Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment

Jid J. Des Marais* Harald Strauss†, Roger E. Summons‡ & J. M. Hayes§

The oxidation of the Earth's crust and the increase in atmospheric oxygen early in Earth history have been linked to the accumulation of reduced carbon in sedimentary rocks. Trends in the carbon isotope composition of sedimentary organic carbon and carbonate show that during the Proterozoic aeon (2.5-0.54 Gyr ago) the organic carbon reservoir grew in size, relative to the carbonate reservoir. This increase, and the concomitant release of oxidizing power in the environment, occurred mostly during phases of global shifting and orogeny.

Isotope effects associated with the enzymatic fixation of carbon and with mass transport of CO₂ are responsible for most of δ₁₃C. The overall fractionation accompanying photosynthesis can be attenuated by limitations in the supply of CO₂ (refs 4, 5). The amounts of carbonate and organic carbon buried depend on global rates of erosion and sedimentation⁸ and on recycling processes at the sea floor⁷. The operation of the carbon cycle can be monitored through an isotopic mass balance

\[ \delta_{\text{in}} = f_{\text{carb}} \delta_{\text{carb}} + f_{\text{org}} \delta_{\text{org}} \]

where \( \delta_{\text{in}} \) represents the isotopic composition of carbon entering the global surface environment comprised of the atmosphere, hydrosphere and biosphere, and the right side of the equation represents the weighted-average isotopic composition of carbon being buried in sediments, \( f_{\text{carb}} \) and \( f_{\text{org}} \) being the fractions of carbon buried in organic and inorganic form (\( f_{\text{carb}} = 1 - f_{\text{org}} \)).

Carbon enters the surface environment by weathering, volcanism and rock metamorphism and, over timescales longer than 100 Myr, \( \delta_{\text{in}} = -5\%_{\circ} \), the average value for crustal carbon⁸. Where values of sedimentary \( \delta_{\text{carb}} \) and \( \delta_{\text{org}} \) can be measured, it is thus possible to determine \( f_{\text{org}} \) for ancient carbon cycles (all δ values in \%_{\circ}):

\[ f_{\text{org}} = (\delta_{\text{in}} - \delta_{\text{carb}}) / (\delta_{\text{in}} - \delta_{\text{carb}}) = (\delta_{\text{carb}} + 5) / \Delta C \]

The carbon isotopic record

Strauss et al.⁹ summarized 731 isotope analyses (Fig. 1) of total organic carbon in Proterozoic sediments. Except for some new low values for rocks older than 2.6 Gyr, the \( \delta^{13}C \) values from earlier work and the new study do not differ substantially. Lines tracing the average values of \( \delta_{\text{carb}} \) and \( \delta_{\text{org}} \) in Fig. 1 are roughly parallel, creating the impression that \( \Delta C \) was invariant throughout the Proterozoic. Some authors have therefore emphasized aspects of uniformity in the Proterozoic carbon cycle and its isotopic record⁹-¹². Episodic \( \delta^{13}C \) variations have, however, been found¹³,¹⁴.

The \( \delta_{\text{org}} \) values in Fig. 1 reflect not only biological and palaeoenvironmental effects, but also postdepositional thermal degradation of the kerogen, which results in preferential loss of \( ^{12}C \)-depleted, hydrogen-rich products. As a result, changes in the H/C ratio and \( \delta_{\text{org}} \) of residual kerogens are correlated¹⁵. As would be expected, older kerogens are more likely to be thermally altered and have lower H/C ratios. Because \( \delta_{\text{org}} \) has been affected, the true magnitudes of \( \Delta C \) and \( f_{\text{org}} \) during the Proterozoic have been obscured.

To minimize isotopic shifts due to extreme thermal alteration or to analytical artefacts, Fig. 2 includes isotopic...
compositions only for kerogens with ash contents less than 25% and H/C values greater than 0.1. Furthermore, the base view of the Proterozoic isotopic record can be obtained by reconstructing the values of δorg before alteration. The characteristic trend relating changes in δorg to values of H/C has been examined in detail. Relationships between changes in H/C and changes in δorg are not significantly dependent on kerogen type or host lithology. The curve which relates the most probable values for this shift (Δδorg) to H/C values (see Fig. 5 of ref. 17) has the form
\[ \Delta \delta_{\text{org}} = 4.05 - 3.05r + 0.785/r + 0.0165/r^2 - 8.79 \times 10^{-5}r^2 \]  
where Δδorg is δorg (as analysed, H/C = r) - δorg (initial, H/C = 1.5). When initial δ values are reconstructed, the isotope record takes the form shown in Fig. 2. Because δcarb is relatively constant, the changes in δ are almost entirely linked to changes in δorg.

**Burial of organic carbon**

When the data of Fig. 2 are used to calculate values of forg for 100-Myr increments between 2.5 and 0.6 Gyr, results indicate a long-term increase (Fig. 3). Complementary changes in δcarb and δorg (Fig. 2) support this trend. This increase was not monotonic but episodic; high values were attained between 2.1 and 1.8 Gyr and between 1.1 and 0.7 Gyr. These changes will have affected the total crustal inventory of organic carbon and, in turn, other aspects of the surface redox environment.

Computed values of forg indicate the average degree of reduction of carbon being stored in accumulating sediments. At the extremes, forg = 0 corresponds to no reduction (all carbon being buried as carbonate) and forg = 1 corresponds to complete reduction (all carbon being buried as organic). This output of carbon from the surface environment is balanced by inputs contributed by erosion and thermal activity. These carbon inputs will be least partly reduced, because they include organic carbon remobilized during destruction of older sediments. If the average degree of reduction of the output differs from that of the input, there must be a net transfer of oxidizing or reducing power to the carbon cycle to the cycle of some other element, possibly iron, sulphur or oxygen.

To reconstruct changes in the crustal inventory of organic carbon during the Proterozoic, we have begun by postulating that the forg value observed at 2.6 Gyr accurately reflects the burial before that time. If so, the crust then contained 500.9 x 10^15 moles of organic carbon (= forg x Corg, where Corg is the total number of moles of carbon in the crust). During the next 100 Myr, the time interval between 2.6 and 2.5 Gyr, a fraction of the crustal inventory of carbon will have been recycled, passing through the surface reaction chamber and being reburied with the forg value characteristic of that era. Quantitatively, variations in the organic carbon reservoir can then be calculated as follows
\[ M_{t} = M_{0} e^{-\tau} + C_{org}(1 - e^{-\tau})f_{org} \]
where M is the quantity of organic carbon in the crust. Present age of sediments deposited at the beginning of the increment (t approaches 0 as time advances), τ is the duration of the increment, forg is based on δ values observed during the time interval t to μ + τ, and k is the first-order decay constant characteristic of the recycling of the sedimentary inventory. For sediment half life of 400 Myr (ref. 19), k = (ln 2)/1.733 Gyr. The first term on the right side of equation (4) represents survival of crustal organic carbon from one increment to the next, the second represents effects of recycling. Simple application of this equation yields the results summarized in Fig. 4.

Uncertainties in M can be discussed mainly in terms of k parameter. First, k is certainly time-variant. Tectonics strongly influence rates at which crustal material is recycled. Rates of erosion and, thus, rates of burial of sediments and organic carbon may be variable over the 2-Gyr interval, and the values used are based on the most recent geological time scale. The use of k = 1.733 Gyr for the entire Proterozoic interval is an overestimation, and the size of the organic carbon reservoir that results from this assumption is too large. However, the results presented in this paper suggest that a broad range of k values will not change the general conclusions reached.

**Episodic relief**

Assuming a hypothetical Proterozoic range of 1.05 x 10^15 to 1.3 x 10^15 m to 1.3 x 10^15 m, our model essentially reduces the t values for the sedimentary sequences for 0.1 to 0.3 Gyr. The lower value of 0.1 Gyr can be thought of as an average time for major episodes of enhanced global tectonic activity and sedimentation during the Proterozoic. The higher value of 0.3 Gyr represents an upper limit on the time scale of these mobile episodes. A discussion of this interval is provided in the Discussion section.
bris, are highest when high mountain terrain is extensive when continental plates experience rifting. Rainfall and erosion are also important and are variable. For the late Proterozoic, the isotopic records of strontium and neodymium have shown significant variations in rates of erosion and organic burial. To examine the sensitivity of our estimates of $M$ to changes in $k$, we have also considered sediment half lives of 0.5 Gyr (Fig. 4).

A second uncertainty related to $k$ concerns the postulate $k_{S} = k$ (value 2.6 Gyr ago) can be estimated from $f_{org}$ value of 0.016 at that time. This estimate seems to at least be consistent with organic sedimentation during the interval 2.7 Gyr. We have not used the entire isotopic record before 2.5 Gyr to estimate variations in $M$ from the beginning of the rock record, because the earlier record is incomplete.

Values of $\delta_{carb}$ have been affected by some extent by postdepositional alteration of carbonates, yet no corrections have been made here. Because of their greater age, early Proterozoic carbonates might be more affected than late Proterozoic carbonates. Wiser et al. obtained a corrected $\delta_{carb}$ value of $0 \pm 1.5\%$ for early Proterozoic marine carbonate, which is in reasonable agreement with the corresponding average $\delta_{carb}$ values in Fig. 3. Postdepositional alteration of carbonates has not significantly compromised the accuracy of the calculations of $M$.

**Necrotic release of oxidizing power**

Using a half life of 0.4 Gyr we find that $M$ increased in the Proterozoic mostly in two increments as follows: from $0.7 \times 10^{21}$ mol between 2.5 and 1.8 Gyr and from $1.05 \times 10^{21}$ mol between 1.3 and 0.7 Gyr. It is instructive to note both the causes of this trend in $M$ and also its consequences for crustal and atmospheric abundances of oxidized species such as Fe$^{3+}$, SO$_{4}^{2-}$ and O$_{2}$. Rates of organic burial and not only on the intensity of production but also on the preservation of organic matter as it is delivered to the oceans and awaits burial. Productivity depends on the efficiency and environmental tolerance of photoautotrophs and the delivery of nutrients to the photic zone$^{31}$. Organic preservation depends on the versatility and aggressiveness of heterotrophs, on the availability of oxidants in the water column and sediments, and on the rate of sedimentation of inorganic debris, rapid burial assisting preservation$^{32,33}$. Thus both productivity and preservation are affected by both biological and geological processes. Although the evolutionary development of oxygenic photosynthesis must have enhanced productivity, it allowed autotrophs to make use of an abundant and ubiquitous electron donor, this evolutionary step occurred during the Archean$^{34-37}$, at least 600 Myr before the time when, according to geochemical evidence, O$_{2}$ accumulated in the atmosphere. Thus the pulses of accelerated organic burial revealed by the Proterozoic record are expected to correlate with times intervals during which tectonically enhanced rates of weathering and erosion delivered more nutrients$^{38}$ and promoted rapid burial.

Most of the O$_{2}$ generated from the photosynthetic production of organic matter is consumed by respiratory processes. The small amount of organic matter that escapes oxidation by being buried (today, $\sim 0.2-0.3\%$ of primary production$^{39}$) allows an equivalent amount of O$_{2}$ to remain in the surface environment$^{1}$. Burial of organic carbon thus releases O$_{2}$, erosion commonly exposes organic carbon, sulphide, and Fe$^{2+}$ which consume O$_{2}$ (refs 2, 3, 30). It is instructive to explore how this balance was affected by tectonic events during the Proterozoic.

**Proterozoic events**

The interval 3.0 to 2.4 Gyr probably saw the first assembly of large, relatively stable continental plates from smaller cratons$^{31}$, setting the stage for extensive cratonic sedimentation$^{32}$. Carbonate platforms having most of the essential features of their Phanerzoic equivalents were well developed by 2.6 to 2.3 Gyr (ref. 33). Indeed, the best-developed Proterozoic carbonate platforms, with evidence of extensive oxygenic photosynthetic stromatolitic communities, are primarily of early Proterozoic age$^{33}$. This evidence for extensive production of O$_{2}$ might seem to conflict with the observation that palaeosols that O$_{2}$ levels were low before 2.0 Gyr (ref. 34). But modern microbial mats remineralize organic matter efficiently (D. E. Canfield and D. J. D., manuscript submitted); the low amounts of organic carbon in early Proterozoic stromatolitic carbonates$^{35}$ are thus not unexpected. Oxidants can be consumed as rapidly as they are produced in these communities. Little organic carbon was buried on the extensive early Proterozoic carbonate platforms, so net accumulation of O$_{2}$ was near zero. This picture is consistent with the low values of $f_{org}$ (0.1) observed for the earliest Proterozoic (Fig. 3). The smaller net production of oxidants was probably consumed by reactions in sea-floor hydrothermal systems$^{36}$, which were more active than today. Accordingly, seawater SO$_{4}^{2-}$, although present, was substantially below modern concentrations$^{37}$. The deposit of Superior-type banded iron formations at that time apparently required an anoxic deep ocean$^{3}$ containing some dissolved Fe$^{2+}$.

Commencing at 2.2-2.1 Gyr, the large continental plates that had assembled for the first time in the late Archean to early Proterozoic underwent rifting and, later, orogeny on a global scale, as evidenced by massive basic and ultrabasic dyke swarms and Andean-type orogenic belts$^{38}$. Post-Archean tectonic cycles display an increasingly prominent early rift stage and a well-developed terminal stage of orogeny$^{39}$. Accordingly, rifting on a global scale probably promoted the development of extensive anoxic basins favourable for organic preservation. A sustained rise in seawater $87Sr/86Sr$ values at that time$^{39}$ indicates enhanced rates of continental erosion. The earliest-known glaciations occurred during this interval$^{40}$, lowering the sea level, exposing more continent, and making conditions more favourable for high rates of erosion and clastic sedimentation$^{40}$. Between 2.1 and 1.7 Gyr, the opening and closing of Atlantic-type ocean basins caused rifting and uplift which accelerated the rate of erosion, release of nutrients for biological production,
near-shore sedimentation and, therefore, organic burial. One such episode of enhanced organic sedimentation at this time might be represented by $^{13}$C-rich carbonates reported by Baker and Fallick.

The idea that growth of the crustal inventory of reduced carbon (M) led to oxidation of other elements is supported by geological evidence. A substantial rise in atmospheric $^{18}$O$_2$ levels is indicated by increase in retention of Fe$^{3+}$ in palaeosols and emergence of extensive red beds. The biosynthesis of sterol precursors requires $^{18}$O$_2$, and the oldest known sterane biomarkers occur in the 1.69 Gyr Barney Creek formation. The deposition of Superior-type banded iron formations was curtailed severely after 1.8 Gyr (ref. 44), perhaps because of oxygenation of the deep ocean. Possibly the oldest known occurrence of massive SO$_2^-$ evaporite deposition is recorded in 1.4-1.8 Gyr sediments of the McArthur basin, Australia.

During the interval 1.7 to 1.2 Gyr, organic activity was not as globally extensive as it was during the preceding period. There is no evidence of glaciation. A supercontinent may have existed, organic activity was more local in nature, and terms such as ‘anoxic magmatism’ and ‘abortive riftting’ have been used to characterize major tectonic events of that time. It is reasonable to conclude that global rates of sedimentation and organic burial were low to moderate. The absence of evidence for large changes in the sizes of the oxidized reservoirs is therefore not surprising. The $^{18}$O content of the atmosphere was apparently maintained at a value intermediate between modern levels and those of the early Proterozoic.

Tectonic activity increased during the interval 1.2 to 0.9 Gyr. The replacement of extensive mafic dyke swarms heralded the breakup of the supercontinent and the widespread dispersal of continental fragments. Modern-style orogenic cycles and glacial episodes became more frequent than before. Once again conditions were favourable for relatively rapid rates of organic sedimentation. Massive evaporites occur during and after this interval in central Africa (Upper Roan group).

FIG. 4 Quantity of organic carbon in the crust (M) against age. Values of M are calculated according to equation (4) (in the text). Symbols represent calculations of M assuming sediment half lives (see derivation of equation (4)) as follows: □, 300 Myr; ●, 400 Myr; △, 500 Myr. Rectangles along the bottom margin depict time intervals of enhanced global rifting and orogeny (see text).

North America (Grenville series) and Australia (Bitter Spring formation).

As indicated in Fig. 4, the crustal organic carbon reservoir increased in a stepwise fashion during each of the two intervals during the early and middle-to-late Proterozoic, with global rifting and orogenies occurred. A third stepwise increase apparently occurred in a brief interval between the Varan glacial episode and the Cambrian boundary. These events are not correlated with the development of new biological $^{18}$O$_2$. Indeed, the last stepwise oxidation is correlated with development of important new $^{18}$O$_2$ consumers, the metazoans. It is instead likely that these events were driven by accelerations of erosion, nutrient release and clastic sedimentary factors that are known to accelerate organic sedimentation throughout Earth history. These observations support earlier proposals that tectonic events strongly affected the biogeochemical cycles of O$_2$, SO$_2^-$ and Fe$^{3+}$, also increased, as predicted by the one cycle model which is particularly appealing for interval 2.1 to 1.8 Gyr (ref. 41). A prediction from the previous findings is that a second large increase in the oxidized reservoir occurred between 1.1 and 0.8 Gyr. A systematic search for evidence should be undertaken.

The role of life

These findings challenge the widely held view that innovations in biological evolution directed the long-term rise of atmospheric oxygen levels. As stated earlier, the development of oxygen photosynthesis occurred at least 600 Myr before O$_2$ (according to biochemical evidence) accumulated in the atmosphere. Eukaryotic organisms, which require O$_2$ for biosynthesis of essential lipids, appear in the palaeontological record at 2.1 Gyr ago, perhaps before the first large O$_2$ increase discovered here. Photosynthesis indeed provided an O$_2$ source strong enough to sustain a major atmospheric increase, but the time and magnitude of O$_2$ accumulation was regulated by tectonic processes controlling erosion and sedimentation. These observations are consistent with the view that chemical processes of the environment that are buffered by large crustal reservoirs (such as crustal organic carbon and sulphur) over long time scales (50-100 Myr) will ultimately be controlled by geologic processes, such as tectonics, which regulate interactions among those reservoirs.

The growth of the crustal organic carbon reservoir and resultant oxidation of the surface environment must have profoundly affected the Earth's biota. Evidence of abundant abiotic organisms appears in the organic geochemical record at 1.7 Gyr ago. Eukaryotes require O$_2$, it is not implausible an increase in their abundances and diversity with rise of O$_2$ that probably accompanied the growth of the organic reservoir between 2.2 and 1.8 Gyr.

The declining $^{13}$C difference between sedimentary carbon and reduced carbon during the Proterozoic (Fig. 2) suggests that isotopic discrimination during biological $^{18}$O$^+$ uptake is decreased in response to declining $^{18}$O$^+$ concentrations in oceans and atmosphere. The fact that the greatest decline discrimination coincides with the episodes of global rifting and orogeny is consistent with the drawdown of atmospheric O$_2$ levels which accompanies high erosion rates. It is therefore likely that the atmospheric ratio of O$_2$ to CO$_2$ increased markedly during these episodes. Evolutionary changes in the end-ribulose bisphosphate carboxylase oxygenase, which both CO$_2$ and O$_2$ as substrates, might have been triggered as these transitions.

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truncated activin receptor inhibits mesoderm induction and formation of axial structures in Xenopus embryos

Hemmati-Brivanlou & Douglas A. Melton

Department of Biochemistry and Molecular Biology, Harvard University, 7 Divinity Avenue, Cambridge, Massachusetts 02138, USA

Activins can induce mesoderm in embryonic explants and have been proposed as the natural inducer of Xenopus. A mutant activin receptor that inhibits activin signalling is used to show that activin is required for the induction of mesoderm in vivo and the patterning of the embryonic body plan. Blocking activin signal transduction pathway also reveals autonomous induction of a neural marker and suggests that the relationship between activin and fibroblast growth factor.

Understanding the processes that lead from a fertilized egg to the formation of germ layers and subsequently to a body plan is a central goal of embryology. Much of what is known about development of a vertebrate body plan comes from studies on amphibians where, at the tadpole stage, the main body axis consists of the dorsal structures notochord, spinal cord and notochord tissue anterior to posterior as head, trunk and tail. Animal tissues derive from the three germ layers and the mesoderm plays a pivotal role in organizing the body axis. Embryonic cells lead the movements of gastrulation, and the activity of the nerve system 4,5, and the development of the notochord gives rise to the muscular, skeletal, circulatory and exocrine systems. Moreover, a portion of the dorsal mesoderm from the gastrula, the Spemann organizer, can induce and organize the body axis following transplantation to another site. Understanding of the development of mesoderm will help clarify how the vertebrate body plan is generated.

Before gastrulation the three germ layers are simply arranged, top to bottom, in a frog blastula. Ectoderm arises from the top, or animal pole; mesoderm from the middle, or marginal zone, and endoderm from the bottom or vegetal pole. Mesoderm can be induced in animal pole cells (animal caps) by signals emanating from the vegetal pole. Several peptide growth factors have been identified that can induce mesoderm in animal caps in vitro. When animal cap tissue is explanted from a blastula embryo and cultured in isolation it develops into a ball of epidermis. But in the presence of an inducing factor, the animal cap will differentiate into mesodermal derivatives, including notochord, muscle and blood 6. Members of the fibroblast growth factor family, in particular basic fibroblast growth factor (bFGF), and the transforming growth factor-ß (TGF-ß) family, notably activins, are potent inducers in this assay.

Xenopus homologues of the Wnt gene family may also have a role in mesoderm induction. Both Xwnt1 (ref. 16) and Xwnt8...