

# CO<sub>2</sub> as a primary driver of Phanerozoic climate

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## ABSTRACT

Recent studies have purported to show a closer correspondence between reconstructed Phanerozoic records of cosmic ray flux and temperature than between CO<sub>2</sub> and temperature. The role of the greenhouse gas CO<sub>2</sub> in controlling global temperatures has therefore been questioned. Here we review the geologic records of CO<sub>2</sub> and glaciations and find that CO<sub>2</sub> was low (<500 ppm) during periods of long-lived and widespread continental glaciations and high (>1000 ppm) during other, warmer periods. The CO<sub>2</sub> record is likely robust because independent proxy records are highly correlated with CO<sub>2</sub> predictions from geochemical models. The Phanerozoic sea surface temperature record as inferred from shallow marine carbonate δ<sup>18</sup>O values has been used to quantitatively test the importance of potential climate forcings, but it fails several first-order tests relative to more well-established paleoclimatic indicators: both the early Paleozoic and Mesozoic are calculated to have been too cold for too long. We explore the possible influence of seawater pH on the δ<sup>18</sup>O record and find that a pH-corrected record matches the glacial record much better. Periodic fluctuations in the cosmic ray flux may be of some climatic significance, but are likely of second-order importance on a multimillion-year timescale.

## INTRODUCTION

Atmospheric CO<sub>2</sub> is an important greenhouse gas, and because of its short residence time (~4 yr) and numerous sources and sinks, it has the potential to regulate climate over a vast range of timescales, from years to millions of years. For example, the 30% rise in atmospheric CO<sub>2</sub> concentrations over the past 100 years has been accompanied by significant global warming (Mann et al., 1999, 2003). Most studies incorporating all known climate forcings implicate CO<sub>2</sub> as the primary driver for this most recent rise in global temperatures (Mann et al., 1998; Crowley, 2000; Mitchell et al., 2001). At the longer timescale of glacial-interglacial cycles (10<sup>5</sup> yr), a tight correlation between CO<sub>2</sub> and polar temperatures has long been established (Barnola et al., 1987; Petit et al., 1999). Although debated for many years, it is clear that CO<sub>2</sub> acted as either a climate driver or an important amplifier (Shackleton, 2000). For pre-Quaternary climates, ice core records do not exist, but a multitude of CO<sub>2</sub> proxies and models have been developed. As with the Recent (10<sup>1</sup> yr) and Quaternary (10<sup>5</sup> yr) records, a close correspondence between CO<sub>2</sub> and temperature has generally been found for the Phanerozoic (e.g., Crowley and Berner, 2001). Taken together, CO<sub>2</sub> appears to be an important driver of climate at all timescales.

The role of CO<sub>2</sub> in regulating climate over Phanerozoic timescales has recently been questioned using δ<sup>18</sup>O records of shallow marine carbonate (Veizer et al., 2000) and modeled patterns of cosmic ray fluxes (Shaviv and Veizer, 2003). The low-latitude δ<sup>18</sup>O compilation (Veizer et al., 1999, 2000), taken to reflect surface water temperatures, is decoupled from the CO<sub>2</sub> record and instead more closely correlates with the cosmic ray flux data. If correct, cosmic rays, ostensibly acting through variations in cloud albedo, may be more important than CO<sub>2</sub> in regulating Phanerozoic climate.

Here we scrutinize the pre-Quaternary records of CO<sub>2</sub>, temperature, and cosmic ray flux in an attempt to resolve current discrepancies. We first compare proxy reconstructions and model predictions of CO<sub>2</sub> to gauge how securely we understand the major patterns of Phanerozoic CO<sub>2</sub>. Using this record of CO<sub>2</sub> and Ca concentrations in Phanerozoic seawater, we then modify the δ<sup>18</sup>O record of Veizer et al. (1999, 2000) to account for the effects of seawater pH. This modified δ<sup>18</sup>O record is then compared to records of continental glaciations and cosmic ray fluxes.

## COMPARISON OF PROXY CO<sub>2</sub> RECORDS TO GEOCARB MODEL RESULTS

Multiple geochemical models of atmospheric CO<sub>2</sub> evolution have been developed in recent years; the most complete models track the exchange of carbon between buried organic and inorganic sedimentary carbon and the atmosphere plus oceans (Berner, 1991; Tajika, 1998; Berner and Kothavala, 2001; Wallmann, 2001; Kashiwagi and Shikazono, 2003). The CO<sub>2</sub> predictions from these models are highly convergent; for the purposes of this study, we will use GEOCARB III (Berner and Kothavala, 2001), which predicts CO<sub>2</sub> over the whole Phanerozoic in 10 m.y. time-steps. The GEOCARB model (Berner, 2004) is based on quantifying over time the uptake of CO<sub>2</sub> during weathering of Ca and Mg silicates and its release during the weathering of sedimentary organic matter. Also considered is the burial of carbonates and organic matter in sediments and the fluxes

of CO<sub>2</sub> to the atmosphere and oceans from the thermal decomposition of carbonates and organic matter at depth. Weathering fluxes are modified over time as changes occur in global temperature, continental size, position and relief, and land plant colonization. This includes incorporating solar radiation, due to the slow stellar evolution of the sun, and the CO<sub>2</sub> greenhouse effect in general circulation model (GCM) calculations of global mean surface temperature and river runoff. Volcanic degassing is guided by the abundance of volcanics, seafloor spreading rates, and the carbonate content of subducting oceanic crust.

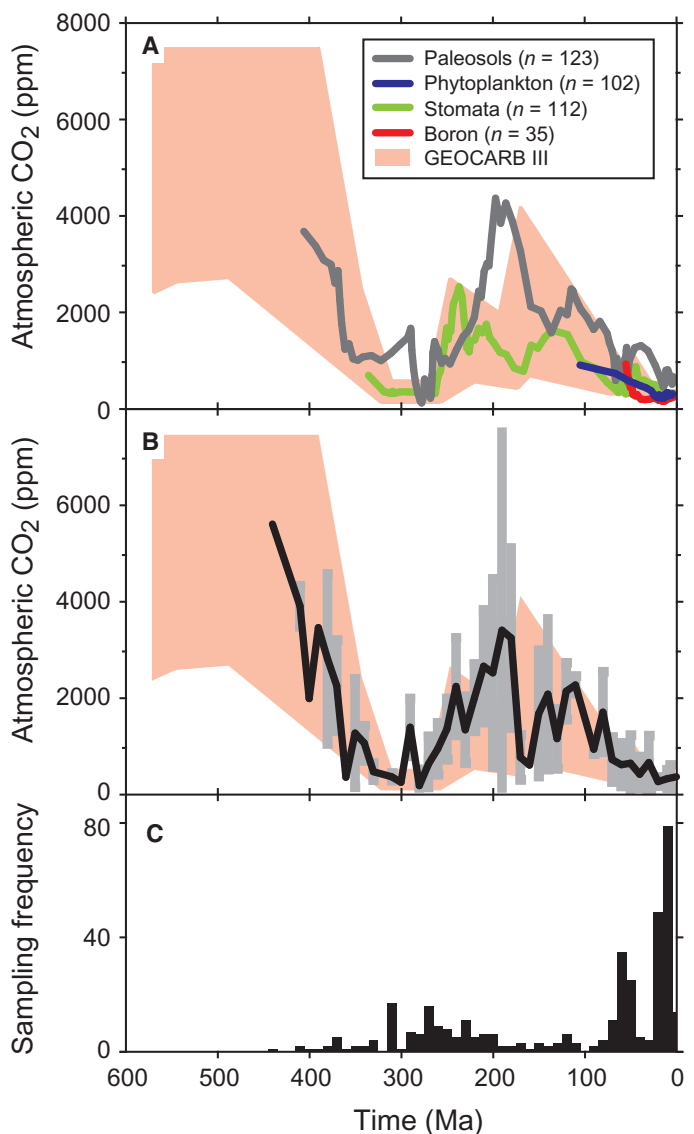
The paleo-CO<sub>2</sub> results of Rothman (2002) and U. Berner and Streif (2001), presented by Shaviv and Veizer (2003) as additional models, are in fact not based on carbon cycle modeling, but constitute an extension of the δ<sup>13</sup>C plankton CO<sub>2</sub> proxy (see below). These authors apply Δ<sup>13</sup>C, the difference between the δ<sup>13</sup>C of bulk organic matter and carbonates (Hayes et al., 1999), to directly calculate paleo-CO<sub>2</sub>. However, bulk organic matter can include non-photosynthetic compounds as well as terrestrial material derived from rivers, and the original method was based strictly on marine photosynthetic compounds (Freeman and Hayes, 1992; cf. Royer et al., 2001a). In addition, changes in Δ<sup>13</sup>C over time can be due to changes in seawater temperature (Rau et al., 1989) or O<sub>2</sub> concentrations (Beerling et al., 2002), and not only atmospheric CO<sub>2</sub>.

Four proxies for pre-Quaternary CO<sub>2</sub> levels have been developed over the past 15 years (consult Royer et al. [2001a] for further details).

1. The δ<sup>13</sup>C of pedogenic minerals (calcium carbonate [Cerling, 1991] or goethite [Yapp and Poths, 1992]). The carbonate in certain pedogenic minerals is formed from biologically and atmospherically derived soil CO<sub>2</sub>. Because these two components differ in their carbon isotopic compositions, the concentration of atmospheric CO<sub>2</sub> (*p*CO<sub>2</sub>) can be estimated assuming some knowledge of the biologically derived *p*CO<sub>2</sub> in the soil, and the δ<sup>13</sup>C of the atmospheric and biogenic constituents. Reliable pedogenic minerals are available back to the Devonian, and the range of errors is comparably small at high CO<sub>2</sub>. Some disadvantages of this proxy include comparably high errors at low CO<sub>2</sub>, and the difficulty of extracting organic carbon from the paleosols that contain these minerals.

2. The δ<sup>13</sup>C of phytoplankton (Freeman and Hayes, 1992; Pagani et al., 1999). Most phytoplankton exert little or no active control on the CO<sub>2</sub> entering their cells. Because of this, the Δ<sup>13</sup>C between seawater CO<sub>2</sub> and phytoplankton photosynthate is affected by seawater *p*CO<sub>2</sub> and can thus be used as a CO<sub>2</sub> proxy. High resolution CO<sub>2</sub> records are obtainable from appropriate marine sediment cores, but factors such as cell geometry and growth rate, which also influence the δ<sup>13</sup>C of phytoplankton, must be carefully considered.

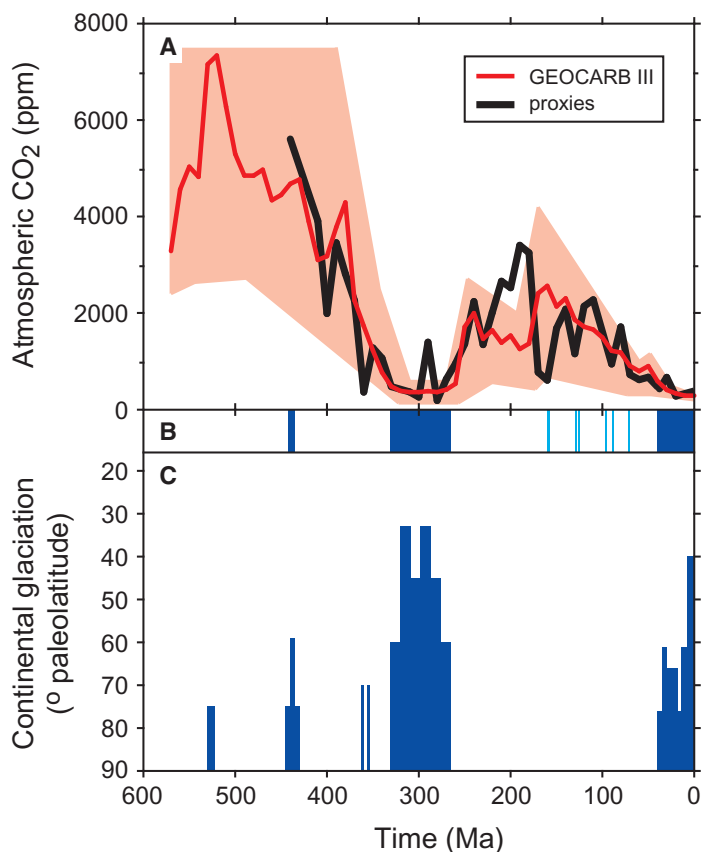
3. The stomatal distribution in the leaves of C<sub>3</sub> plants (Van der Burgh et al., 1993; McElwain and Chaloner, 1995). Unlike phytoplankton, most higher land plants have pores that enable them to control the flux of CO<sub>2</sub> entering their leaves. Because the proportion of these stomatal pores to all the cells on the leaf epidermis inversely relates to *p*CO<sub>2</sub>, information on the ancient CO<sub>2</sub> content of the atmosphere can be ex-



**Figure 1.** Details of CO<sub>2</sub> proxy data set used in this study. **A:** Five-point running averages of individual proxies (see footnote 1). Range in error of GEOCARB III model also shown for comparison. **B:** Combined atmospheric CO<sub>2</sub> concentration record as determined from multiple proxies in (A). Black curve represents average values in 10 m.y. time-steps. Gray boxes are standard deviations (± 1σ) for each time-step. **C:** Frequency distribution of CO<sub>2</sub> data set, expressed in 10 m.y. time-steps. All data are calibrated to the timescale of Harland et al. (1990).

tracted using fossil plants. High resolution, high precision CO<sub>2</sub> records are possible, but because the stomatal response to CO<sub>2</sub> is species-specific, care must be exercised in pre-Cretaceous material.

4. The δ<sup>11</sup>B of planktonic foraminifera (Pearson and Palmer, 2000). The relative proportions of the two dominant species of boron in seawater are partially pH-dependent. Because these two species differ in their isotopic compositions, *p*CO<sub>2</sub> information can be retrieved from carbonate tests containing trace amounts of boron. As with the phytoplankton proxy, high resolution CO<sub>2</sub> records are possible, but only after vital effects and the influence of the total alkalinity and δ<sup>11</sup>B of the ocean are removed.



**Figure 2.** CO<sub>2</sub> and climate. **A:** Comparison of model predictions (GEOCARB III; Berner and Kothavala, 2001) and proxy reconstructions of CO<sub>2</sub>. 10 m.y. time-steps are used in both curves. Shaded area represents range of error for model predictions. **B:** Intervals of glacial (dark blue) or cool climates (light blue; see text). **C:** Latitudinal distribution of direct glacial evidence (tillites, striated bedrock, etc.) throughout the Phanerozoic (Crowley, 1998).

Here we have compiled 372 published observations of paleoatmospheric CO<sub>2</sub> (Figs. 1A-B; see GSA Data Repository<sup>1</sup>). The most well-represented intervals are the late Carboniferous to Triassic (315–205 Ma) and Cenozoic (past 65 m.y.) (Fig. 1C). This proxy record differs from previously published compilations (e.g., Crowley and Berner, 2001; Royer et al., 2001a) most significantly in that the Permo-Carboniferous CO<sub>2</sub> estimates of Ekart et al. (1999) have been revised downward based on a higher resolution, more comprehensive data set. In addition, the Paleogene CO<sub>2</sub> estimates of Pearson and Palmer (2000) have also been lowered (Demico et al., 2003), which reduces the previously large disparities among CO<sub>2</sub> proxies at this time (Fig. 1A; cf. Royer et al., 2001b). The various proxies are in general agreement for the Phanerozoic; the moderate mismatches during the early Mesozoic are likely due to sparse coverage (Fig. 1).

In order to compare the proxy record to the model output, the raw proxy data were combined and averaged into 10 m.y.

time-steps. The combination of CO<sub>2</sub> data from different techniques maximizes the statistical power of the resulting data set. Because the various methods produce similar estimates of CO<sub>2</sub> over multimillion-year timescales (Fig. 1A), method-dependent biases are not significant. The binning of the proxy data into 10 m.y. time-steps reduces their ability to discern short-term events, but makes for the fairest comparison to the GEOCARB output. The resulting proxy-based curve is highly correlated with the “best-guess” predictions of GEOCARB III (Fig. 2A;  $r = 0.71$ ;  $P = 0.0002$ )<sup>2</sup>, indicating that the multimillion-year scale patterns are a reasonable approximation of the overall trend of Phanerozoic CO<sub>2</sub>.

### COMPARISON OF CO<sub>2</sub> RECORDS TO PHANEROZOIC CLIMATE

The rock record of glacial deposits offers the most conservative approach for reconstructing Phanerozoic climate. It is difficult to envision globally warm climates coexisting with long-lived, widespread continental ice masses, particularly when the ice reached mid-latitudes. The Phanerozoic record of tillites and other direct evidences for glaciation (compiled by Crowley [1998]) is shown in Fig. 2C. It is important to note that the length of the late Ordovician glaciation has been revised downward from 35 m.y. as reported by Frakes et al. (1992) and adopted by Veizer et al. (2000) and Shaviv and Veizer (2003) to <15 m.y. (Brenchley et al., 1994; Crowell, 1999; Pope and Steffen, 2003). The CO<sub>2</sub> record compares predictably with the glacial record, with low values (<500 ppm) during periods of intense and long-lived glaciation (Permo-Carboniferous [330–260 Ma] and late Cenozoic [past 30 m.y.]) and high values (>1000 ppm) at all other times. The late Ordovician (~440 Ma) represents the only interval during which glacial conditions apparently coexisted with a CO<sub>2</sub>-rich atmosphere. Critically, though, widespread ice sheets likely lasted <1 m.y. (Brenchley et al., 1994, 2003; Sutcliffe et al., 2000). Given the coarse temporal resolution of the GEOCARB model (10 m.y.) and poor proxy coverage across this interval (Fig. 1C), it is perhaps unsurprising that a short-lived drop in CO<sub>2</sub> has not yet been captured. Moreover, geochemical evidence is consistent with a late Ordovician CO<sub>2</sub>-drawdown (Kump et al., 1999), suggesting that CO<sub>2</sub> and temperature did in fact remain coupled. Further work, however, is needed to more clearly decipher this important period.

The traditional view of a uniformly warm Mesozoic has been increasingly questioned. For example, Frakes et al. (1992) consider the middle Jurassic to early Cretaceous (~183–105 Ma) a “cool mode.” If correct, these purported cool climates must be reconciled with the high reconstructed CO<sub>2</sub> levels (Fig. 2A). While a cool mode designation is useful for differentiating it from a uniformly warm mode, this has the unfortunate side-effect of conflating it with other classic cool modes, such as the Permo-Carboniferous and late Cenozoic. Critically, the climate mode of the middle Jurassic to early

<sup>1</sup>GSA Data Repository Item 2004041, compilation of Phanerozoic CO<sub>2</sub> records, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, editing@geosociety.org, or at www.geosociety.org/pubs/ft2004.htm.

<sup>2</sup>The correlation coefficient,  $r$ , was calculated by correlating the first differences of the two series ( $y_t - \rho y_{t-1}$ ), where  $\rho$  is the lag-one autocorrelation coefficient. The significance test,  $P$ , was calculated using the actual series, but with the degrees of freedom ( $n$ ) modified by:  $n' = n(1 - \rho_1\rho_2)/(1 + \rho_1\rho_2)$ . Bins represented by  $\leq 3$  proxy observations were not included in the analyses

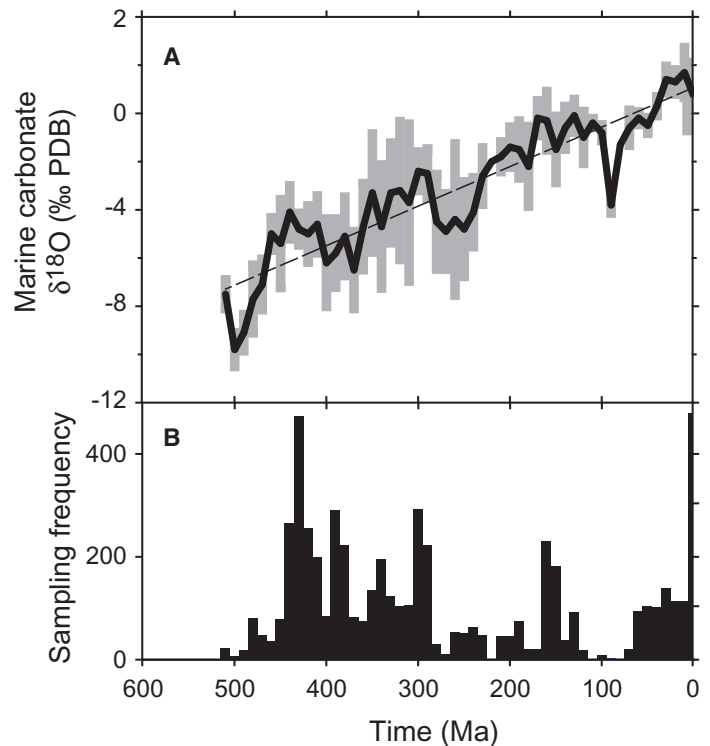
Cretaceous is fundamentally different from the Permo-Carboniferous and late Cenozoic. The existence of productive polar forests during much of the Mesozoic (e.g., Vakhrameev, 1991; Huber et al., 2000) is incompatible with the long-lived ice caps that characterize true glacial periods. Indirect evidence for seasonal or alpine ice exists, but these intervals were likely brief “cold snaps” within an otherwise warm Mesozoic (e.g., Price, 1999). Moreover, indirect evidence such as ice-rafted debris should be treated cautiously, as such deposits are found in every Phanerozoic Period except the Triassic (Frakes et al., 1992).

The best indirect evidence for Mesozoic ice combines sea-level considerations with oxygen isotope and strontium content records (Stoll and Schrag, 1996, 2000; Dromart et al., 2003; Lécuyer et al., 2003; Miller et al., 2003). These studies corroborate the notion of brief icy intervals (<2 m.y.; see light blue bands in Fig. 2B) within a globally warm Mesozoic. The possible presence of brief cold snaps should therefore not be used as a sole criterion for a cool mode: It is increasingly being recognized that globally warm climates previously considered stable are in fact quite dynamic (e.g., mid-Cretaceous: Wilson and Norris [2001]; Eocene: Wade and Kroon [2002]; Holocene: Indermühle et al. [1999]). For example, although the Turonian (~90 Ma) is one of the best-documented intervals of extreme global warmth in Earth’s history (Wilson et al., 2002; Bice et al., 2003), it is straddled by two of the proposed icy intervals (Fig. 2B). This entire “cool-warm-cool” sequence lies within the late Cretaceous to early Tertiary “warm mode” of Frakes et al. (1992).

Regardless of semantics, the important issue is determining the forcings responsible for global climate change. To this end, Dromart et al. (2003) reported evidence for a temporary drawdown in atmospheric CO<sub>2</sub> across the 160 Ma icy event. If correct, a CO<sub>2</sub>-driven reverse greenhouse effect appears responsible for this brief cool period. The proxy record of CO<sub>2</sub> not only records a local CO<sub>2</sub> minimum during this event, providing independent support for the findings of Dromart et al. (2003), but also during the other five proposed icy events (Fig. 2, A and B). These brief perturbations in the carbon cycle are likely not resolvable with GEOCARB because of the model’s coarse time resolution. As with the bulk of the Phanerozoic, a coupling between CO<sub>2</sub> and temperature appears strong for the Mesozoic Era.

### THE EFFECT OF SEAWATER pH ON THE δ<sup>18</sup>O OF MARINE CARBONATE

The rock record of glacial deposits can only be qualitatively compared to other records of climate, such as CO<sub>2</sub>. It is within this context that the low-latitude paleotemperature data of Veizer et al. (2000) and Shaviv and Veizer (2003), based on the shallow-marine δ<sup>18</sup>O carbonate record of Veizer et al. (1999; Fig. 3A), is so appealing. These data are compiled from a range of taxa, including belemnites, brachiopods, conodonts, and foraminifera. The most well-represented intervals are the middle Paleozoic (445–285 Ma), late Jurassic (165–145 Ma) and Cenozoic (Fig. 3B). The signal:noise ratio in this data set can be assessed by comparing the proportion of the plotted standard deviations (1σ; Fig. 3A) to the total range in values (11.2‰). These proportions range from 0.02



**Figure 3.** Details of δ<sup>18</sup>O data set used in this study. **A:** Low-latitude, shallow-marine δ<sup>18</sup>O carbonate record of Veizer et al. (1999). The statistical parameters represented by the black curve and gray boxes are as in Fig. 1B. Dashed line represents linear regression of data points composing black curve. **B:** Frequency distribution of δ<sup>18</sup>O data set, expressed in 10 m.y. time-steps. All data are calibrated to the timescale of Harland et al. (1990).

to 0.29 (median = 0.10). For comparison, in the CO<sub>2</sub> proxy data set, proportions range from 0.01 to 0.36 (median = 0.11; total range = 5354 ppm; data point at 190 Ma excluded). The oxygen isotope and CO<sub>2</sub> curves are therefore comparable in terms of their signal:noise ratios.

After detrending the secular 8‰ shift in δ<sup>18</sup>O across the Phanerozoic (Veizer et al., 2000; Fig. 3A), however, the resulting paleotemperature curve fails two first-order tests with the more robust glacial deposit record: the Ordovician-Silurian and Mesozoic intervals are too cold for too long. The oxygen isotope record suggests a 50 m.y. cool interval of equivalent severity to the Permo-Carboniferous and late Cenozoic between 450 and 400 Ma, but other climate indicators only support a 15 m.y. long intermittent cool phase at this time (Crowell, 1999; Pope and Steffen, 2003), with widespread glaciation likely lasting <1 m.y. (Brenchley et al., 1994, 2003; Sutcliffe et al., 2000). During the Mesozoic, oxygen isotopes suggest another 100 m.y. cool interval of similar severity (220–120 Ma), but, as discussed above, independent evidence for a long-lived glaciation at this time is completely lacking. Other factors must therefore influence the δ<sup>18</sup>O of marine calcite such as alteration during diagenesis (Schrag et al., 1995). Here we explore an additional possible bias of δ<sup>18</sup>O-derived temperatures due to the carbonate ion effect on oxygen isotope incorporation in carbonates controlled by temporal changes in the pH of seawater (Zeebe, 1999).

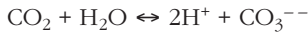
Zeebe (2001) derived the expression:

$$\Delta T_{\text{pH}} = b s \Delta \text{pH} \quad (1)$$

where:

$\Delta \text{pH}$  = pH at present – pH at some past time;  
 $\Delta T_{\text{pH}}$  = correction for change in “temperature” due to the effect of change in pH on  $\delta^{18}\text{O}$  of carbonates ( $\Delta T = T$  at present –  $T$  in past);  
 $b$  = coefficient of the linear term of the  $\delta^{18}\text{O}$  paleo-temperature equation ( $b = -4.80$  °C per ‰); and  
 $s$  = slope of  $\delta^{18}\text{O}$  versus pH from theory and experiments ( $s = -1.42$  ‰ per unit pH).

For a surficial ocean which, over time, is saturated with  $\text{CaCO}_3$  (or at constant supersaturation—see below) and equilibrated with atmospheric  $\text{CO}_2$ , for the reactions:



and



we have the equilibrium expressions

$$[\text{H}^+]^2 [\text{CO}_3^{--}] / p\text{CO}_2 = K_0 K_1 K_2 \quad (2)$$

and

$$[\text{Ca}^{++}] [\text{CO}_3^{--}] = K_{\text{sp}} \quad (3),$$

where the brackets represent activities,  $p\text{CO}_2$  the partial pressure of  $\text{CO}_2$  in the atmosphere and  $K_0$ ,  $K_1$ ,  $K_2$  and  $K_{\text{sp}}$  are, respectively, the constants for solubility equilibrium of  $\text{CO}_2$ , the first and second dissociations of carbonic acid and the solubility of calcium carbonate. Combining (2) and (3) and taking common logarithms:

$$2 \log [\text{H}^+] - \log p\text{CO}_2 - \log [\text{Ca}^{++}] = \log (K_0 K_1 K_2 / K_{\text{sp}}) \quad (4).$$

For a past time ( $t$ ) and the present (0), using the definition of  $\text{pH} = -\log [\text{H}^+]$  and assuming that the equilibrium constants do not change appreciably with time due to minor temperature changes:

$$2 \text{pH}(0) - 2 \text{pH}(t) - \log [p\text{CO}_2(t)/p\text{CO}_2(0)] - \log [(Ca)(t)/(Ca)(0)] = 0 \quad (5)$$

Introducing the definitions

$$RCO_2 = p\text{CO}_2(t)/p\text{CO}_2(0) \quad (6)$$

and

$$\Delta \text{pH} = \text{pH}(0) - \text{pH}(t) \quad (7)$$

we obtain

$$\Delta \text{pH} = 0.5 \{ \log RCO_2 + \log [(Ca)(t)/(Ca)(0)] \} \quad (8),$$

where  $RCO_2$  is the ratio of mass of atmospheric  $\text{CO}_2$  at a past time to that for the pre-industrial present (280 ppm), and  $(Ca)$  is the mean concentration of dissolved calcium in seawater.

It is assumed that the ratios of Ca concentrations in seawater at time ( $t$ ) and the present (0) are essentially the same as the ratios of their activities, which is reasonable for small changes in temperature and chemical composition or salinity.

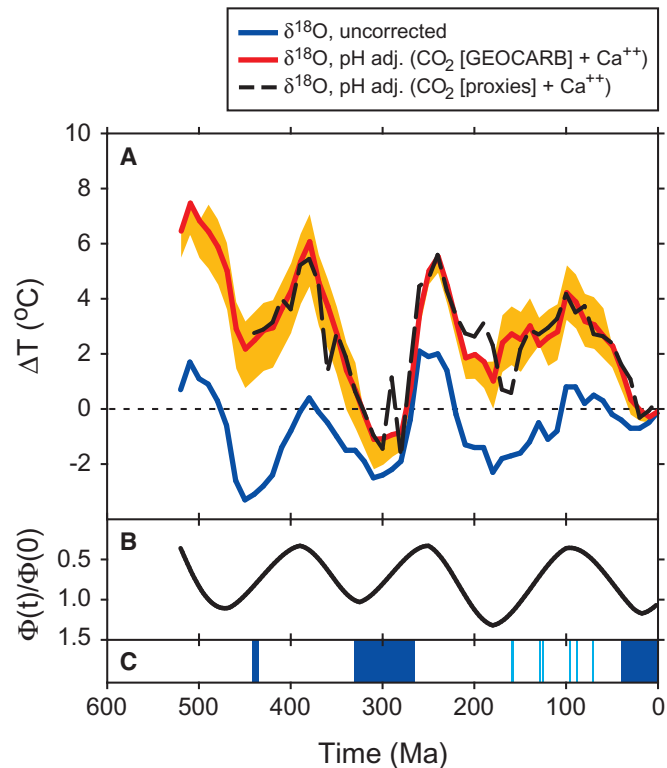
In actuality, the surficial oceans, where those carbonates analyzed for oxygen isotopes formed, were probably su-

persaturated with respect to both calcite and aragonite as at present. If the oceans remained at the same degree of supersaturation over time, cancellation of the terms involving the equilibrium constants of equation (4) for the past and present would still be justified. However, the value  $\Omega = [\text{Ca}^{++}][\text{CO}_3^{--}] / K_{\text{sp}}$  for calcite may have varied over time from past values of 2–4 to the present value of 6 (Demichco et al., 2003). To consider this variation, equation (8) based on equation (4) is modified to:

$$\Delta \text{pH} = 0.5 \{ \log RCO_2 + \log [(Ca)(t)/(Ca)(0)] + \log [\Omega(0)/\Omega(t)] \} \quad (9).$$

Here we assume that values of  $\Omega(0)/\Omega(t)$  for “calcite seas” (500–330 Ma, 180–60 Ma) were equal to 2 and for aragonite seas (550–500 Ma, 330–180 Ma, 60–0 Ma) were equal to 1 (Demichco et al., 2003).

Finally, to obtain the correction for the false “temperature” change due to a change in pH we obtain from expressions (1) and (8) upon substituting the values for  $b$  and  $s$  in (1):



**Figure 4.** pH-correction for shallow-marine  $\delta^{18}\text{O}$  carbonate curve. **A:** The blue curve corresponds to temperature deviations relative to today calculated by Shaviv and Veizer (2003) from the “10/50”  $\delta^{18}\text{O}$  compilation presented in Veizer et al. (2000), where the original data (Veizer et al., 1999) were detrended and then averaged in 10 m.y. time-steps using a 50 m.y. moving window. In the two remaining curves, data from the blue curve have been adjusted for pH effects due to changes in seawater  $\text{Ca}^{++}$  concentration (after Horita et al., 2002), and  $\text{CO}_2$  based either on GEOCARB III or proxies. A sensitivity analysis was performed on the GEOCARB +  $\text{Ca}^{++}$  curve by holding  $\text{Ca}^{++}$  levels constant (lower bound of orange band), or by allowing the saturation state of  $\text{CaCO}_3$  in the ocean to vary through time ( $\Omega$ ; upper bound; see text for details). **B:** Cosmic ray flux (relative to the present day) as reconstructed by Shaviv (2002). **C:** Intervals of glacial and cool climates, as in Fig. 2B.

$$\Delta T_{\text{pH}} = 3.4\{\log R\text{CO}_2 + \log[(\text{Ca})(t)/(\text{Ca})(0)]\} \quad (10),$$

or alternatively:

$$\Delta T_{\text{pH}} = 3.4\{\log R\text{CO}_2 + \log[(\text{Ca})(t)/(\text{Ca})(0)] + \log(\Omega(0)/\Omega(t))\} \quad (11).$$

These are the expressions that can be applied to correcting inferred paleotemperatures, based on carbonate  $\delta^{18}\text{O}$  values, for changes in pH of the oceans due to changes in the  $\text{CO}_2$  level of the atmosphere and changes in Ca concentrations and calcium carbonate saturation state in seawater.

Based on the  $\text{CO}_2$  data from GEOCARB III and proxies (Fig. 2A), plus data for paleo-concentrations of Ca in seawater (Horita et al., 2002; Lowenstein et al., 2003), equations (10) and (11) have been used to calculate pH corrections that can be applied to the low-latitude  $\Delta T$  data of Veizer et al. (2000) and Shaviv and Veizer (2003). (Alternative use of the Horita vs. the Lowenstein data leads to almost indistinguishable differences in results.) A comparison of the original Veizer  $\Delta T$  curve with pH-corrected  $\Delta T$  curves is shown in Fig. 4A. The corrected curves incorporate changes in pH due to changes in  $\text{CO}_2$  alone (constant  $\text{Ca}^{++}$  concentration), changes in  $\text{Ca}^{++}$  and  $\text{CO}_2$  using GEOCARB and proxy  $\text{CO}_2$  data, and inclusion of the additional term for changes in  $\text{CaCO}_3$  saturation state. (Calculated  $\Delta\text{pH}$  values for the Eocene of 0.3–0.4 are in the middle of the range 0.1–0.7 calculated via the boron isotope paleo-pH method by Pearson and Palmer [2000].)

The corrected curves record, on average, higher past temperatures than that at present, which is in accord with paleoclimatological observations, especially for the Mesozoic (Vakhrameev, 1991; Huber et al., 2000, 2002). The original uncorrected Veizer curve and the cosmic ray flux curve record too cold a Phanerozoic past (Fig. 4). Also, the large coolings of the uncorrected curve for the Ordovician-Silurian (480–400 Ma) and the Triassic-Cretaceous (220–100 Ma) that correlate with intense cosmic ray fluxes, are, with corrections for pH, only lesser coolings superimposed on generally warm periods (Fig. 4). The cosmic ray fluxes and the uncorrected  $\Delta T$  curve predict long-lived and extensive glaciations during these time periods but there were none, except for a very short glaciation lasting at most a few million years at the end of the Ordovician (Fig. 4C). By contrast, the corrected Veizer curves predict the two major glaciations correctly. These are during the two times when low latitude temperature was about the same as, or less than, that at present: the Permo-Carboniferous glaciation (centered around 300 Ma) and the late Cenozoic glaciation (past 30 m.y.).

## CONCLUSIONS

We conclude the following from these considerations.

1. Proxy estimates of paleo- $\text{CO}_2$  agree, within modeling errors, with GEOCARB model results.
2. There is a good correlation between low levels of atmospheric  $\text{CO}_2$  and the presence of well-documented, long-lived, and aerially extensive continental glaciations.
3. The uncorrected Veizer temperature curve predicts long periods of intense global cooling that do not agree with independent observations of paleoclimate, especially during the Mesozoic. When corrected for pH effects, however, the temperature curve matches the glacial record much better.

4. The global temperatures inferred from the cosmic ray flux model of Shaviv and Veizer (2003) do *not* correlate in amplitude with the temperatures recorded by Veizer et al. (2000) when corrected for past changes in oceanic pH. Additional problems with this correction have been shown by Rahmstaf et al. (2004). Changes in cosmic ray flux may affect climate but they are not the dominant climate driver on a multimillion-year time scale.

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