The Rise of Oxygen over the Past 205 Million Years and the Evolution of Large Placental Mammals

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On the basis of a carbon isotopic record of both marine carbonates and organic matter from the Triassic-Jurassic boundary to the present, we modeled oxygen concentrations over the past 205 million years. Our analysis indicates that atmospheric oxygen approximately doubled over this period, with relatively rapid increases in the early Jurassic and the Eocene. We suggest that the overall increase in oxygen, mediated by the formation of passive continental margins along the Atlantic Ocean during the opening phase of the current Wilson cycle, was a critical factor in the evolution, radiation, and subsequent increase in average size of placental mammals.

It has long been recognized that atmospheric oxygen levels play a key role in the evolution of metazoans (1), yet our understanding of precisely how oxygen concentrations influence specific animal evolutionary traits is limited. Although many metazoans are capable of acclimating to hypoxic conditions by lowering metabolic rates and/or operating the tricarboxylic acid cycle partially in reverse (2), these physiological modifications cannot be sustained indefinitely. Controls of atmospheric oxygen by the carbon and sulfur cycles (3, 4) have led to models based on analyses of the isotopic composition of carbonates and sulfur (3, 5) or on the relative abundance of different rock types (6), which suggest that atmospheric oxygen concentrations varied throughout the Phanerozoic, with a maximum ~300 million years ago (Ma), a minimum ~200 Ma, and an overall rise from ~200 Ma to the present (5, 6). However, the range and underlying causes of these variations in oxygen are not well understood. Here, we provide an isotopic record for organic carbon, which we analyzed in conjunction with isotopic records for carbonates and sulfates for the past 205 million years (My). Our analysis suggests that ambient oxygen levels approximately doubled from ~10% by volume (76 Torr) to 21% (160 Torr) over this period. Concurrent examination of the fossil record suggests that this change in oxygen tension was potentially a key factor leading to the evolution of large placental mammals in the Cenozoic.

On time scales of millions of years, the oxidation state of the atmosphere and surface ocean is determined by the balance of electron equivalents sequestered in the lithosphere relative to that consumed primarily in reactions at Earth's surface (3, 5). In principle, changes in the net electron balance through time can be inferred from the isotopic composition of carbon (carbonates and/or organic matter) and sulfur (sulfate and/or pyrite) sinks; the simultaneous use of both isotopic signatures best constrains the analysis (7, 8).

We determined the isotopic composition of both carbonates (9, 10) and organic matter (this study) from a series of marine sediment cores from the Lower Jurassic through the Cenozoic (Fig. 1). These carbon isotope data are coeval, high-resolution (225,000-year average sampling interval) records from both carbonates and organic matter that cover the past 205 My, providing full constraint on the carbon sinks. Correlations to shorter duration records of transient $\delta^{13}C$ excursions and 3- to 20-My-long $\delta^{13}C$ events establish the global nature of our data set (10); here, we focus instead on the 100-My-scale trends. The isotopic data for carbonates reveal a long-term increase in $\delta^{13}C_{carb}$ of 1.1 per mil (‰) from the beginning of the record to ~15 Ma, followed by a sharp reversal amounting to about 2.5‰. Statistical analysis of the regression of the inferred long-term increase (205 to 15 Ma) indicates that the slope is significantly different from zero ($P < 0.05$). Over the same time period, buried organic matter ($\delta^{13}C_{org}$) became depleted in the light isotope by ~5‰. Statistical analysis of this record also reveals a long-term secular trend. The isotopic records of both carbonates and organic carbon require increases in both the extraction of ^{12}C from, and supply of ^{13}C to, the mobile carbon reservoirs through (i) increase in net burial of organic carbon in the

lithosphere, with an implied increase in net oxidation of the atmosphere, and (ii) increase in $\delta^{13}C$ signature of carbon introduced to the mobile carbon reservoir from volcanic outgassing and weathering of continental rocks. Sensitivity tests establish that neither factor alone can account for the measured $\delta^{13}C$ changes (10, 11). The long-term depletion of CO_2 associated with greater organic carbon burial may also have been a key factor that selected for the β carboxylation in marine diatoms (12) and C_4 photosynthetic pathways in terrestrial plants (13, 14). Indeed, the evolution of these alternative photosynthetic pathways appears to have led to an increase in $\delta^{13}C_{org}$ as ^{13}C-enriched organic matter was buried over the latter half of the Cenozoic and ultimately contributed to the $\delta^{13}C_{carb}$ decrease that began in the mid-Miocene (10).
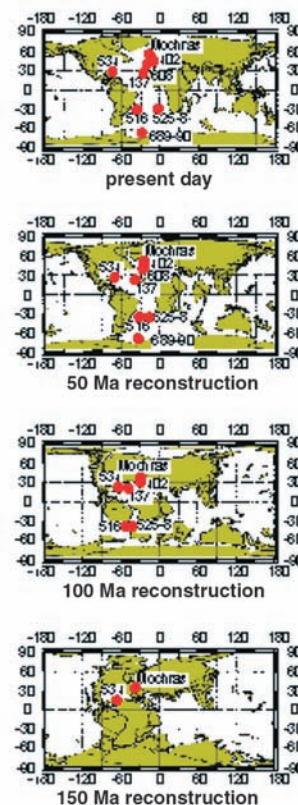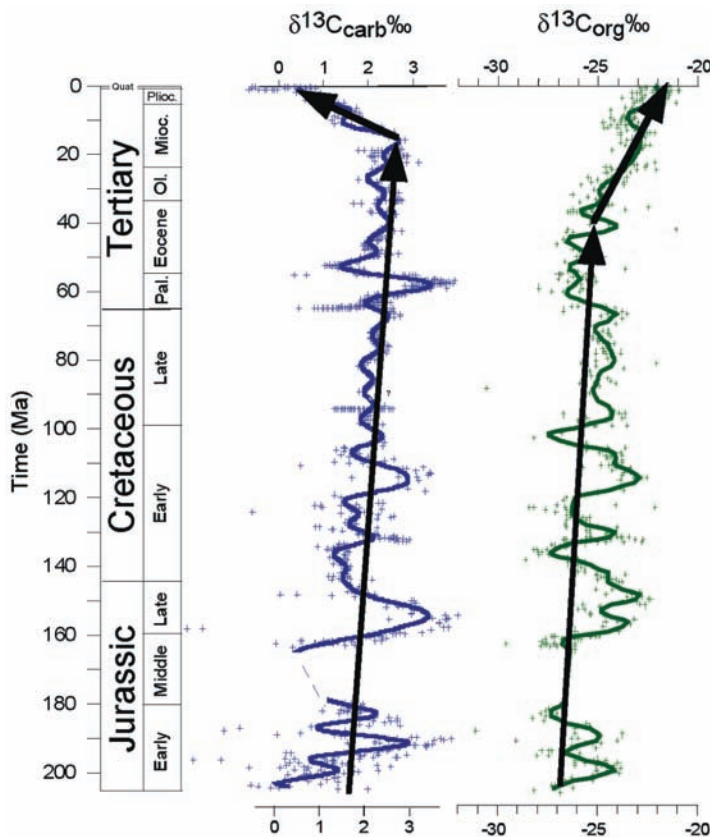
Using three isotopic signatures ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and $\delta^{34}S_{sulf}$), we reconstructed the history of O_2 over the past 205 My by hindcasting from the present value of 21% using the model of Berner (11) (Fig. 2). The results suggest that atmospheric O_2 was at a nadir in the Triassic and increased throughout the Mesozoic to approximately 18% of the total atmospheric volume. There appears to have been a relatively large spike in O_2 in the Eocene, when levels may have reached as high as 23%, followed by a small decline over the past 10 My. These results are qualitatively similar to those obtained by Huey and Ward (15), with the important difference that our results suggest that the rise in O_2 to contemporary levels was obtained by 50 Ma.

Net oxidation of Earth's surface reservoirs requires a net burial of organic matter and/or pyrite (5). Over the past 205 My, the burial efficiency of organic matter in marine sediments was greatly enhanced by the evolution of relatively large, nonmotile phytoplankton taxa, especially coccolithophorids and diatoms (16). The radiation and expansion of the latter phytoplankton taxa occurred concurrently with the fragmentation of Pangea, marking the initiation of the current Wilson cycle, and the opening of the Atlantic Ocean basin. The formation of extensive passive continental margins in the circum-Atlantic region has provided a long-term storehouse for organic matter since the early Mesozoic (10). Indeed, most of the world's known petroleum reserves originated from the burial of biomass produced by eukaryotic phytoplankton in the Mesozoic and early Cenozoic on continental margins and shallow seas (17). The rise in O_2 in the Eocene and Oligocene corresponds to a major radiation of diatoms (16), which are responsible for a large fraction of organic carbon buried on continental margins (18). The net oxidation of Earth's atmosphere, driven largely by the burial of organic matter in marine sediments along continental margins supplemented by burial

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Fig. 1. Composite bulk sediment $\delta^{13}C_{carb}$ (9, 10) and $\delta^{13}C_{org}$ (this study) records for the Jurassic through the Cenozoic. Samples are primarily from open ocean Atlantic Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) boreholes; the epicontinental Mochras Borehole (Wales) was used for the Lower Jurassic because there is little to no pre–Middle Jurassic ocean floor left. Site locations are shown in a series of paleogeographic reconstructions at 50 My intervals (www.odsn.de/odsn/index.html). We used least-squares regression (95% confidence interval) to determine the long-term trends in $\delta^{13}C$, where x = age and y = $\delta^{13}C$: (i) $\Delta\delta^{13}C_{carb}$ = −2.52‰ for 0 to 15 Ma, y = (0.168 ± 0.024)x + (0.049 ± 0.17), R = 0.89; (ii) $\Delta\delta^{13}C_{carb}$ = 1.1‰ for 16 to 205 Ma, y = (−0.006 ± 0.001)x + (2.64 ± 0.12), R = 0.38; (iii) $\Delta\delta^{13}C_{org}$ = 3.2‰ for 0 to 40 Ma, y = (−0.08 ± 0.01)x + (−22.1 ± 0.02), R = 0.78; (iv) $\Delta\delta^{13}C_{org}$ = 0.8‰ for 40 to 205 Ma, y = (−0.005 ± 0.003)x + (−24.8 ± 0.38), R = 0.17. We note that including the Lower Jurassic section (Mochras borehole data) in the linear regression produces a lower rate of increase in $\delta^{13}C$, which yields a more conservative estimate of the magnitude of the long-term increase. We used a singular spectrum analysis to highlight the long-term $\delta^{13}C$ variations; $\delta^{13}C$ data were linearly interpolated (100,000-year sampling interval) and analyzed using the SSA-MTM Toolkit from www.atmos.ucla.edu/tcd/ssa (30). Singular spectrum analysis (SSA) was performed using a 205-point (~20 My) window with the Broomhead and King method for constructing the covariance matrix; the six highest variance components were added together to reconstruct the long-term $\delta^{13}C$ variations.

on land (6), appears to have had a profound influence on the evolutionary trajectories of metazoans.

Whereas the relatively rapid decline in oxygen at the end-Permian and early Triassic is suggested to have been a major factor contributing to the extinction of terrestrial animals (mostly reptiles) at this time (15), the rise of oxygen over the ensuing 150 My almost certainly contributed to evolution of large animals. Animals with relatively high oxygen demands, including theropod dinosaurs (the group that includes living birds) and small mammals (19, 20), evolved by the Late Triassic. Avian and mammalian metabolic demands are three to six times as high per unit biomass as those of reptiles (21). Although the reproductive strategies of the earliest mammals are not known with certainty, both the fossil record and molecular divergence indicate that superordinal diversification of placental mammals occurred between 65 and 100 Ma (20, 22, 23). This radiation corresponds to a period of relatively high and stable oxygen levels in the atmosphere (Fig. 2). Although placental evolution is not unique to mammals (24), this reproductive strategy, which can facilitate geographic expansion of a species, requires relatively high ambient oxy-
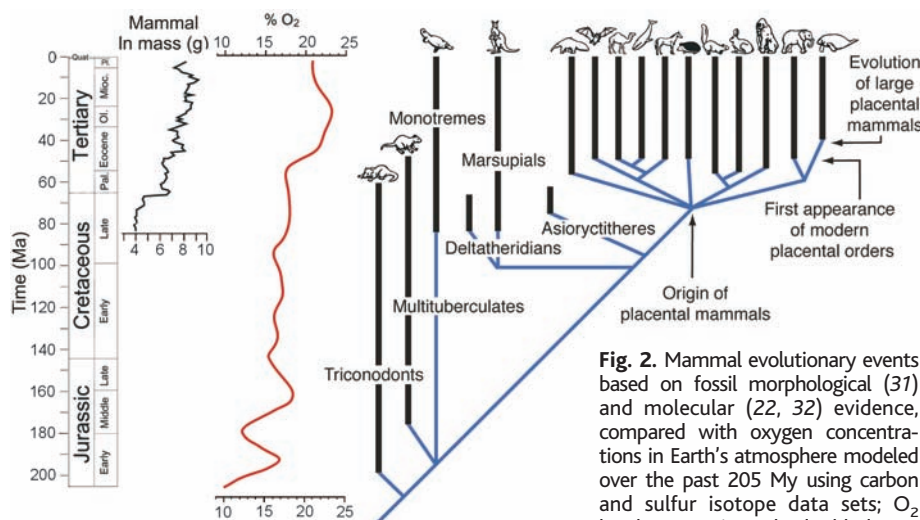
Fig. 2. Mammal evolutionary events based on fossil morphological (31) and molecular (22, 32) evidence, compared with oxygen concentrations in Earth's atmosphere modeled over the past 205 My using carbon and sulfur isotope data sets; O_2 levels approximately doubled over this time from 10% to 21%, punctuated by rapid increases in the Early Jurassic and in the Eocene. Changes in average mammalian body mass is taken from (27). Vertical black bars represent known fossil ranges, blue lines represent inferred phylogenetic branching. Only some of the ordinal-level placental mammals are shown.

gen concentrations (25, 26). In the placenta, maternal arterial blood, with oxygen levels near ambient alveolar pressure, mixes with placental venous blood in a sinuslike vascular structure. Fetal umbilical arterial (really venous) blood arrives in a capillary network in the maternal sinus where oxygen diffuses into the fetal blood. The nature of this exchanger requires the mammalian fetus to live at a very low arterial oxygen pressure. Al-

though at low oxygen, placental hemoglobin binding affinity for O_2 is modified by pH (i.e., the Bohr effect), with exceptions, few extant mammals reproduce above elevations of ~4500 m, corresponding to atmospheric oxygen levels in the Early Jurassic (15).

Whereas a bolide impact at the Cretaceous-Tertiary (K-T) boundary and the ensuing extinction of dinosaurs provided ecological opportunity for the radiation of placental mammals, the rise of oxygen in the Eocene corresponds to a large increase in average mammalian body size (27). The density of capillaries per unit muscle scales to the 0.87 power of size in mammals (28); hence, larger animals require high ambient O_2 levels to obtain maximal metabolic rates. Comprehensive study of body mass of nearly 2000 fossil mammals in the North American record indicates a steady expansion in size range throughout the Cenozoic, tracked by mean body size due to the static lower limit of size (27). Data show a rapid increase from small to medium-sized mammals in the first few million years after the K-T event (Fig. 2). This size contrast is blurred slightly with the recent discovery of larger Cretaceous mammals (29), but this trend does not appear to be driven by oxygen. A second upward surge in mean body mass is recorded for the early through middle Eocene (50 to 40 Ma) (27), followed by further but less dramatic size increases through the Miocene. This trend tracks a change in oxygen. The early to middle Eocene, an interval characterized by the highest global mean annual temperatures and the broadest latitudinal span of warm subtropical to temperate faunas and floras for the Cenozoic, was also a time of high morphological disparity in North American placental mammals. One might infer that this indicates a proliferation of ecological roles in the North American mammalian fauna. Notably, many of the living placental orders appear in the early Eocene, and artiodactyls, the dominant large terrestrial herbivores today, underwent a massive radiation in the mid-Eocene (27). Data from other continents are more limited, but there is reason to argue that North America serves as a model for broader patterns, at least in the northern hemisphere. The substantially improving records in Europe and Asia, especially, will provide an interesting test of the pattern.

The data presented here provide evidence of a secular increase in atmospheric oxygen over the past 205 My that broadly corresponds with three main aspects of vertebrate evolution, namely endothermy, placentation, and size. Particularly notable are high stable O_2 levels during the time of placental mammal origins and diversification and a close correspondence between marked increases in both atmospheric oxygen levels and mammalian body size during the early to middle Eocene. Although increases in mammalian body size,

morphological disparity, and inferred ecological heterogeneity during this interval may have been influenced as well by other environmental factors such as warm global temperatures and the spread of tropical and subtropical habitats, the correlation between evolutionary changes in mammalian body size and increased atmospheric O_2 has a physiological basis related to placental mammal reproduction. The changes in oxygen appear to have been driven by tectonics and increased burial efficiency of organic matter on continental margins.

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Preindustrial to Modern Interdecadal Variability in Coral Reef pH

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The oceans are becoming more acidic due to absorption of anthropogenic carbon dioxide from the atmosphere. The impact of ocean acidification on marine ecosystems is unclear, but it will likely depend on species adaptability and the rate of change of seawater pH relative to its natural variability. To constrain the natural variability in reef-water pH, we measured boron isotopic compositions in a ~300-year-old massive *Porites* coral from the southwestern Pacific. Large variations in pH are found over ~50-year cycles that covary with the Interdecadal Pacific Oscillation of ocean-atmosphere anomalies, suggesting that natural pH cycles can modulate the impact of ocean acidification on coral reef ecosystems.

Since the beginning of the industrial revolution, the burning of fossil fuels has increased the CO_2 content of the atmosphere from ~280 to more than 370 parts per million per volume (ppmv), a level unprecedented in the last 420,000 years (1). To date, a large part of anthropogenic CO_2 emissions has been absorbed by the oceans (2), which have become

more acidic, thus reducing their capacity to continue to absorb CO_2. Estimates of global oceanic pH trends to the year 2000 indicate that the oceans have already acidified by 0.1 pH units relative to preindustrial times (3, 4). Geochemical models forecast an exponential decrease of nearly 0.8 pH units by 2300 (4), a scenario for which there is no obvious