berner, R. A., and Beerling, D. J. 2001. Phanerozoic atmospheric CO₂ change: evaluating geochemical and paleobiological approaches. *Earth-Science Reviews*, 54 (4), 349-392.
- Sandberg, P. A. 1975. New interpretations of Great Salt Lake ooids and of ancient nonskeletal carbonate mineralogy. *Sedimentology*, 22, 497-538.
- . 1983. An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy, *Nature*, 305 (5929), 19-22.
- Spencer, R. J., and Hardie, L. A. 1990. Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines. *Geochemical Society Special Publication*, 2, 409-419.
- Stanley, S. M., and Hardie, L. A. 1998. Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 144 (1-2), 3-19.
- Stumm, W., and Morgan, J. J. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3rd edition. Wiley, New York, 1022 pp.
- Tappan, H., and Loeblich, A. R., Jr. 1973. Evolution of the oceanic plankton. *Earth-Science Reviews*, 9, 207-240.
- Van Andel, T. H. 1975. Mesozoic/Cenozoic calcite compensation depth and the global distribution of calcareous sediments. *Earth and Planetary Science Letters*, 26, 187-194.
- Veizer, J.; Godderis, Y., and Francois, L. M. 2000. Evidence for decoupling of atmospheric CO₂ and global climate during the Phanerozoic eon. *Nature*, 408 (6813), 698-701.
- Walker, J. C. G.; Hays, P. B., and Kasting, J. F. 1981. A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *Journal of Geophysical Research*, 86, 9776-9782.
- Webb, G. E. 2001. Biologically induced carbonate precipitation in reefs through time. In: *The history and sedimentology of ancient reef systems* (Ed. G. D. Stanley). Kluwer Academic/Plenum Publishers, New York, 159-203.
- Wendt, J., and Aigner, T. 1985. Facies patterns and depositional environments of Palaeozoic cephalopod limestones. *Sedimentary Geology*, 44, 263-300.
- Wilkinson, B. H. 1979. Biomineralization, paleoceanography, and the evolution of calcareous marine organisms. *Geology*, 7, 524-527.
- Wilkinson, B. H.; Owen, R. M., and Carroll, A. R. 1985. Submarine hydrothermal weathering, global eustasy, and carbonate polymorphism in Phanerozoic marine oolites. *Journal of Sedimentary Petrology*, 55 (2), 171-183.
- Wilkinson, B. H., and Walker, J. C. G. 1989. Phanerozoic cycling of sedimentary carbonate. *American Journal of Science*, 289, 525-548.
- Woods, A. D.; Bottjer, D. J.; Mutti, M., and Morrison, J. 1999. Lower Triassic large sea-floor carbonate cements: their origin and a mechanism for the prolonged biotic recovery from the end-Permian mass extinction. *Geology*, 27, 645-648.
- Zeebe, R. E. 2001. Seawater pH and isotopic paleotemperatures of Cretaceous oceans, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 170, 49-57.
- Zhong, S. J., and Mucci, A. 1989. Calcite and aragonite precipitation from seawater solutions of various salinities - precipitation rates and overgrowth compositions. *Chemical Geology*, 78 (3-4), 283-299.

MANUSCRITO RECIBIDO: 14 abril, 2004

MANUSCRITO ACEPTADO: 27 diciembre, 2004