only diopside and andesine, the algorithm is run again with an end-member set that includes all feldspars and clinoptyroxenes that are spectrally similar to andesine and diopside but excludes all other mineral spectra. This commonly improved the fit and reduces the possibility that a correct end-member is accidentally thrown out in the iterative process. The mineral end-member set is currently limited to 200 cm\(^{-1}\) and, as a result, the analysis was not performed between 200 and 400 cm\(^{-1}\).

Most of the minerals used are from P. R. Christensen et al., J. Geophys. Res., in press. For a complete list, see the supplemental data available at Science Online at www.sciencemag.org/feature/data/1047493.shl.

V. E. Hamilton, P. R. Christensen, J. Geophys. Res. 102, 25593 (1997).


The glass end-member used in the analysis is an rhyolite obsidian with a high silica (74% SiO\(_2\)) content (25).

Christensen et al. (3) performed a similar analysis on a surface spectrum from Terra Cimmeria to test the confidence of minor mineral percentages (<15%).

The spectra used were limited to surfaces warmer than 245 K, dust extinctions of <0.25, ice extinctions of <0.15, and RMS fits of measured to modeled spectra of <0.03. Because of the computationally extensive nature of temperature profile retrieval, dust and water-ice opacities were unavailable at the time of analysis. However, although opacity does not correlate perfectly with extinction, low extinctions will limit opacity for surfaces warmer than the atmosphere. Limiting the RMS error of the least-squares fit provides a quick method for filtering highly anomalous data due to errors such as lost bits, mislabeled calibration pairs, and compression errors. These criteria are less restrictive than those used to retrieve the spectral types because the fitting routine is more constrained with fewer end-members. TES emissivity spectra of warm surfaces under a variety of atmospheric and topographic conditions may be modeled with only dust, water-ice, and surface spectral shapes.

Isotope Fractionation and Atmospheric Oxygen: Implications for Phanerozoic O\(_2\) Evolution

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Models describing the evolution of the partial pressure of atmospheric oxygen over Phanerozoic time are constrained by the mass balances required between the inputs and outputs of carbon and sulfur to the oceans. This constraint has limited the applicability of proposed negative feedback mechanisms for maintaining levels of atmospheric O\(_2\) at biologically permissible levels. Here we describe a modeling approach that incorporates O\(_2\)-dependent carbon and sulfur isotope fractionation using data obtained from laboratory experiments on carbon-13 discrimination by vascular land plants and marine plankton. The model allows us to calculate a Phanerozoic O\(_2\) history that agrees with independent models and with biological and physical constraints and supports the hypothesis of a high atmospheric O\(_2\) content during the Carboniferous (300 million years ago), a time when insect gigantism was widespread.

A dominant feature of Earth’s atmosphere is the presence of abundant free oxygen (O\(_2\)), which signifies an active aerobic biosphere. Much attention has been directed toward understanding the rise of O\(_2\) during the Precambrian (1–5). Of equal interest, however, is the relative lack of...
variability in the partial pressure of atmospheric oxygen ($p_{O_2}$) during the Phanerozoic (the past 600 million years). Physical and biological constraints based on the fossil record of charcoal and forest fires limit extreme atmospheric composition variations to roughly 10 to 40% $O_2$ at constant $N_2$ mass (6, 7). This range is remarkably constant considering the potential variation in atmospheric $O_2$ production and consumption rates that may have occurred over geologic time. On hundred- to thousand-year scales, $O_2$ is controlled by global rates of photosynthesis and respiration. On longer time scales, the burial of organic matter (OM) and pyrite ($FeS_2$) in sediments and the oxidative weathering of these materials on the continents (plus oxidation of $C$ and $S$-containing gases liberated from them at depth) become the dominant contributions and the oxidative weathering of these materials on the continents (plus oxidation of $C$ and $S$-containing gases liberated from them at depth) become the dominant contributors to $O_2$ variability (8, 9). To maintain approximate constancy of $p_{O_2}$ through time, strong negative feedbacks must exist within global biogeochemical cycles. Proposed feedbacks include links between $p_{O_2}$ and forest fires (7, 10) and between the concentration of dissolved oxygen ($[O_2]_{aq}$) and nutrient availability in the oceans (11–13); however, none of these feedbacks have been formulated into a model that is consistent with constraints imposed by chemical and isotopic mass balances for carbon and sulfur.

The calculation of changes in $p_{O_2}$ on geologic time scales can be achieved if reasonably accurate estimates of burial rates and weathering rates of OM and pyrite can be developed (14). Models based on the abundance of organic carbon and pyrite sulfur in sedimentary rocks through time (15) provide one approach to the modeling of Phanerozoic $p_{O_2}$ variations. Another approach is the use of mathematical models driven by organic and sulfur isotope variations (9). In brief, the abundance of $^{13}C$ in seawater dissolved inorganic carbon reflects the partitioning of carbon between total global masses of carbonate and OM in sedimentary rocks; likewise, $^{34}S$ abundance in seawater $SO_4^{2-}$ reflects partitioning of sulfur between global sedimentary sulfate and sulfide. These features arise because during photosynthetic fixation of $CO_2$ there is a strong discrimination in favor of $^{13}C$; photosynthetic biomass is significantly depleted in $^{13}C$ relative to ambient $CO_2$ (17, 18). Analogously, bacterial sulfate reduction exhibits a strong discrimination in favor of $^{32}S$; biogenic sulfate minerals are significantly depleted in $^{34}S$ relative to ambient dissolved sulfate (19). Several studies (16, 20–22) have attempted to use these features of the carbon and sulfur isotope systems to resolve $p_{O_2}$ variations based on the isotopic records of marine carbonates and sulfates, which serve as proxies for oceanic values of $^{13}C/^{12}C$ and $^{34}S/^{32}S$. None has generated a Phanerozoic $O_2$ history that is consistent with physical and biological constraints or the rock abundance model. Indeed, the use of geologically and biologically reasonable feedbacks in isotope-driven $O_2$ models results in unavoidable positive feedbacks and catastrophic modeled $O_2$ histories (16, 23).

The possible dependence on $p_{O_2}$ of net carbon isotope discrimination during photosynthesis and biogenic sulfur production are two potentially important factors currently omitted from isotope-driven $O_2$ modeling studies, although theoretical considerations indicate that both are likely. Increased rates of plant photosynthesis under high ambient $O_2/CO_2$ are predicted because of the dual carboxylase-oxygenase function of Rubisco (24), potentially leading to a greater fraction of biomass being derived from $^{13}C$-depleted respired $CO_2$ (25). Sulfur cycling in marine sediments is related to $O_2$ availability, and more recycling results in a greater net biogenic sulfate $^{34}S$ depletion (19). Therefore, to address the sensitivity of these current uncertainties on Phanerozoic $O_2$ change, we report results from experiments determining the influence of elevated $p_{O_2}$ on the net $^{13}C$ discrimination of a herbaceous angiosperm ($Ranunculus repens$), a cycad ($Macrozamia communis$), and a marine diatom ($Phaeodactylum tricornutum$), all grown in the laboratory under a variety of $CO_2$ and $O_2$ concentrations. These data have been used, together with a best-guess estimate of sulfur isotope fractionation with $O_2$ content, to derive a new mass balance model of $O_2$ for calculating a revised Phanerozoic $O_2$ history.

Each species of vascular land plant was grown under similar environmental conditions (i.e., light intensity, temperature, humidity, $p_{CO_2}$, and nutrient supply) but contrasting atmospheric $O_2/CO_2$ ratios (21 and 35% $O_2$ with 330 parts per million (ppm) $CO_2$) in controlled environment chambers described previously (26, 27). The upper $p_{O_2}$ value was taken to represent a previous upper estimate of the past 300 million years (15).

Table 1 shows the C isotopic composition, expressed as per mil (%) deviation from the Pee Dee Belemnitite standard, of $CO_2$ in growth chamber air ($\delta_{cham}$) and of the plant samples ($\delta_{plant}$) grown at ambient and elevated $O_2$ concentrations and the net carbon isotope discrimination $\Delta_C$ ($[O_2]_{aq}$, $[CO_2]_{aq}$, but in equilibrium with 21% O2) (21 and 32.5%), whereas $[CO_2]_{aq}$ varied from 3.7 to 20.1 $\mu$mol kg$^{-1}$. Previous work has demonstrated that carbon isotopic fractionation in marine microalgae varies as a function of both $[CO_2]_{aq}$ and algal growth rate (28, 29). The isotopic fractionation for $P. tricornutum$ grown under similar ranges of growth rate (µ) and $[CO_2]_{aq}$ but in equilibrium with 21% $O_2$ (30), were compared with the results of the present study in order to determine the effect of varying $O_2/CO_2$ on isotope fractionation corrected for fractionation due to varying $CO_2$ (Table 2) (31).

The results of the experiments can be applied to calculate the partial pressure of atmospheric $O_2$ during the Phanerozoic. The $O_2$ curve is based on estimates of $O_2$ burial rates and photosynthesis rates of the fossil record of charcoal and forest fires. The resulting $O_2$ curve shows a gradual increase from the Proterozoic to the Phanerozoic, with a peak during the Carboniferous period. The $O_2$ curve is then used to calculate the apparent $O_2$ values for the Phanerozoic, which are then compared with the calculated $O_2$ values.
plied directly to an isotope-driven O₂ mass balance model by calculating the relation between Δₐ and O₂ as

\[ \Delta_c = \delta^{13}C_{\text{gas}} - \delta^{13}C_{\text{plant}} = (\Delta_c)_0 + J(O_2/38) - 1 \] (1)

where Δₐ is isotope fractionation (discrimination) for vascular land plant or algal carbon (in ‰); (Δₐ)_0 = 25‰ for the present level of O₂ but for an average higher-than-atmospheric O₂ content (Equation 1 closely mirrors that expected from empirical coefficients used for curve fitting.

33‰); (Δₐ)_0 = 25‰ for the present level of O₂ but for an average higher-than-atmospheric O₂ content (Equation 1 closely mirrors that expected from empirical coefficients used for curve fitting. For vascular land plant or algal carbon (in ‰); (Δₐ)_0 = 25‰ for the present level of O₂ but for an average higher-than-atmospheric O₂ content (Equation 1 closely mirrors that expected from empirical coefficients used for curve fitting.

Equation 1 closely mirrors that expected from theoretical modeling of photosynthesis and carbon isotope fractionation to the same increase in atmospheric O₂ content (34).

Because of the complex effects of oxidation of sulfide and multiple fractionation during diagenetic recycling (19), no straightforward experiments on the effects of pO₂ on sulfur isotope discrimination during bacterial sulfate discrimination are possible. As an initial approximation, we assume a simple linear proportionality

\[ \Delta_s = \delta^{34}S_{\text{sulfate}} - \delta^{34}S_{\text{plant}} = (\Delta_s)_0(O_2/38) \] (2)

where Δₕ is fractionation for sulfur (in ‰) and (Δₕ)_0 is the average fractionation for the present level of O₂ (35‰).

The utility of a model that involves C and S isotopic fractionation depends on how O₂ variations are calculated from carbonate and sulfate isotopic records. Changes with time toward 13C-enriched carbonates indicate an increase in the total mass of OM in sediments and sedimentary rocks, either through increased OM burial or decreased OM weathering. Increased OM burial (or decreased weathering) rates correspond to elevated O₂ production and increasing atmospheric pO₂. However, at constant carbon and sulfur isotope discrimination during biomass production, the variations in atmospheric O₂ calculated from observed variations in the δ¹³C of carbonate and δ³⁴S of sulfate are too large to be realistic, resulting even in highly negative values for pO₂. By allowing photosynthetic carbon and sulfur isotope discrimination to vary with atmospheric O₂ changes in carbonate ¹³C and/or sulfate ³⁴S content result in damped O₂ variations as compared with O₂ variations derived without the O₂ functionality.

The isotope model used in the present study is that of Garrels and Lerman (9), but with O₂-dependent isotope discrimination and the use of both the carbon and sulfur isotopic record to calculate rates of weathering and burial of organic carbon and pyrite sulfur. Also included is rapid recycling analogous to what was done in modeling rock abundance data (15). Rapid recycling is a means of incorporating into a model the observation that younger rocks are more likely to be exposed and weathered on the continents than are older rocks. The change in atmospheric oxygen mass (O₃) with time was calculated from the expression

\[ \frac{dO_2}{dt} = F_{dp} - F_{w} + 15/8(F_{bp} - F_{wp}) \] (3)

where F refers to fluxes in mass per unit of time, the subscripts b and w refer to burial and weathering (including oxidation of reduced gases derived from deep processes), and the subscripts g and p refer to organic carbon and pyrite sulfur, respectively.

For carbon isotope fractionation, the values of J in Eq. 1 were varied to obtain an O₂ history bounded between 10 and 40% O₂, which at the same time fitted our experimental plant and plankton growth results (Fig. 1). A curve for J = 2.5 is fit to the experimental data, although a somewhat higher value of J is more likely because cycads [showing the highest Δ(Δₐ)] represent a primitive life form that is more representative of the burial of ancient terrestrial OM, as emphasized in the present study. Extensive sensitivity analysis showed that the variation of J from 0 to 5 results in a lowering of the peak value of O₂ at 280 million years before the present (My B.P.) (Fig. 2) by about 25% and that values of O₂ for 450 to 350 My B.P. are affected more by the inclusion of O₂ dependence in sulfur isotope fractionation than by its inclusion in carbon isotope fractionation.

The modeling results for the Phanerozoic history of atmospheric O₂ based on Eqs. 1 through 3 and the isotopic composition of sedimentary carbonates (35, 36) and sulfates (16, 37, 38) as proxies for seawater isotopic composition are shown in Fig. 2 and are compared with the results of the sediment abundance model of Berner and Canfield (15). There is surprisingly good agreement between the results of these two totally independent approaches.

The most obvious feature in Fig. 2 is the large pO₂ maximum centered around 300 million years ago, thought to be a response to the evolution of large vascular plants on the continents (8, 15, 16). Production of new sources of biomass (such as lignin) that were resistant to the then available pathways of OM degradation likely led to enhanced OM burial in swamps and in marine sediments after transport to the oceans by rivers. This explanation is consistent both with the abundance of coal deposits and OM in general that were preserved at this time (15, 16) and with the most severe enrichment in oceanic ¹³C content measured during the Phanerozoic (16, 36).

It has been suggested that variations in globally averaged Δₐ values between sedimentary carbonate and OM correspond largely to variations in atmospheric CO₂ content (33). This relation certainly holds for specific classes of organic compounds that show a strong relation.
between $^{13}$C depletion and ambient $p$CO$_2$ values (39–41). However, $\Delta_4$ values for the Permo-Carboniferous are larger than values immediately before and after this time span, a feature difficult to explain in terms of greatly increased $p$CO$_2$. Indeed, Permo-Carboniferous $CO_2$ concentration is likely to have been decid-

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