

Atmospheric $p\text{CO}_2$ since 60 Ma from records of seawater pH, calcium, and primary carbonate mineralogy

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ABSTRACT

A 60 m.y. record of atmospheric $p\text{CO}_2$ has been refined from knowledge of (1) secular changes in the major ion composition of seawater (particularly Ca and Mg) and (2) oscillations in the mineralogy of primary oceanic carbonate sediments. Both factors have had a significant impact on the chemistry of the ocean carbonate buffer system. Calculated atmospheric $p\text{CO}_2$ oscillated between values of 100–300 ppm and to maxima of 1200–2500 ppm from 60 to 40 Ma and varied between 100 and 300 ppm from 25 Ma to the present. The refined $p\text{CO}_2$ values are significantly lower than previous estimates made from seawater pH data where total dissolved inorganic carbon was assumed constant and more in line with modeling and stomatal index estimations of atmospheric $p\text{CO}_2$ for the Tertiary.

Keywords: carbon dioxide, seawater chemistry variation, atmospheric history, equilibrium, geochemistry.

INTRODUCTION

One important control of the global climate system is the concentration of atmospheric greenhouse gases, particularly CO_2 . Direct measurements of atmospheric $p\text{CO}_2$ are available for only the past 420 k.y. from ice cores (Petit et al., 1999). Prior to that, geochemical modeling (Berner et al., 1983; Berner and Kothavala, 2001) and proxy measures, such as stable carbon isotopes from paleosols (Ekart et al., 1999) and stomatal density of leaves (Retallack, 2001; Royer et al., 2001), give variable results that have led to disparate conclusions about the role of atmospheric CO_2 in climate change (Pagani et al., 1999; Viezer et al., 2000; Boucot and Gray, 2001). The ocean's carbonate buffer system responds directly to changes in atmospheric composition, and therefore the chemistry of ancient marine carbonates (e.g., boron isotopes) has been used to calculate ancient atmospheric $p\text{CO}_2$ concentrations (Pearson and Palmer, 1999, 2000). Here we present new estimates of atmospheric $p\text{CO}_2$ over the past 60 m.y. in light of growing evidence that the major ion chemistry of seawater (in particular Ca and Mg) and the mineralogy of marine carbonate phases (aragonite vs. calcite) have undergone secular variations (Sandberg, 1983; Hardie, 1996; Lowenstein et al., 2001).

Pearson and Palmer (1999) used the boron isotope composition ($\delta^{11}\text{B}$) of middle Eocene planktonic foraminiferal tests to estimate that

43 Ma mid-Pacific surface seawater had a pH of 8.05. On the basis of the assumption that total dissolved inorganic carbon (TDIC) has not changed over time, they calculated that middle Eocene atmospheric $p\text{CO}_2$ was between ~ 170 and 570 ppm. Pearson and Palmer (1999) concluded that their estimate of middle Eocene $p\text{CO}_2$ implied either that Earth's climate is very sensitive to small changes in $p\text{CO}_2$ or that global cooling since the Eocene resulted from other changes in the climate system (e.g., changes in ocean circulation). Caldeira and Berner (1999, p. 2043a) argued that oceanic TDIC "could be expected to vary over time" but that oceanic $[\text{Ca}^{2+}]$ (and hence oceanic $[\text{CO}_3^{2-}]$) has remained constant. On the basis of the assumption of constant $[\text{CO}_3^{2-}]$, Caldeira and Berner (1999) used a pH = 8.05 from Pearson and Palmer (1999) to calculate a middle Eocene atmospheric $p\text{CO}_2$ of ~ 750 ppm. This $p\text{CO}_2$ value is more than 2.5 times that of the preindustrial value of 280 ppm, a large enough increase in the view of Caldeira and Berner (1999) to account for warmer global climates during the middle Eocene. Pearson and Palmer (2000) also applied their boron isotope method to calculate the variations in pH of mid-Pacific surface seawater and atmospheric $p\text{CO}_2$ over the past 60 m.y. The method they used requires that values for either TDIC or alkalinity of surface seawater be known over the past 60 m.y. But, as they noted, no reliable record of variations in either parameter exists over the time scale covered by their study. They recognized that

variations in seawater $[\text{Ca}^{2+}]$ due to secular changes in riverine flux are likely. In the absence of a measure of such variations, they assumed that seawater $[\text{Ca}^{2+}]$ has remained proportional to alkalinity and calculated surface-ocean alkalinity and TDIC by "assuming that the increases in these parameters with depth have remained the same as modern western equatorial Pacific Ocean," an assumption they recognized "may not be correct" (Pearson and Palmer, 2000, p. 697). Their estimated atmospheric $p\text{CO}_2$ concentrations indicate values that oscillated between 2000 and 3500 ppm during the late Paleocene and early Eocene, values that oscillated between 500 and 2500 ppm during the middle Eocene, and stable values close to modern values over the past 25 m.y.

VARIATIONS IN SEAWATER CHEMISTRY WITH TIME

Secular variations in seawater $[\text{Ca}^{2+}]$ are known from direct chemical analyses of primary fluid inclusions in ancient chevron halites from marine evaporites (Lowenstein et al., 2001; Horita et al., 2002) and have been modeled (Hardie, 1996) (Fig. 1A). Chemical analyses of fluid inclusions in halite crystals of ancient marine evaporites are from two sources using two different techniques: (1) direct measurements of small (tens of micrometers) frozen inclusions in primary chevron halite crystals using an environmental scanning electron microscope with an X-ray energy-dispersive spectrometry system (Lowenstein et

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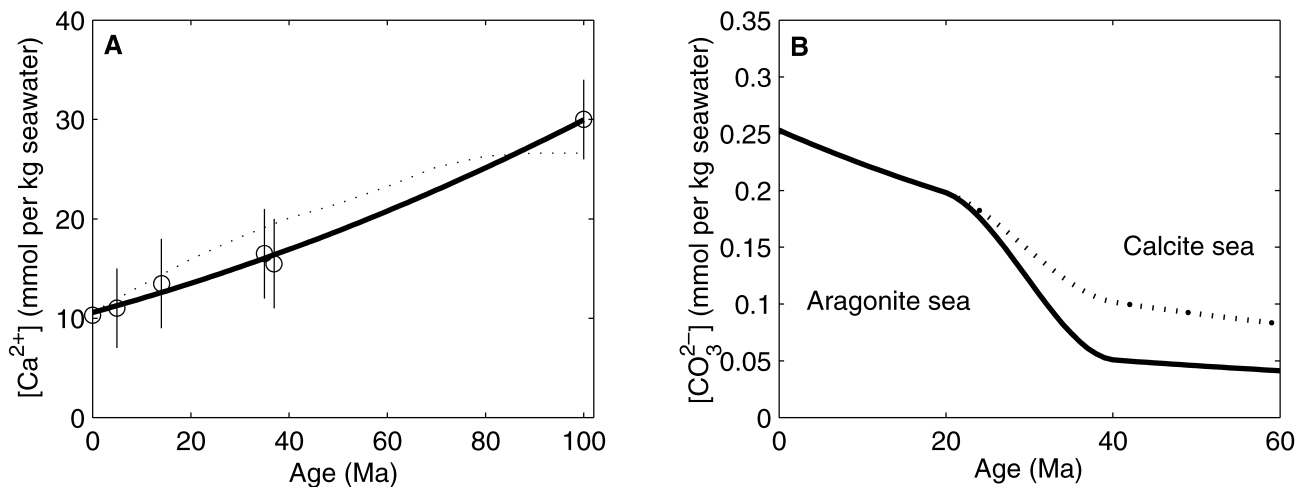


Figure 1. A: Plot of $[Ca^{2+}]$ in ancient seawater determined by Lowenstein et al. (2001) and Horita et al. (2002) vs. age from 100 Ma to present. Modern ocean $[Ca^{2+}]$ is 10.2 mmol and increases to Late Cretaceous value of 30 mmol. Solid line is quadratic best fit through data. Dotted line is from modeling of Hardie (1996). **B:** Plot of modeled $[CO_3^{2-}]$ (mmol) vs. age. From present to 20 Ma, oceans are modeled as four times supersaturated with aragonite. Dotted line—oceans modeled from 40 Ma to 60 Ma as four times supersaturated with calcite. Solid line—oceans modeled from 40 Ma to 60 Ma as two times supersaturated with calcite. Modern ocean $[CO_3^{2-}]$ is ~ 0.26 mmol/kg (Zeebe and Wolf-Gladrow, 2001).

al., 2001) and chemical analyses of brines extracted from large inclusions with a micropipette (Horita et al., 2002). Both techniques indicate that seawater $[Ca^{2+}]$ progressively decreased from the Late Cretaceous to the present (Fig. 1A), a finding in agreement with the seawater $[Ca^{2+}]$ values predicted by a first-order model in which paleo-seawater chemistry varies as a function of mid-ocean-ridge hydrothermal brine flux and seafloor-spreading rates (Hardie, 1996) (Fig. 1A).

Our calculations assume that throughout the past 60 m.y., $CaCO_3$ crystalline phases have precipitated from surface seawater as either calcite or aragonite, depending on the Mg/Ca ratio in seawater during the time period under consideration: the phase precipitated is specified in the expression “aragonite seas” (0–40 Ma when Mg/Ca was >2) or “calcite seas” (40–60+ Ma when Mg/Ca was <2) (Sandberg, 1983; Stanley and Hardie, 1998; Lowenstein et al., 2001). This assumption allows the calculation of secular variation of seawater $[CO_3^{2-}]$ directly from the measured values of seawater $[Ca^{2+}]$ over the past 60 m.y. (Fig. 1B) because at equilibrium between surface seawater and a crystalline $CaCO_3$ phase at constant temperature, the $[Ca^{2+}]$ and $[CO_3^{2-}]$ ion concentrations in seawater are governed by the solubility-product constant $[Ca^{2+}][CO_3^{2-}]$ for the particular carbonate phase under consideration. Once seawater pH and $[CO_3^{2-}]$ are known, the pCO_2 of the atmosphere in equilibrium with surface seawater can be calculated from the relationship $pCO_2 = [H^+]^2[CO_3^{2-}]/K_1K_2K_H$, where K_H is the Henry’s law constant for $CO_{2(g)}$, and K_1 and K_2 are the first and second dissociation constants for carbonic acid (Zeebe and Wolf-

Gladrow, 2001). For these calculations we used the so-called stoichiometric equilibrium constants recommended by Zeebe and Wolf-Gladrow (2001), i.e., K_{sp} for calcite and K_{sp} for aragonite from Mucci (1983); K_1 and K_2 from Dickson and Eoyet (1994); and K_H from Weiss (1974). Stoichiometric equilibrium constants for seawater are based on concentrations rather than activities, and therefore depend on temperature, pressure, and salinity.

From 40 Ma to the present, aragonite has been the principal $CaCO_3$ chemical precipitate (aragonite seas), and our modeling of seawater $[CO_3^{2-}]$ (Fig. 1B) assumes that during this time period, surface seawater, like today’s seawater, was highly supersaturated with both aragonite and calcite such that the solubility product $[Ca^{2+}][CO_3^{2-}]$ was approximately four times the equilibrium value for aragonite and six times that for calcite. High supersaturation results from the high Mg ion concentration in the seawater during aragonite seas that kinetically retards the nucleation and growth of low-magnesian calcite (<4 mol% $MgCO_3$), allowing the $[Ca^{2+}][CO_3^{2-}]$ solubility product to rise, promoting the nucleation of metastable aragonite (Berner, 1975). The state of saturation of surface seawater is not known during times of calcite seas. The dashed line in Figure 1B was calculated by assuming that the $[Ca^{2+}][CO_3^{2-}]$ solubility product during calcite seas remained at four times supersaturation with respect to calcite. However, it is plausible that during times when seawater $[Mg^{2+}]$ was lower than modern values (Lowenstein et al., 2001), the high $[Mg^{2+}]$ kinetic barrier to calcite precipitation was removed, and the $[Ca^{2+}][CO_3^{2-}]$ solubility product may have been lower than four times supersaturated.

This second scenario is shown as the solid line in Figure 1B, where $[CO_3^{2-}]$ is calculated when the $[Ca^{2+}][CO_3^{2-}]$ solubility product is two times the equilibrium value for calcite.

MODELING RESULTS AND DISCUSSION

Figure 2 shows the calculated variations in atmospheric pCO_2 over the past 60 m.y. based on the assumptions of the secular variations in surface seawater pH from Pearson and Palmer (2000) and ocean-chemistry history presented here. Uncertainties in the model arise from four sources. The first source of error stems from analytical uncertainties in the boron isotope analyses in the original pH estimates of Pearson and Palmer (2000). It is important to note that there has been considerable discussion in the literature about larger uncertainties in this technique, including vital effects and the long-term variation of trends in the boron isotope composition of seawater. A second source of error arises from analytical uncertainties in the $[Ca^{2+}]$ measurements from the fluid inclusions. The third source of error results from the uncertainty of the saturation state of a calcite-precipitating ocean. Errors in the analytical uncertainties are denoted by the dotted lines in Figure 2, whereas the shaded area denotes uncertainty in the calcite saturation state of a calcite-precipitating ocean (lower saturation state yields lower pCO_2 estimates). Finally, small variations arise from the choice of stoichiometric equilibrium constant used and the temperature, salinity, and seawater chemistry chosen.

Our results are similar to those of Pearson and Palmer (2000) for the past 25 m.y., i.e., relatively stable, low pCO_2 values (~ 200 – 300

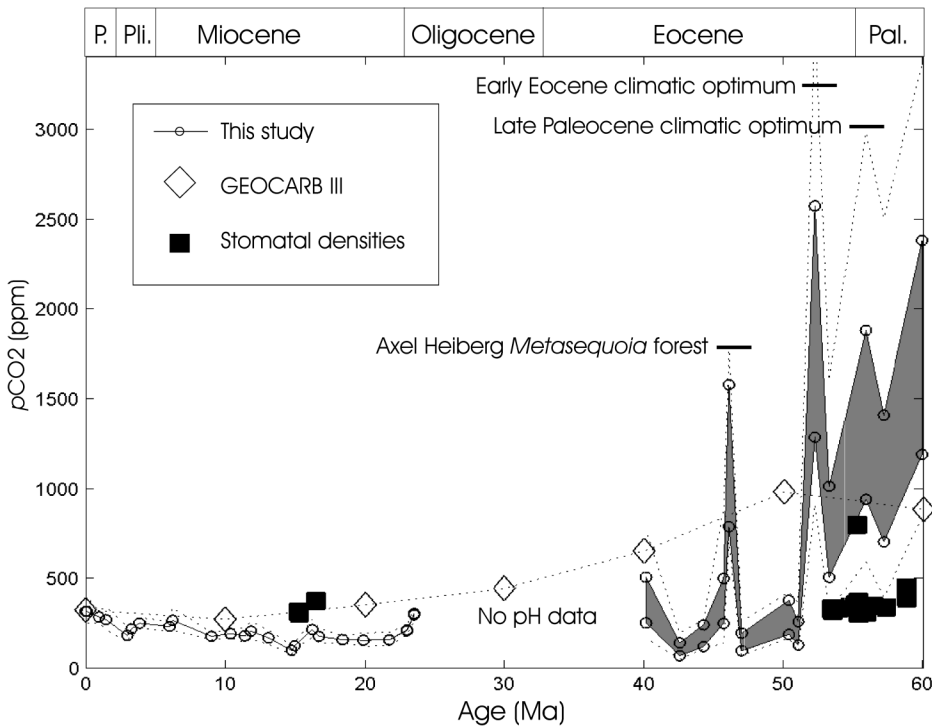


Figure 2. Atmospheric $p\text{CO}_2$ (in parts per million by volume) over past 60 m.y. calculated from $[\text{CO}_3^{2-}]$ values from Figure 1B and pH values from Pearson and Palmer (2000). Open circles are $p\text{CO}_2$ calculated here by using four times supersaturation with aragonite for aragonite seas from present to 20 Ma and two states of saturation with calcite for calcite seas from 40 Ma to 60 Ma (lower $p\text{CO}_2$ values = lower saturation state; see Fig. 1B). Open diamonds—GEOCARB III values of Berner and Kothavala (2001). Filled squares—values from stomatal density data of Royer et al. (2001). Climatic events from Jahren and Sternberg (2002) and Zachos et al. (2001). P. = Pleistocene, Pli. = Pliocene, and Pal. = Paleocene.

ppm) close to the modern preindustrial value of 280 ppm. However, for the middle Eocene to the late Paleocene (40–60 Ma), atmospheric $p\text{CO}_2$ is predicted to have oscillated considerably. Atmospheric $p\text{CO}_2$ values determined by Pearson and Palmer (2000) fluctuated between 400 and 3500 ppm over this time span, whereas the values predicted here are lower overall and range between 100 and 2500 ppm (Fig. 2). A temperature of 27 °C was used in order to compare these results with those of Pearson and Palmer (2000). However, this modeling indicates that a change of 2 °C is equivalent to a change in $p\text{CO}_2$ of ~200 ppm; the higher the temperature, the lower the $p\text{CO}_2$. Likewise, different values for K_1 and K_2 lead to slight variations in the results. For example, using of values for K_1 and K_2 from Lueker et al. (2000) leads to a maximum increase of ~150 ppm at the highest $p\text{CO}_2$ values. If slight corrections for the effects of variable Mg^{2+} on the stoichiometric equilibrium constants are incorporated (cf. Mucci and Morse, 1984; Ben-Yaakov and Goldhaber, 1973), then maximum $p\text{CO}_2$ values are lowered by ~200 ppm. Increasing or decreasing the salinity of seawater also has a similar slight effect on the final $p\text{CO}_2$ values calculated.

There are spikes of high atmospheric $p\text{CO}_2$ values ca. 46 Ma (coincident with the *Metasequoia* forests preserved on Axel Heiberg Island, Canada, reported by Jahren and Sternberg, 2002), ca. 52 Ma (coincident with the early Eocene climate optimum), and ca. 55 Ma (coincident with the late Paleocene thermal maximum) (Pearson and Palmer, 2000; Zachos et al., 2001).

For comparison, Figure 2 shows the $p\text{CO}_2$ values predicted by Berner and Kothavala (2001, their Fig. 13) for the period 0–60 Ma from their GEOCARB III model and the values predicted by Royer et al. (2001) based on leaf stomatal indices for fossil *Ginkgo* and *Metasequoia* from the middle Miocene (15.2–16.5 Ma) and early Eocene–middle Paleocene (53.4–58.5 Ma) time periods. Berner and Kothavala's values, which they calculated at 10 m.y. intervals, range from ~300 to ~1000 ppm over the past 60 m.y., in reasonably good agreement with the range of values calculated here (Fig. 2). The $p\text{CO}_2$ values of 307–377 ppm given by Royer et al. (2001) for the middle Miocene are above the calculated values, whereas their values for the early Eocene–middle Paleocene are 200–1000 ppm below our curve, with the exception of a single spike of 798 ppm at 55.2 Ma coincident with our

lower estimate. However, the “training sets” determined by growing saplings in CO_2 -controlled greenhouses used by Royer et al. (2001) yielded curves of stomatal index (SI%) vs. CO_2 (ppmv) that flatten out markedly at $\text{SI} = \sim 8 \pm 1$ and a CO_2 value of ~350 ppmv, considerably lowering the sensitivity of SI at higher $p\text{CO}_2$ values (Royer et al., 2001, their Fig. 1).

CONCLUSIONS

We conclude that the different methods of predicting atmospheric $p\text{CO}_2$ discussed in this paper are in good agreement with each other for the Neogene (0–25 Ma), yielding low values in the range of 100–300 ppm not unlike the $p\text{CO}_2$ values determined from ice cores over the past 420 k.y. For the period 40–60 Ma, the $p\text{CO}_2$ values predicted here oscillate between minimum values of 100–300 ppm and maxima of 1000–2500 ppm, a range within which some of the variations in atmospheric $p\text{CO}_2$ predicted by both Berner and Kothavala (2001) and Royer et al. (2001) fall (Fig. 2). Because we used the pH values determined by Pearson and Palmer (2000), the difference between their values and our overall lower values between 52 and 60 Ma clearly lies in the different assumptions made for seawater $[\text{CO}_3^{2-}]$ concentrations. Our approach utilized independently determined calcium concentrations that vary significantly as a function of geologic time, coupled with the recognition that the CaCO_3 crystalline phase (whether of abiogenic or biogenic origin) precipitating from the oceans has varied, both factors having a significant impact on the chemistry of the ocean carbonate buffer system. It would appear that the results of disparate methods for estimating ancient atmospheric $p\text{CO}_2$ are converging on a limited range of values. Moreover, agreements between calculated atmospheric $p\text{CO}_2$ values and events such as the early Eocene climate optimum and the late Paleocene thermal maximum suggest that CO_2 may have been a significant factor in climate variability over the past 60 m.y.

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Manuscript received 8 April 2003
 Revised manuscript received 29 May 2003
 Manuscript accepted 30 May 2003

Printed in USA