

The Sulfur-Isotopic Composition of Cenozoic Seawater Sulfate: Implications for Pyrite Burial and Atmospheric Oxygen

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Abstract

The availability of high-temporal-resolution C- and S-isotope curves for the Cenozoic permit for the first time modeling of the influence of the C and S cycles on the partial pressure of atmospheric O₂ on comparable time scales. A simple isotope mass-balance model was used to calculate atmospheric O₂ levels from the burial rates of organic C and pyrite S. Burial rates were derived from the C- and S-isotope records of seawater-dissolved inorganic C and sulfate. Results indicate that in the early Cenozoic atmospheric O₂ levels were about 16% higher than current levels. Extension of the model to Phanerozoic time scales yields atmospheric O₂ levels that are inconsistent with geological evidence that suggests that the mass of atmospheric O₂ has not changed by more than a factor of two from the present atmospheric level since the Cambrian (Berkner and Marshall, 1974; Watson et al., 1978; Jones and Chaloner, 1991).

These results indicate that either our knowledge of the parameters controlling atmospheric O₂ is incomplete, or that the assumptions used in such models inadequately represent the complexity of the natural systems. Here we critically examine the assumptions inherent in isotope mass-balance models to determine whether they may be the source of the model-data discord. A major problem with these models is the extreme sensitivity of the mass of atmospheric O₂ to very small changes in the much larger masses of oxidized and reduced C and S reservoirs. For example, small variations in continental weathering fluxes and the associated isotope ratios of river input have profound effects on calculated O₂ levels and need to be accounted for. Similarly, variations in the isotopic composition of pyrite and organic C buried in sediments, which are strongly influenced by changes in isotopic fractionation, dramatically influence calculated O₂ concentrations. Thus, constant fractionation factors should not be applied in such models. In addition, the assumption that the isotopic composition of dissolved inorganic C is controlled only by the relative amounts of reduced and oxidized C buried in sediments and their respective isotope ratios is questionable. Isotope mass-balance models do not adequately encompass and simulate the actual processes being modeled because of the simplifications and assumptions made. More "realistic" models are required to achieve stabilization of atmospheric O₂ over geological time.

Introduction

THE ELEMENT SULFUR (S) is an important constituent of the Earth's exogenic cycle. Global changes in climate and atmospheric chemistry are intimately related to the S sedimentary cycle. Seawater sulfate represents the main reservoir of S for the exogenic cycle; therefore, knowledge of its chemical and isotopic composition over time is important for understanding numerous geochemical cycles on Earth (Berner, 1989; Holland, 1984). S is commonly present in seawater and marine sediments in one of two redox states, in its oxidized state as sulfate and

sulfate minerals and in its reduced form as H₂S and sulfide minerals. The $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{13}\text{C}_{\text{carbonate}}$ records provide estimates for the relative partitioning of C and S between their respective oxidized and reduced reservoirs through time, and thus are sensitive indicators of change in the geological, geochemical, and biological environments (Strauss, 1997; Berner, 1999).

The total amount of oceanic sulfate and its $\delta^{34}\text{S}$ value are controlled by the input and output fluxes of S to the ocean and by their isotopic values. The largest input today is from river runoff from the continent. The $\delta^{34}\text{S}$ value of this source is variable (0 to

TABLE 1. Parameters Used in the Model

Element	Fw, 10 ¹⁸ mol/yr	Fw _{red} ¹ , 10 ¹⁸ mol/yr	δw, ‰	δb, ‰	δo, ‰
Carbon	14.0	3.93	-4.95	-23.7	Shackleton, 1987
Sulfur	1.53	0.53	7.88	-15.0	Paytan et al., 1998

¹Fw_{red} is the weathering flux of reduced components (e.g., organic C or pyrite).

10‰), but typically is lower than seawater, depending on the relative amount of gypsum and pyrite in the drainage basin. Volcanism and hydrothermal activity also are small sources of S to the ocean, with δ³⁴S close to 0‰. The output flux is via deposition of evaporites (δ³⁴S_{evaporite} ≡ δ³⁴S_{seawater}) and sulfides with δ³⁴S_{pyrite} ≡ -15‰. The typically light-isotope ratios of sulfides are a result of the strong S-isotope fractionation involved in bacterial sulfate reduction, the precursor for sulfide mineral formation (Krouse, 1980; Kaplan, 1983). This results in the S-isotope ratios of seawater sulfate being heavier than any of the input sources to the ocean.

The evidence that the S-isotopic composition of seawater sulfate has fluctuated significantly until recently was based on comprehensive, although not continuous, isotope data sets obtained from marine evaporitic sulfate deposits and pyrite (Claypool et al., 1980; Strauss, 1993). Recently, marine barite was used to construct a continuous, high-resolution S curve for the Cenozoic (Paytan et al., 1998). The new data show considerably more detail than—and fills significant gaps in—the former data set, revealing previously unrecognized structure.

The availability of this high-resolution record enables modeling of the C and S cycles on comparable time scales. Because C and S exist in both oxidized (CaSO₄, CaCO₃) and reduced (FeS₂, organic C) states in rocks, and because they are the dominant elements involved in surficial redox cycling (Holland, 1978), the global conversion between oxidation states for one element, if not perfectly balanced by a reciprocal conversion for the other, ultimately involves changes in the level of atmospheric O₂ (Garrels and Perry, 1974). Calculation of the effect of change in the global C and S cycles over geologic time on atmospheric O₂ has been attempted through the use of isotope mass-balance models (Garrels et al., 1976; Schidlowski et al., 1977; Holland, 1978; Veizer et al., 1980; Garrels and Lerman,

1984; Francois and Gerard, 1986; Kump and Garrels, 1986; Walker, 1986; Berner, 1987, 1989; Lasaga, 1989; Mackenzie et al., 1993; Carpenter and Lohmann, 1997; Petsch and Berner, 1998). In all of the above modeling efforts, the S-isotope curves used were characterized by inadequate and irregular temporal spacing and the timing constrains were not precise. The C-isotope record, on the other hand, was based on relatively high resolution data. Thus, simultaneous interpretation of the C and S records was complicated by the different time averaging of the data. Using the high-resolution S-isotope curve of Paytan et al. (1998) enables correlation between the C- and S-isotope records on time scales of 1 million years or less and provide the means for a better representation of the observed natural fluctuations in the cycles of these elements.

Carbon- and Sulfur-Isotope Modeling

The detailed δ¹³C curve of marine carbonate strata, averaged over one-million-year intervals (Fig. 1), and the S isotope curve were used in a simple model of atmospheric O₂ concentration (*sensu* Kump and Garrels, 1986). In this model, changes in atmospheric O₂ concentrations are driven by pyrite and organic C burial rates that are computed from the respective isotope records and the assumption of isotope mass balance. C and S are assumed to exist in oxidized and reduced sedimentary reservoirs within the sediments and the ocean. It has been assumed that the total C and S inputs to the ocean, and their isotopic composition, are constant over time (a simplification) and that the isotopic composition of all reservoirs is homogeneous. The isotopic composition of buried organic C and pyrite also is assumed to be constant over time (Table 1).

The burial of organic C and pyrite are computed using the relation

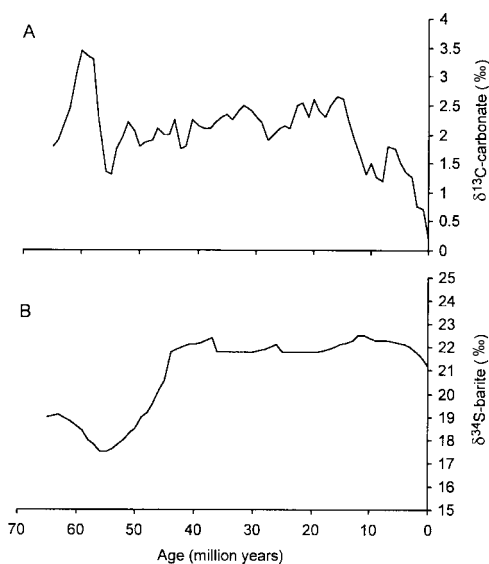
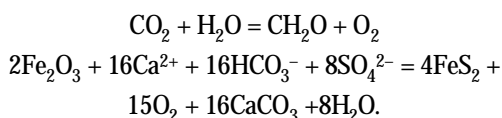


FIG. 1. Changes in seawater-dissolved inorganic C- and S-isotopic composition for $\delta^{13}\text{C}$ bulk carbonate (Shackleton, 1987) (A) and $\delta^{34}\text{S}$ barite (Paytan et al. 1998) (B).

$$Fb = \frac{\delta o - \delta w}{\delta o - \delta b} Fw \quad (1)$$

where Fb is the burial flux of organic C or pyrite, δo is the $\delta^{13}\text{C}$ or $\delta^{34}\text{S}$ of the ocean as recorded in carbonates and barite, respectively (from Fig. 1), δw is the mean $\delta^{13}\text{C}$ or $\delta^{34}\text{S}$ of river input (assumed constant), δb is the isotopic composition of buried organic matter or pyrite (assumed constant), and Fw is the total weathering flux of all C or S compounds (assumed constant).

O_2 concentrations are calculated using a simple stoichiometric relationship based on the weathering and burial reactions of organic C and pyrite



The rate of change of atmospheric O_2 is calculated as

$$\begin{aligned} \frac{d\text{O}_2}{dt} &= (Fb_{\text{orgC}} - Fw_{\text{orgC}}) + \\ &\frac{15}{8}(Fb_{\text{pyrite}} - Fw_{\text{pyrite}}) \quad (2) \end{aligned}$$

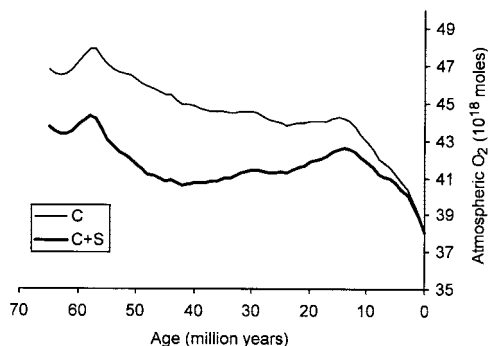


FIG. 2. Changes in atmospheric O_2 levels computed by Equation 2. The thin line represents the effect of organic C burial alone and the thick line also includes the effect of pyrite.

where Fb_{orgC} and Fw_{orgC} are the burial and weathering fluxes, respectively, of organic C, and Fb_{pyrite} and Fw_{pyrite} are the burial and weathering fluxes, respectively, of pyrite. The model was run starting at 65 Ma with a tie point to the present-day conditions. The cumulative effects of variation in the organic C and pyrite S accumulation rates on atmospheric O_2 concentrations are presented in Figure 2.

Applying the combined burial histories yields atmospheric O_2 concentrations for the early Paleocene that are 16% higher than present ($\sim 44 \times 10^{18}$ moles compared to 38×10^{18} moles today). Although these results are plausible, extension of this model to the Phanerozoic results in atmospheric O_2 concentrations that fluctuate considerably below and above current levels. Such results are inconsistent with geological evidence that suggests the mass of atmospheric O_2 has not changed by more than a factor of two from the present atmospheric level since the onset of the Cambrian (Berkner and Marshall, 1965; Watson et al., 1978; Jones and Chaloner, 1991). This inconsistency indicates that coupling between the C and S systems is not the sole mechanism maintaining relatively constant atmospheric O_2 concentrations on time scales of one to a few million years. Processes such as iron oxidation, phosphate cycling, and volcanism have been advanced (Schidlowski and Junge, 1981; Walker, 1986; Coleman et al., 1996; Van Cappellen and Ingall, 1996; Carpenter and Lohmann, 1997) and should be taken into account. Including these components in the models, however, does not change substantially the results obtained for this time interval (Petsch and Berner, 1998). Therefore, we conclude that although

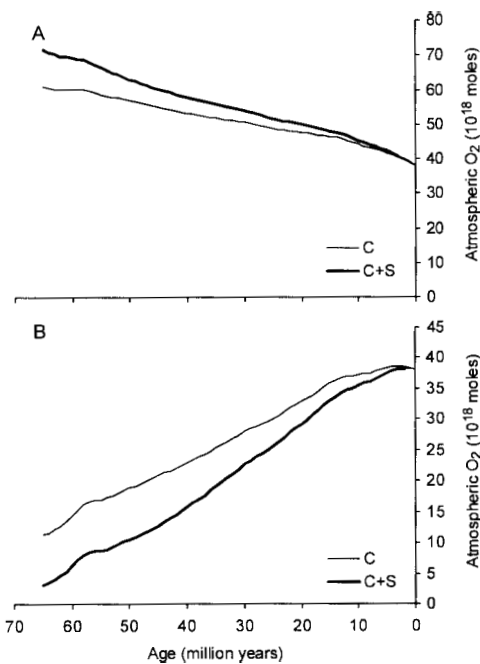


FIG. 3. Sensitivity of computed atmospheric O₂ concentrations to changes in (A) weathering rate (20% decrease) and (B) isotopic composition (1‰ decrease) of the weathering flux of both total C and S.

a reasonable understanding of the controls on the partial pressure of atmospheric O₂ exist, the current models do not account for the complexity of the natural system. Thus, an assessment of the assumptions and simplifications made in such models is required.

A major problem with models that calculate past O₂ levels based on isotope mass-balance considerations is the extreme sensitivity of the reservoirs of atmospheric O₂ to very small relative changes in the much larger masses of oxidized and reduced C and S. These models assign all isotope shifts to variations in burial, e.g. correlating a rise in the ³⁴S content of seawater to an increase in pyrite burial, and assume constant weathering fluxes. Testing the model sensitivity to changes in weathering flux indicates that small changes result in considerable variation in atmospheric O₂. For example, lowering weathering rates by ~20%, a reasonable value for the early Paleocene based on interpretation of the Sr-isotope record (Raymo et al., 1988; Hodell et al., 1990; Francois and Walker, 1992; Richter et al., 1992), leads to calculated atmospheric O₂ levels for

the Paleocene that are 90% greater than present-day values (Fig. 3A).

A more realistic approach would allow for temporal variations in continental weathering flux. Weathering rate has been calculated from the total continental land area and global temperature (Berner and Lasaga, 1989), and from Sr-isotope-based erosion rates (Raymo et al., 1988). However, weathering rate also depends on topography, vegetation, precipitation, rock type and age, and additional factors that are not accounted for. In addition, because the Sr-isotope record is affected by hydrothermal exchange and the isotopic composition of the rocks being eroded at any given time (Kump and Arthur, 1997), it cannot be interpreted uniquely as a weathering-rate proxy. Another problem is that the isotopic composition of the weathered material is likely to change regardless of the absolute weathering flux. For example, it has been argued that for Sr, most of the observed variation in isotopic composition in the Cenozoic results from changes in the mean river isotopic composition and not to global weathering rates (Kump and Arthur, 1997). Changes in the geographic distribution of the type of rocks being weathered may significantly alter the isotopic composition of rivers. Present-day ranges of C- and S-isotope composition in different drainage basins are quite large, with values ranging between -1 and -12‰ for C and 0 to 10‰ for S (Anderson and Arthur, 1983; Kaplan, 1983). Decreasing the isotopic composition of the weathered fluxes of C and S by 1‰ in the model resulted in computed Cenozoic O₂ concentrations that are >90% lower than present (Fig. 3B). This change is driven predominantly by the changes in the burial fluxes required to maintain mass balance. Until reliable quantitative proxies for weathering rates and silicate/carbonate/shale/evaporite weathering ratios are established, the reliability of models like the C-S-O isotope mass-balance model is limited.

Variations in the isotopic composition of pyrite and organic C buried in sediments are strongly influenced by changes in isotope fractionation. The fractionation of S isotopes during sedimentary pyrite formation can vary considerably depending on sulfate concentrations, rates of sulfate reduction, the degree of openness of the sediment to sulfate in the overlying seawater, and other factors (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979; Strauss, 1997). C-isotope fractionation is sensitive to atmospheric CO₂ and O₂ concentrations (Popp et al., 1989; Berner et al.,

2000) and to the carbonate-ion concentrations (Spero et al., 1997). C-isotope ratios recorded in biogenic carbonate also are complicated by physiological and/or environmental artifacts (Berger et al., 1978; Spero and Williams, 1988; Oppo and Fairbanks, 1989; Mackensen et al., 1993; McCorkle et al., 1995; Spero and Lea, 1996). Most models applied for investigating the long-term changes in organic C and pyrite burial assume that the isotope ratio differences between the oxidized and reduced materials deposited from the ocean ($\Delta^{13}\text{C}$, $\Delta^{34}\text{S}$) are constant (Berner and Raiswell, 1983; Lasaga et al., 1985; Francois and Gerard, 1986; Kump and Garrels, 1986; Walker, 1986; Berner, 1987). For C, this is based on the observation that the mean isotopic composition of C in carbonates ($\delta^{13}\text{C} = 0\text{‰}$) and organic matter ($\delta^{13}\text{C} = -23.7\text{‰}$) preserved in sedimentary rocks has not changed much for the past 3.5 b.y. (Schidlowski et al., 1983). For S, the assumption of constant isotopic fractionation is less robust, both for lack of a continuous record of the isotopic composition of pyrite, and for a large variability in the record that does exist (Strauss, 1997). Regardless of the mean values of $\Delta^{13}\text{C}$ and $\Delta^{34}\text{S}$, a large range of ratios is reported for most geological time intervals (Schidlowski et al., 1983; Claypool et al., 1980; Strauss, 1993).

Because there are indications that atmospheric pCO_2 (Arthur et al., 1985; Freeman and Hayes, 1992) and possibly marine sulfate concentrations (Canfield et al., 2000) have changed over geological time, it is quite likely that the isotopic fractionation of both organic C and pyrite have not remained constant. The effect of lowering the mean isotopic ratio of buried organic C and pyrite by 1‰ on calculated atmospheric O_2 is substantial, increasing to 45% above present values when the isotopic composition of reduced buried fraction is lowered by 1‰ (Fig. 4). Therefore, models of the C-S-O system must accommodate this variability by explicitly using the isotope-ratio difference between oxidized and reduced phases of the same age instead of applying a constant fractionation. Alternatively, a relationship between a reconstructed paleo- CO_2 , paleo- O_2 , paleo-sulfate, and paleo-carbonate ion concentrations and the fractionation factors should be applied. Such records are difficult to construct and are not yet widely available. Until variations in the fractionation factors through time are included in isotope mass-balance models, results obtained from these models with respect to atmospheric O_2 are questionable.

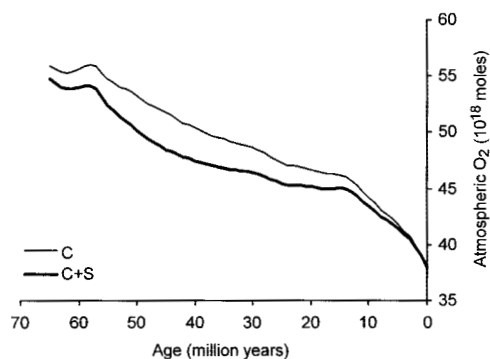


FIG. 4. Sensitivity of computed atmospheric O_2 concentrations to a 1‰ decrease in the isotopic composition of buried organic C and pyrite.

Another assumption that is embedded in all isotope mass-balance models is that the $\delta^{13}\text{C}$ of the dissolved inorganic C (DIC), as recorded in carbonate shells, is controlled only by the amount of organic C buried, its isotopic composition, and its physiological effects. It has been recognized recently that other sources of C can contribute to the DIC pool. For example, methane from gas-hydrate dissociation that is oxidized in the water column can have, at least for short time intervals, large effects on the isotopic composition of DIC (Dickens et al., 1995, 1997). The global effect of such sources on the isotopic composition recorded by marine organisms and used in the models has not been quantified. It is yet unclear how the signal of low $\delta^{13}\text{C}$ associated with methane sources can be separated from low $\delta^{13}\text{C}$ values that result from lower burial rates of organic matter. Interpretation of very low $\delta^{13}\text{C}$ ratios only in terms of organic C burial could result in a large underestimate of the amount of organic C buried, with considerable implications for atmospheric O_2 . These effects on the C-isotope record should be considered in future models.

Finally, feedback mechanisms are normally invoked in geochemical-cycle models to return to geologically reasonable conditions after a perturbation. Such feedback mechanisms for the C-S-O cycle include both rapid recycling of young sediments (Berner, 1987), O_2 -sensitive weathering and burial (Berner, 1987; Lasaga, 1989; Van Cappellen and Ingall, 1996), links between atmospheric O_2 and forest fires (Watson et al., 1978; Robinson, 1989), or nutrient availability (Van Cappellen and Ingall, 1996; Colman et al., 1996) and dependence

of the fractionation factors on the atmospheric O₂ content (Berner et al., 2000). In many cases, including such feedback in models involves an unavoidable positive feedback that results in even less plausible O₂ concentrations (Berner, 1987; Lasaga, 1989; Berner and Petsch, 1998). To date, no negative feedback involving atmospheric O₂ has been identified that is well behaved in an isotope-driven model, and there is still a need to find a way to accomplish O₂ stabilization in isotope mass-balance models.

Conclusions

In sum, the long and productive history of work that resulted in the current generation of models provide a fundamental framework for understanding the complexity of global exogenic cycles and their interaction and for reconstructing atmospheric O₂ fluctuations over geologic time. However, the simplifying assumptions required by these isotope mass-balance models appear to be insufficient for realistic simulation of processes that control atmospheric O₂ concentrations. This results in part from the sensitivity of the models to the small uncertainty that currently exists in the isotopic composition of buried C and S and to incomplete knowledge of other processes that control the feedbacks in the C-S-O cycles. As our understanding of the feedbacks that exist within these complex systems and the subtleties that control the processes involved increases, so will our ability to accurately simulate them. This should result in generation of additional data permitting better representation of this dynamic system and therefore, the production of a more reliable O₂ curve in the future.

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