



Atmospheric oxygenation driven by unsteady growth of the continental sedimentary reservoir

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ABSTRACT

Atmospheric oxygen concentration has increased over Earth history, from ~0 before 2.5 billion years ago to its present-day concentration of 21%. The initial rise in pO_2 approximately 2.3 billion years ago required oxygenic photosynthesis, but the evolution of this key metabolic pathway was not sufficient to propel atmospheric oxygen to modern levels, which were not sustained until approximately two billion years later. The protracted lag between the origin of oxygenic photosynthesis and abundant O_2 in the surface environment has many implications for the evolution of animals, but the reasons for the delay remain unknown. Here we show that the history of sediment accumulation on continental crust covaries with the history of atmospheric oxygen concentration. A forward model based on the empirical record of net organic carbon burial and oxidative weathering of the crust predicts two significant rises in pO_2 separated by three comparatively stable plateaus, a pattern that reproduces major biological transitions and proxy-based pO_2 records. These results suggest that the two-phased oxygenation of Earth's surface environment, and the long delays between the origin of life, the evolution of metazoans, and their subsequent diversification during the Cambrian Explosion, was caused by step-wise shifts in the ability of the continents to accumulate and store sedimentary organic carbon. The geodynamic mechanisms that promote and inhibit sediment accumulation on continental crust have, therefore, exerted a first-order control on the evolution of Earth's life and environment.

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1. Introduction

The extraction and burning of organic carbon-based fossil fuels is reversing the processes of photosynthesis and sedimentation, thereby causing a rise in CO_2 and concomitant O_2 drop in Earth's atmosphere (Keeling and Piper, 1996). Although the global climate consequences of the former are cause for concern, the industrial-scale consumption of O_2 is not considered a threat, despite the necessity of oxygen for animal life. The difference is caused by the large quantity of free O_2 in the surface environment, a product of organic carbon burial and sequestration in sediments. With respect to the history of atmospheric oxygen, this discrepancy highlights a critically important fact: biological photosynthesis is a necessary condition for the rise of atmospheric oxygen, but it is insufficient to produce an O_2 -rich atmosphere unless it is coupled to the sequestration of organic carbon in sedimentary deposits (Hayes and Waldbauer, 2006).

The notion that Earth's surface chemistry is controlled, at the most fundamental level, by mass exchanges between the sur-

face environment and the lithosphere has been recognized for over 100 years (Chamberlin, 1899). However, because data with which to constrain global mass fluxes into and out of the sedimentary reservoir are difficult to assemble, proxy records are used typically to interrogate the evolution of Earth's surface environment. For example, measurements of mass-independent fractionation (MIF) of sulfur isotopes (Farquhar et al., 2000) define an initial rise in atmospheric oxygen by ~2300 million years ago (Ma) – an event referred to as the 'Great Oxidation Event' ('GOE', Holland, 1999). Measuring levels of atmospheric oxygen from the GOE to its present concentration of 21% is notoriously difficult. Nevertheless, a proxy-based history has emerged in which pO_2 was stable but low throughout the Proterozoic (~2300–~635 Ma), with an anoxic deep ocean (Reinhard et al., 2013; Scott et al., 2008). This long-term plateau ended in the terminal Proterozoic (Sahoo et al., 2012), with a rise that may have been gradual (Bergman et al., 2004; Sperling et al., 2015) or sudden (Berner and Canfield, 1989), but that achieved modern levels by the early Paleozoic (~400 Ma). Ideas about pO_2 variability within the Phanerozoic (Fig. 1) are informed primarily by numerical models coupled to proxy constraints (Berner, 2005; Bergman et al., 2004).

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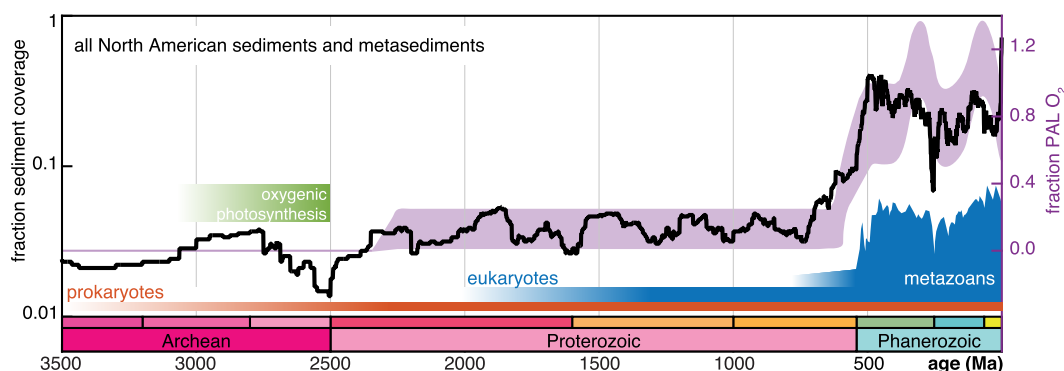


Fig. 1. Empirical sedimentary and metasedimentary coverage in North America (left logarithmic y-axis, measured as proportion of geologic columns containing any sediment of a given age) is displayed along with the canonical history of atmospheric oxygen (right linear y-axis, Lyons et al., 2014). A schematic depiction of major biological events in the Earth system is depicted also, including the origins of oxygenic photosynthesizers (Lyons et al., 2014), eukaryotes (Lyons et al., 2014) and metazoans (Erwin et al., 2011), and scaled biodiversity of Phanerozoic marine animals (Hannisdal and Peters, 2011).

A ‘three phase’ hypothesis for atmospheric oxygen levels (Fig. 1) is emerging as a fundamental feature of Earth history, albeit one that continues to be tested and challenged (Lyons et al., 2014). The potential mechanisms driving this history, however, are less well known. An O_2 -free Archean has been explained by more reducing volcanism (Holland, 1984) or an absent biological O_2 source (Kirschvink and Kopp, 2008), but the long-term maintenance of an intermediate Proterozoic plateau in atmospheric pO_2 (Fig. 1) is difficult to explain. Carbon isotopic measurements of Proterozoic marine carbonates (Bartley and Kah, 2004; Knoll et al., 1986; Halverson et al., 2005) imply sustained organic carbon burial rates that were $\sim 1\text{--}2\times$ Phanerozoic levels, assuming exogenic carbon mass fluxes and their isotopic compositions were approximately equivalent (Hayes and Waldbauer, 2006). Such high net O_2 production rates are potentially incongruent with low pO_2 in the Proterozoic (Johnston et al., 2009; Schrag et al., 2013; Laakso and Schrag, 2014; Derry, 2015).

Earth’s sedimentary shell contains 1.25×10^{21} moles of organic carbon (Bernier and Canfield, 1989), equivalent to ~ 33 modern atmospheres of oxygen. Despite representing a large, net source of O_2 , the integrated history of deposition and erosion on the continents that has yielded this mass of organic carbon remains unknown. Although some organic carbon burial does occur on oceanic crust ($<10\%$ today, Hedges and Keil, 1995), recycling of most or all of this sediment can occur as this crust is consumed at convergent margins, with a seafloor half-life of ~ 62.4 Myr in the modern (Rowley, 2002). A recent survey suggests that little carbon is returned to the convecting mantle via downgoing slabs, either migrating into the overlying mantle and crustal lithosphere or volatilizing through arc volcanoes and diffuse outgassing (Kelemen and Manning, 2015). The fate of the reducing power of subducted sediments is a related but more complex question. It has, however, been suggested that most or all of the reducing power of deep sea sediments is returned to the surface environment during seafloor destruction, at least presently (Hayes and Waldbauer, 2006). If correct, while carbon storage on ocean crust is significant compared to the residence time of atmospheric O_2 (<1 Myr, Hedges and Keil, 1995), the most important determinant of atmospheric O_2 on billion year timescales is the net accumulation of organic carbon in continental sedimentary deposits – a conceptual approach that has been widely applied (e.g., Bernier and Canfield, 1989; Hayes and Waldbauer, 2006; Lee et al., 2016). Here, we consider explicitly the connection between the net growth of Earth’s continental carbon reservoir and atmospheric oxygenation. We first measure net sedimentary burial in continental settings and then use this history to constrain a simple forward model for pO_2 .

2. Methods

2.1. Macrostrat database

Macrostrat (<https://macrostrat.org>) is a relational geospatial database that describes the chronological age and spatial distribution of rocks and sediments in the upper crust. Data here derive from the North American component, characterized by 23,813 lithostratigraphic units contained within 949 geographic columns (Fig. S1). Units in Macrostrat are assigned a variety of physical attributes, including thicknesses, dominant and subordinate lithologies, attributes that modify lithologies (e.g. ‘black shale,’ ‘stromatolitic limestone’), lithostratigraphic nomenclature and age estimates. All Macrostrat units have at least one dominant lithology, but multiple lithologies, and the relative proportional abundances of each, can be recorded.

Each unit acquires a modeled numerical age by using basic correlations to chronostratigraphic intervals and the contact relationships among units in the same column. For example, if there are 5 vertically stacked sedimentary units bounded by hiatuses in a column, and if together those units spanned one chronostratigraphic time bin (e.g., the Frasnian), then the time represented by the chronostratigraphic bin would be distributed, in a relative sense, equally and sequentially between each successive unit.

Parsing time in the sedimentary rock record is more difficult in the Precambrian as compared to the Phanerozoic, owing to the absence of widespread index fossils in the former. Thus, even in the absence of direct radiometric dating of a stratigraphic succession, biostratigraphic arguments potentially allow for the construction of a basic age model for many Phanerozoic sediments. The lack of a biological chronostratigraphic tool may explain the observed longer mean duration of Precambrian ‘sedimentary packages’ – defined here as an interval of sedimentation bound by hiatuses of at least 1 Myr duration (Peters, 2006). Consistent recognition of Precambrian hiatuses may be more challenging without chronostratigraphic biozones, thereby leading to longer-duration sedimentary packages (Fig. 2a). However, Precambrian packages are also, on average, thicker (Fig. 2b). Thus, the distributions of Precambrian and Phanerozoic rates of sediment accumulation are quite similar (Fig. 2c).

Data to create Fig. 1 are available via the Macrostrat application program interface (API) at:

https://macrostrat.org/api/v2/units?lith_class=sedimentary&lith_type=metasedimentary&project_id=1&response=long

The number of columns that have sediments or metasediments are tabulated for each one million year increment, with the minimum

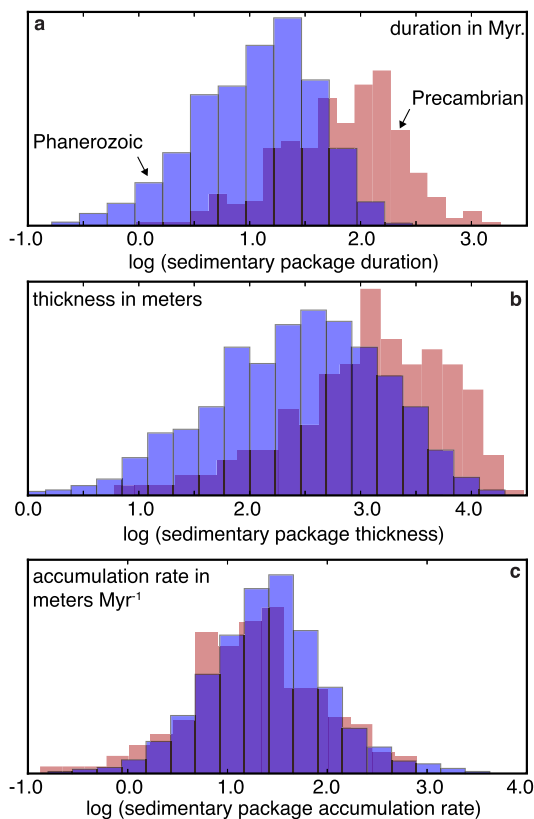


Fig. 2. Distribution of durations (a), thicknesses (b) and accumulation rates (c) for Precambrian and Phanerozoic sedimentary packages (i.e., an interval of sediment accumulation bound by hiatuses) as defined by Macrostrat's age model.

possible value being 0 and the maximum 949 (if all regions are occupied by sediment of that age). The sediment coverage record (Fig. 1) is then built by normalizing the time series to the maximum value (i.e., a value of 1 would indicate all of Laurentia is accumulating sediment at a given time point). For flux calculations, the volume of each rock unit is distributed linearly between its bottom and top age. The Macrostrat API output is produced dynamically from the current information in the database. The specific data used here, as well as the summarized sediment coverage record, are archived in Dataset S1.

2.2. Modeling global sediment volumes

One challenge in using Macrostrat as a basis for exploring global sedimentary processes is that, at present, it only covers ~16% of continental land area (Fig. S1). A model must, therefore, be used to scale Macrostrat sediment volumes to global values. Here, we base this model on a comparison to the work of Alexander Ronov (Ronov et al., 1980; Ronov, 1982), who generated globally comprehensive rock volume estimates for general lithologies and epochs (or longer duration time intervals) in the Phanerozoic and latest Precambrian. Sediment fluxes from this compilation are shown in Fig. 3a, derived by normalizing sediment volumes by bin duration. A Macrostrat-based sediment volume flux model can be produced at the same time resolution as Ronov's, using rock unit thicknesses, areal extents and age estimates (Fig. S1). This time series can become an initial global model (blue in Fig. 3a) by multiplying the ratio of global continental area captured by Ronov's synthesis to Macrostrat's areal coverage (~6.07).

As is the case for any proxy dataset, Ronov's sediment volume compilation is not perfect and has its limitations. Of these, the most relevant for this work are the coarse temporal reso-

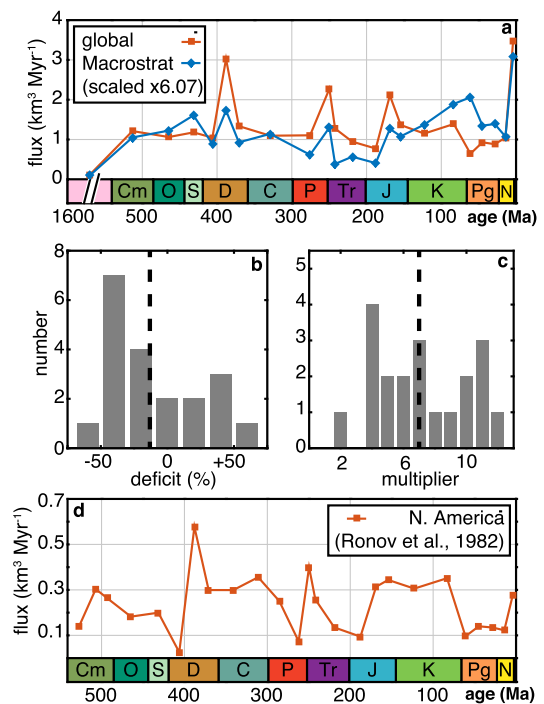


Fig. 3. (a) Time series of global (red curve, Ronov et al., 1980) and Macrostrat sediment volume fluxes (blue curve, scaled by a constant factor of 6.07 to become a global estimate) are displayed. (b) Comparison of the red and blue curves in (a) can be expressed as a distribution of misfits between the models, defined as (Macrostrat/global) – 1 and expressed as percent deficit – note that the Paleocene (+221%) is not shown. (c) Distribution of multiplicative factors needed to bring Macrostrat's global model into agreement with Ronov's estimate – note that the Middle Triassic (20.1×) is not shown. Dashed lines in b and c are median values for each distribution. (d) Ronov's estimate for sediment flux for North America alone (Ronov, 1982). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

lution at which data were compiled (~15 Myr bin durations or greater) and the difficulty in editing binned sediment volume estimates as correlations, age models and timescales are updated and improved. However, it remains the only compilation of global sediment volume for the Phanerozoic and latest Proterozoic, and was constructed independently of Macrostrat. Thus, the two syntheses can be compared, with commonalities between them constituting meaningful evidence that each are useful models of extant sediment volumes.

Both datasets yield congruent time series of global sediment volume (partial correlation on first-differences with changes in interval duration held constant: Spearman's $\rho = 0.50$, $P = 0.02$; Pearson product-moment $r = 0.79$, $P = 0.00002$). The total amount of Phanerozoic sediment in Ronov's synthesis is 639 million km³; the simple area-based scaling of Macrostrat's Phanerozoic estimate ($\times 6.07$) is within 3% of this value (620 million km³). By comparison, the scaled estimate for Macrostrat's Precambrian sediment volume is 222 million km³, an amount equivalent to approximately one third of the Phanerozoic total, despite representing ~6× more elapsed geologic time.

If North American volumes are removed from Ronov's global time series, the correlation between Macrostrat and Ronov persists ($\rho = 0.47$, $P = 0.04$; $r = 0.64$, $P = 0.003$). This finding is consistent with Ronov's conclusion that global processes predominate over local processes in governing changes in sediment quantity (Ronov et al., 1980). The distribution of residuals between the initial Macrostrat and Ronov models are shown in Fig. 3b; for example, the scaled Macrostrat model predicts 2.2× more sediment in the Paleocene as seen in Ronov's compilation. The scale factors needed to bring Macrostrat's global sediment volume estimate into strict

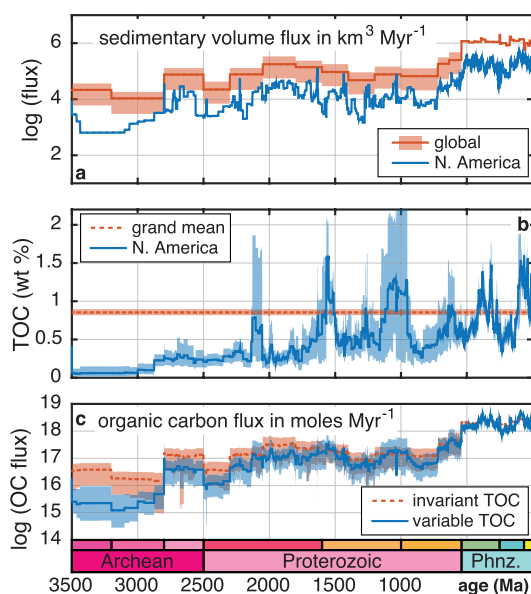


Fig. 4. (a) Continental sediment flux models are shown for North America (blue curve) and the globe (red curve). (b) Using Macrostrat's lithological descriptions (supplementary online material section S2), the TOC content of bulk sediment in North America is predicted. (c) By combining (a) with (b), two end-member global organic carbon burial models are produced (red and blue curves). Shaded regions in (a–c) cover 95% of values produced by random assignment of properties defining sediment and organic carbon fluxes (supplementary online material section S2). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

agreement with Ronov's are shown in Fig. 3c. Although few in number, the scaling factors are distributed around the initial scaling (6.07), with the Middle Triassic being the only outlier.

These scale factors (Fig. 3c) are used to generate the Phanerozoic global sediment volume flux model presented in Fig. 4a. The only exception is the Middle Devonian; the scale factor needed to yield agreement is 10.6, but the initial model is used. This adjustment is justified by an examination of Ronov's compilation, parsed by region (Fig. 3d). In North America, the Middle Devonian is predicted to have the highest flux in the entire Phanerozoic, while the Early Devonian is predicted to have the lowest. We find this scenario unlikely, and believe it indicates correlation issues in Ronov's original compilation, wherein what is now considered Early Devonian strata was then placed in the Middle Devonian. This particular change, however, has no effect on the most important implication of these results – the dramatic increase in continental sediment accumulation seen across the Proterozoic–Phanerozoic boundary (Fig. 1).

Lastly, Ronov (Ronov et al., 1980) does include a Precambrian estimate, but its bin duration is too coarse (~1000 Myr), and correlations are too uncertain to justify strict usage. Thus, in each model instance, a scale factor for each Precambrian period bin is sampled with replacement from the observed distribution of Phanerozoic factors (Fig. 3c). The global sedimentation model is run 1000 times, with the shaded red region in Fig. 4a covering 95% of the Precambrian model outputs.

3. Results

3.1. Continental sedimentation history

Sedimentary and metasedimentary rock coverage, a presence-absence measure of rock quantity compiled from 949 regions in the North American component of the Macrostrat database (Methods, Fig. S1), is low in the Archean, rises to a higher value in the Proterozoic, and then again rises dramatically during the early

Phanerozoic (Fig. 1). Previous analysis of the Phanerozoic portion of this record identified quantitative signals of global tectonics, notably the supercontinental coalescence and breakup cycle (Meyers and Peters, 2011). The presence of modes in sedimentation within the Proterozoic that are similarly spaced by ~400 Myr (Fig. 1) suggests that a supercontinent-like tectonic cycle may have exerted a first-order control on continental sediment accumulation within the Proterozoic as well.

The prevalence of a global tectonic signal within the Phanerozoic (Meyers and Peters, 2011), and possibly within the Proterozoic (Fig. 1), does not help to explain the dramatic increase in sediment quantity that is observed during the Proterozoic–Phanerozoic transition. Intrinsic measurements of sedimentary systems (i.e., estimated accumulation rates) show no change across this boundary (Fig. 2), thus indicating that the implied increase in sediment accumulation is not an artifact of the Macrostrat database and its ability to estimate Precambrian vs. Phanerozoic stratigraphic properties. Instead, this boundary marks a major step-wise increase in the extent of continental flooding that coincided with, and perhaps resulted in, a step-wise increase in the accumulation of sediments on the continents (Peters and Gaines, 2012). It is notable that exponential decay in surviving rock quantity with increasing age, as expected by models of rock cycling (Gregor, 1968; Garrels and Mackenzie, 1969; Gregor, 1970; Wold and Hay, 1990), is not apparent in the empirical rock quantity-age data (Fig. 1). Variation in original rates of erosion and/or deposition could result in higher frequency rises and falls in surviving sedimentary rock quantity, but if erosion were the dominant process, then these fluctuations would still be superimposed on an approximately exponential decrease in surviving sediment quantity with increasing age (Garrels and Mackenzie, 1971b, 1971a; Mackenzie and Pigott, 1981).

The lack of the expected, approximately exponential decrease in sediment quantity was also noted by Alexander Ronov (Ronov et al., 1980), whose global sediment volume compilation for the Phanerozoic and latest Proterozoic produces a very similar trajectory to that documented in Fig. 1 (see Fig. 3). Ronov concluded from this observation that the main factor driving the observed fluctuations in sediment abundance on the continents must reflect primarily variation in net sediment accumulation, not subsequent modification of sediments by erosion (Ronov et al., 1980). This conclusion does not require that erosion plays no measurable role in shaping the rock record. For example, the last five million years shows a precipitous increase in sediment abundance towards the present, caused by the inclusion of non-marine sedimentary rocks in the analysis (Fig. 1). This clear secular trend indicates that at least some portion of these non-marine rocks are transient, temporarily stored on continental crust as they are eroded and transported to other sedimentary settings, and are not part of the net sedimentary record that dominates the continental rock record (i.e., 5–3500 Ma on Fig. 1).

If the most recent estimate of global sediment flux from Fig. 4a represents total sediment flux (~6 million km³/Myr) through the surface environment (i.e., global transport by rivers), and this rate has remained relatively constant throughout Earth history, the full history in Fig. 4a implies that only a fraction of this gross sediment delivery is destined for preservation on continental crust – ~20% on average in the Phanerozoic, ~2% in the Proterozoic, and ~0.5% in the Archean. This fraction constitutes the long-term net record of sediment accumulation, the process most important for surface oxygenation on billion-year timescales (Hayes and Wald-bauer, 2006). Importantly, the observed sediment quantity-age data suggest that the global sediment mass stored on the continents has not remained constant, but has instead undergone episodes of net growth. Although we do consider the implication of an erosion-dominant process interpretation for the entirety of Fig. 1, this sce-

nario requires contrived, time-varying rates of sedimentation and erosion (see section 4).

Given that variation in the sedimentary record is a proxy for changes in net sedimentation on the continents, an important next step is scaling our Macrostrat-derived record (Fig. 1) to arrive at a global model (Methods). Previous work has argued for global relevance of the Phanerozoic portion of the dataset by documenting a strong correlation with independent global biological, geochemical, and eustatic sea level records (Meyers and Peters, 2011; Hannisdal and Peters, 2011). Analogously, the overall time series of North American continental sediment abundance is strikingly similar to the global history of atmospheric oxygen concentration and major transitions in the global fossil record (Fig. 1). This covariation, alone, is notable and suggests that there is a process connection. Comparisons between the Macrostrat data (Fig. 1), Ronov's global rock volume data (Ronov et al., 1980), global geological maps, and Australian stratigraphic nomenclature data further indicate that North America is a sufficiently large sample of the continental crust (~16% of present-day continental area), to be globally representative (see supplementary online material section S1 and Figs. 3, S2 and S3).

3.2. Organic carbon accumulation on continental crust

To estimate net global continental sediment accumulation across Earth history, we scale Macrostrat's sediment volume flux (blue curve in Fig. 4a, Methods) upward to become a global model (red curve in Fig. 4a) using Ronov's global Phanerozoic and late Proterozoic compilation (Ronov et al., 1980, Methods and Fig. 3). To estimate the total organic carbon (TOC) content of this sediment, we used 49,803 sedimentary lithological characterizations in Macrostrat supplemented with 5,466 weight percent TOC measurements from the USGS National Geochemical Database (USGS, 2008) (supplementary online material section S2, Fig. S4). The time varying lithological properties of North American sediment (e.g., temporal shifts in the abundance of coal) translates into a changing expectation for the average sediment TOC content over time (Fig. 4b). The organic carbon burial flux in North America is estimated from both its sedimentary volume flux (blue line in Fig. 4a) and its lithology-dependent TOC estimate (blue line in Fig. 4b).

Given the empirical record of North America (Fig. 1), there are two approaches to characterizing the TOC content of the global continental sedimentary reservoir (Fig. 4): either TOC of sediment outside of North America mirrors the temporal variability expressed in the North American record (blue line in Fig. 4b), or the TOC content of the remaining global flux is invariant and equal to bulk average sedimentary composition (red, dashed line in Fig. 4b). When integrated, the 'variable TOC' model (blue line in Fig. 4c) predicts that the total amount of organic carbon in Earth's continental sedimentary shell is between 1.0 to 2.0×10^{21} moles, with a median prediction of 1.37×10^{21} moles. This estimate for the global mass of organic carbon in sedimentary deposits is within 10% of other independent global estimates (Bernier and Canfield, 1989). The median prediction of the 'invariant TOC' model (red, dashed line in Fig. 4c) predicts a slightly higher total integrated value (1.6×10^{21} moles).

An important consideration when combining net continental sediment flux (Fig. 4a) with lithology-specific TOC estimates (Fig. 4b) in order to estimate net organic carbon burial over time (Fig. 4c) is whether the TOC content of Precambrian sediments differ systematically from those of the Phanerozoic. We test this possibility for shale lithologies, using 3,346 TOC measurements from the USGS database (USGS, 2008), as well as 2,398 measurements from Partin et al. (2013). These data are combined, and the distributions of Precambrian and Phanerozoic TOC values are plotted together in Fig. 5. The two distributions are similar, diverging

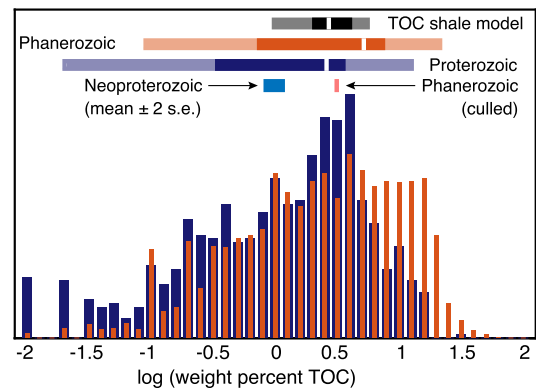


Fig. 5. Normalized Precambrian (blue bars) and Phanerozoic distributions (red, thinner bars) of shale weight percent TOC measurements from the USGS National Geochemical Database ($n = 3,346$, USGS, 2008) and from Partin et al. (2013) ($n = 2,398$). Percentiles (2.5, 25, 75 and 97.5) for the distributions of modeled, formation-scale TOC values for shales, Phanerozoic data, and Precambrian data are included at the top. White lines are the means for each distribution. The model values shown are only for shale bodies not described as 'red' (see supplementary online material section S2). Data summaries (mean $\pm$ 2 standard errors) of data subsets (Neoproterozoic data and Phanerozoic data for units with TOC values $\leq 20\%$) are also included for comparison. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

most strongly only at high TOC values (>10 weight percent). If the stratigraphic units with TOC values $>20\%$, which are known to be unusual, are culled from the data, then the Phanerozoic mean is very close to the Precambrian mean (lighter red horizontal bar in Fig. 5). In either case, there is little difference between Precambrian and Phanerozoic shale TOC content, at least among shales for which measurements have been made (USGS, 2008; Partin et al., 2013). The distributions of formation-scale TOC values assigned to shale volumes in our model (see supplementary online material section S2) are also congruent with the empirical distributions (grey, black and white horizontal bar in Fig. 5).

4. Discussion

Without compelling evidence for markedly different average sediment properties in the Precambrian compared to the Phanerozoic (Fig. 5), the notable concordance between empirical sediment abundance and pO_2 histories shown in Fig. 1 becomes sensible in the context of total net organic carbon accumulation – i.e., burial in stable continental sediments which constitute the net sedimentary rock record, an idea first developed for Ronov's global Phanerozoic syntheses (Budyko et al., 1987; Bernier and Canfield, 1989). Previous pO_2 models included pyrite burial as a source of O_2 because the reduction of seawater sulfate via microbial respiration transfers reducing power from organic carbon to pyrite (Bernier and Canfield, 1989). Because pyrite burial is not a direct source of oxygen, we do not include it here; nevertheless, results are comparable when pyrite burial is included (supplementary online material section S3, Fig. S5).

To model sinks of O_2 , we empirically parameterize the oxidation of iron in oceanic crust (Lécuyer and Ricard, 1999) and the oxidative weathering of sediments on land (Lasaga and Ohmoto, 2002). The numerical model for pO_2 is:

$$\frac{dM}{dt} = F_{org} - k_1 M - k_2 B_{org} \sqrt{M}, \quad (1)$$

where M is the mass of O_2 in the surface environment (in moles), F_{org} is the net burial of organic carbon in continental settings (in moles/Myr), B_{org} is total accumulated sedimentary organic carbon (in moles), $k_1 M$ is the consumption of O_2 via iron oxidation, and $k_2 B_{org} \sqrt{M}$ is the oxidation of reduced phases (i.e., organic carbon

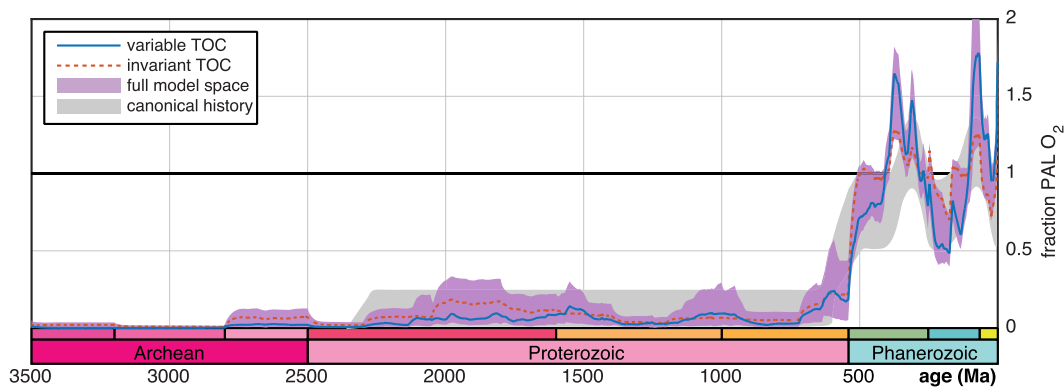


Fig. 6. Following Equation (1) of the text, atmospheric pO_2 is predicted. The 'variable TOC' model uses the blue curve in Fig. 4c as the F_{org} term, whereas the 'invariant TOC' model uses the red, dashed curve. Any solution between these end-members is viable. The full model space (shaded region) also includes uncertainties in the end-member F_{org} models estimated by 1000 randomizations of sediment properties used to define organic carbon flux (supplementary online material section S2). Displayed in grey is the independently derived canonical history of atmospheric oxygen (Lyons et al., 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and pyrite) in Earth's sedimentary shell (supplementary online material section S4).

Possible functions for F_{org} include any linear combination of the burial histories in Fig. 4c, which in turn defines a family of solutions for the history of atmospheric oxygen (Fig. 6). In all model predictions, atmospheric oxygen is present only transiently in the Archean, which is suggestive of O_2 'whiffs' implied by certain proxy records (Lyons et al., 2014). The first permanent rise in O_2 occurs at ~ 2300 Ma. For the rest of the Proterozoic, pO_2 remains low (ranging from ~ 0.01 to 0.30 PAL, with a mean value of ~ 0.09 PAL). Atmospheric pO_2 then begins to rise in the Neoproterozoic, but does not achieve modern-like values until the late Cambrian at ~ 500 Ma under the 'invariant TOC' model, and not until the Early Devonian (~ 400 Ma) under the 'variable TOC' forcing. After the second large rise in the early to middle Paleozoic, pO_2 ranges between ~ 0.5 to 2 PAL, a dynamic range that is comparable to other pO_2 models for the past 500 Myr (Bernier and Canfield, 1989; Bergman et al., 2004).

Equation (1) is a simple forward model for atmospheric oxygen that encompasses continental organic carbon burial and aspects of oxidative weathering. More complex variations of the model could include, for example, more reducing volcanism in the Archean (Holland, 1984), the effects of a growing marine sulfate reservoir and pyrite deposition (Bernier and Canfield, 1989), and feedbacks between pO_2 and the TOC content of sediments (Hedges and Keil, 1995). However, our principal insight is not a specific model formulation, but is instead the empirical evidence that organic carbon accumulation on continental crust has evolved substantially across Earth history. Major inflection points in the record of net sediment storage coincide in timing and in relative magnitude with state changes in the history of pO_2 and major transitions in the biosphere (Fig. 1). Model variants postulating that there has been no such change in continental sediment accumulation, and that the observed sedimentary record is dominated by the effects of post-depositional erosion, requires that the hypothetical missing sediments had properties that are different than all surviving sediments (supplementary online material section S5 and Figs. S6, S7), or that oxygen sinks were far higher in the Proterozoic, which lacks independent evidence (Derry, 2015; Keller and Schoene, 2012).

The suggestion that sources of O_2 must have been weak to maintain low Proterozoic pO_2 is not new, but in the absence of direct estimates for F_{org} (Fig. 4c), this condition has previously been attributed to a variety of factors. Examples include a dominance of anoxygenic photosynthesis in the Proterozoic (Johnston et al., 2009), although biomarker tests of this hypothesis are incon-

clusive (French et al., 2015), as well as phosphorus limitation on biological productivity (Laakso and Schrag, 2014; Derry, 2015). The latter stands in contrast to isotope-based models of the Proterozoic carbon cycle. Although previous work has noted isotopic evidence for transient increases in fractional organic carbon burial near the end-Archean and end-Proterozoic boundaries (Knoll et al., 1986; Des Marais et al., 1992), background Proterozoic organic carbon burial fluxes have been interpreted as comparable to the Phanerozoic average (Krissansen-Totton et al., 2015) despite putatively low Proterozoic pO_2 (Fig. 1). This potential inconsistency has led to challenges against canonical models that invert carbon isotopic time series for organic carbon burial histories (Schrag et al., 2013).

A full treatment of the implications of our results for carbon isotopic records is beyond the scope of the present paper, but expectations for two end-member hypotheses can be articulated. The first is that low continental sediment accumulation in the Precambrian (Figs. 1 and 4) reflects overall lower exogenic carbon flux to the surface system, such that while isotopic determinations of fractional organic carbon burial in the Precambrian may be broadly correct, the implied absolute fluxes may be vastly different from those in the Phanerozoic. The second hypothesis stems from the fact that we demonstrate covariation between proxy records of atmospheric oxygen concentration and continental organic carbon storage (Fig. 1). The latter can diverge from the total carbon burial flux if the locus of that burial shifts from the stable continents to the tectonically less stable ocean floor, with implications dependent upon the long-term fate of buried carbon (see Hayes and Waldbauer (2006) and supplementary online material section S6). Determining which of these scenarios, if either, is correct depends upon identifying the ultimate cause for the increase in continental sediment storage (Fig. 1) and its potentially much broader implications for the Precambrian Earth system.

Regardless, it is apparent that the empirically determined record of net sediment accumulation on the continents contains considerable explanatory power for the history of atmospheric oxygen, even in the absence of a specific model for carbon burial (Fig. 1). The forward model presented here (Fig. 6), calibrated with sedimentary volumes (Fig. 4) and total organic carbon measurements (Fig. 5), makes several predictions that are congruent with previous notions about the trajectory of pO_2 across geologic time: O_2 concentration began a protracted rise during the end-Proterozoic (Sahoo et al., 2012), remained below modern levels until well into the Paleozoic (Bergman et al., 2004; Sperling et al., 2015), reached maxima during the Carboniferous and Cretaceous (Bernier and Canfield, 1989; Bergman et al., 2004), and dropped to

a Phanerozoic minimum at the end-Paleozoic/early-Mesozoic transition (Berner, 2005). The emerging idea that pO_2 may have been near-modern levels following the GOE (Lyons et al., 2014) also has some amount of support, if we tenuously hypothesize that a small peak in Paleoproterozoic sediment area represents an initial Great Unconformity-like episode (Peters and Gaines, 2012) of continental sediment accumulation that was removed prior to the initiation of a second, Phanerozoic iteration of the same process (supplementary online material section S7, Fig. S9).

5. Conclusions

Given the overall dependence of net O_2 production on the net burial of organic carbon in sedimentary deposits, it is not surprising that the empirical history of long-term, net continental sediment accumulation and its organic carbon content (Figs. 1, 4) has similarities to the empirical history of atmospheric pO_2 (Fig. 6). What is surprising, and as yet unexplained, is why the continents should undergo such a large step-wise transition in their capacity to act as long-term net sediment storage reservoirs. A potential mechanism includes changes in the average amount of continental crust that is flooded by shallow seas, possibly driven by changes in continental freeboard and the growth of the continental crust, neither of which is well known (Lee et al., 2016). A notable challenge for geoscience is identifying the specific causes of the abrupt transition in continental sediment accumulation that occurs at the start of the Phanerozoic.

Regardless of the ultimate mechanisms that drive changes in the ability of the continents to serve as long-term sediment storage reservoirs, recognizing that geodynamic factors, operating in conjunction with biological production of O_2 , have governed the timing and magnitude of major transitions in Earth's surface redox state must affect our understanding of the long-term evolution of life and environment. In this view, delays between the origin of eukaryotes and the appearance of metabolically demanding metazoan body plans during the Cambrian (Erwin et al., 2011) depended little on biological factors. Instead, animal diversification was determined largely by the timing of a state transition in the capacity of the continents to sequester photosynthetic organic carbon and, therefore, to serve as sources of O_2 . A corollary of this hypothesis is that returns to low Precambrian-like rates of continental sediment storage may be threats to complex animal life (Fig. 1). It is likely that just such a forcing, driven tectonically by the formation of Pangea (Hannisdal and Peters, 2011) and subsequent subaerial exposure of continental shelves, contributed to the severity of the end-Permian mass extinction (Knoll et al., 2007). Earth's ability to sequester sediments in tectonically stable continental settings is, therefore, a planetary process that is necessary for both the initial evolution of complex O_2 -metabolizing animal life and its long-term maintenance.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2016.12.012>.

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