6.11 Atmospheric CO$_2$ and O$_2$ During the Phanerozoic: Tools, Patterns, and Impacts

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6.11.1 Introduction

The partial pressures of CO$_2$ and O$_2$ impart a first-order control on Earth’s climatic and biotic systems. CO$_2$ is an important greenhouse gas and is a fundamental building block for most life, while O$_2$ 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 CO$_2$ 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 O$_2$ (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 CO$_2$ and O$_2$, including their limitations, and to present several geologic case studies that highlight the impacts of CO$_2$ and O$_2$ on climate and life. The review is not exhaustive and focuses mainly on developments within the last decade.

6.11.2 Models for Atmospheric CO$_2$ and O$_2$ Estimation

6.11.2.1 Key Principles

The flow of CO$_2$ and O$_2$ 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 CO$_2$ and O$_2$ 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 CO$_2$ and O$_2$ 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 CO$_2$ over multimillion-year timescales. The first is the formation and burial of carbonates whose ionic components (Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$) derive from the weathering of Ca and Mg silicate rocks. Carbonate formation releases a stoichiometrically
equivalent amount of CO$_2$, but the weathering of one mole of silicate mineral consumes two moles of HCO$_3^-$, 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 CO$_2$:

Weathering of a generalized calcium silicate:

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

Precipitation of calcium carbonate:

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

Sum of eqns [1] and [2]:

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

The second major sink for CO$_2$ 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 O$_2$, the burial of organic matter leads to the buildup of atmospheric O$_2$ and its weathering (oxidation) to O$_2$ consumption. These processes can be conceptualized as ‘geo’-photosynthesis (eqn [4] from left to right) and ‘geo’-respiration (eqn [4] from right to left):

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

The cycling of sulfur between rocks and the surface Earth also impacts atmospheric O$_2$. 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, FeS$_2$), then the O$_2$ 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 O$_2$:

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

Similarly, if oxidized sulfur enters the rock reservoir (typically as gypsum, CaSO$_4$), then this can lead to a drawdown of O$_2$ 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 O$_2$. During the Phanerozoic, the sulfur cycle is typically secondary to the organic carbon cycle for impacting O$_2$, but the effects are nevertheless nonnegligible (Berner, 2004).

It is clear from this discussion that the long-term controls of atmospheric CO$_2$ and O$_2$ are linked via the carbon cycle. For processes related to the cycling of organic matter, there are opposing but stoichiometrically equivalent impacts on CO$_2$ and O$_2$. The burial of organic matter leads to a drop in CO$_2$ and equal rise in O$_2$, and vice versa for organic-matter weathering. It may be expected, then, that CO$_2$ and O$_2$ show opposing patterns over time. However, other processes only impact CO$_2$ (e.g., silicate weathering) or O$_2$ (e.g., pyrite formation). Thus, changes in CO$_2$ and O$_2$ can be decoupled.

The processes that control the long-term evolution of CO$_2$ and O$_2$ 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 CO$_2$ and O$_2$. 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 CO$_2$ over timescales of approximately $<10^5$ years and the long-term carbon cycle for timescales of $>10^5$ 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
multimillion-year patterns in CO\textsubscript{2} and O\textsubscript{2}, respectively. Berner and colleagues have since expanded and refined these original studies (Berner, 1991, 1994, 2001, 2004, 2006a,c, 2008, 2009; Berner and Kothavala, 2001; Berner et al., 2000). The model began as GEOCARB, a model for Phanerozoic CO\textsubscript{2} based only on the long-term carbon cycle, and subsequently evolved to its latest iteration, GEOCARBSULFvolc, a model for CO\textsubscript{2} and O\textsubscript{2} based on both the carbon and sulfur cycles. The discussion here is based mainly on GEOCARBSULFvolc.

Critical for the GEOCARB family of models is the correct parameterization of the processes described earlier (Section 6.11.2.1). In other words, how have the burial, weathering, and degassing fluxes changed over time? The overarching framework of the model is an isotopic mass balance, where the mass and stable isotopic composition of carbon and sulfur in the surface Earth system at a given time in the past is related to the flux and isotopic values of carbon and sulfur moving into and out of the system (Berner, 2004). Tracking isotopes are helpful because many of the major reservoirs (Figure 1) have distinct values.

### 6.11.2.2.1 Silicate weathering

The chemical weathering of Ca and Mg silicates has received considerable attention because it is a key, negative climate feedback for maintaining long-term global temperatures within a narrow range (Berner et al., 1983; Pagani et al., 2009; Walker et al., 1981; Zeebe and Caldeira, 2008; see also Chapter 6.15). Both CO\textsubscript{2} and temperature impact chemical weathering rates: these effects have been documented in field studies (Andrews and Schlesinger, 2001; Baars et al., 2008; Gislason et al., 2009) and for events in the geological past (Dallanave et al., 2010). Temperature is inferred partly via climate sensitivity to CO\textsubscript{2}; a value of 3 °C per CO\textsubscript{2} doubling is typical, but estimates of higher climate sensitivity, especially for glacial periods (Hansen et al., 2008; Pagani et al., 2010; Park and Royer, 2011; see also Section 6.11.4.1), may call for a re-parameterization (Berner, 2004). Changing paleogeography, for example, changing land area or poleward drift of a continent (Worsley and Kidder, 1991), also affects weathering. Proper treatment of this factor requires coupling paleogeographic reconstructions with climate model simulations (e.g., Otto-Bliesner, 1995); some progress in this area has been made (Donnadieu et al., 2006a; Le Hir et al., 2011).

Vegetation strongly impacts rock weathering rate by acidifying the soil, increasing soil moisture, and lengthening water–mineral contact time (Berner, 1992). Vegetation factors presently considered in GEOCARB are the transition from a minimally vegetated to forested land surface and the transition from gymnosperms to angiosperms (Baars et al., 2008; Moulton and Berner, 1998; Moulton et al., 2000). Another possible important factor that is presently excluded is the mycorrhizal associations (Taylor et al., 2009). These vegetation processes are some of the least constrained in GEOCARB and are responsible for considerable uncertainty in the CO\textsubscript{2} calculations (Berner, 2004; Berner and Kothavala, 2001).

Mean continental relief affects chemical weathering via the confounding influence of physical erosion and runoff. This relief factor has been estimated via strontium isotopes and abundance of sedimentary rocks (Berner, 2004). Also, because volcanic rocks weather more quickly than nonvolcanic silicate rocks, their changing proportions over time are incorporated (Berner, 2006c, 2008; Wallmann, 2001).

### 6.11.2.2.2 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 O\textsubscript{2} dependency for organic matter weathering (e.g., Bergman et al., 2004), but this dependency is typically weak (Bolton et al., 2006; Wildman et al., 2004). For carbonates, factors related to plant evolution and the direct weathering effect of CO\textsubscript{2} 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.

### 6.11.2.2.3 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 δ\textsuperscript{13}C 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 O\textsubscript{2} dependency on the carbon isotopic fractionation during photosynthesis (both for plants and phytoplankton) (Beerling 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 O\textsubscript{2} 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 O\textsubscript{2} (Berner, 2001, 2004; Berner et al., 2000).

### 6.11.2.2.4 Degassing

CO\textsubscript{2} 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 \( \text{CO}_2 \) and \( \text{O}_2 \) 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 \( \text{CO}_2 \) and \( \text{O}_2 \) can be computed (Figure 2). These are computed in units of mass abundance (i.e., partial pressure), but for convenience have been converted to volumetric fraction (ppm) assuming unity at sea level (e.g., a doubling in mass equals a doubling in volumetric fraction). \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{O}_2 \) 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 \( \text{CO}_2 \) and \( \text{O}_2 \) Reconstruction

There are other long-term geochemical models that calculate Phanerozoic \( \text{CO}_2 \) and \( \text{O}_2 \). 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 \( \text{CO}_2 \) and \( \text{O}_2 \) calculations are similar to GEOCARB except for lower \( \text{CO}_2 \) during the Cambrian–Silurian and an additional large \( \text{O}_2 \) 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 \( \text{O}_2 \) for the past 205 My. Tajika (1998) and Kashiwagi and Shikazono (2003) model \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{O}_2 \) and marine P via organic matter burial (Van Cappellen and Ingall, 1996).
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.