6.11 Atmospheric CO2 and O2 During the Phanerozoic: Tools, Patterns, and Impacts

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6.11.1 Introduction

The partial pressures of CO2 and O2 impart a first-order control on Earth’s climatic and biotic systems. CO2 is an important greenhouse gas and is a fundamental building block for most life, while O2 is intimately linked to metabolism. The levels of these two critical gases are not static: their temporal variability over millennial and longer timescales has been long noted (Beerling, 2007; Lane, 2002; Weart, 2003). This temporal behavior potentially offers tremendous explanatory power for making sense of the geologic record. For example, over a century ago, Arrhenius (1896) and Chamberlin (1897, 1898, 1899) argued for the importance of CO2 in regulating global climate over geologic timescales. In recent decades, attention has also been turned to the two-way interplay over time between life and atmospheric composition (e.g., Beerling, 2007), for example, how the evolution of forests may have facilitated insect gigantism via atmospheric O2 (Section 6.11.4.2). Equally important, studies of the ancient Earth system, including paleoclimate, have increasingly been used as analogues to help predict the future trajectory of the current Earth system (e.g., IPCC, 2007).

The goal of this review is to describe the major model- and proxy-based approaches for reconstructing pre-Pleistocene CO2 and O2, including their limitations, and to present several geologic case studies that highlight the impacts of CO2 and O2 on climate and life. The review is not exhaustive and focuses mainly on developments within the last decade.

6.11.2 Models for Atmospheric CO2 and O2 Estimation

6.11.2.1 Key Principles

The flow of CO2 and O2 into and out of the atmosphere over multimillion-year timescales is largely controlled by a handful of processes (Figure 1). These processes primarily act to transfer CO2 and O2 between rocks and surficial reservoirs (atmosphere, ocean, and land surfaces). Critically, if the rate of the processes over time can be determined, then the geologic trajectories of CO2 and O2 can be quantified.

The key processes were enumerated in 1845 by French chemist and mining engineer J.J. Ebelmen (1845; see also Berner and Maasch, 1996), with more modern treatments given by Urey (1952), Garrels and Perry (1974), Holland (1978), Walker et al. (1981), Berner et al. (1983), Garrels and Lerman (1984), Berner and Canfield (1989), and Berner (1991, 2004). There are two main sinks for CO2 over multimillion-year timescales. The first is the formation and burial of carbonates whose ionic components (Ca2+, Mg2+, and HCO3–) derive from the weathering of Ca and Mg silicate rocks. Carbonate formation releases a stoichiometrically...
equivalent amount of CO₂, but the weathering of one mole of silicate mineral consumes two moles of HCO₃⁻. Thus, assuming no large, long-term change in ocean alkalinity (Holland, 1984), the weathering of Ca and Mg silicate rocks consumes a stoichiometrically equivalent amount of CO₂:

Weathering of a generalized calcium silicate:

\[ 2\text{CO}_2 + \text{H}_2\text{O} + \text{CaSiO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2 \]  \[ \text{[1]} \]

Precipitation of calcium carbonate:

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]  \[ \text{[2]} \]

Sum of eqns [1] and [2]:

\[ \text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \]  \[ \text{[3]} \]

The second major sink for CO₂ is the burial of organic matter (on land or in the ocean). This burial process physically separates the carbon from the surface Earth system until, tens to hundreds of millions of years later, tectonic forces return the carbon to the atmosphere via degassing or direct chemical weathering (respiration) of organic-rich rocks. Because the formation of organic matter also involves the release of O₂, the burial of organic matter leads to the buildup of atmospheric O₂ and its weathering (oxidation) to O₂ consumption. These processes can be conceptualized as ‘geo’-photosynthesis (eqn [4] from left to right) and ‘geo’-respiration (eqn [4] from right to left):

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{CH}_2\text{O} + \text{O}_2 \]  \[ \text{[4]} \]

The cycling of sulfur between rocks and the surface Earth also impacts atmospheric O₂. This is because the dominant pathway for reducing sulfur is through sulfur-reducing bacteria, who metabolize organic matter without consuming oxygen. If the reduced sulfur is then buried (typically as pyrite, FeS₂), then the O₂ that was released when the associated organic matter was synthesized remains in the atmosphere. Over long timescales, this can lead to the buildup of atmospheric O₂:

\[ 2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2-} + 16\text{H}^+ \rightarrow 15\text{O}_2 + 4\text{FeS}_2 + 8\text{H}_2\text{O} \]  \[ \text{[5]} \]

Similarly, if oxidized sulfur enters the rock reservoir (typically as gypsum, CaSO₄), then this can lead to a drawdown of O₂ because less sulfur is available for pyrite formation. When reduced sulfur is released into the surface Earth system via degassing or direct pyrite weathering, oxygen is consumed via oxidation (eqn [5] from right to left). For opposite reasons, the return of oxidized sulfur to the surface Earth leads to the retention of atmospheric O₂. During the Phanerozoic, the sulfur cycle is typically secondary to the organic carbon cycle for impacting O₂, but the effects are nevertheless nonnegligible (Berner, 2004).

It is clear from this discussion that the long-term controls of atmospheric CO₂ and O₂ are linked via the carbon cycle. For processes related to the cycling of organic matter, there are opposing but stoichiometrically equivalent impacts on CO₂ and O₂. The burial of organic matter leads to a drop in CO₂ and equal rise in O₂, and vice versa for organic-matter weathering. It may be expected, then, that CO₂ and O₂ show opposing patterns over time. However, other processes only impact CO₂ (e.g., silicate weathering) or O₂ (e.g., pyrite formation). Thus, changes in CO₂ and O₂ can be decoupled.

The processes that control the long-term evolution of CO₂ and O₂ are distinct from their short-term control. Most noticeably, the more familiar short-term carbon cycle, which involves the transfer of carbon within the surface Earth system, is not directly relevant to the long-term control of atmospheric CO₂ and O₂. This is because any large change in the size of these reservoirs (e.g., soil, marine inorganic carbon) cannot be sustained over geologically relevant timescales. Over long timescales, these reservoirs can be assumed to be in quasi steady state (Berner, 2004). As a result, the short-term carbon cycle dominates the control of atmospheric CO₂ over timescales of approximately <10⁵ years and the long-term carbon cycle for timescales of >10⁵ years.

### 6.11.2.2 GEOCARB Models

Berner et al. (1983) and Berner and Canfield (1989) applied the principles described in Section 6.11.2.1 to quantify
6.11.2.2 Weathering of carbonates, organic matter, pyrite, and gypsum

The weathering of carbonates, organic matter, pyrite, and sulfate minerals is treated in a manner similar to silicate weathering (Section 6.11.2.2.1), but with different rate constants. Factors for carbonate and organic matter weathering include uplift (runoff), paleogeography (and its climatic consequences), and land area. Some carbon-cycle models include an O2 dependency for organic matter weathering (e.g., Bergman et al., 2004), but this dependency is typically weak (Bolton et al., 2006; Wildman et al., 2004a). For carbonates, factors related to plant evolution and the direct weathering effect of CO2 and temperature are also included. The weathering of pyrite is linked to land area (calculated from rock abundances and associated reduced sulfur contents of marine and coal basin sediments) and uplift, while the weathering of gypsum is linked to sulfate abundance and the paleogeographic impact on climate (because sulfate minerals are highly soluble) (Berner, 2006a).

A final modifying parameter is related to the observation that younger rocks are more likely to weather than older rocks because they tend to be closer to the Earth’s surface (‘rapid recycling’; Garrels and Mackenzie, 1971). In GEOCARB, the relative proportions of two age classes (young and old) are computed from rock abundance data.

6.11.2.3 Burial of organic matter and pyrite

The burial flux of organic matter is estimated in two ways (Berner, 2004): through rock abundance data and their associated organic carbon contents and through the carbon isotopic history of shallow marine carbonates, which serve as a proxy for the atmosphere. Because the δ13C of organic matter is distinctly more negative than the atmosphere, an increased burial flux causes an isotopic enrichment in the atmosphere and oceans. Such an enrichment is clearly seen during the Carboniferous and Permian (Prokoph et al., 2008; Veizer et al., 1999). An additional factor is included to account for the O2 dependency on the carbon isotopic fractionation during photosynthesis (both for plants and phytoplankton) (Beaumont et al., 2002b; Berner, 2009; Berner et al., 2000; Berry et al., 1972).

Pyrite burial has also been modeled from both rock abundance data and the sulfur isotopic history of sulfate in shallow marine carbonates, which, as with carbon, serve as an atmospheric proxy. The biologically mediated process of pyrite formation incorporates isotopically depleted sulfur, meaning an increased burial flux in pyrite leads to an isotopic enrichment in the atmosphere and oceans. A modifying parameter to account for the inverse effect of atmospheric O2 on the isotopic fractionation of sulfur is included (Berner, 2001; Berner et al., 2000).

For both organic matter and pyrite burial, the two approaches (mass balance and isotopic mass balance) yield similar estimates of O2 (Berner, 2001, 2004; Berner et al., 2000).

6.11.2.4 Degassing

CO2 degassing from volcanic, metamorphic, and diagenetic processes is one of the least-constrained components of long-term carbon cycle models (Berner, 2004). Seafloor spreading
rates are often considered a proxy for degassing (e.g., Berner et al., 1983). Spreading rates can be inferred from the volume of intact seafloor (Seton et al., 2009) and, for times predating intact seafloor (>180 Ma), from global sea level (Gaffin, 1987). Kerrick (2001) considers this approach too simplified and instead proposes that global degassing scales more directly with volcanic rock volume. Following this approach, Berner (2004) found no first-order disagreement with the spreading rate approach.

Before 150 Ma, deep-sea carbonate formation was rare because most calcareous plankton had not yet evolved (Wilkinson and Walker, 1989). Because deep-sea sediment is more likely to be subducted than sediment deposited on shelves, the evolutionary radiation of calcareous plankton likely influenced degassing (Ridgwell and Zeebe, 2005). In GEOCARB, the effect is modeled as a linear increase in subducted carbonate beginning at 150 Ma (Berner, 1994).

### 6.11.2.2.5 Estimates of CO₂ and O₂ from the GEOCARB Model

Following the parameterizations outlined earlier (Sections 6.11.2.2.1–6.11.2.2.4), the Phanerozoic histories of atmospheric CO₂ and O₂ can be computed (Figure 2). These are computed in units of mass abundance (i.e., partial pressure), but for convenience have been converted here to volumetric fraction (ppm) assuming unity at sea level (e.g., a doubling in mass equals a doubling in volumetric fraction). CO₂ was high (above 2000 ppm) for much of the early Paleozoic, followed by a precipitous drop to present-day levels (<500 ppm) near the end of the Devonian. This CO₂ drop was triggered largely by the origin and expansion of forests, which increased chemical weathering rates (Section 6.11.2.2.1) and permitted increased burial of organic carbon (Section 6.11.2.2.3). Increased degassing (Section 6.11.2.2.4) led to elevated CO₂ levels during the Cretaceous (~1000 ppm), followed by a steady decline to the present day (Figure 2(a)), due in part to relief-driven changes in silicate weathering.

Atmospheric O₂ levels oscillated between 15% and 25% for much of the Phanerozoic, with one large, positive excursion to >30% centered on the late Carboniferous and Permian (Figure 2(b)). This spike was largely caused by an increase in organic carbon burial (see also Section 6.11.4.2).

### 6.11.2.3 Other Models for CO₂ and O₂ Reconstruction

There are other long-term geochemical models that calculate Phanerozoic CO₂ and O₂. Most are grounded in the principles outlined earlier (Section 6.11.2.1) and thus share many traits with the GEOCARB family of models. For example, Budyko et al. (1987) track the mass abundance of carbon- and sulfur-bearing rocks much like GEOCARB, but they do not incorporate isotopes and include fewer modifying parameters. Their CO₂ and O₂ calculations are similar to GEOCARB except for lower CO₂ during the Cambrian–Silurian and an additional large O₂ spike during the Cretaceous.

Falkowski et al. (2003) use the oxygen model of Berner (2001) and updated sulfur and carbon isotope records to reconstruct atmospheric O₂ for the past 205 My. Tajika (1998) and Kashiwagi and Shikazono (2003) model CO₂ for the last 150 and 65 My, respectively, in a manner similar to GEOCARB except for expanded treatments of degassing. The results from these three models broadly match those from GEOCARB. Wallmann (2001, 2004) developed a set of independent GEOCARB-style models, with an additional focus on the submarine weathering of basalt. However, most studies point to submarine weathering having only a minor role in long-term CO₂ control (see Berner, 2004 for summary). In Wallmann (2004), reconstructions of galactic cosmic radiation modify the temperature inputs; however, cosmic ray reconstructions and their possible impact on climate are poorly understood (Rahmstorf et al., 2004; Royer et al., 2004).

Three models have expanded beyond the carbon–oxygen–sulfur system to include other elements, such as phosphorus and iron (Arvidson et al., 2006; Bergman et al., 2004; Hansen and Wallmann, 2003). This allows for the inclusion of more feedback processes, for example, the negative feedback between atmospheric O₂ and marine P via organic matter burial (Van Cappellen and Ingall, 1996).

Figure 2  Phanerozoic history of atmospheric CO₂ and O₂ from the GEOCARBSULFvolc model. CO₂ history is from Berner (2008), assuming a basalt/granite weathering rate ratio (VNV) of 5, a present-day basalt–seawater reaction rate (fB(0)) of 4, and a strontium isotope variability in granites over time (NV) of 0.015. The error envelope, which captures the likely range of the input parameters, is updated from Berner and Kothavala (2001). O₂ history is from Berner (2009). The error envelope is updated from Berner (2006a).
Most long-term carbon- and oxygen-cycle models have coarse time resolution. The GEOCARB model, for example, typically has a 10 My time step. An obvious drawback to this approach is that short-term events, such as the Paleocene–Eocene thermal maximum and the K–T boundary bolide impact, are not captured. However, a coarse time resolution is not intrinsic to these models; it simply reflects the difficulty in resolving processes, such as runoff and chemical weathering, especially during the Paleozoic and early Mesozoic. While no high-resolution model exists yet for the entire Phanerozoic, there are some high-resolution models for targeted intervals (e.g., Berner, 2005; Gibbs et al., 1997; Saltzman et al., 2011; Tajika, 1998).

Other models emphasize one aspect of long-term geochemical cycles. For example, the GEOCLIM model is a GEOCARB-style model for CO2 estimation but with a sophisticated, spatially resolved module for silicate weathering (Donnadieu et al., 2006b; 2009; Goddéris et al., 2008; Le Hir et al., 2011). Clearly, there is simultaneous movement in long-term geochemical models to shorten time steps and to more completely describe the processes that control the long-term evolution of CO2 and O2.

### 6.11.3 Proxies for Atmospheric Reconstruction

Atmospheric CO2 and O2 cannot be measured directly for the pre-Pleistocene. However, CO2 and O2 covary with many elements in the Earth system today, and some of these elements can be measured in rocks. These proxies provide an alternative approach for reconstructing CO2 and O2 that are independent from geochemical models. The foundational caveat for all proxies is that the uniformitarian assumption that their governing processes have not changed over time.

There has been an explosion of paleo-CO2 proxies over the past two decades. The six leading methods are described here (Sections 6.11.3.1–6.11.3.5). Proxies for atmospheric O2, while less quantitative, are described too (Section 6.11.3.7). In both cases, recent developments are emphasized. More exhaustive reviews can be found elsewhere (Berner et al., 2003; Freeman and Pagani, 2005; Pagani, 2002; Royer, 2001; Royer et al., 2001a; Sheldon and Tabor, 2009). With the exception of the paleosol proxies (Section 6.11.3.3), all CO2 proxies described here respond to pCO2; for convenience, all reconstructions are expressed in units of volumetric fraction (ppm) assuming unity at sea level (e.g., a doubling in pressure corresponds to a doubling in volumetric fraction).

#### 6.11.3.1 CO2: Stomata

Stomata are the microscopic pores on leaf surfaces that facilitate gas exchange with the atmosphere, namely, CO2, O2, and H2O. Approximately 200% and 16% of the total content of atmospheric water vapor and CO2 are cycled through stomata each year (Hetherington and Woodward, 2003). As such, stomata are finely tuned to the atmosphere. Woodward (1986) demonstrated that stomatal density typically increases with elevation. This response, replicated in experiments (Woodward and Bazzaz, 1988), is largely driven by lower pCO2 and the plant’s requirement to maintain photosynthetic rates but with a transpirational cost (Royer et al., 2001a; Woodward, 1987). Because both atmospheric pressure and atmospheric CO2 mass affect pCO2, if pressure is controlled for CO2 concentration (ppm) can be reconstructed. Typically, stomatal index (100 × stomatal density/[stomatal density + epidermal cell density]), not stomatal density, is used for CO2 reconstruction because stomatal index is influenced by fewer environmental factors (Royer, 2001). For example, stomatal density is more sensitive to water potential gradients within leaves and canopies (including sun and shade leaves) because water stress affects epidermal cell size (and thus stomatal density) but not stomatal initiation rates (and thus stomatal index) (Kürschner, 1997; Royer, 2001; Sun et al., 2003). Light intensity affects both stomatal density and stomatal index (Lake et al., 2001); however, in natural forest systems, the impact on stomatal index appears minor (Royer, 2001; Sun et al., 2003).

A strength of the stomatal approach for quantifying paleo-CO2 is that the genetic (Casson and Gray, 2008; Gray et al., 2000), functional (Kleidon, 2007; Konrad et al., 2008; Wynn, 2003), and signaling (Lake et al., 2001, 2002) pathways that underpin the inverse relationship are fairly well understood. Stomata-based CO2 reconstructions also compare favorably to coeval estimates from Pleistocene and Holocene ice cores (McElwain et al., 2002; Rundgren and Beerling, 1999, 2003; Rundgren et al., 2005).

The principal limitation of the proxy is that the stomata lose sensitivity at high CO2 faster than the other proxies (Figure 3). Above ~700 ppm, the upper error limits for most stomata-based CO2 estimates are unbounded. Another constraint on using the stomata to reconstruct CO2 is that atmospheric pressure needs to be considered. Thus, fossil studies must account for paleoelevation; in most cases, if the paleoelevation of a site is <1000 m, then the impact of atmospheric pressure is minor (Beerling and Royer, 2002). The final constraint is that the stomatal responses to CO2 are commonly species-specific (Beerling, 2005; Haworth et al., 2010; Jordan, 2011; Royer et al., 2001a).

![Figure 3](image-url) Error analysis for atmospheric CO2 proxies. Curves are regression fits (CO2 vs. associated error) of the data presented in Figure 4. Positive and negative errors are computed separately. Dashed green lines represent data based on the stomatal ratio proxy.
et al., 2001a). This means that measurements from fossil species should be calibrated to the same extant species. An alternative approach is to compare closely related (but not identical) species; the ratio of the two stomatal measurements is then directly related to CO₂ (McElwain and Chaloner, 1995). The errors associated with this stomatal ratio approach are considerably smaller (green dashed lines in Figure 3). But because a stomatal–CO₂ relationship is assumed, not calculated, the CO₂ estimates are semiquantitative, including the associated errors.

A superior alternative is to reconstruct CO₂ from stomatal dimensions and gas exchange considerations alone (Grein et al., 2011). This approach retains sensitivity even at high CO₂ (e.g., standard deviation for an estimate of 2000 ppm is ~200 ppm) and does not require an extant calibration between CO₂ and stomatal index, opening up much more of the paleobotanical record (i.e., species that are extinct today). However, as with the traditional approaches, it requires some uniformitarian assumptions, specifically about photosynthetic and conductance parameters.

### 6.11.3.2 CO₂: Phytoplankton and Liverworts

In contrast to stomata-bearing plants, most phytoplankton cannot actively control the throughput of CO₂ through their cells. If the concentration of CO₂ rises in the surrounding water, then more CO₂ will pass through their cells. Because photosynthesis fractionates against the heavy isotope $^{13}$C (Degens et al., 1968), the carbon isotopic fractionation between CO₂ in ambient seawater and photosynthate, $\Delta_{\text{sea-photo}} = \left(\frac{\delta^{13}C_{\text{sea}} - \delta^{13}C_{\text{photo}}}{1 + \delta^{13}C_{\text{photo}}/1000}\right)$, increases in a high-CO₂ environment. This is because the phytoplankton–CO₂ system is more open in a Rayleigh fractionation context. At low CO₂, with a correspondingly low-CO₂ throughput, more $^{13}$C is incorporated into photosynthate and $\Delta_{\text{sea-photo}}$ declines (Popp et al., 1989).

The $\delta^{13}$C and $\delta^{18}$O of marine carbonate can be used to reconstruct $\delta^{13}$C$_{\text{sea}}$. By coupling isotopic measurements of carbonates with coexisting organic matter ($\delta^{13}$C$_{\text{photo}}$), atmospheric CO₂ can be reconstructed. Many studies use the $\delta^{13}$C of bulk organic matter as a proxy for $\delta^{13}$C$_{\text{photo}}$ (Arthur et al., 1985; Cramer and Saltzman, 2007; Freeman and Hayes, 1992; Holland and McKenzie, 1991; Kienast et al., 2001; Kump et al., 1999; Popp et al., 1989; Rothman, 2002; Sarkar et al., 2003; Young et al., 2010). However, even in deep-sea settings, marine nonphotosynthetic and terrestrial organic matter are present in bulk samples (Hayes et al., 1989; Pagani et al., 2000). Also, vital effects related to active HCO$_3^-$ transport (Hinga et al., 1994), growth rate (Fry and Wainwright, 1991), and cell volume/surface area (Popp et al., 1998) can impact $\Delta_{\text{sea-photo}}$. As a result, most studies no longer measure bulk $\delta^{13}$C but instead, a subset of biomarkers that today are found in a limited number of species. Jasper and Hayes (1990) pioneered the use of C$_{\pi}$ diunsaturated alkenones, which today are produced mostly by two closely related species of haptophytic algae (Conte et al., 1994). The influence of cell geometry can be calibrated with the appropriate extant taxa (Henderiks and Pagani, 2007) and applied to fossils (Henderiks and Pagani, 2007, 2008), although the fossil measurements are very laborious. The growth rate in fossil algae has proved more difficult to model. Most paleo-CO₂ studies apply the present-day relationship between the growth rate in haptophytic algae and seawater PO$_4^{3-}$ concentration (Bidigare et al., 1997; Pagani, 2002). However, reconstructing paleo-PO$_4^{3-}$ is difficult; most fossil studies use marine sediment cores with strong evidence for oligotrophy and apply PO$_4^{3-}$ concentrations from putatively similar modern seawater (e.g., Pagani et al., 1999b).

Further work is needed to improve the characterization of growth rate in fossil studies, especially considering that some experimental studies find $\Delta_{\text{sea-photo}}$ more strongly impacted by growth rate than by CO₂ concentration (e.g., Benthien et al., 2007). Indeed, the anomalously high CO₂ estimates from the high-latitude sites of Pagani et al. (2005b) may reflect differences in growth rate rather than CO₂. A temporal limitation of the alkenone-based approach is that alkenones are unknown from before the Cretaceous (Farrimond et al., 1986) and remain rare until the middle Eocene. Presently, all alkenone-based CO₂ estimates postdate the early Eocene.

Bryophytes (mosses, liverworts, and hornworts) typically lack stomata in their vegetative tissues. For the purposes of reconstructing CO₂, then, these plants can be considered terrestrial equivalents of phytoplankton. As atmospheric CO₂ rises, the $\delta^{13}$C of the plant tissue declines, reflecting a more open Rayleigh fractionation system, and vice versa when CO₂ drops. White and colleagues pioneered this proxy, reconstructing Holocene CO₂ from Sphagnum moss bogs (Figge and White, 1995; White et al., 1994). As with phytoplankton, an additional control on the $\delta^{13}$C of bryophytes is growth rate, which is strongly controlled by water content (Price et al., 1997; Rice and Giles, 1996). Fletcher et al. (2005) demonstrated that liverworts have much more stable water contents than most mosses and, thus, are the best candidates for paleo-CO₂ estimation. Fletcher et al. (2006) developed a process-based model for liverwort photosynthesis that calculates atmospheric CO₂ from $\delta^{13}$C$_{\text{photo}}$, $\delta^{13}$C$_{\text{air}}$ temperature, O₂ concentration, irradiance, and a suite of physiological parameters. This proxy is quite young; as more groups use the method, improvements will no doubt come, especially with respect to modeling the physiological parameters.

### 6.11.3.3 CO₂: Paleosols (Calcite and Goethite)

In arid and semiarid climates, calcite commonly precipitates in soils (Royer, 1999). For soils with noncarbonate parent material and little diagenetic or groundwater influence (Quast et al., 2006), the carbon has two sources: biological respiration within the soil and diffusion of atmospheric CO₂ into the soil. Because the $\delta^{13}$C of these sources is distinct, an isotopic mass balance can be constructed to calculate atmospheric CO₂ concentration (Cerling, 1984, 1991, 1999):

$$ CO_{2\text{[atm]}} = S(z) \frac{\delta{C}}{\delta{C}_s} - 1.0044 \frac{\delta{O}}{\delta{O}_s} - 4.4 \frac{\delta{O}}{\delta{O}_s} $$

where $S(z)$ is the concentration of soil-respired CO₂ and $\delta{C}_s$, $\delta{O}_s$, and $\delta{O}_s$ are the $\delta^{13}$C of soil CO₂ (inferred from soil calcite), soil-respired CO₂ (inferred from organic matter), and atmospheric CO₂ (inferred from coeval shallow marine carbonate). Because carbonate-bearing soils often have little preserved organic matter, atmospheric $\delta^{13}$C records (e.g., from shallow marine
carbonates) are sometimes used as a proxy (e.g., Ekart et al., 1999), but such an approach is fraught with uncertainty (Beerling and Royer, 2002). Even when the $\delta^{13}$C of coexisting organic matter can be measured, care must be taken to account for isotopic fractionation during microbial decomposition (Bowen and Beerling, 2004; Wynn, 2007).

Estimating the concentration of soil-respired CO$_2$ ($S(z)$) is difficult. Older studies typically assumed values of ~5000 ppm based on annually integrated measurements in present-day soils (e.g., Brook et al., 1983). However, Breecker et al. (2009) demonstrated that calcite precipitation is thermodynamically favorable only during the warmer and drier parts of the year. During these times, $S(z)$ is low (usually <2000 ppm). Because atmospheric CO$_2$ estimates scale directly with $S(z)$, many published estimates may be too high by over a factor of 2 (see also Schroeder et al., 2006). Recognition of this overestimation has been critical for improving paleo-CO$_2$ records, but the application of a single, revised $S(z)$ (Breecker et al., 2010) ignores the full range of possible $S(z)$. Future work will be directed toward developing more refined indicators of $S(z)$ (Retallack, 2009b).

An analogous atmospheric CO$_2$ proxy is based on trace carbonate in goethite (Fe(CO$_3$)OH) (Feng and Yapp, 2009; Tabor and Yapp, 2005; Tabor et al., 2004; Yapp, 2004; Yapp and Poths, 1992, 1996). As with the calcite-based proxy, the $\delta^{13}$C of the carbonate and coexisting organic matter is inputted into a two-end-member mixing model. Critically, the concentration of the trace carbonate scales with the concentration of soil CO$_2$ (Yapp, 1987; Yapp and Poths, 1991). Thus, in contrast to the calcite method, the concentration of soil-respired CO$_2$ ($S(z)$) can be computed directly. However, molecular dynamic simulations and quantum chemistry calculations demonstrate that carbonate in goethite is incorporated through two pathways, each with its own carbon isotope fractionation factor (Rustad and Zarzycki, 2008). The standard goethite paleo-CO$_2$ model assumes a constant fractionation factor and thus needs revision in light of these new results. Changes in soil moisture content and the residence time of soil carbon can also affect CO$_2$ estimates (Gulbranson et al., 2011).

### 6.11.3.4 CO$_2$: Boron ($\delta^{11}$B and B/Ca)

The relative proportions of the two major boron species in the ocean, B(OH)$_3$ and B(OH)$_4^-$, vary with pH. Because the boron isotopic composition ($\delta^{11}$B) of these two species differs, the $\delta^{11}$B of marine carbonate is a proxy for seawater pH (Hemming and Hanson, 1992; Palmer et al., 1998; Sanjal et al., 1995, 1996; Spivack et al., 1993; Vengosh et al., 1991). With assumptions about the total alkalinity or dissolved inorganic carbon (DIC) concentration of ancient seawater, atmospheric CO$_2$ can be inferred from pH (Hönisch and Hemming, 2005; Hönisch et al., 2009; Pearson and Palmer, 1999, 2000; Pearson et al., 2009).

Several critical objections have been raised about this CO$_2$ method. First, the fractionation factor between B(OH)$_3$ and B(OH)$_4^-$ used by earlier studies (Hönisch and Hemming, 2005; Pearson and Palmer, 1999, 2000) is incorrect (Klochko et al., 2006; Liu and Tossell, 2005; Pagani et al., 2005a; Rustad et al., 2010; Zeebe, 2005). Also, the $\delta^{11}$B in biologically produced carbonate is usually offset from the theoretical fractionation, and this offset is generally species-specific (e.g., Blamart et al., 2007; Hönisch et al., 2003; Sanjal et al., 1996; Zeebe et al., 2003). At minimum, fossil studies should be calibrated to the same extant species. The boron proxy assumes that only B(OH)$_4^-$ is incorporated into carbonate, but Klochko et al. (2009) determined that B(OH)$_3$ may be active too, and the proportionality of uptake between the two species is pH-dependent; this behavior may explain some of the reported ‘vital effects’ and further complicates the proxy. Early CO$_2$ reconstructions assumed constant alkalinity (Pearson and Palmer, 1999), but this is not realistic (Caldeira et al., 1999). More recent reconstructions have used increasingly sophisticated models for alkalinity and DIC (Demico et al., 2003; Pearson et al., 2009; Roberts and Tripati, 2009; Tyrrell and Zeebe, 2004). Knowledge of the $\delta^{11}$B of seawater is also needed for pH reconstructions, but quantifying its evolution is difficult (Lemarchand et al., 2000, 2002; Simon et al., 2006). Diagenesis may also impact the $\delta^{11}$B of carbonate (Hönisch and Hemming, 2004; Spivack and You, 1997; Wara et al., 2003). The impact of diagenesis is particularly worrisome in light of the recognition that carbonate considered pristine using traditional screening protocols may in reality be highly altered isotopically (Pearson et al., 2001). A final roadblock for the boron proxy is that methodological differences have led to interlab differences in $\delta^{11}$B measurements that exceed the stated precision by eightfold (Foster et al., 2006). A new method based on MC-ICPMS may resolve this precision problem, but further interlab testing is needed (Foster, 2008; Ni et al., 2010).

The CO$_2$ reconstructions of Pearson and Palmer (1999, 2000) should be considered suspect due to the use of an incorrect fractionation factor, the strong possibility of diagenesis, and the primitive modeling of alkalinity and seawater $\delta^{11}$B. Newer CO$_2$ reconstructions have made progress on all these fronts (Pearson et al., 2009; Seki et al., 2010), but more work is needed to understand the long-term controls of seawater $\delta^{11}$B and the species-specific nature of the pH responses. For example, the seawater $\delta^{11}$B record of Paris et al. (2010) suggests that most pre-Pleistocene CO$_2$ estimates require substantial downward revision.

Recently, the B/Ca ratio in marine carbonate has been proposed as a proxy for pH and atmospheric CO$_2$ (Yu et al., 2007). If B(OH)$_4^-$ is the only boron species incorporated into carbonate and its concentration is controlled in part by pH, then the B/Ca ratio in carbonate should reflect pH. This proxy is highly related to the $\delta^{11}$B proxy, and as such, many of the concerns already outlined are pertinent here (Foster, 2008; Ni et al., 2007; Yu et al., 2007, 2010). Additionally, Allen et al. (2011) report that CO$_2$ as carbonate is more important than pH in controlling B/Ca and that B/Ca covaries with seawater B concentration and salinity. The controls over boron uptake in shells clearly warrant further study.

### 6.11.3.5 CO$_2$: Nahcolite

Nahcolite is a rare sodium carbonate mineral (NaHCO$_3$). Equilibrium experiments demonstrate that in the nahcolite-trona–natron system, nahcolite only precipitates at high CO$_2$ (>1330 ppm, >1125 ppm if coprecipitated with halite) (Eugster, 1966). The presence of nahcolite may therefore establish a minimum level of atmospheric CO$_2$. Key assumptions

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*Atmospheric CO$_2$ and O$_2$ During the Phanerozoic: Tools, Patterns, and Impacts*
with this proxy are that the nahcolite precipitates at the air–water interface and that in situ generation of biologically respired CO2 is minimal (Lowenstein and Demicco, 2006). Application of the proxy is limited because nahcolite is rare: the only geologic deposits are from the Eocene. Nevertheless, the classic nahcolite deposits from the Green River Formation date to the peak of Cenozoic warmth (early Eocene climatic optimum), suggesting a CO2–temperature link (Lowenstein and Demicco, 2006). Trona, which precipitates at lower CO2, is also found in coeval Green River deposits, but it lacks primary sedimentary textures and is interpreted to have formed diagenetically at higher temperatures where it is stable. Importantly, new equilibrium experiments find that nahcolite can precipitate at lower CO2 (Iagniecki et al., 2010), suggesting a downward revision of CO2 estimates from >1330 ppm to ~1000 ppm.

6.11.3.6 Estimates of Phanerozoic CO2 from Proxies

A Phanerozoic CO2 history from proxies is presented in Figure 4(a). Two points are worth noting: First, although there is some scatter at any given time interval, the variability

Table 1 Sources of CO2 data presented in Figures 4–7

<table>
<thead>
<tr>
<th>CO2 proxy</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stomata</td>
<td>van der Burgh et al. (1993); Kürschner et al. (1996, 2001, 2008); Beering et al. (1998, 2002a); McElwain (1998); McElwain et al. (1999, 2005); Chen et al. (2001); Royer et al. (2001b); Beering (2002); Beering and Royer (2002); Greenwood et al. (2003); Roth-Nebelsick and Konrad (2003); Royer (2003); Haworth et al. (2005); Sun et al. (2007); Passalà (2008); Quan et al. (2009); Retallack (2009a); Yan et al. (2009); Barclay et al. (2010); Bonis et al. (2010); Smith et al. (2010); Doria et al. (2011); Steinthorsdottir et al. (2011); Stults et al. (2011); Grein et al. (2011); Wan et al. (2011)</td>
</tr>
<tr>
<td>Phytoplankton</td>
<td>Pagani et al. (1999a,b, 2005b, 2011); Seki et al. (2010)</td>
</tr>
<tr>
<td>Liverworts</td>
<td>Fletcher et al. (2008)</td>
</tr>
<tr>
<td>Paleosol carbonate</td>
<td>Suchecki et al. (1988); Platt (1989); Cerling (1991, 1992); Koch et al. (1992); Muczelh et al. (1993); Sinha and Stott (1994); Andrews et al. (1995); Mora et al. (1996); Ekart et al. (1999); Lee (1999); Lee and Hisada (1999); Driese et al. (2000); Cox et al. (2001); Royer et al. (2001b); Tanner et al. (2001); Nordt et al. (2002, 2003); Robinson et al. (2002); Tabor et al. (2004); Ghosh et al. (2005); Prochnow et al. (2006); Sandler (2006); Montañez et al. (2007); Cleveland et al. (2008); Leier et al. (2009); Retallack (2009b); Schaller et al. (2011)</td>
</tr>
<tr>
<td>Boron (δ13B)</td>
<td>Pearson et al. (2009); Seki et al. (2010)</td>
</tr>
<tr>
<td>Boron (B/Ca)</td>
<td>Tripati et al. (2009)</td>
</tr>
<tr>
<td>Nahcolite</td>
<td>Lowenstein and Demicco (2006)</td>
</tr>
</tbody>
</table>

Notes: All dates are calibrated to the timescale of Gradstein et al. (2004). Many individual CO2 estimates are based on multiple measurements of the same material; consult sources for details. The boron-based estimates of Pearson and Palmer (2000) are omitted owing to their lack of reliability (Section 6.11.3.4). No goethite-based estimates are presented owing to the poor knowledge of some of the isotopic fractionation factors (Section 6.11.3.3). Liverwort estimates have been updated using the atmospheric δ13C record of Tipple et al. (2010). Paleosol carbonate estimates have been recalculated assuming a soil respiration concentration of 2000 ppm (Breecker et al., 2009). Stomatal ratio estimates have been recalculated following the procedure of Beering and Royer (2002). For Retallack (2009a), which emend Retallack (2001, 2002), only estimates based on >4 cuticles (Royer, 2003) and from the genus Ginkgo (Vörding and Kerp, 2008) are included; for fossil species other than Ginkgo adiantoides, the stomatal ratio method was applied. The high-resolution record of Doria et al. (2011) has been combined into a single estimate. Some Permo–Carboniferous data of Ekart et al. (1999) have been updated by Tabor et al. (2004) and Montañez et al. (2007). Beering et al. (2009) emend the estimates of Royer et al. (2001b), Beering et al. (2002a), Royer (2003), and Kürschner et al. (2008). Ghosh et al. (2005) emend the estimates of Ghosh et al. (1995, 2001), and Henderiks and Pagani (2008) emend the estimates of Pagani et al. (1999a,b, 2005b). Southern high-latitude sites from Pagani et al. (2005b, 2011) are excluded; see Pagani et al. (2011) for justification. Estimates from Pagani et al. (2011) follow their Figure 4.
is typically less than twofold. Second, there is a broad agreement among methods (see also Figures 5–7). This contrasts with earlier compilations that found much higher variability (e.g., >3000 ppm for the early Paleogene; Royer, 2003). Much of the discrepancy has been resolved through the downward revision of paleosol estimates (Breecker et al., 2010), the upward revision of stomatal estimates (Beerling et al., 2009), and the exclusion of suspect boron estimates (see Section 6.11.3.4). An example of reconciliation is drawn from Royer et al. (2001b), who reported pairs of CO2 estimates from the paleosol and stomatal methods. Here, the large discrepancies between methods largely disappear after incorporating the revisions of Beerling et al. (2009) and Breecker et al. (2010) (Figure 5).

Proxy estimates broadly match the independently derived model estimates (Figure 4(b)). Both show a ‘double hump’ pattern of CO2, with elevated CO2 during the early Paleozoic and mid-Mesozoic, and a possible secondary ‘hump’ during the early Cenozoic. Together, they bolster confidence that the long-term (10 My time step) patterns of atmospheric CO2 are well described.

6.11.3.7 O2 Proxies

Proxy development for atmospheric O2 lags far behind that for CO2. Combustion experiments suggest a minimum oxygen content of 15% to support wildfire (Belcher and McElwain, 2008; Belcher et al., 2010). Charcoal is a product of wildfire and is present in the geologic record, with few exceptions, throughout the last 420 My when vascular plants were common (Chaloner, 1989; Cope and Chaloner, 1980; Glasspool et al., 2004; Scott, 2000). This suggests that atmospheric O2 exceeded 15% for much of the Phanerozoic, a result in accord with geochemical calculations (Figure 2(b)).

Upper O2 limits are less constrained by proxies. Early combustion experiments suggested runaway wildfires at levels above ~25%, but newer experiments do not support this claim (Berner et al., 2003; Wildman et al., 2004b). During the Carboniferous and Permian, when geochemical models predict O2 levels up to 35% (Figure 2(b)), charcoal is more abundant than at most other times during the Phanerozoic (Robinson, 1991; Scott, 2000). Indeed, the fraction of charcoal macerals in coal quantitatively tracks the rise of O2 into the Carboniferous as predicted from geochemical models (Diessel, 2010; Glasspool and Scott, 2010; Scott and Glasspool, 2006), providing strong, independent support for an O2 spike at that time.

6.11.4 Impacts of CO2 and O2 on Climate and Life

6.11.4.1 CO2–Temperature Coupling

A rich body of evidence supports a strong link between atmospheric CO2 and temperature for much of the Phanerozoic (e.g., Berner, 1991; Bijl et al., 2010; Came et al., 2007; Crowley and Berner, 2001; Montañez et al., 2007; Royer, 2006; Vaughan, 2007). In particular, the two most long-lived Phanerozoic glaciations during the Permo–Carboniferous

![Figure 5](image-url) Atmospheric CO2 estimates from the Bighorn Basin, Wyoming. Each CO2 pair corresponds to stratigraphically equivalent beds (within 15 m or ~30 ky). Original estimates (open symbols) are from Royer et al. (2001b). Stomatal estimates have been revised following the error propagation method of Beerling et al. (2009). Paleosol carbonate estimates have been recalculated assuming a soil respiration concentration of 2000 ppm (Breecker et al., 2009).

![Figure 6](image-url) CO2—temperature coupling during the Cenozoic. (a) Global-mean surface temperature, as calculated from the benthic δ18O compilation of Zachos et al. (2008) and following the protocol of Hansen et al. (2008). Temperature is expressed relative to the preindustrial. (b) Individual CO2 estimates, coded by proxy type. See Table 1 for data sources. Estimates with arrows are unbounded. Red bands correspond to pulses in global warmth; the blue band corresponds to the rapid cooling coincident with the inception of Antarctic ice growth (Zachos et al., 2008). Dashed line represents preindustrial CO2 concentration (280 ppm). This figure is updated from Beerling and Royer (2011).
CO₂ rose during the Paleocene, peaking at 1000 ppm during the early Eocene, corresponding with the peak of Cenozoic warmth. CO₂ then fell during the Eocene, tracking cooling global temperatures, before plummeting at the Eocene–Oligocene boundary, a time marked by the onset of glaciation on Antarctica. Two CO₂ peaks during the late Oligocene and Middle Miocene coincide with well-known warm periods (Figures 6 and 7). Despite this apparent coupling, several inconsistencies remain: First, the phytoplankton method does not pick up the Middle Miocene CO₂ spike, but three other methods do (stomata, paleosols, and B/Ca) (Figure 7). Second, Paleocene CO₂ levels are low – similar to Oligocene values – despite clear evidence that temperatures were warmer during the Paleocene. Either climate sensitivity to CO₂ was high during the Paleocene or the CO₂ data are in error.

For some parts of the Phanerozoic, CO₂ and temperature records are sufficiently robust (numerous, convergent estimates) to compute climate sensitivity. During the Pleistocene, climate sensitivity was ~6 °C per CO₂ doubling (Hansen et al., 2008). Critically, this is approximately double the value typically calculated from global climate models and historical records from the last 1000 years (~3 °C) (IPCC, 2007). The discrepancy is due to models and historical data not capturing long-term processes, such as the waxing and waning of continental ice sheets (Hansen et al., 2008). For geological studies, the longer-term response, sometimes called Earth system sensitivity (Lunt et al., 2010), is more appropriate. Although the computation of Earth system sensitivity is a frontier area, a pattern is emerging of 6–9 °C sensitivity during glacial times and 3–6 °C during nonglacial times (Hansen et al., 2008; Lunt et al., 2010; Pagani et al., 2010; Park and Royer, 2011; Royer, 2010; Royer et al., 2007; see also Chapter 6.13). The amplification during glacial times is probably due to a stronger ice–albedo climate feedback, but even during nonglacial times, Earth system sensitivity is higher than what is calculated for the present day. The underlying reason for this is unclear but points to the presence of presently unknown climate feedbacks (see Chapter 6.13). Identifying these feedbacks will greatly expand the fundamental understanding of the ice-free Earth system, for example, the long-standing enigma of flatter latitudinal temperature gradients during ice-free times (e.g., Ballantyne et al., 2010; Bijl et al., 2009; Hollis et al., 2009).

6.11.4.2 Linking Trees to Giant Insects During the Carboniferous and Permian

One elegant case study that highlights the two-way interplay between evolution and geochemical cycling is the evolution of forests during the Devonian facilitating the evolution of giant insects during the Carboniferous and Permian. As discussed earlier (Section 6.11.2.2.1), plants enhance the chemical weathering rate of silicate minerals, a process that shuttles carbon from the atmosphere to the carbonate rock reservoir (Figure 1). As a result, the evolution of forests during the Devonian probably led to a global increase in weathering rate, which was brought back into balance through the attendant CO₂ drawdown and associated cooling (Berner, 1997, 1998). The evolution of forests also significantly increased the amount of carbon stored on land, principally in the form of wood and soil organic matter. Further, components of wood...
atmospheric oxygen levels reached 35%, then total atmospheric oxygen needs (e.g., Robinson, 1990). The geologic record strongly supports this scenario: the Phanerozoic peak in organic matter burial occurs during the Carboniferous and Permian (Berner, 2003). The massive coal deposits from this interval are the most obvious manifestation of this burial.

The evolution of forests and its attendant increase in organic matter burial would have two first-order impacts on atmospheric composition (Figure 1): a drop in CO2 and a rise in O2 (Figure 8). The CO2 drop was likely a critical driver for the Permo-Carboniferous glaciation, the most intense and long-lived glaciation during the Phanerozoic (Section 6.11.4.1). Equally important, the O2 rise probably profoundly impacted evolution. A general link between oxygen and evolution is well established (Berner et al., 2007), and glaciation from Isbell et al. (2003).

like lignin, which did not exist in abundance before the rise of woody plants, are highly resistant to decomposition. Taken together, both the size and chemical composition of this new reservoir of reduced carbon increased the likelihood for organic matter burial (e.g., Robinson, 1990). The geologic record strongly supports this scenario: the Phanerozoic peak in organic matter burial occurs during the Carboniferous and Permian (Berner, 2003). The massive coal deposits from this interval are the most obvious manifestation of this burial.

The evolution of forests and its attendant increase in organic matter burial would have two first-order impacts on atmospheric composition (Figure 1): a drop in CO2 and a rise in O2 (Figure 8). The CO2 drop was likely a critical driver for the Permo-Carboniferous glaciation, the most intense and long-lived glaciation during the Phanerozoic (Section 6.11.4.1). Equally important, the O2 rise probably profoundly impacted evolution. A general link between oxygen and evolution is well established (Berner et al., 2007; Budyko et al., 1987; McAlester, 1970). Animals, in particular, are sensitive owing to their intensive oxygen needs (Chapter 6.10). In the fossil record, the most pronounced interval of insect gigantism coincides with the Permo-Carboniferous O2 spike (Figure 8) (Berner et al., 2003, 2007; Graham et al., 1995). Insects were up to ten times larger than similar extant groups, including dragonflies with 70 cm wingspans and 2 m long millipedes (Graham et al., 1995; Harrison et al., 2010). All insects rely on tracheal networks for respiration, whose volumetric contribution to body volume may place an upper limit on body size that scales with atmospheric O2 concentration (Kaiser et al., 2007; VandenBrooks et al., 2012). A growing body of experimental evidence links atmospheric O2 content to body size and metabolism in insects (see summaries in Berner et al., 2003; Harrison et al., 2010). If atmospheric oxygen levels reached 35%, then total atmospheric pressure would have increased by 25% relative to the Devonian (Berner, 2006b). For flying insects, this may have also relaxed upper limits on body size (Dudley, 2000).

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