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Geobiology of microbial carbonates: metazoan and seawater saturation state influences on secular trends during the Phanerozoic

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Abstract

Microbial carbonates are long-ranging, essentially bacterial, aquatic sediments. Their calcification is dependent on ambient water chemistry and their growth is influenced by competition with other organisms, such as metazoans. In this paper, these relationships are examined by comparing the geological record of microbial carbonates with metazoan history and secular variations in $CaCO_3$ saturation state of seawater. Marine abundance data show that microbial carbonates episodically declined during the Phanerozoic Eon (past 545 Myr) from a peak 500 Myr ago. This abundance trend is generally inverse to that of marine metazoan taxonomic diversity, supporting the view that metazoan competition has progressively limited the formation of microbial carbonates. Lack of empirical values concerning variables such as seawater ionic composition, atmospheric partial pressure of CO_2, and pH currently restricts calculation of $CaCO_3$ saturation state for the Phanerozoic as a whole to the use of modeled values. These data, together with palaeotemperature data from oxygen isotope analyses, allow calculation of seawater $CaCO_3$ saturation trends. Microbial carbonate abundance shows broad positive correspondence with calculated seawater saturation state for $CaCO_3$ minerals during the interval 150–545 Myr ago, consistent with the likelihood that seawater chemistry has influenced the calcification and therefore accretion and preservation of microbial carbonates. These comparisons suggest that both metazoan influence and seawater saturation state have combined to determine the broad pattern of marine microbial carbonate abundance throughout much of the Phanerozoic. In contrast, for the major part of the Precambrian it would seem reasonable to expect that seawater saturation state, together with microbial evolution, was the principal factor determining microbial carbonate development. Interrelationships such as these, with feedbacks influencing organisms, sediments, and the environment, are central to geobiology.

Keywords: metazoan diversity; microbial carbonates; Phanerozoic; saturation state; seawater chemistry

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1. Introduction

Throughout the 545 Myr of the Phanerozoic Eon, marine organisms have extensively used the calcium carbonate minerals aragonite and calcite to create organic skeletons. From much earlier times additional deposits have resulted from algal and bacterial processes, such as photosynthesis and sulphate reduction, that promote carbonate precipitation in microenvironments adjacent to cells. In marine environments over geological timescales these processes of $CaCO_3$ biomineralization have had great significance for the fossil record. They have also contributed to the generation of large quantities of carbonate sediment. The resulting long-lived accumulations of limestones and dolostones constitute important sedimentary records in oceanic and crustal rocks. This carbon reservoir, dependent upon the presence of a hydrosphere on Earth, is much larger than that in modern biomass and fossil fuels (Rubey, 1951; Holland, 1978; Stumm and Morgan, 1996). Such large-scale sequestration of CO_2 in carbonate rocks dominates the long-term carbon cycle and is therefore likely to have been a key influence on Earth's climate (Walker et al., 1981; Berner et al., 1983; Kasting and Catling, 2003). It follows that the relationship between water chemistry and biomineralization in aquatic organisms is a major research area for geobiology at the interface between palaeobiology and carbonate sedimentology, with broad implications for Earth's surface environment.

Microbial carbonates have particular relevance in this field for two reasons. Firstly, microbial carbonates are very long ranging, with probably the longest geological record and most extensive facies distribution of any biogenic sediment (Riding, 2000). Secondly, microbial carbonates are very susceptible to environmental influence, both for the growth of the micro-organisms that localize them and for the precipitation processes that determine their sedimentary accretion and geological preservation. One of the most widely appreciated features of the secular distribution of microbial carbonates is the suggestion that they have declined in abundance from a peak in the Proterozoic. Phanerozoic stromatolite decline was noted by Fischer (1965) and Cloud and Semikhatov (1969) but recognition of its longer term pattern, and possible link to metazoan competition, resulted from study of gastropod grazing on the Bahama Banks (Garrett, 1970) coupled with compilation of late Proterozoic reduction in stromatolite diversity (Awramik, 1971). Nonetheless, decline in microbial carbonates has also long been linked to changes in calcification (Fischer, 1965; Monty, 1973, 1977; Serebryakov and Semikhatov, 1974; Gebelein, 1976; Grotzinger, 1990), ultimately related to seawater chemistry.

Here we examine the Phanerozoic distribution of microbial carbonates in general and consider to what extent it may be possible to relate their secular abundance to competition with metazoans and to changes in seawater chemistry. This enquiry necessarily involves a number of assumptions, e.g., that metazoan diversity may be a proxy for metazoan abundance and, therefore, competition in its broadest sense, and also that currently available modeled estimates of Phanerozoic atmospheric and seawater composition may provide a window into changes in past seawater saturation state. Not the least aim of this study is to encourage further work that will lead to more robust information on which these interpretations can be based. Our approach to these questions is therefore essentially to compare secular variation in microbial carbonate abundance, metazoan abundance, and seawater saturation state for the Phanerozoic.

2. Microbial carbonates

Microbial carbonates can be regarded mainly as products of bacterial, and also algal, processes that promote the precipitation of $CaCO_3$ minerals such as aragonite and calcite, and trap sedimentary particles. Some microbial carbonates are difficult to confidently recognize in ancient carbonate sediments even though they are likely to have been volumetrically important. These may include micritic particles precipitated in the water column by pelagic microbes (Thompson, 2000) and those produced by the disintegration on the seafloor of calcified bacteria such as *Girvanella* (Pratt, 2001). In contrast, benthic microbial carbonates (Burne and Moore, 1987) produced by calcified microbial mats and biofilms are much more readily recognizable. These deposits include forms such as stromatolites and thrombolites that can be regarded as reef-builders along with skeletal algae and invertebrates.

Biocalcification in aquatic organisms ranges from biologically controlled, where organisms closely regulate their calcification, to biologically induced, where calcification is metabolically mediated but dependent on ambient water chemistry (Lowenstam, 1981; Leadbeater and Riding, 1986; Mann, 2001). In bacteria, a wide range of processes can lead to localized pH increase which affects carbonate speciation and favours $CaCO_3$ precipitation. In microbial mats these processes differ significantly, although over minute distances, between surface mat and sub-mat microenvironments. In oxic illuminated mat-surface environments, cyanobacterial photosynthetic uptake of CO_2 and/or HCO_3^- raises pH in ambient waters and in protective mucilaginous sheaths around the cyanobacterial cells, promoting calcification (Pentecost and Riding, 1986; Merz, 1992; Merz-Preiß, 2000; Arp et al., 2001). In sub-mat environments, anaerobic degradation of photosynthetic mat material by organotrophic bacteria can result in pH rise and $CaCO_3$ precipitation. These latter energy yielding processes include ammonification, denitrification, and sulphate reduction (references in Riding, 2000). In all these cases, bacterial calcification is not obligate, and it is dependent on suitable environmental and micro-environmental conditions. It is therefore biologically induced. This limits it to environments, whether in open water bodies or in sediment pores, where ambient waters are significantly oversaturated with respect to $CaCO_3$ minerals.

3. Phanerozoic abundance of microbial carbonates

Until recently, data regarding microbial carbonate Phanerozoic abundance have been scarce. Awramik (1971) used measures of diversity, based on form–genera and form–species, to show marked Neoproterozoic decline in stromatolites. However, comparable data are sparse for the Phanerozoic although it is well-known that microbial carbonates continued to be prominent, especially in reefs (Pratt, 1982; Webb, 2001). Riding (1992, 1993) qualitatively assessed Phanerozoic variation in the abundance of marine calcified cyanobacteria and found that their abundance can broadly coincide with that of ooids and marine cements, e.g., in the Cambrian–Early Ordovician, Late Devonian, and Permian–Triassic. More recently, improved data sets have been compiled for microbial carbonate abundance. On the basis of extensive literature review, Arp et al. (2001) plotted 864 reported occurrences of Phanerozoic calcified marine cyanobacteria, normalized to 10 Myr intervals. Kiessling and Flügel (2002) collected semiquantitive data from a literature search of 3050 global Phanerozoic reef sites to establish a Paleoreef Database (PaleoReefs). Using this data set, Kiessling (2002) reduced the fourteen reef-builder categories to nine, one of which is microbes, to show the 'number of reefs in which a particular reef-building group is dominant' and plotted these data against thirty-two 'supersequence' time-slices (Kiessling, 2002, Fig. 16). Riding (in press) replotted these microbial reef data using time ranges for each supersequence based on Golonka and Kiessling's, 2002) evaluation of absolute ages. Kiessling's (2002) reefal microbial

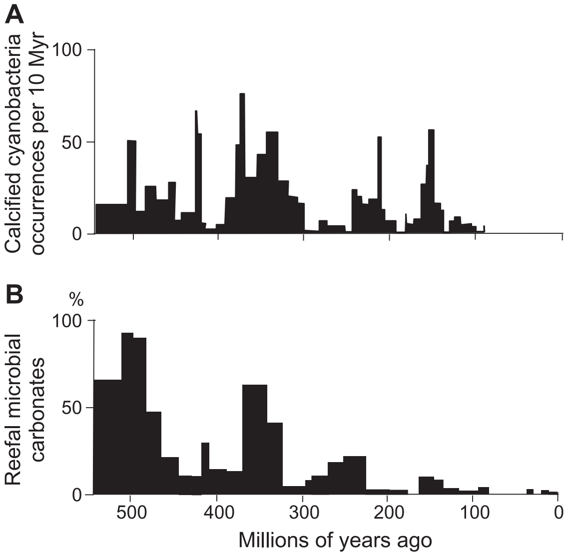

Fig. 1. Phanerozoic secular distribution of microbial carbonates. (A) Reported occurrences of calcified cyanobacteria per 10 Myr Phanerozoic (from Arp et al., 2001). (B) Relative abundance of reefal microbial carbonates replotted from Kiessling (2002, Fig. 16) using Golonka and Kiessling's (2002, Fig. 1, pp. 13–18) time intervals for each supersequence supersequences (see Riding, in press).

carbonate abundance data, together with occurrences of calcified cyanobacteria compiled by Arp et al. (2001), are shown in Fig. 1. Kiessling's (2002) data show a steep Early Palaeozoic decline in reefal microbial carbonate relative abundance that becomes a more gradual decline towards the present-day. However, marked oscillations are superimposed on this trend, with successively diminishing peaks of relative abundance at about 500, 350, 240, and 150 Myr ago (Riding, in press). In contrast, Arp et al.'s (2001) data show more occurrences of marine calcified cyanobacteria prior to ~300 Myr ago, fewer 300–100 Myr ago, and hardly any in the past 100 Myr (Fig. 1). There are peaks in occurrence about 500, 420, 370, 330, 210, and 150 Myr ago. These peaks are similar in size except near 420 and 370 Myr, when they are a little larger.

4. Metazoan diversity

Marine metazoan diversity, as compiled by Sepkoski (1997) shows exponential Early Cambrian to Late Ordovician increase, lesser overall change until marked Late Permian decline ~250 Myr ago, and then increase to the present-day, with the general diversity level of the Palaeozoic being exceeded by ~100 Myr ago during the Cretaceous (Fig. 2). This diversification resulted in the number of genera increasing from zero to ~2500 over the Phanerozoic as a whole.

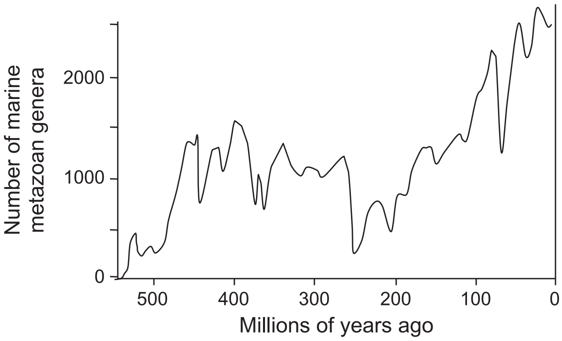

Fig. 2. Marine metazoan generic diversity data (from Sepkoski, 1997) showing exponential Early Cambrian to Late Ordovician increase, lesser overall change until marked Late Permian decline ~250 Myr ago, followed by increase to the present-day.

5. Seawater chemistry

Fundamental controls on marine carbonate precipitation through time can be expected to include saturation state of seawater with respect to aragonite and calcite (Kempe and Kazmierczak, 1990; Opdyke and Wilkinson, 1990; Webb, 2001) and biologically controlled biomineralization processes (Bosscher and Schlager, 1993). Mg^{2+}/Ca^{2+} ratio affects the kinetics of calcite precipitation, and is widely believed to have produced alternate calcite and aragonite seas through time (Sandberg, 1975, 1983; Stanley and Hardie, 1998). The relative importance of these controls on carbonate sedimentation for the Phanerozoic as a whole is still unclear (Opdyke and Wilkinson, 1990; Bosscher and Schlager, 1993; Stanley and Hardie, 1998; Leeder, 1999). Suggested broad stability of ocean water composition during the past 1000 Myr (Holland, 1978) does not preclude variations in Ca^{2+}, Mg^{2+}, carbonate alkalinity, seawater pH, and temperature (e.g., Berner et al., 1983; Sandberg, 1983; Karhu and Epstein, 1986; Morse and Mackenzie, 1990; Hardie, 1996; Berner and Kothavala, 2001; Stanley and Hardie, 1998; Veizer et al., 1999) that could significantly affect the precipitation of aragonite and calcite. In particular, such variations in seawater chemistry would influence saturation states with respect to these minerals (Arvidson et al., 2000; Riding and Liang, 2004, in press). Variation in marine abundances of aragonite and calcite has been recognized throughout the Phanerozoic (Sandberg, 1983; Burton and Walter, 1987; Wilkinson and Algeo, 1989; Mackenzie and Morse, 1992), but calculation of the saturation state of seawater for $CaCO_3$ minerals is more problematic, particularly prior to 100 Myr ago (Riding and Liang, 2004, in press).

6. Seawater saturation state

Saturation state with respect to $CaCO_3$ minerals, defined by $\Omega=\{Ca^{2+}\}\{CO_3^{2-}\}/K_{sp}$ (where Ω signifies saturation ratio, and { } signifies activity), is determined by activity product of calcium and carbonate over the solubility constant at a given temperature and pressure condition (Stumm and Morgan, 1996). Arvidson et al. (2000, p. 2) calculated saturation for calcite and dolomite for the past 100 Myr using partial pressure of CO_2 (p_{CO2}) and seawater composition data of Berner et al. (1983) and showed that saturation state declined towards the present-day. Calculation of saturation state for periods prior to 100 Myr has been hindered by lack of estimates of oceanic carbonate speciation. In order to constrain the system it is necessary to know at least two of the four key parameters: carbonate alkalinity, p_{CO2}, dissolved inorganic carbon (DIC), and pH (Stumm and Morgan, 1996). Estimated values for p_{CO2} can be derived from the model named GEOCARB III (Berner and Kothavala, 2001), but additional information is needed to estimate carbonate species for the Phanerozoic. In the absence of pH data, Riding and Liang (2004, in press) determined carbonate concentration by estimating DIC from the correlation established for p_{CO2} and HCO_3^- for the last 100 Myr by Lasaga et al. (1985) who revised data originally obtained by Berner et al. (1983) using the so-called BLAG model.

Using this approach, together with published estimates of other major ions (Hardie, 1996; Stanley and Hardie, 1998), Riding and Liang (2004, in press) calculated $\Omega_{aragonite}$, $\Omega_{calcite}$, and $\Omega_{dolomite}$ for the Phanerozoic assuming chemical equilibrium. A constant temperature (15 °C) was used in the calculations. They found that the resulting calculated trends of $\Omega_{aragonite}$ and $\Omega_{calcite}$ exhibit broad positive covariation with carbonate platform accretion rate (see Bosscher and Schlager, 1993) and with periods of abundance of microbial and nonskeletal $CaCO_3$ precipitates (Riding and Liang, 2004, in press). Riding and Liang (2004, in press) concluded that these relationships suggest a primary control by seawater chemistry on limestone formation in general and microbial carbonates in particular. In addition, they found that higher values of saturation state and limestone accumulation correspond with ‘calcite seas’, and lower values with ‘aragonite seas’.

7. Development of saturation ratio estimates

Previously, we calculated past seawater saturation state for major carbonate minerals ($\Omega_{aragonite}$, $\Omega_{calcite}$, and $\Omega_{dolomite}$) with a stoichiometric chemical equilibrium approach (Riding and Liang, 2004, in press). Numerical calculations were performed using the PHREEQC code, for phase reaction equilibria written in the C programming language (version 2, Parkhurst and Appelo, 1999). Estimation of activity coefficients in PHREEQC employs the extended Debye–Hückel limiting law (Debye and Hückel, 1923) for aqueous species. However, for concentrated solutions, including seawater and brines, Pitzer’s (1991) approximation is deemed more appropriate to account for ionic interactions and to compute activity coefficients (Stumm and Morgan, 1996). Furthermore, Riding and Liang (2004, in press) simplified calculations by using a constant temperature of 15 °C, whereas global sea surface temperatures are likely to have fluctuated substantially during the Phanerozoic (Karhu and Epstein, 1986; Frakes et al., 1992). Stable oxygen isotope ($\delta^{18}O$) data from marine invertebrate shells provide a means of assessing Phanerozoic temperature variation (Veizer et al., 1999). However, such palaeotemperature estimation is complicated by a long-term rising $\delta^{18}O$ trend (Veizer et al., 1999), that might indicate a long-term control on seawater $\delta^{18}O$ by mid-ocean ridge and riverine fluxes, in addition to temperature (Veizer et al., 2000). Accordingly, Veizer et al. (2000) derived detrended values by subtracting the least-squares linear fit from the data.

Recognizing the limitations with regard to activity coefficients and temperature in the previous modeling approach, here we recalculate calcite saturation state ($\Omega_{calcite}$) for the Phanerozoic Eon. In these new calculations, the input chemistry data, such as Ca, Mg, K, SO_4^{2-}, p_{CO2}, DIC, etc. remain the same as in Riding and Liang (2004, in press). However, two

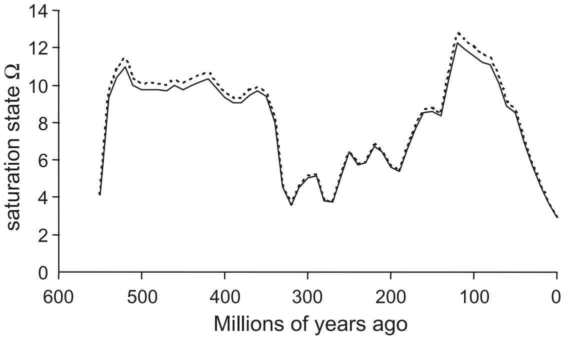

Fig. 3. Riding and Liang (2004, in press) $\Omega_{calcite}$ Phanerozoic trend (dashed line), compared with the same data recalculated using Pitzer equations (solid line). Use of Pitzer equations results in slightly (<5%) lower saturation ratio values.

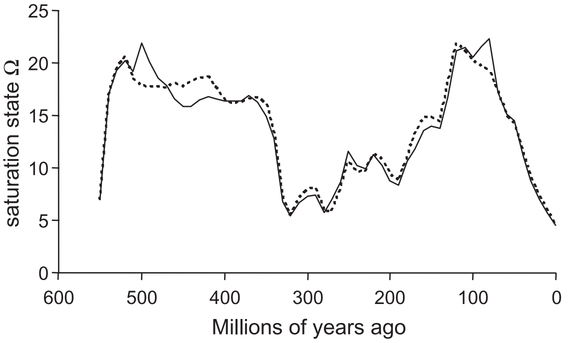

Fig. 4. Riding and Liang (2004, in press) Ω_{calcite} Phanerozoic trend recalculated at 25 °C (dashed line), compared with the same data incorporating Veizer et al's (2000, Fig. 3) temperature anomalies (solid line). The most conspicuous changes in saturation state resulting from incorporation of these temperature values are ~400–500 Myr ago and ~80 Myr ago.

additional factors are examined: (i) effect of ionic interaction, using an improved Pitzer formulations to calculate activity coefficients (Fig. 3); (ii) effect of temperature, using detrended temperature anomaly values in the range −4 °C and +6 °C, based on samples from low latitudes (Veizer et al., 2000, Fig. 3). The latter is implemented with a baseline of 25 °C, representing present-day mean tropical sea-surface temperature, to approximate temperatures during the Phanerozoic (Fig. 4).

8. Results

8.1. Saturation ratio trends

Ω_{calcite}, recalculated using Pitzer equations from the input data of (Riding and Liang, 2004, in press), is compared with the original Ω_{calcite} trend in Fig. 3. Use of Pitzer equations results in slightly lower saturation ratio values, but the maximum deviation in calculated Ω_{calcite} is <5%. For example, calculated saturation ratio at its Phanerozoic peak 120 Myr ago is reduced from 12.8 to 12.3. The improvement by using Pitzer's formulation is small compared to the quality of the input data. For example, the error estimates on calculated GEOCARB p_{CO2} CO_2 values are generally very large (Berner and Kothavala, 2001). For this reason, the remaining comparisons are made here using results obtained from extended Debye–Hückel limiting law.

The Ω_{calcite} Phanerozoic trend recalculated using Veizer et al's (2000, Fig. 3) temperature anomaly data is shown in Fig. 4, together with the Ω_{calcite} values recalculated at 25 °C. Calculated saturation ratio rises rapidly from 545 Myr ago to peaks ~500 Myr ago, declines to a high plateau between ~450 and 375 Myr, declines rapidly to low points ~320 and 280 Myr ago, rises to low peaks ~250 and 220 Myr ago, declines to ~190 Myr ago, and rises to high peaks ~100 Myr before steeply declining to the present day.

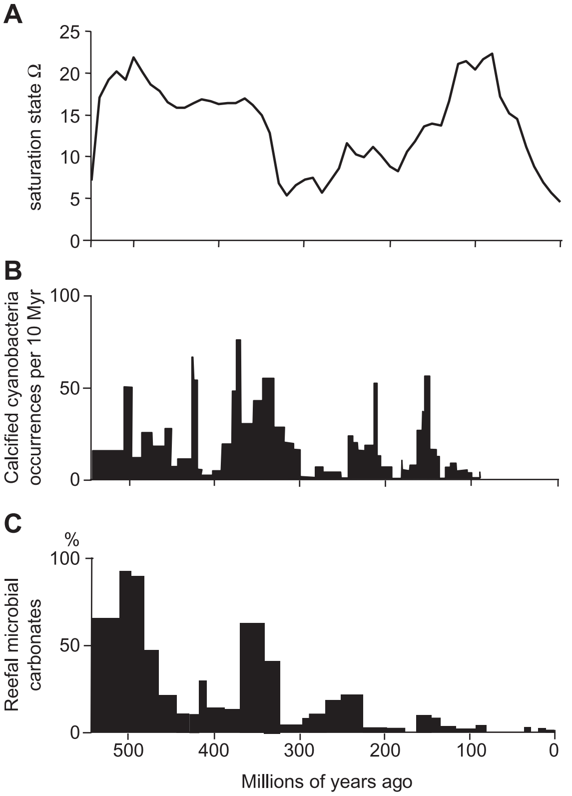

Fig. 5. (A) Ω_{calcite} incorporating Veizer et al's (2000, Fig. 3) temperature anomalies with 25 °C baseline (solid line in Fig. 4) compared with microbial carbonate abundance data of (B) Arp et al. (2001) and (C) Kiessling (2002). Periods of increased abundance of calcified cyanobacteria and reefal microbial carbonates prior to ~150 Myr ago broadly coincide with peaks of calculated saturation ratio. However, an anomaly occurs ~120–80 Myr ago when calculated saturation ratio is high and microbial carbonate abundance is low. This is suggested to reflect pelagic carbonate deposition by plankton. This removal, that would have reduced saturation state, is not incorporated into the saturation state values calculated here.

8.2. Saturation state and microbial carbonate abundance

The $\Omega_{calcite}$ trend (with temperature correction) is compared with microbial carbonate abundance data of Arp et al. (2001) and Kiessling (2002) in Fig. 5. Periods of increased abundance of calcified cyanobacteria and reefal microbial carbonates (e.g., ~500, 420, 370, 250–220, and 160 Myr ago) appear to coincide with peaks of calculated saturation ratio. However, whereas microbial carbonates decline in the past 150 Myr, calculated saturation ratio rises to marked peaks ~120–80 Myr ago.

8.3. Microbial carbonates and metazoan diversity

Phanerozoic abundance of microbial carbonates (Arp et al., 2001; Kiessling, 2002, Fig. 16) is compared with an inverse plot of marine metazoan generic diversity (data from Sepkoski, 1997) in Fig. 6. In general, microbial carbonates decline in abundance as metazoan diversity increases, and in some cases sharp declines (major extinctions) in diversity correspond with increases in microbial carbonates (e.g., ~370–360 and ~245 Myr ago).

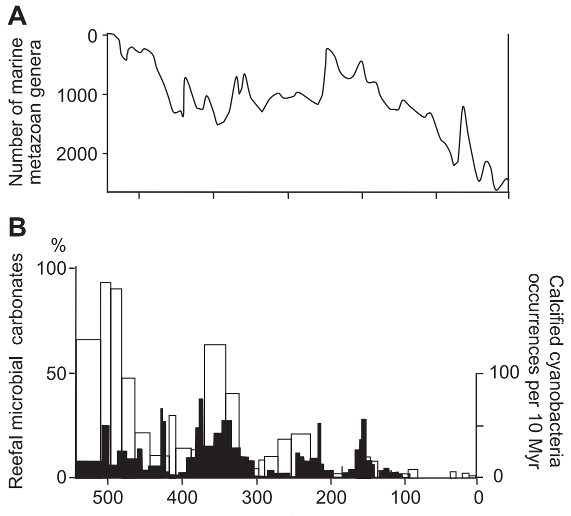

Fig. 6. (A) Inverse plot of marine metazoan generic diversity (data from Sepkoski, 1997). (B) Relative abundance of reefal microbial carbonates during the Phanerozoic. Open bar data from Riding (in press), replotted from Kiessling (2002, Fig. 16) using Golonka and Kiessling's, (2002, Fig. 1, pp. 13–18) time intervals for super-sequences. Filled bars show reported occurrences of calcified cyanobacteria per 10 Myr Phanerozoic from Arp et al. (2001). The broadly inverse relationship supports the view that microbial carbonates declined through the Phanerozoic as metazoans diversified.

9. Discussion

9.1. Constraints on saturation state estimates

As stated above (6, Seawater saturation state), calculation of $\Omega_{aragonite}$, $\Omega_{calcite}$, and $\Omega_{dolomite}$ is based on modeled values of atmospheric CO_2 (Berner and Kothavala, 2001), seawater major ion composition (Hardie, 1996; Stanley and Hardie, 1998), and a correlation established for p_{CO2} and HCO_3^- for the past 100 Myr (Lasaga et al., 1985). Many of the assumptions underlying these modeled values remain to be confirmed. For example, inference of seafloor spreading rates from changes in sealevel (Gaffin, 1987) is not supported for the past 180 Myr by estimates based on area–age distribution of oceanic crust (Parsons, 1982; Rowley, 2002). Nonetheless, Hardie's (1996) and Stanley and Hardie's (1998) modeled estimates of Phanerozoic Ca^{2+} and Mg^{2+} values are generally consistent with analyses of fluid inclusions preserved in marine halite (Lowenstein et al., 2001; Horita et al., 2002). Furthermore, model estimates of p_{CO2} from GEOCARB, with GEOCARB III (Berner and Kothavala, 2001) being the most recent version, for the Phanerozoic have broad support from p_{CO2} proxy data such as $\delta^{13}C$ values of palaeosols and fossil plant stomata (Ekart et al., 1999; Royer et al., 2001; Crowley and Berner, 2001). An additional difficulty concerns the lack of knowledge of variations in the carbonate system over time. In the absence of published data for either DIC, alkalinity, or pH for the Phanerozoic as a whole, Riding and Liang (2004, in press) estimated DIC using the correlation established for p_{CO2} and HCO_3^- for the last 100 Myr in the revised BLAG data (Lasaga et al., 1985) and extrapolated it to earlier periods from GEOCARB III p_{CO2} data. There are objections to this approach. In the first place, underlying modeling assumptions of Lasaga et al. (1985) differ from those of Hardie (1996) and Stanley and Hardie (1998), thus raising questions on consistency of the data. Furthermore, seawater chemistry of the earlier Phanerozoic is likely to differ from that of past 100 Myr, due to the varying inputs from continental weathering via rivers and inputs and outputs due to changes in mid-ocean ridge brine fluxes and reactions in sediments (Holland, 2004). Fundamentally, the relationship between p_{CO2} and DIC depends on ocean pH, and this is debatable even for the past 100 Myr (e.g., Pearson and Palmer, 2000; LeMarchand et al., 2000).

Given these uncertainties, how might we attempt to establish broad constraints on secular changes in this system? As mentioned earlier, if p_{CO2} is known the carbonate system can be constrained by either DIC, alkalinity or pH. Riding and Liang (2004, in press) used estimated DIC values to calculate saturation state. It is therefore relevant to compare the effects of (i) alkalinity and (ii) pH on carbonate saturation state.

(i) With the same input data but using present-day levels of seawater alkalinity (~2.3 mM), very different saturation states from those of Riding and Liang (2004, in press) are obtained. These new values are close to undersaturation in the Early Palaeozoic (~400 Myr ago; Fig. 7A) when modeled p_{CO2} was high. Holding alkalinity constant lowers seawater pH due to lack of buffering capacity. This appears unrealistic, since increased p_{CO2} can be expected to have increased subaerial weathering, supplying Ca^{2+}, Mg^{2+}, HCO_3^-, and other dissolved species, with the result that seawater alkalinity should increase and saturation state should rise. This is not seen where alkalinity is held constant (Fig. 7A).

(ii) The effect of holding pH constant is shown in Fig. 7B. Absolute saturation values differ markedly depending on the pH selected. For example, at constant pH 7.6, calculated saturation state becomes <1 at times of low p_{CO2}, whereas at constant pH 8.2 calculated saturation state reaches values >200 when p_{CO2} is very high. Despite these differences in absolute values, the saturation trends in both these cases are identical in shape, and although different in detail from that of Riding and Liang (2004, in press) remain similar in terms of most maxima and minima. When pH is held constant, alkalinity is allowed to increase to accommodate p_{CO2} increase and carbonate species dominate the system. Thus, it is not surprising that the resulting saturation curve reflects the p_{CO2} curve. Of course, the extent of alkalinity increase at very high p_{CO2} could become unreasonable, as seen in the very high saturation state under these conditions. Nonetheless, this simple evaluation indicates that, compared with the constant alkalinity approach, the constant pH method is more reasonable because it permits the feedback mechanisms that increase alkalinity. We conclude that, although it is not possible to quantitatively constrain the carbonate system prior to 100 Myr ago, there is reason to consider that the

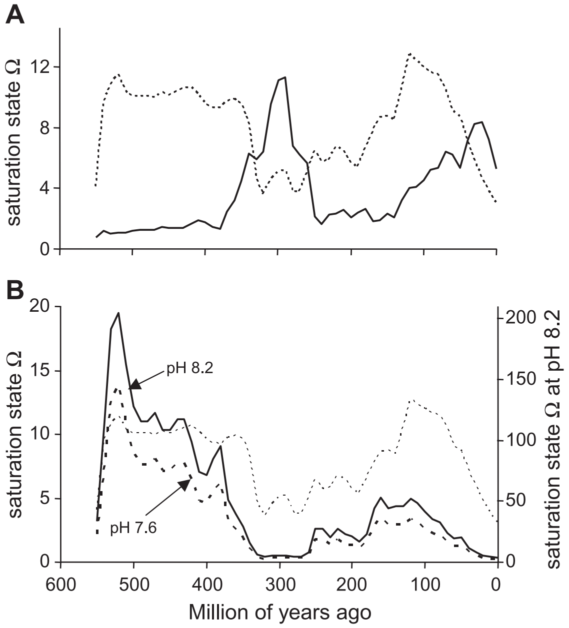

Fig. 7. (A) Saturation state ($\Omega_{calcite}$) calculated with alkalinity held constant at present-day level (~2.3 mM; solid line) compared with previous calculation (dashed line; Riding and Liang, 2004, in press). (B) Saturation state ($\Omega_{calcite}$) calculated with pH held constant at 7.6 (dark dashed line) and 8.2 (solid line), compared with previous calculation (thin dashed line; Riding and Liang, 2004, in press). Assumption of constant alkalinity (A) results in low saturation values at high p_{CO2}. This appears unrealistic, since increased p_{CO2} can be expected to increase subaerial weathering, supplying Ca^{2+}, Mg^{2+}, HCO_3^-, and other dissolved species. This in turn would result in increase in seawater alkalinity and corresponding increase in saturation state that is not seen in (A). In contrast, holding pH constant (B) permits alkalinity to increase with p_{CO2}. This is accompanied by increase in carbonate species and therefore results in higher saturation state.

revised BLAG relationship between p_{CO2} and HCO_3^- (Lasaga et al., 1985) used by Riding and Liang (2004, in press) may not be unrealistic.

Using this approach for the carbonate system, previous calculation yielded pH values in the range 7.6–8.2 (Riding and Liang, 2004, in press), which are within the ranges of sea-surface pH estimates for the past 300 Myr (Caldeira and Wickett, 2003; Pearson and Palmer, 2000; Zeebe, 2001). Furthermore, since change in alkalinity should be constrained by carbonate and silicate weathering, oceanic pH need not vary significantly even over longer timescales than the Phanerozoic (Grotzinger and Kasting, 1993). We conclude that, although the limitations on saturation state calculation noted above remain inescapable at present, it may be that absence of robust information regarding Phanerozoic DIC, alkalinity, or pH does not completely negate attempts to reconstruct secular variation in surface ocean saturation state.

9.2. Microbial carbonates compared with saturation trends incorporating temperature data

The recalculated $\Omega_{calcite}$ Phanerozoic trend, using Veizer et al.'s (2000, Fig. 3) temperature anomaly data (Fig. 4) is broadly similar to that of Riding and Liang (2004, in press) but with the following differences: a marked peak at ~500 Myr, an enhanced peak at ~420 Myr, a slight shift to a peak at ~370 Myr, and a marked peak at ~80 Myr ago. The earlier three of these peaks correspond with successive Palaeozoic peaks in calcified cyanobacteria abundance of Arp et al. (2001) and with Kiessling's (2002) Palaeozoic peaks of reefal microbial carbonate abundance (Fig. 5). Elevated sea-surface temperatures can be expected to increase saturation state, and therefore $CaCO_3$ precipitation, and also to stimulate microbial growth. It may not be coincidental, therefore, that intervals of higher temperatures in the Late Cambrian–Early Ordovician (~500 Myr), Late Devonian (~370 Myr), and Late Permian–Early Triassic (~250 Myr) recognized by Veizer et al. (2000, Fig. 3) from oxygen isotope analyses, broadly correspond with increased abundance of microbial carbonates (see also Riding, 1992).

However, steady decline in reefal microbial carbonate abundance peaks during the Phanerozoic to quite low values during the past 200 Myr (Fig. 5C) creates marked discrepancy between low microbial carbonate abundance and elevated calculated saturation ratio ~80–120 Myr ago. Riding and Liang (2004, in press) noted a similar discrepancy with shallow-water limestone accumulation rate measured by Bosscher and Schlager (1993). They suggested that this might reflect the Late Cretaceous period of increased deposition of deep-sea carbonates in response to pelagic biomineralization. There is need, therefore, to incorporate biologically controlled $CaCO_3$ removal into geochemical models of global budgets. Notwithstanding uncertainties such as these, we conclude that, overall, there is a degree of coincidence between this newly calculated saturation state trend and microbial carbonate abundance measures prior to ~150 Myr ago that suggests a causal relationship.

9.3. Microbial carbonates compared with metazoan diversity

Comparisons between microbial carbonates and metazoan diversity rely on the assumption that taxonomic diversity may be a proxy for competitive interference, and this requires support. Nonetheless, the broadly inverse relationship between microbial carbonate abundance and marine metazoan generic diversity (Fig. 6) tends to support the view that microbial carbonates declined through the Phanerozoic as metazoans diversified and, directly or indirectly, provided competitive interference (Garrett, 1970; Awramik, 1971).

9.4. Dual control on microbial carbonates

Earlier assessments of the Phanerozoic history of microbial carbonates recognized a long-term decline (e.g., Maslov, 1959, Fischer, 1965) that was patterned by marked fluctuations in abundance (Riding, 1992, 1993), but there was a lack of stratigraphically resolved data to test this further. Data subsequently extracted from the literature for calcified cyanobacteria (Arp et al., 2001) and reefal microbial carbonates (Kiessling, 2002, Fig. 16) confirm a long-term pattern of fluctuating decline. Furthermore, comparisons between these measures of microbial carbonate abundance and both estimated saturation state and metazoan diversity data strengthen the likelihood that these have operated in conjunction as controlling factors.

In hindsight, therefore, it appears that suggestions concerning the importance of early lithification that go back many years (e.g., Walcott, 1914; Logan, 1961, p. 520; Fischer, 1965), and of interactions with eukaryotes in general and metazoans in particular (e.g., Fischer, 1965; Garrett, 1970; Awramik, 1971), including the related concept of stromatolites as ‘disaster forms’ resurging when metazoans are reduced (Schubert and Bottjer, 1992), have been on the right track. But it is also evident that neither factor should be considered in isolation. Riding (in press) concluded that microbial carbonates were most abundant when elevated saturation state coincided with low metazoan diversity (e.g., Cambrian–Early Ordovician and Late Silurian, and following Late Devonian, end-Permian, and end-Jurassic extinctions; Fig. 8) and were least abundant when reduced saturation state coincided with high metazoan diversity (e.g., Late Carboniferous, Early–Mid Jurassic, and Cenozoic). In other words, maxima and minima of microbial carbonate abundance depended on whether the effects of metazoan diversity and carbonate saturation state reinforced or countered one another.

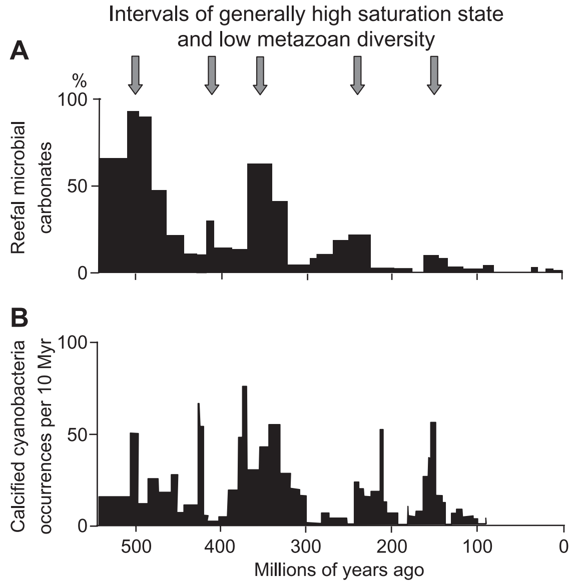

Fig. 8. Phanerozoic periods of microbial carbonate abundance (A, Kiessling, 2002; B, Arp et al., 2001) broadly coincide with intervals (arrows) when saturation state was elevated and metazoan diversity reduced.

9.5. Microbial carbonates and biocalcification

Confirmation that competition and early lithification have combined to determine the secular pattern of microbial carbonates observed in the Phanerozoic suggests a number of questions. For example, is it possible to judge whether – at different times – one of these factors was more important than another? Even more intriguingly, is it likely that these organisms – whether prokaryote or eukaryote – have not only competed for resources such as space and nutrients but also for the resources that promote biomineralization? In other words, could the link observed between metazoan increase and microbial carbonate decline reflect, inter alia, competition for $CaCO_3$? This focuses attention on the relationships between saturation state and biologically induced calcification on the one hand and biologically controlled calcification on the other. It could 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. Preliminary comparisons of calculated seawater saturation state with patterns of marine calcified organisms during the Phanerozoic Eon suggest 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. In contrast, organisms with relatively controlled calcification, such as molluscs, brachiopods, bryozoans, and echinoderms, appear to have been relatively unaffected by saturation state. This could indicate that $CaCO_3$ availability – governed by saturation state – has significantly influenced the diversity of organisms with biologically induced calcification. This could involve many tropical marine algae and invertebrates, especially those that are most involved in reef building. Thus, despite its apparent abundance, it may be that $CaCO_3$ has been so widely employed in biomineralization by aquatic organisms during the past ~550 million years that it has constituted a limiting resource, partitioned between organisms that biologically control and biologically induce their calcification, with the surplus being inorganically precipitated.

In contrast, for the major part of the Precambrian not only would metazoan interference have been reduced or absent (Awramik, 1971) but so would competition for $CaCO_3$, because controlled biomineralization was scarce prior to the Phanerozoic (Lowenstam, 1981). In these circumstances, seawater saturation state, together with microbial evolution, would have been the principal factors determining microbial carbonate development during the Precambrian (Grotzinger, 1994). The advent of biologically controlled calcification in the Palaeozoic is likely to have significantly affected this system. As a first approximation, we can envisage that marine carbonate sedimentation prior to the advent of controlled biocalcification would have reflected seawater $CaCO_3$ saturation state equilibrium. Other factors being equal, the evolutionary rise of organisms with controlled biocalcification (Lowenstam, 1981) must have reduced seawater saturation state and, thus, inorganic and biologically induced precipitation. During the Phanerozoic it seems likely that this switch from induced to controlled biocalcification progressively increased. Certainly, the record of microbial carbonates reflects long-term decline in microbially induced calcification. Biological influences on $CaCO_3$ precipitation would have been mediated by evolution and habitat availability, and by fluctuations in seawater saturation state-determined by global cycling—such as those that we endeavour to use here to estimate changes in saturation ratio. So long as most biocalcifiers were benthic, a prime control on habitat availability would have been the extent of shallow seas, and therefore dependent on sealevel fluctuations (Grotzinger, 1994). Cretaceous radiation of coccolithophore algae and globigerine foraminifers (Tappan and Loeblich, 1973) can be seen as part of the long-term rise in controlled biocalcification. But this substantial increase in oceanic planktic calcifiers also delivered large quantities of $CaCO_3$ to the deep-ocean rather than to shallow shelves (Hay, 1985; Opdyke and Wilkinson, 1988). This should have impacted negatively on shelf carbonate sedimentation (Wilkinson and Walker, 1989). Furthermore, because these pelagic carbonates were prone to dissolution in deep water prior to burial, they could be rapidly recycled in response to changes in global ocean chemistry. This has introduced a stabilizing factor into the marine carbonate system (Ridgewell et al., 2003) that continues to the present-day (Broecker and Clark, 2001). On the other hand, the rate at which buried deep-sea carbonates are subducted could be quite irregular, and this may have been a factor contributing to low present-day p_{CO2} (Edmond and Huh, 2003). This in turn would have influenced current low seawater saturation state and reduced abundance of microbial carbonates. By this type of reasoning it should be possible to integrate the biological evolution of calcification, patterns of carbonate sedimentation, and variation in seawater chemistry over extensive timescales. This remains to be further elucidated.

10. Summary and conclusions

It has long been suggested that the geological distribution of microbial carbonates could reflect not only the rise of eukaryotes in general, and metazoans in particular, but also changes in seawater chemistry that determined the extent of microbial calcification (Fischer, 1965). Compilations of abundance data for calcified cyanobacteria (Arp et al., 2001) and reefal microbial carbonates (Kiessling, 2002) suggest that marine microbial carbonates in general have undergone long-term episodic decline since the Early Palaeozoic. A broadly inverse relationship between this pattern and that of metazoan diversity (Sepkoski, 1997) supports the view that microbial carbonates became less widespread as metazoans expanded (Riding, in press). Riding and Liang (2004, in press) calculated variation in saturation state for the Phanerozoic using published estimates of past seawater ionic composition and atmospheric CO_2 levels, and assuming constant temperature of 15 °C. They found broad positive coincidence between the secular trend of $\Omega_{calcite}$, shallow-water limestone accumulation rate (Bosscher and Schlager, 1993), and periods of increased abundance of microbial carbonates. These results suggest that microbial carbonate abundance responded to changes in the saturation state of seawater, as well as to changes in the presence of metazoans (Fig. 9), and that both of these factors need to be considered to understand the Phanerozoic history of marine microbial carbonates (Riding, in press), as Fischer (1965) anticipated.

Recognition of the likely importance of changes in seawater saturation state for understanding many aspects of limestone precipitation and biocalcification, including microbial carbonates (Kempe and Kaz-

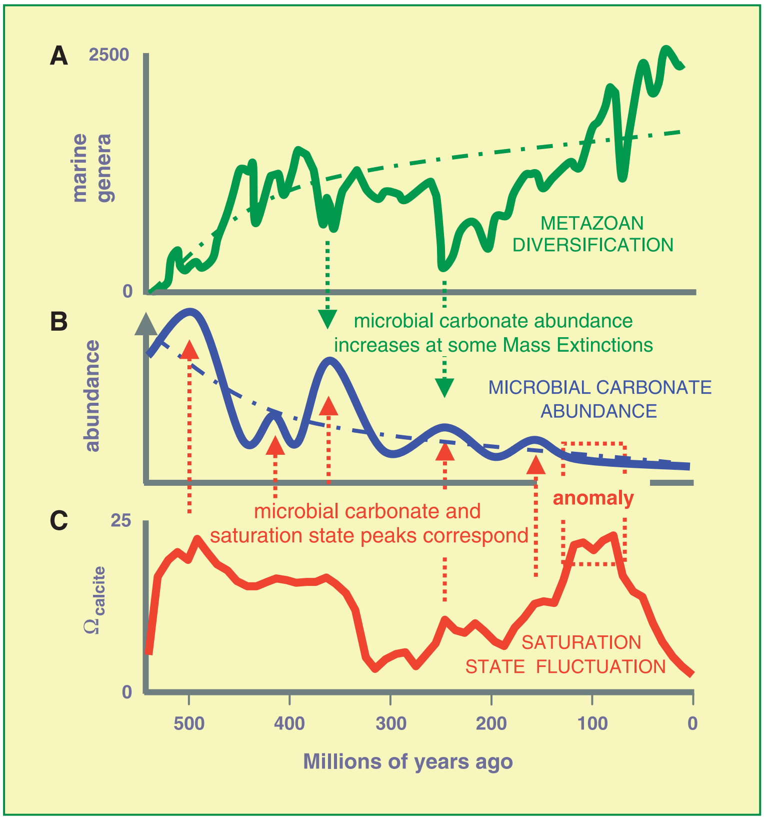

Fig. 9. Comparison of (A) marine metazoan generic diversity (Sepkoski, 1997), (B) microbial carbonate abundance generalized from Arp et al. (2001) and Kiessling (2002), and (C) calcite saturation ratio calculated in this paper. Microbial carbonates show oscillatory decline. The overall trend of microbial carbonate decline inversely mirrors that of metazoan diversification. Peaks of microbial carbonate abundance superimposed on the overall trend broadly coincide with periods of raised calcite saturation ratio (red arrows). An anomaly ~80–120 Myr ago occurs where high calculated saturation state does not correspond to increase in microbial carbonates. This could reflect reduction in saturation state due to Late Cretaceous increase in deep-sea carbonates; this has not been taken into account in calculating saturation state. Some peaks of microbial carbonate abundance also correspond with marked reductions (Mass Extinctions) in metazoan diversity (green arrows), although not all Mass Extinctions can be seen to have had this effect. This summary indicates that the Phanerozoic trend of microbial carbonate abundance broadly reflects the influence of both metazoan interference and seawater saturation state with respect to $CaCO_3$ minerals.

mierczak, 1990; Opdyke and Wilkinson, 1990; Webb, 2001), is not new. Unfortunately, calculation of past seawater saturation state is fraught with difficulty, particularly prior to 100 Myr ago. Comprehensive values of seawater ionic composition (e.g., Hardie, 1996; Stanley and Hardie, 1998) and atmospheric CO_2 levels (e.g., Berner and Kothavala, 2001) available for the Phanerozoic as a whole are modeled estimates. Interpretation of palaeotemperatures based on oxygen isotope ($\delta^{18}O$) data from marine invertebrate shells is complicated by an overall rising $\delta^{18}O$ trend (Veizer et al., 1999). Furthermore, there is a lack of information concerning seawater pH, alkalinity, or DIC, one of which is required to constrain the carbonate system and calculate $\{CO_3^{2-}\}$.

Here we have endeavoured to improve estimation of Phanerozoic seawater saturation state by using Pitzer equations (Pitzer, 1991) to compute activity coefficients for seawater species, and by incorporating temperature anomaly data (Veizer et al., 2000, Fig. 3). We cannot overcome the lack of robust information concerning changes in Phanerozoic seawater pH. Nonetheless, we find that holding pH constant (e.g., at 7.6 and 8.2), while using the same ionic and p_{CO2} input data, results in $\Omega_{aragonite}$ and $\Omega_{calcite}$ trends that are not very dissimilar from those of Riding and Liang

(2004, in press) who determined carbonate concentration by applying the correlation established for p_{CO2} and HCO_3^- for the last 100 Myr in the revised BLAG data (Lasaga et al., 1985) to the entire Phanerozoic. This calculation yielded pH variation between 7.6 and 8.2 (Riding and Liang, 2004, in press), with the change inversely linked to p_{CO2} increase, permitting feedback mechanisms to increase alkalinity to a reasonable level. Holding pH constant implies that as p_{CO2} increases, carbonate increases accordingly and controls seawater saturation state, resulting in similarity between the trends of saturation state and p_{CO2}. Similarities between the saturation ratio trend and the geological record therefore tend to substantiate GEOCARB III p_{CO2} values from which $\Omega_{\mathrm{calcite}}$ was calculated. The $\Omega_{\mathrm{calcite}}$ trend for the Phanerozoic, recalculated using temperature anomaly data from Veizer et al. (2000), shows correspondence with peaks of microbial carbonate abundance prior to ~150 Myr ago. The modeled estimates we have used are based primarily on global budgets of physico-chemical processes, and do not take account of biologically controlled removal of $CaCO_3$. Thus, contrast between (elevated) saturation state and (low) microbial carbonate abundance ~100 Myr ago could be due to the fact that calculated saturation ratio does not take account of $CaCO_3$ removed from the system by biologically controlled calcification such as pelagic plankton.

Long-term secular variation in seawater saturation state with respect to $CaCO_3$ minerals is of interest for a variety of reasons, not least for elucidating fundamental controls on $CaCO_3$ precipitation and recognizing their effects on geological patterns of sedimentation, as well as for its role in carbon sequestration. We conclude that similarities between calculated saturation state and the geological records of both limestone accumulation rate (Riding and Liang, 2004, in press) and microbial carbonate abundance provide evidence that secular variation in saturation state has significantly influenced marine carbonate formation. Improved estimates of seawater ionic composition (e.g., from fluid inclusion data), and of atmospheric p_{CO2} and past pH are needed for confident seawater saturation state calculation. Better measures of microbial and other non-skeletal carbonates through time are also required to further explore these questions.

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References

Arp, G., Reimer, A., Reitner, J., 2001. Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. Science 292, 1701–1704.

Arvidson, R.S., Mackenzie, F.T., Guidry, M.W., 2000. Ocean/atmosphere history and carbonate precipitation rates: a solution to the ã dolomite problemã. In: Glenn, C.R., Prévôt-Lucas, L., Lucas, J. (Eds.), Marine authigenesis: from global to microbial. SEPM Special Publication 66, Tulsa, OK, pp. 1–5.

Awramik, S.M., 1971. Precambrian columnar stromatolite diversity: reflection of metazoan appearance. Science 174, 825–827.

Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO2 over Phanerozoic time. Am. J. Sci. 301, 182–204.

Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon-dioxide over the past 100 million years. Am. J. Sci. 283, 641–683.

Bosscher, H., Schlager, W., 1993. Accumulation rates of carbonate platforms. J. Geol. 101, 345–355.

Broecker, W.S., Clark, E., 2001. Glacial-to-Holocene redistribution of carbonate ion in the deep sea. Science 294, 2152–2154.

Burne, R.V., Moore, L.S., 1987. Microbialites: organosedimentary deposits of benthic microbial communities. Palaios 2, 241–254.

Burton, E.A., Walter, L.M., 1987. Relative precipitation rates of aragonite and Mg calcite from seawater: temperature or carbonate ion control? Geology 15, 111–114.

Caldeira, K., Wickett, M.E., 2003. Anthropogenic carbon and ocean pH. Nature 425, 365.

Cloud, P.E., Semikhatov, M.A., 1969. Proterozoic stromatolite zonation. Am. J. Sci. 267, 1017–1061.

Crowley, T.J., Berner, R.A., 2001. Paleoclimate-CO_2 and climate change. Science 292, 870–872.

Debye, P., Hückel, E., 1923. Zur Theorie der Elektrolyte. Phys. Z. 24, 185–206.

Edmond, J.M., Huh, Y., 2003. Non-steady state carbonate recycling and implications for the evolution of atmospheric P_{CO2}. Earth Planet. Sci. Lett. 216, 125–139.

Ekart, D.D., Cerling, T.E., Montanez, I.P., Tabor, N.J., 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. Am. J. Sci. 299, 805–827.

Fischer, A.G., 1965. Fossils, early life, and atmospheric history. Proc. Natl. Acad. Sci. 53, 1205–1215.

Frakes, L.A., Francis, J.E., Syktus, J.I., 1992. Climate Modes of the Phanerozoic: The History of the Earth's Climate Over rhe Past

600 Million Years. Cambridge University Press, Cambridge, England (274 pp.).

Gaffin, S., 1987. Ridge volume dependence on sea-floor generation rate and inversion using long-term sea-level change. Am. J. Sci. 287, 596–611.

Garrett, P., 1970. Phanerozoic stromatolites: noncompetitive ecologic restriction by grazing and burrowing animals. Science 169, 171–173.

Gebelein, C.D., 1976. The effects of the physical, chemical and biological evolution of the earth. In: Walter, M.R. (Ed.), Stromatolites, Developments in Sedimentology, vol. 20. Elsevier, Amsterdam, pp. 499–515.

Golonka, J., Kiessling, W., 2002. Phanerozoic time scale and definition of time slices. In: Kiessling, W., Flügel, E., Golonka, J. (Eds.), Phanerozoic Reef Patterns, SEPM Special Publication, vol. 72, pp. 11–20.

Grotzinger, J.P., 1990. Geochemical model for Proterozoic stromatolite decline. Am. J. Sci. 290-A, 80–103.

Grotzinger, J.P., 1994. Trends in Precambrian carbonate sediments and their implication for understanding evolution. In: Bengtson, S. (Ed.), Early Life on Earth, Nobel Symposium, vol. 84. Columbia University Press, New York, pp. 245–258.

Grotzinger, J.P., Kasting, J.F., 1993. New constraints on Precambrian ocean composition. J. Geol. 101, 235–243.

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, 279–283.

Hay, W.W., 1985. Potential errors in estimates of carbonate rock accumulating through geologic time. In: Sundquist, E.T., Broecker, W.S. (Eds.), The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present, Geophysical Monograph, vol. 32. American Geophysical Union, Washington, DC, pp. 563–573.

Holland, H.D., 1978. The Chemistry of the Atmosphere and Oceans. Wiley, New York (351 pp.).

Holland, H.D., 2004. The geologic history of seawater. In: Elderfield, H. (Ed.), The Oceans and Marine Geochemistry, pp. 583–625., Vol. 6. Treatise on Geochemistry (Holland, H.D., Turekian, K.K., Eds.), Elsevier-Pergamon, Oxford, 646 pp.

Horita, J., Zimmermann, H., Holland, H.D., 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporates. Geochim. Cosmochim. Acta 66, 3733–3756.

Karhu, J., Epstein, S., 1986. The implication of the oxygen isotope records in coexisting cherts and phosphates. Geochim. Cosmochim. Acta 50, 1745–1756.

Kasting, J.F., Catling, D., 2003. Evolution of a habitable planet. Annu. Rev. Astron. Astrophys. 41, 429–463.

Kempe, S., Kazmierczak, J., 1990. Calcium carbonate supersaturation and the formation of in situ calcified stromatolites. In: Ittekot, V., Kempe, S., Michaelis, W., Spitzy, A. (Eds.), Facets of Modern Biogeochemistry. Springer, Berlin, pp. 255–278.

Kiessling, W., 2002. Secular variations in the Phanerozoic reef ecosystem. In: Kiessling, W., Flügel, E., Golonka, J. (Eds.), Phanerozoic reef patterns, SEPM Special Publication, vol. 72, pp. 625–690.

Kiessling, W., Flügel, E., 2002. Paleoreefs—a database on Phanerozoic reefs. In: Kiessling, W., Flügel, E., Golonka, J. (Eds.), Phanerozoic reef patterns, SEPM Special Publication, vol. 72, pp. 77–92.

Lasaga, A.C., Berner, R.A., Garrels, R.M., 1985. An improved geochemical model of atmospheric CO_2 fluctuations over the past 100 million years. In: Sundquist, E.T., Broecker, W.S. (Eds.), The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present, Geophysical Monograph, vol. 32. American Geophysical Union, Washington, DC, pp. 397–411.

Leadbeater, B.S.C., Riding, R. (Eds.), 1986. Biomineralization in Lower Plants and Animals. Special Volume, vol. 30. Systematics Association, Clarendon, Oxford (401 pp.).

Leeder, M., 1999. Sedimentology and Sedimentary Basins: From Turbulence to Tectonics. Blackwell, Oxford (592 pp.).

LeMarchand, D., Gaillardet, J., Lewin, E., Allegre, C.J., 2000. The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH. Nature 408, 951–954.

Logan, B.W., 1961. *Cryptozoon* and associated stromatolites from the Recent, Shark Bay, Western Australia. J. Geol. 69, 517–533.

Lowenstam, H.A., 1981. Minerals formed by organisms. Science 211, 1126–1131.

Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., Demicco, R.V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. Science 294, 1086–1088.

Mackenzie, F.T., Morse, J.W., 1992. Sedimentary carbonates through Phanerozoic time. Geochim. Cosmochim. Acta 56, 3281–3295.

Mann, S., 2001. Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry. Oxford University Press, Oxford (240 pp.).

Maslov, V.P., 1959. Stromatolites and facies. Dokl. Akad. Nauk SSSR 125, 1085–1088. (in Russian).

Merz, M., 1992. The biology of carbonate precipitation by cyanobacteria. Facies 26, 81–102.

Merz-Preiß, M., 2000. Calcification in cyanobacteria. In: Riding, R., Awramik, S.M. (Eds.), Microbial sediments. Springer-Verlag, Berlin, pp. 50–56.

Monty, C.L.V., 1973. Precambrian background and Phanerozoic history of stromatolitic communities, an overview. Ann. Soc. Geol. Belg. 96, 585–624.

Monty, C.L.V., 1977. Evolving concepts on the nature and the ecological significance of stromatolites. In: Flügel, E. (Ed.), Fossil Algae, Recent Results and Developments. Springer-Verlag, Berlin, pp. 15–35.

Morse, J.W., Mackenzie, F.T., 1990. Geochemistry of sedimentary carbonates. Developments in sedimentology. Elsevier, Amsterdam (707 pp.).

Opdyke, B.N., Wilkinson, B.H., 1988. Surface area control of shallow cratonic to deep marine carbonate accumulation. Paleoceanography 3, 685–703.

Opdyke, B.N., Wilkinson, B.H., 1990. Paleolatitude distribution of Phanerozoic marine ooids and cements. Palaeogeogr. Palaeoclimatol. Palaeoecol. 78, 135–148.

Parkhurst, D.L., 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.

Parsons, B., 1982. Causes and consequences of the relation between area and age of the ocean floor. J. Geophys. Res. 87, 289–302.

Pearson, P.N., Palmer, M.R., 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. Nature 406, 695–699.

Pentecost, A., Riding, R., 1986. Calcification in cyanobacteria. In: Leadbeater, B.S.C., Riding, R. (Eds.), Biomineralization in Lower Plants and Animals, Systematics Association, Special Vol., vol. 30. Clarendon Press, Oxford, pp. 73–90.

Pitzer, K.S., 1991. Ion interaction approach: theory and data correlation. In: Pitzer, K.S. (Ed.), Activity Coefficients in Electrolyte Solutions. CRC Press, Boca Raton, Florida, pp. 75–153.

Pratt, B.R., 1982. Stromatolite decline—a reconsideration. Geology 10, 512–515.

Pratt, B.R., 2001. Calcification of cyanobacterial filaments; *Girvanella* and the origin of lower Paleozoic lime mud. Geology 29, 763–766.

Ridgewell, A.J., Kennedy, M.J., Caldeira, K., 2003. Carbonate deposition, climate stability, and Neoproterozoic ice ages. Science 302, 859–862.

Riding, R., 1992. Temporal variation in calcification in marine cyanobacteria. J. Geol. Soc. (Lond.) 149, 979–989.

Riding, R., 1993. Phanerozoic patterns of marine $CaCO_3$ precipitation. Naturwissenschaften 80, 513–516.

Riding, R., 2000. Microbial carbonates: the geological record of calcified bacterial–algal mats and biofilms. Sedimentology 47 (Suppl. 1), 179–214.

Riding, R., in press. Phanerozoic reefal microbial carbonate abundance: comparisons with metazoan diversity, mass extinction events, and seawater saturation state. Revista Española de Micropaleontología.

Riding, R., Liang, L., 2004. Marine limestone accumulation over the past 550 million years—control by seawater chemistry. Goldschmidt Conference 2004, Copenhagen, Conference Supplement. Geochim. Cosmochim. Acta, A354.

Riding, R., Liang, L., in press. Seawater chemistry control of marine limestone accumulation over the past 550 million years. Revista Española de Micropaleontología.

Rowley, D.B., 2002. Rate of plate creation and destruction: 180 Ma to present. Geol. Soc. Amer. Bull. 114, 927–933.

Royer, D.L., Wing, S.L., Beerling, D.J., Jolley, D.W., Koch, P.L., Hickey, L.J., Berner, R.A., 2001. Paleobotanical evidence for near present-day levels of atmospheric CO_2 during part of the Tertiary. Science 292, 2310–2313.

Rubey, W.W., 1951. Geologic history of seawater: an attempt to state the problem. Geol. Soc. Amer. Bull. 62, 1111–1147.

Sandberg, P.A., 1975. New interpretations of Great Salt Lake ooids and of ancient nonskeletal carbonate mineralogy. Sedimentology 22, 497–538.

Sandberg, P.A., 1983. An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy. Nature 305, 19–22.

Schubert, J.K., Bottjer, D.J., 1992. Early Triassic stromatolites as post-mass extinction disaster forms. Geology 20, 883–886.

Sepkoski Jr., J.J., 1997. Biodiversity; past, present, and future. J. Paleontol. 71, 533–539.

Serebryakov, S.N., Semikhatov, M.A., 1974. Riphean and recent stromatolites: a comparison. Am. J. Sci. 274, 556–574.

Stanley, S.M., 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. Palaeogeogr. Palaeoclimatol. Palaeoecol. 144, 3–19.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed. Wiley, New York (1022 pp.).

Tappan, H., Loeblich Jr., A.R., 1973. Evolution of the oceanic plankton. Earth-Sci. Rev. 9, 207–240.

Thompson, J.B., 2000. Microbial whitings. In: Riding, R., Awramik, S.M. (Eds.), Microbial Sediments. Springer-Verlag, Berlin, pp. 250–260.

Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebneth, S., Goddéris, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H., 1999. 87Sr/86Sr, δ13C and δ18O evolution of Phanerozoic seawater. Chem. Geol. 161, 59–88.

Veizer, J., Godderis, Y., Francois, L.M., 2000. Evidence for decoupling of atmospheric CO2 and global climate during the Phanerozoic eon. Nature 408, 698–701.

Walcott, C.D., 1914. Cambrian geology and paleontology: III. Precambrian Algonkian algal flora. Smithson. Misc. Collect. 64, 77–156.

Walker, J.C.G., Hays, P.B., Kasting, J.F., 1981. A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. J. Geophys. Res. 86, 9776–9782.

Webb, G.E., 2001. Biologically induced carbonate precipitation in reefs through time. In: Stanley, G.D. (Ed.), The History and Sedimentology of Ancient Reef Systems. Kluwer Academic/Plenum Publishers, New York, pp. 159–203.

Wilkinson, B.H., Algeo, T.J., 1989. Sedimentary carbonate record of Ca–Mg cycling at the Earth's surface. Am. J. Sci. 289, 1158–1194.

Wilkinson, B.H., Walker, J.C.G., 1989. Phanerozoic cycling of sedimentary carbonate. Am. J. Sci. 289, 525–548.

Zeebe, R.E., 2001. Seawater pH and isotopic paleotemperatures of Cretaceous oceans. Palaeogeogr. Palaeoclimatol. Palaeoecol. 170, 49–57.