The rise of oxygen and siderite oxidation during the Lomagundi Event

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Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved April 14, 2015 (received for review November 21, 2014)

The Paleoproterozoic Lomagundi Event is an interval of 130–250 million years, ca. 2.3–2.1 billion years ago, in which extraordinarily 13C enriched (>10%) limestones and dolostones occur globally. The high levels of organic carbon burial implied by the positive δ13C values suggest the production of vast quantities of O2 as well as an alkalinity imbalance demanding extremely low levels of weathering. The oxidation of sulfides has been proposed as a mechanism capable of ameliorating these imbalances: It is a potent sink for O2 as well as a source of acidity. However, sulfide oxidation consumes more O2 than it can supply CO2, leading to insurmountable imbalances in both carbon and oxygen. In contrast, the oxidation of siderite (FeCO3 proper, as well as other Fe2+–bearing carbonate minerals), produces 4 times more CO2 than it consumes O2 and is a common—although often overlooked—constituent of Archean and Early Proterozoic sedimentary successions. Here we propose that following the initial rise of O2 in the atmosphere, oxidation of siderite provided the necessary carbon for the continued oxidation of sulfides, burial of organic carbon, and, most importantly, accumulation of free O2. The duration and magnitude of the Lomagundi Event were determined by the size of the preexisting Archean siderite reservoir, which was consumed through oxidative weathering. Our proposal helps resolve a long-standing conundrum and advances our understanding of the geologic history of atmospheric O2.

carbon isotopes | oxygen | siderite | carbon cycle | Great Oxidation Event

Reconstructing the geologic history of atmospheric oxygen is among the foremost scientific challenges of our time (1). The level of atmospheric oxygen (pO2) without doubt played a key role in the evolution of the Earth System (2), exerting a major influence on the biosphere, especially the evolution of metazoans (3). With no direct way of measuring oxygen concentrations in deep geologic time, the stable isotopes of carbon recorded in marine limestones provide key constraints (4). Carbon enters the ocean–atmosphere system through volcanoes and weathering of carbon-bearing sedimentary rocks and can exit in one of two ways: (i) uptake during photosynthesis and burial of organic carbon leading to O2 production and (ii) reaction during weathering and formation of CaCO3 in the ocean. The carbon isotopic record tells us how carbon was partitioned between these two sinks: A δ13C value of 0‰ indicates that ~80% of incoming carbon was buried as carbonate carbon and 20% as organic carbon. Positive excursions in δ13C are unusual and indicate that a larger fraction of carbon was fixed and buried as organic carbon and, with it, a larger amount of O2 was produced.

Following the indications for the first rise of O2 in the atmosphere (5, 6) is the largest and most protracted period of 13C enrichment in the geologic record, known as the Lomagundi Event (Fig. 1). Limestones and dolostones with extreme carbon isotopic values of +8% to greater than +15%ø occur globally (6–8), and a duration of between 128 million years (m.y.) and 249 m.y. is suggested by current age constraints (9). The highly elevated δ13C values indicate the burial of tremendous amounts of organic carbon, and the production of correspondingly vast amounts of O2. In fact, the duration and magnitude of the isotopic excursion in δ13C bespeak of O2 fluxes so large that they challenge our understanding of geochemical cycles. Calculations indicate an integrated production of far larger amounts of O2 than currently exist—or likely ever existed—in Earth’s atmosphere, implying the concurrent existence of effective O2 sinks (10).

A second, hitherto unrecognized problem exists as well. The elevated δ13C values indicate a repartitioning of the incoming carbon in favor of organic carbon burial. However, if the total amount of carbon entering the ocean–atmosphere system remains unchanged, then any increase in the organic carbon burial flux can only be at the expense of the other output flux, that of carbonate. However, the burial of carbonate carbon represents the carbon not only of carbon but also of alkalinity, and thus a decrease in its magnitude demands a commensurate decrease in the input of alkalinity from weathering. Critically, δ13C values of +10‰ indicate the burial of so large a fraction of organic carbon that a 90% reduction in carbonate burial, and hence weathering, would have been necessary to balance it (see SI Appendix for calculation). Assuming that weathering is proportional to pCO2 to the 0.3 power (11, 12), a 90% reduction in weathering would have entailed a decline from a pCO2 baseline of 10,000 ppm to single part per million levels. Consequently, in the face of such high levels of organic carbon burial, without an additional source of CO2 or sink for alkalinity, a near-complete shutdown of weathering would have been required to balance the inputs and outputs of carbon.

The more plausible alternative is that during Lomagundi times processes that consume O2 and release CO2 compensated the inferred imbalances such that pCO2 levels were bolstered and pO2 levels moderated. The oxidation of sedimentary sulfides is an attractive option for alleviating the attendant imbalances, as it is a potent sink for oxygen (13) and, in conjunction with acidification of carbonates, a source of CO2 (14). The oxidation of sulfides following the first rise of oxygen is supported by evidence

Significance

The evolution of Earth’s oxygen-rich atmosphere occurred in two major steps, the first of which took place approximately 2.4 billion years ago. Following the initial rise of oxygen, carbon isotope evidence indicates the burial of vast quantities of organic carbon and the production of correspondingly large amounts of oxygen. However, if not accompanied by an additional supply of carbon, the extreme levels of organic carbon burial imply nonphysically low atmospheric pCO2 levels. Here we propose that the initial rise in O2 led to the oxidation of a large preexisting reservoir of siderite (FeCO3), which provided the necessary carbon for the burial of organic matter, production of further O2, and substantial accumulation of oxygen in Earth’s atmosphere for the first time.

Author contributions: A.B. and L.R.K. designed research, performed research, and wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.orglookup/suppl/doi:10.1073/pnas.1422319112/-/DCSupplemental.

www.pnas.org/cgi/doi/10.1073/pnas.1422319112

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including the disappearance of detrital pyrites (15, 16), the appearance of sedimentary evaporites (17), and Cr enrichment in iron-rich sedimentary rocks indicating a highly acidic weathering regime (18).

Nonetheless, sulfide oxidation alone could not have fully compensated the imbalances resulting from the elevated burial of organic carbon during the Lomagundi Event. Close examination of Eqs. 1-3 reveals that pyrite oxidation coupled to acidification of carbonates leads to unavoidable imbalances in carbon and oxygen due to the stoichiometry of the overall reaction, which consumes more oxygen than it releases carbon. The oxidation of 4 mol of pyrite requires 15 mol of \(O_2\) (Eq. 1), while the associated acidification of carbonates can release at most only 8 mol of \(CO_2\) (Eq. 2). Thus, on the whole, pyrite oxidation consumes 15 mol of \(O_2\) but produces only 8 mol of \(CO_2\) (Eq. 3).

\[
\begin{align*}
4\text{FeS}_2 + \text{15O}_2 + 8\text{H}_2\text{O} &\rightarrow 8\text{H}_2\text{SO}_4 + 2\text{Fe}_2\text{O}_3 \quad [1] \\
8\text{CaCO}_3 + 8\text{H}_2\text{SO}_4 &\rightarrow 8\text{CaSO}_4 + 8\text{H}_2\text{O} + 8\text{CO}_2 \quad [2] \\
4\text{FeS}_2 + \text{15O}_2 + 8\text{CaCO}_3 &\rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{CaSO}_4 + 8\text{CO}_2 \quad [3]
\end{align*}
\]

However, the continued oxidation of pyrite requires the burial of 15 mol of \(CO_2\) as organic carbon (Eq. 4)—7 mol more than can be supplied by pyrite oxidation coupled to the acidification of carbonates.

\[
\begin{align*}
\text{15CO}_2 + 15\text{H}_2\text{O} &\rightarrow 15\text{CH}_2\text{O} + \text{15O}_2 \quad [4]
\end{align*}
\]

Conversely, if the amount of \(CO_2\) required by organic carbon burial is assumed to balance the amount that can be supplied by pyrite oxidation coupled to acidification of carbonates (8 mol), not enough oxygen is produced during organic carbon burial (8 mol) to balance the demand of pyrite oxidation (15 mol), such that any pyrite oxidation would grind to a halt. Consequently, the oxidation of sulfides cannot be a sustained source of carbon over geological timescales, even during intervals of highly elevated oxygen production, and much less so during periods when this is not the case (14).

Here we suggest that siderite oxidation (including siderite proper, \(\text{FeCO}_3\), as well as other \(\text{Fe}^{2+}\) bearing carbonate minerals) provided the necessary \(CO_2\) during Lomagundi times. Siderite is a major constituent of Archean and Early Proterozoic sediments: It is extremely abundant in banded iron formations, often even more so than iron oxides (19). Siderite is also found in anomalously high concentrations in Proterozoic limestones and dolomites (20), where it arises from the replacement of \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) by \(\text{Fe}^{2+}\) in the carbonate mineral lattice. Crucially, the oxidation of siderite produces 4 times more \(CO_2\) than it requires \(O_2\). The oxidation of siderite (Eq. 5) followed by photosynthetic \(CO_2\) fixation (Eq. 6) is a net source of oxygen (Eq. 7).

\[
\begin{align*}
4\text{FeCO}_3 + \text{O}_2 &\rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2 \quad [5] \\
4\text{CO}_2 + 4\text{H}_2\text{O} &\rightarrow 4\text{CH}_2\text{O} + 4\text{O}_2 \quad [6] \\
4\text{FeCO}_3 + 4\text{H}_2\text{O} &\rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{CH}_2\text{O} + 3\text{SO}_2 \quad [7]
\end{align*}
\]

Hence, in principle, the burial of the \(CO_2\) evolved from siderite oxidation as organic carbon can produce oxygen 3 times in excess of the \(O_2\) required by siderite oxidation, with the surplus going to the oxidation of sulfide, oxidation of reduced crustal iron, and the accumulation of free \(O_2\) (21).

**Calculations and Numerical Results**

Siderite oxidation would have contributed to transient \(^{13}C\) enrichment of the exogenic reservoir in two principle ways. First, by the delivery of \(^{13}C\) enriched carbon. Massively bedded Archean and Proterozoic marine siderites have an average carbon isotopic composition of \(-9.9\%\) (19), \(-4\%\) more enriched than the average weathering input. Second, siderite oxidation could drive up exogenic \(^{13}C\) by changing the ratio of organic to carbonate carbon burial fluxes as governed by the stochiometries of siderite, sulfide, and iron silicate oxidation. Consider first the oxidation of siderite coupled to the burial of organic carbon and oxidation of iron silicates (Eq. 8):

\[
\text{FeCO}_3 + 3\text{FeSiO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 + 3\text{SiO}_2 + \text{CH}_2\text{O}. \quad [8]
\]

Neither \(O_2\) nor \(CO_2\) appears in the above reaction; it is balanced for both. The burial of 1 mol of organic carbon consumes 1 mol of \(CO_2\), which is supplied by the oxidation of 1 mol of siderite. One quarter of the resulting mol of \(O_2\) that is produced goes to the oxidation of siderite, while the other 3/4 mol goes to the oxidation of iron silicates. Siderite oxidation coupled to iron silicate oxidation and organic carbon burial can thus drive an increase in the \(^{13}C\) of the exogenic pool with no imbalances in oxygen or carbon.

Consider next the effects of sulfide oxidation (Eq. 3) on the carbon cycle: The acidity produced by sulfide oxidation is neutralized by the release of calcium from limestones and silicates, which releases carbon. We need not distinguish between the direct acidification of limestones by sulfuric acid (Eq. 2) and the sulfuric acid weathering of silicates; both reactions equally lead to net release of carbon dioxide: the first by the conversion of carbonate to \(CO_2\), and the second by replacing carboxylic acid weathering with sulfuric acid weathering and thus allowing volatilized \(CO_2\) to go unconsumed. Equally, viewed from the product side, the production of calcium sulfate makes available carbon that would otherwise be tied to the burial of calcium carbonate. Coupled to siderite oxidation, a \(CO_2\) and \(O_2\) neutral reaction can be written (Eq. 9):

\[
3\text{FeS}_2 + 6\text{CaCO}_3 + 7\text{FeCO}_3 + 13\text{H}_2\text{O} \rightarrow 5\text{Fe}_2\text{O}_3 + 6\text{CaSO}_4 + 13\text{CH}_2\text{O}. \quad [9]
\]

We can use Eqs. 8 and 9 to construct a carbon isotopic mass balance. We assume that some fraction, \(\alpha\), of the siderite is oxidized according to Eq. 8, and the rest, \(1 - \alpha\), according to Eq. 9. From the resulting isotopic mass balance, an expression can be obtained
for the isotopic composition of limestones as a function of the siderite oxidation flux (see SI Appendix):

$$\delta^{13}C_{\text{carb}} = \frac{F_{\text{sid}}^{w} (\delta^{13}C_{\text{sid}} + \varepsilon \alpha)}{F_{\text{in}} + \alpha F_{\text{sid}}^{w}}$$

where $\alpha = \frac{1}{2} - \frac{1}{2} \delta$. When the siderite oxidation flux is zero, Eq. 10 gives the long-term isotopic composition of marine carbonates of 0‰. As the net flux of siderite oxidation increases, so does the isotopic value of marine carbonates (Fig. 2). For the middle range of $\delta^{13}C$ values observed in carbonates belonging to the Lomagundi Event ($+8‰ < \delta^{13}C < +10‰$), a siderite oxidation flux between 13 Tmol yr$^{-1}$ (10$^{12}$ moly) and 35.5 Tmol yr$^{-1}$ is required (dotted lines in Fig. 2).

To further evaluate the time-dependent behaviors of CO$_2$ and O$_2$, as well as place bounds on the quantities of reactants involved in the Lomagundi Event, we use a simple model of the sedimentary and oceanic carbon cycles. The model includes the sedimentary reservoirs of organic and carbonate carbon, sulfate and sulfide sulfur, siderite, and reduced iron. It also includes the oceanic reservoirs for calcium, sulfate, phosphate, and alkalinity, and the ocean–atmosphere reservoirs for carbon and oxygen. The carbonate system parameters (pH, pCO$_2$, and the carbonate saturation, $\Omega$) are calculated at every time step. Full model description and code are available in SI Appendix. We set the initial model conditions to postulated pre-Lomagundi conditions: low sulfate (50 $\mu$M), low O$_2$ (10$^{-5}$ present atmospheric level), and high pCO$_2$ (10,500 ppm).

We first use the model to explore the impacts of organic carbon burial without accompanying oxidation of siderite. We then add the oxidation of siderite and iron silicates and evaluate the resultant changes in pCO$_2$ and O$_2$. Forcing organic carbon burial for 130 m.y. so that a +10‰ positive $\delta^{13}C$ excursion arises results in a dramatic drop in pCO$_2$ (Fig. 3, solid black line). Without additional CO$_2$ input from siderite oxidation, organic carbon burial consumes more carbon than can be supplied by sulfide oxidation forcing a precipitous decline in pCO$_2$ to 46 ppm. Following the cessation of this forcing, as organic carbon burial ceases to consume carbon, and sulfide oxidation begins to consume oxygen at a rapid pace, pCO$_2$ rises to 20 × 10$^3$ ppm (2× model baseline). The extremely low minimum pCO$_2$ levels that result in this model run suggest that this scenario is implausible. Conversely, with increasing input of carbon from siderite oxidation, minimum pCO$_2$ levels increase (Fig. 3). With a low amount of FeCO$_3$ oxidized (813 Emol, 10$^{20}$ mol), pCO$_2$ is reduced from the initial 10,800 ppm to 2,800 ppm (red dash-dotted line in Fig. 3). Oxidizing 1,118 Emol of FeCO$_3$ results in a more moderate pCO$_2$ decline to 7,600 ppm (green dashed line in Fig. 3). Increasing the amount of siderite to 1,424 Emol of FeCO$_3$ results in pCO$_2$ not being reduced by any significant amount (solid blue line in Fig. 3). In all cases, the modeled pO$_2$ rises substantially in association with the positive $\delta^{13}C$ excursion. Minimum modeled pO$_2$ is 0.14 atm, or approximately two thirds the modern value, suggesting substantial oxygen accumulation in association with the Lomagundi Event. Overall, the modeling indicates that, when accompanied by siderite oxidation, the Lomagundi Event can be successfully accommodated without it giving rise to nonphysical ocean or atmospheric chemistries.

![Fig. 2](image_url)

**Fig. 2.** Effect of siderite oxidation and organic carbon burial on the carbon isotopic composition of the exogenic carbon pool. Calculated according to Eq. 10 using a total carbon input flux of 50 Tmol yr$^{-1}$. The range of values observed during Lomagundi times, $8‰ < \delta^{13}C < 10‰$, require the oxidation of 13–35.5 Tmol yr$^{-1}$ (10$^{12}$ moly) of siderite (dashed lines), depending on the relative proportions of siderite oxidized together with sulfide ($\alpha = 0$, blue line) versus siderite oxidized together with FeSiO$_3$ ($\alpha = 1$, green line).

![Fig. 3](image_url)

**Fig. 3.** Dynamic model runs simulating the Lomagundi Event. In all model runs, organic carbon burial is increased such that a large (+10‰) positive $\delta^{13}C$ excursion lasting 130 m.y. is generated (A). With increasing amounts of siderite and iron silicate oxidation (B), minimum pCO$_2$ values rise (C), while peak pO$_2$ values decline (D). When organic carbon burial is not accompanied by any siderite oxidation (solid black line), the deficit in CO$_2$ for organic carbon burial drives pCO$_2$ to the extremely low level of 46 ppm. With a small amount of siderite oxidized (red dash-dotted line), pCO$_2$ declines to a more moderate 2,800 ppm; with an intermediate amount (dashed green line), pCO$_2$ declines to 7,600 ppm; and with a high amount (blue solid line), pCO$_2$ does not decline at all. In all cases, O$_2$ rises in association with the $\delta^{13}C$ excursion. Minimum modeled pO$_2$ is 0.14 atm, or approximately two thirds the modern value, suggesting substantial oxygen accumulation in association with the Lomagundi Event. Overall, the modeling indicates that, when accompanied by siderite oxidation, the Lomagundi Event can be successfully accommodated without it giving rise to nonphysical ocean or atmospheric chemistries.
calculated value is consistent with evidence for moderate sea water sulfate concentrations and gypsum precipitation at 2.1 Ga (23). Thus, the oxidation of a large preexisting sedimentary reservoir of siderite, following the rise of O$_2$ in the atmosphere, can successfully accommodate the existence of a large, protracted, positive carbon isotope excursion, driven by organic carbon burial, without it resulting in nonphysical ocean or atmospheric chemistries or violation of global mass balance constraints.

**Discussion**

Our proposal that siderite oxidation played a key role in the Lomagundi Event helps resolve several conundrums related to its timing and duration. It has been pointed out (4) that the order of oxygenation (as indicated by the disappearance of the mass independent fractionation of sulfur isotopes; Fig. 1) and the organic carbon burial event (as evidenced by the positive $\delta^{13}$C values 200 m.y. later) is reversed from what would be expected if organic carbon burial was responsible for the rise of O$_2$. Our mechanism offers a plausible explanation for the observed order of events. Geologically slow processes, such as changes in plate tectonic regime, secular mantle cooling, or a shift in the locus of volcanism leading to changes in volcanic gas composition [among numerous proposed mechanisms (24)], were likely responsible for driving a gradual long-term increase in $p$O$_2$. We postulate that superimposed on this long-term increase in atmospheric $p$O$_2$ was a pulse of O$_2$ production: Once the threshold for oxidation of siderite was surpassed, a positive feedback was triggered whereby siderite oxidation supplied CO$_2$ for organic carbon burial, which in turn supplied oxygen for further siderite, sulfide, and iron silicate oxidation. The siderite was likely oxidized both subaerially, where ex- posed, and in reaction with oxidizing groundwaters that would have penetrated the continental shelves and intracratonic basins for the first time (25). Concomitantly, the burial of siderite would have diminished as a result of a reduction in the inputs of Fe$^{2+}$ from both terrestrial weathering and hydrothermal inputs. Delivery of ferrous iron from terrestrial settings would have ceased under a high-O$_2$ atmosphere, and hydrothermal inputs of reduced iron would have likely diminished in an ocean bearing appreciable quantities of sulfate (26). The oxidation of siderite and burial of organic carbon would have continued until the siderite reservoir was consumed, on the timescale of hundreds of millions of years. Once the large Archean reservoirs of reduced minerals were exhausted and abundant crustal oxidants were produced, little siderite remained to fuel organic carbon burial, and O$_2$ production was curtailed.

Our model, which shows an initial drop in $p$CO$_2$ (Fig. 3), is further consistent with the occurrence of glacial episodes preceding the Lomagundi Event. It is also consistent with the pattern of $\delta^{34}$S changes that occur during the Lomagundi interval. Measurements of both carbonate-associated sulfate (CAS) and evaporite sulfate (27) show an increase in $\delta^{34}$S followed by a protracted decrease, which coincides with the peak of the $\delta^{13}$C excursion, followed by another increase (Fig. 4). These trends have been interpreted as reflecting the balance of sulfide burial to sulfide oxidation in response to changing O$_2$ levels, during, and in the wake of, the Lomagundi Event (27). Our model agrees with and refines this interpretation. In our model, there is an initial increase in $\delta^{34}$S that is driven by an increase in the fractionation factor associated with an increase in sulfate concentrations (28). The $\delta^{34}$S values then decline as large amounts of relatively light sulfate (+7%e) are delivered to the ocean from the oxidation of sulfides, then rise again as that flux wanes, and finally fall as sulfate concentrations decline once more. In the model, 14–18% of the total S reservoir is oxidized to sulfate and sulfate concentrations in the ocean reach a peak of 4 mM, which is ~15% of their modern value. Following this modest burst of sulfate production and deposition during the Lomagundi Event, the $\delta^{34}$S of sedimentary pyrite indicate that pyrite burial became predominant once more, and that dominance was maintained until the second rise of oxygen in the Neoproterozoic (29).

Incidentally, the pattern of $\delta^{13}$C and $\delta^{34}$S variation argues against two otherwise interesting hypotheses that have been put forth in an effort to account for the Lomagundi Event. The first hypothesis postulates that in response to rising $p$O$_2$, methanogenic activity in the shallow marine realm led to the creation of pools of highly $\delta^{13}$C enriched carbon, which was then incorporated into Lomagundi-aged carbonates (4). However, under this scenario, carbonate-associated sulfate incorporated during the precipitation of these carbonates should be extremely $\delta^{34}$S enriched, in contrast to the moderate $\delta^{34}$S values that are observed (27)—although

![Fig. 4. $\delta^{34}$S data from Lomagundi age sediments (27). Light gray boxes are $\delta^{34}$S values measured in sulfate from evaporites (gypsum and anhydrite), and dark gray boxes are $\delta^{34}$S measured in carbonate associated sulfate. Lines are the same model outputs as in Fig. 3. In the model, the initial increase in $\delta^{34}$S is driven by an increase in the fractionation factor associated with an increase in sulfate concentrations (28). The subsequent decline arises from the input of light sulfur (+7%) from sulfide oxidation; the $\delta^{34}$S values then rise again as that flux wanes, and finally fall as sulfate concentrations decline once more. Modeled oceanic sulfate levels reach a peak value of 4 mM, which is ~15% of their modern value.](image-url)
the controls on incorporation of CAS during carbonate precipitation remain incompletely understood. A stronger case can be made against the second hypothesis, that the source of δ13C enrichment in Lomagundi-aged carbonates was the burial of 13C-depleted authigenic carbonates in other (unsampled) settings (30). Oxidation of organic carbon via bacterial sulfate reduction during early diagenesis would have led to the precipitation of authigenic carbonates but, at the same time, would have also led to the precipitation of δ34S-depleted pyrite, resulting in correlating enrichments in both δ13C and δ34S in shelf carbonates, in contradiction with the observed inverse correlation.

A key remaining question is the mechanism by which the carbon produced by siderite and pyrite oxidation was directed to organic productivity. Increased carbon input is a necessary, but not sufficient, condition for increased organic carbon burial and O2 production. Additional limitations arise from the nutrient requirements of organisms, chiefly phosphate (31). However, a simple increase in weathering and delivery of phosphate to the ocean would not generate a positive δ13C excursion, since the resulting increase in organic carbon burial would be coupled to an identical increase in carbonate carbon burial arising from increased delivery of alkalinity. To generate a large positive δ13C excursion, the delivery of phosphate from weathering must be decoupled from the delivery of alkalinity to the ocean. Sulfuric acid weathering is a particularly effective way to mobilize P from apatite (18), allowing for increased organic carbon burial without the concomitant delivery of alkalinity that would demand carbonate burial. An additional effective way to supply phosphate for organic productivity is to reduce the output flux of P relative to that of organic carbon. More-efficient remineralization of phosphate allows for the export of more organic carbon per unit phosphate buried. Our model indicates a fivefold increase in C:P ratios through the event (from 106 to 500), which, although large, is still far less than the values found in much younger black shales (∼ 4,000). The mechanisms by which the C:P burial ratio increased (and by inference, why it was kept low before and after the Lomagundi Event) are still contested (32, 33). We speculate that a combination of the two aforementioned mechanisms may have been at play: Following the initial increase in pCO2, oxidation of sulfides allowed for increased P delivery concomitant with increased availability of sulfate. The development of euxinic (H2S-rich) bottom waters (34) facilitated mobilization of phosphate back into the water column. Increased P delivery together with more efficient P utilization allowed for continued organic productivity and organic carbon burial. This mechanism was curtailed following the exhaustion of the siderite reservoir and concomitant drop in sulfate levels (27).

A second key question pertains to the size of the Archean reduced sedimentary reservoirs that were subsequently oxidized. Estimates are uncertain, as they are extrapolated from preserved Archean sedimentary volumes, and thus depend on poorly known parameters such as the areal extent of Archean continents and the geologic history of sediment recycling. Nonetheless, it is reasonable to expect that siderite and sulfide, as well as other reduced crustal minerals, were oxidized following the initial rise of O2. The question of whether the supply of CO2 and acidity from these oxidizing species played a pivotal role in driving O2 production hinges critically on the interpretation of the carbon isotopic record. If the highly δ13C enriched values were representative of the exogenic carbon pool, and large amounts of organic carbon were buried during the Lomagundi event, then mass balance demands that large amounts of siderite and pyrite were oxidized concurrently to compensate for the enhanced pCO2 drawdown and O2 production.

We conclude by noting that Garrels and Perry (21), in a paper predating much of our understanding of Precambrian redox dynamics, presciently underscored the importance of siderite oxidation in determining the current redox state of the atmosphere: “The role of the oxidation of FeCO3 in creating free oxygen should be emphasized. The level of oxygen in the present steady-state atmosphere would seem to be fortuitous, in that it apparently was controlled by the relative amount of siderite in the preoxygen rocks.” Once the transfer of carbon from the siderite to the organic carbon reservoir was complete, a modern oxidizing atmosphere was established, and Earth settled into its long Mesoproterozoic stasis.

ACKNOWLEDGMENTS. We thank Jim Kasting, Chester Harman, Ying Cui, and Jeff Havig for valuable comments. We thank Noah Planavsky and an anonymous reviewer for constructive reviews. A.B. thanks the Canadian Institute for Advanced Research for a postdoctoral fellowship given through the Earth Systems Evolution Program. L.R.K. acknowledges support from the National Aeronautics and Space Administration Astrobiology Institute, the US National Science Foundation Geobiology and Low-Temperature Geochemistry Program, and the Canadian Institute for Advanced Research.


Supplemental Material

S1 Weathering reduction associated with an increase in organic carbon burial

What is the impact of increased organic carbon burial on weathering and $pCO_2$? The following reasoning might at first glance appear sound. Utilizing the traditional carbon isotope mass balance (Equation S1):

$$\delta^{13}C_{in} = \delta^{13}C_{carb} - f_{org} \times \epsilon$$

Then, applying $\delta^{13}C_{in} = -5\%e$, $\epsilon = 25\%e$, and an organic carbon burial fraction ($f_{org}$) of 0.2 gives the canonical value of 0 \%e. Increasing $f_{org}$ from 0.2 to 0.6 yields a value of +10 \%e. Hence, if during the Lomagundi Event the organic carbon burial fraction increased from 20% to 60%, then carbonate carbon burial must have decreased from 80% to 40% of the total, i.e. by 50%, thus requiring a 50% reduction in weathering.

However, this estimate is erroneous, as it does not take into account the constraints imposed by alkalinity, which imply a far greater reduction—on the order of 91%. To illustrate the underlying logic, we employ a more complete description of the carbon cycle, one which includes alkalinity (Figure S1). For the magnitudes of the fluxes we use values modified from Kump and Arthur (1): $F^w_{volc} = 5$, $F^w_{carb} = 36$, $F^w_{sil} = 4$, $F^w_{org} = 9$, and $F^b_{org} = 10$, $F^b_{carb} = 40$, all in Tmol/yr.

An increase in the fraction of organic carbon burial ($f$) of 0.2 to 0.6 implies an increase in the burial of organic carbon ($F^b_{org}$) from 10 to 30 Tmol/yr and a commensurate reduction in the burial of carbonate carbon ($F^b_{carb}$) from 40 to 20 Tmol/yr. To balance the reduction in carbonate burial, the input of alkalinity from the weathering of silicates and carbonates ($F^w_{sil} + F^w_{carb}$) would have to decline from 40 to 20 Tmol/yr as well. But then not enough carbon is brought in to balance the total carbon output: only $18 + 9 + 5 = 32$ Tmol/yr are brought in but 40 Tmol/yr
are removed. Thus, an additional decline in burial of carbonate and organic carbon is required, which requires another decrease in the weathering flux, and so forth. Consequently, the overall resulting reduction in weathering is far larger than the simplistic estimate of a 50% reduction.

The procedure for calculating the inputs and outputs of carbon and alkalinity, for a specified fraction of organic carbon burial, is given below. We make only three assumptions: 1) that the system is at steady-state, 2) that the only inputs of carbon into the system are from volcanism and the weathering of carbonate and organic carbon, and 3) that the only inputs of alkalinity are from the weathering of carbonate and silicate rocks.

![Basic carbon cycle model for the ocean-atmosphere carbon pool. Modified from Kump and Arthur (1). Units in Tmol/yr.](image)

We begin by expressing the equality between the inputs and outputs of carbon that must exist at steady-state (Equation S2). We introduce a multiplier, $\beta$, which represents the decrease (or increase) in the weathering derived fluxes relative to their original steady-state values (for instance a 20% reduction would be $\beta = 0.8$). The multiplication of the weathering of organic and carbonate carbon fluxes by $\beta$ indicates that they are surficial fluxes subject to physical and
chemical weathering processes, whereas volcanic carbon input is not.

\[ F_{\text{volc}} + (F_{\text{org}}^w + F_{\text{carb}}^w) \beta = F_{\text{org}}^b + F_{\text{carb}}^b \]  
(S2)

Dividing by \( F_{\text{carb}}^b \) gives:

\[ \frac{F_{\text{volc}} + (F_{\text{org}}^w + F_{\text{carb}}^w) \beta}{F_{\text{carb}}^b} = \frac{F_{\text{org}}^b}{F_{\text{carb}}^b} + 1 \]  
(S3)

The ratio of the organic to carbonate carbon burial fluxes, on the left, can be expressed in terms of the organic carbon burial fraction \( f_{\text{org}} \):

\[ \frac{F_{\text{org}}}{F_{\text{carb}}^b} = \frac{f_{\text{org}}}{1 - f_{\text{org}}} \]  
(S4)

So that:

\[ \frac{F_{\text{volc}} + (F_{\text{org}}^w + F_{\text{carb}}^w) \beta}{F_{\text{carb}}^b} = \frac{f_{\text{org}}}{1 - f_{\text{org}}} + 1 = \frac{1}{1 - f_{\text{org}}} \]  
(S5)

Now we take into consideration the fact that the carbonate burial flux must conserve the contribution of alkalinity from the carbonate and silicate weathering fluxes:

\[ (F_{\text{carb}}^w + F_{\text{sil}}^w) \beta = F_{\text{carb}}^b \]  
(S6)

We substitute the alkalinity constraint back into the expression obtained from the carbon mass balance:

\[ \frac{F_{\text{volc}} + (F_{\text{org}}^w + F_{\text{carb}}^w) \beta}{(F_{\text{carb}}^w + F_{\text{sil}}^w) \beta} = \frac{1}{1 - f_{\text{org}}} \]  
(S7)

Rearranging for \( \beta \) yields the final expression:

\[ \beta = \frac{F_{\text{volc}}}{\left( \frac{1}{1 - f_{\text{org}}} \right) \left( F_{\text{carb}}^w + F_{\text{sil}}^w \right) - (F_{\text{org}}^w + F_{\text{carb}}^w)} \]  
(S8)

Substituting the values for the weathering fluxes and volcanic input allows estimating \( \beta \) for a given \( f_{\text{org}} \). If we further assume \( \beta = RCO_2^{0.3} \) we can estimate \( RCO_2 \), defined as the ratio of
Table S1: Values of $\beta$ calculated in accordance with Equation S8. Also shown are the corresponding $\delta^{13}$C values (assuming the canonical values of -5‰ and 25‰ for the carbon input and photosynthetic fractionation), the RCO$_2$ value, and the $p$CO$_2$ value required to maintain steady-state.

<table>
<thead>
<tr>
<th>f$_{org}$</th>
<th>$\delta^{13}$C</th>
<th>$\beta$</th>
<th>RCO$_2$</th>
<th>$p$CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>10,000</td>
</tr>
<tr>
<td>0.4</td>
<td>5</td>
<td>0.23</td>
<td>0.0075</td>
<td>75.3</td>
</tr>
<tr>
<td>0.6</td>
<td>10</td>
<td>0.09</td>
<td>0.00033</td>
<td>3.37</td>
</tr>
<tr>
<td>0.8</td>
<td>15</td>
<td>0.03</td>
<td>1.0685$x10^{-5}$</td>
<td>0.1</td>
</tr>
</tbody>
</table>

As can be seen in the values in Table S1, the values of $\beta$ decline precipitously as the values of $f_{org}$ increase. At high values of $f_{org}$ (and $\delta^{13}$C), $\beta$ is dramatically reduced suggesting that non-physically low levels of weathering are required.

S2 Volcanic carbon inputs and organic carbon burial

Could a long-lived, but temporary increase in carbon inputs potentially prevent atmospheric CO$_2$ levels from crashing, while still allowing increased organic matter burial? To estimate the required increase in carbon input the following calculation might be carried out: carbon isotope mass balance requires that $f_{org}$ be equal to 0.6 for $\delta^{13}$C$_{carb}$ to reach +10‰ (if epsilon is 25‰). Then, assuming the total influx is composed of the initial influx ($x$), 20% of which is buried as organic matter, and an additional influx ($y$), 100% of which is buried as organic matter, the carbon isotope mass balance is:

$$\delta^{13}\text{C}_{\text{in}} \times (x + y) = \delta^{13}\text{C}_{\text{carb}} \times 0.8 \times x + \delta^{13}\text{C}_{\text{org}} \times 0.2 \times x + \delta^{13}\text{C}_{\text{org}} \times y$$  \hspace{1cm} (S9)
Then, substituting the values for \( \delta^{13}C_{\text{carb}} (+10\%) \) and \( \delta^{13}C_{\text{org}} (-15\%) \):

\[
-5 \times (x + y) = 10 \times 0.8 \times x - 15 \times 0.2 \times x - 15 \times y
\]  
(S10)

\[-5x - 5y = 8x - 3x - 15y\]  
(S11)

\[10y = 10x\]  
(S12)

\[y = x\]  
(S13)

So a doubling of the total carbon input is implied, i.e.:

\[\frac{y}{y + x} = 2\]  
(S14)

However, this calculation, similarly to the calculation presented in the opening to Section S1, fails to take into account the constraints imposed by alkalinity. Using the framework presented in S1 we can carry out a more refined calculation and show the difficulty with this proposed solution. We include an additional carbon flux to the mass balance so that it becomes:

\[
\frac{F_{\text{volc}} + F_{\text{extra}} + (F_{w\text{org}} + F_{w\text{carb}})\beta}{(F_{w\text{carb}} + F_{w\text{sil}})\beta} = \frac{1}{1 - f_{\text{org}}}
\]  
(S15)

The magnitude of \( F_{\text{extra}} \) should be large enough so that no reduction in weathering occurs (\( \beta \geq 1 \)), and it must also honor the isotopic constraints which suggest that 60\% of incoming carbon was buried as organic carbon (\( f_{\text{org}} = 0.6 \)). Using the same values for the fluxes as in Section S1 (\( F_{\text{volc}} = 5; F_{w\text{carb}} = 36; F_{w\text{org}} = 9; F_{w\text{sil}} = 4 \)), substituting \( \beta = 1 \) and \( f_{\text{org}} = 0.6 \), and then solving for \( F_{\text{extra}} \) yields:

\[
\frac{5 + F_{\text{extra}} + 9 + 36}{36 + 4} = \frac{1}{1 - 0.6}
\]  
(S16)

\[
\frac{50 + F_{\text{extra}}}{40} = 2.5
\]  
(S17)
So, the results indicate that 50 Tmol/yr of extra carbon are required, an amount that is equal to the total baseline input flux of carbon ($F_{\text{volc}} + F_{\text{wcarb}} + F_{\text{worg}}$). Thus, this calculation indicates that a doubling of the total input flux of carbon is required, exactly as indicated by the simple calculation above, but now the difficulty becomes apparent: the extra carbon has to be supplied in “volcanic” form, that is as $\text{CO}_2$ and not $\text{HCO}_3^-$ or $\text{CO}_3^{2-}$. The reason is that carbon in the form of carbonate alkalinity ($\text{HCO}_3^- + \text{CO}_3^{2-}$), such as supplied by the weathering of calcium silicates and carbonates, is already tied to burial of carbonates and thus is unavailable for organic carbon burial (or at least without causing an imbalance in alkalinity and a decline in $p\text{CO}_2$). An increase in the organic carbon weathering flux is also out of the question since it would simply undo the $^{13}\text{C}$ enrichment effected by the elevated organic carbon burial. Consequently, an eleven-fold increase in volcanism is required (from 5 to 55 Tmol/yr), and not simply a two fold increase in total carbon input. This required increase in volcanic input is very large, and, even if such an increase were geologically plausible, it would only solve half the problem: an increase in volcanic $\text{CO}_2$ input would resolve the conundrum of $\text{CO}_2$ deficit, but not answer the difficulty of $\text{O}_2$ accumulation. Thus, other sources of $\text{CO}_2$ which also consume $\text{O}_2$, such as siderite and sulfide oxidation, must be seriously considered.

### S3 Organic carbon burial accompanied by pyrite oxidation

An increase in organic carbon burial, unaccompanied by increased carbon input, leads to non-physically low levels of weathering because of the resulting imbalance in alkalinity. Pyrite oxidation can ameliorate this imbalance by supplying acidity, thus bolstering $p\text{CO}_2$ levels. As stated in the main text, both the acidification of limestones by sulfuric acid and the sulfuric acid
weathering of silicates equally lead to the release of carbon dioxide. The former acts by direct conversion of carbonate to CO$_2$, while the latter by replacing carbonic acid weathering with sulfuric acid weathering and thus allowing volcanic CO$_2$ to go un-consumed. Consequently, the resulting CO$_2$ is available for organic carbon burial without any charge balance constraints, in contrast to carbonate alkalinity ([HCO$_3^-$],[CO$_3^{2-}$]). It is, nonetheless, important to note that the supply of carbon from the sulfuric acid weathering of silicates should not exceed the flux of volcanic carbon that would otherwise exit as CaCO$_3$ (4 Tmol/yr). Acidification of Ca-silicates in excess of this quantity would lead to an increase in CaCO$_3$ burial and a decrease in the $\delta^{13}$C of the ocean-atmosphere system.

To constrain the required fluxes we augment our previous carbon cycle model with a sulfate box, with one input flux of sulfate from pyrite oxidation and one output flux of CaSO$_4$ (Figure S2):

Figure S2: Basic carbon cycle model for the ocean-atmosphere carbon pool with a sulfate box. X is the variable pyrite oxidation flux. Modified from Kump and Arthur (1). Units in Tmol/yr.
We start with the three mass balance equations, one for each element:

\[ C : \quad F_{volc}^w + F_{org}^w + F_{carb}^w = F_{org}^b + F_{carb}^b \]  
\[ Ca : \quad F_{sil}^w + F_{carb}^w = F_{carb}^b + F_{sulf}^b \]  
\[ S : \quad F_{pyr}^{ox} = F_{sulf}^b \]

Rearranging we get:

\[ F_{sil}^w + F_{carb}^w - F_{pyr}^{ox} = F_{carb}^b \]  
\[ \frac{F_{volc}^w + F_{org}^w + F_{carb}^w}{F_{carb}^b} = \frac{1}{1 - f} \]

Dividing by \( F_{carb}^b \)

\[ F_{volc}^w + F_{org}^w + F_{carb}^w = \frac{1}{1 - f} \]

And substituting back into the expression for carbon:

\[ F_{pyr}^{ox} = (F_{sil}^w + F_{carb}^w) - (1 - f)(F_{volc}^w + F_{org}^w + F_{carb}^w) \]

We can then calculate the necessary pyrite oxidation fluxes required to balance the burial of organic carbon by removal of calcium as gypsum (Table S2):

<table>
<thead>
<tr>
<th>( f )</th>
<th>( \delta^{13}C )</th>
<th>( F_{pyr}^{ox} )</th>
<th>( O_2 ) imbalance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>2.5</td>
<td>5</td>
<td>-4.375</td>
</tr>
<tr>
<td>0.4</td>
<td>5</td>
<td>10</td>
<td>-8.75</td>
</tr>
<tr>
<td>0.6</td>
<td>10</td>
<td>20</td>
<td>-17.5</td>
</tr>
<tr>
<td>0.8</td>
<td>15</td>
<td>30</td>
<td>-26.25</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>-35</td>
</tr>
</tbody>
</table>

Table S2: Pyrite oxidation flux required to balance elevated organic carbon burial, in Tmol/yr. The \( O_2 \) imbalance is the extra \( O_2 \) required for pyrite oxidation beyond that which is produced by organic carbon burial, in Tmol/yr.
As an example of how pyrite oxidation makes CO$_2$ available for organic carbon burial, consider the end-member case where $f = 1$, i.e. all the carbon coming in is buried as organic carbon and none as carbonate carbon. In this case carbonic acid weathering of silicates and carbonates must be zero. For $p$CO$_2$ to remain elevated, carbonic acid weathering must be replaced by sulfuric acid weathering. Thus, a SO$_4$ flux of 40 Tmol/yr, with 4 coming from sulfuric acid weathering of Ca-silicates and 36 from acidification of carbonates completely compensates for missing carbonic acid weathering. Now, 40 Tmol/yr of Ca that would otherwise exit as CaCO$_3$ get buried as gypsum (or accumulate in the ocean), making available for organic carbon burial 40 Tmol/yr of carbon. The only remaining problem is that pyrite oxidation requires 15/8*40 = 75 Tmol/yr of O$_2$, which is 35 Tmol/yr more than organic carbon burial can supply.

It is pertinent to note that the oxygen deficit would be even more severe if sulfide oxidation and carbonate dissolution occurred without a concomitant increase in organic carbon burial. In the framework of the above example 75 Tmol/yr of O$_2$ would be consumed and not just 35 Tmol/yr. Consequently, the oxygen imbalance which arises during sulfide oxidation argues against recent claims for sulfide oxidation as a long-term source of carbon (2). And, if sulfide oxidation did make a significant contribution of carbon during Himalayan uplift, as argued by Torres et al. (2), it would have driven a substantial drop in $p$O$_2$ during the Cenozoic, something for which there is no evidence.

S4 Siderite Oxidation and $\delta^{13}$C

Siderite oxidation can be called upon as a source of carbon over geologic timescales since, in contrast to sulfide oxidation, it produces more CO$_2$ than it consumes O$_2$ (Equation S26) and so can supply CO$_2$ in excess of the amount that is required by organic carbon burial to keep the process going. However, in the context of the Lomagundi Event, the oxidation of siderite

9
must have also been coupled to processes that produce acidity (sulfide oxidation) or consume
O\textsubscript{2} (iron silicate oxidation) as siderite oxidation alone together with the simple (carbonic acid)
weathering silicates could not have generated the Lomagundi Event. The reason is that the
alkalinity generated during the consumption of the excess carbon by silicate weathering would
have negated the \textsuperscript{13}C enrichment effected by organic carbon burial.

To appreciate this difficulty, and more generally, some of the intricacies of siderite oxidation,
consider the oxidation of siderite coupled to weathering of silicates and the burial of organic
carbon and carbonate carbon:

\begin{equation}
4\text{FeCO}_3 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2 \quad \text{(S26)}
\end{equation}

\begin{equation}
\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \quad \text{/ \_ x} \quad \text{(S27)}
\end{equation}

\begin{equation}
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \quad \text{/ \_ y} \quad \text{(S28)}
\end{equation}

One could combine these equations in two ways: first, as an overall CO\textsubscript{2}-neutral reaction (x +
y = 4), and second, as an O\textsubscript{2}-neutral reaction (y = 1). Together with the constraints from the
carbon isotope record \( f_{org} = y/(y + x) = 0.6 \) one can obtain the desired stoichiometries. In
the O\textsubscript{2} neutral case y = 1 and x = 2/3, and in the CO\textsubscript{2} neutral case x = 1.6 and y = 2.4. Hence,
the CO\textsubscript{2}-neutral reaction leads to net release of O\textsubscript{2} at a rate of 1.4 moles of O\textsubscript{2} per 4 moles of
siderite oxidized, while the O\textsubscript{2} neutral reaction leads to net release of CO\textsubscript{2}, at a rate of 2 1/3
moles per 4 moles of siderite oxidized.

These imbalances cannot be maintained over timescales of hundreds of m.y. of years over which
the Lomagundi Event occurs. In the CO\textsubscript{2} neutral reaction one is left with with a large excess of
O\textsubscript{2}, and in the O\textsubscript{2} neutral reaction case one is left with a large excess of CO\textsubscript{2}. The duration of
the event is such that if the organic carbon burial were not fully compensated in terms of both
CO\textsubscript{2} and O\textsubscript{2} physically non-permissible atmospheric compositions would quickly arise (i.e. \( p_{O_2} \))
or $p_{CO_2} \gg 1$ atm). Thus, $CO_2$ or $O_2$ must not appear in the overall reaction for oxidation of siderite together with the weathering of calcium silicates; nor for that matter should they appear in any other reaction which is postulated to have taken place over the duration of the Lomagundi Event. Below we give the appropriate reactions for siderite oxidation coupled to calcium silicate weathering, siderite oxidation coupled to Fe-silicate weathering, and siderite oxidation coupled to Fe-sulfide oxidation and acidification of carbonates.

$$4FeCO_3 + 3CaSiO_3 + H_2O \rightarrow 2Fe_2O_3 + 3CaCO_3 + 3SiO_2 + CH_2O \quad (S29)$$

$$FeCO_3 + 3FeSiO_3 + H_2O \rightarrow 2Fe_2O_3 + 3SiO_2 + CH_2O \quad (S30)$$

$$3FeS_2 + 6CaCO_3 + 7FeCO_3 + 13H_2O \rightarrow 5Fe_2O_3 + 6CaSO_4 + 13CH_2O \quad (S31)$$

What are the biggest differences between the three reactions? Examine the first reaction above (Equation S29): the 1 mol of oxygen produced during the burial of organic matter is balanced by the oxidation of 4 moles of siderite which produces 4 moles of $CO_2$. One mole of the 4 moles of $CO_2$ which is produced goes to the burial of organic carbon while the other 3 to the weathering of silicates. The overall result is an $f_{org}$ ratio of 0.25. Thus, this reaction is nearly isotopically transparent. The increase in the burial of organic carbon in this case is balanced by an increase in the burial of carbonate carbon at a ratio that is very near the long term average $\delta^{13}C$ of the exogenic cycle. Such a reaction would have contributed little to $^{13}C$ enrichment during the Lomagundi Event, and even then mostly via the relatively heavy $\delta^{13}C$ value of the siderite carbon. Contrast Equation S29 with Equations S30 and S31. In the latter two reactions the burial of organic carbon is not accompanied by the offsetting burial of carbonates making them much more effective in driving $^{13}C$ enrichment.

Thus, there are more and less efficient ways to drive $^{13}C$ enrichment via siderite oxidation coupled to organic carbon burial. When inverting the $\delta^{13}C$ record, one is given a degree of freedom
in choosing the varying proportions of the three reactions. By choosing a large proportion of siderite oxidation coupled to non-Fe-silicate weathering (Equation S29) one could explain the Lomagundi Event in a way that involves an amount of reactants that exceeds those which were likely available for oxidation or leads to the production of more products than can be accounted for.

Does such a worst-case-scenario calculation does invalidate the hypothesis? No, it is the best case scenario which is the test: if it can be shown that even under the most propitious circumstances the hypothesis fails, then it can be confidently rejected. Hence, in our tables and model runs below we focus on the most effective ways to drive the Lomagundi Event and show that these do not violate mass balance constraints. We do not claim that back reactions (sulfide burial, oxidation of organic carbon) or the weathering of non-Fe-silicates did not occur, but we do maintain that these must have been minor in relation to the forward reactions, as demanded by constraints imposed by the global mass balance on the one hand and the $\delta^{13}\text{C}$ (and $\delta^{34}\text{S}$) record on the other.

**S5 Derivation of Equation 10**

We can use Equations S30 and S31 to construct a carbon isotopic mass balance. We assume that some fraction, $\alpha$, of the siderite is oxidized together with Fe-silicates according to Equation S30, and the rest, $(1 - \alpha)$, reacts with sulfides and carbonates according to Equation S31. The first reaction (Equation S30) implies that the burial of organic carbon occurs at a 1:1 ratio with siderite oxidation, such that a certain portion of organic carbon burial is proportional to the siderite oxidation flux associated with iron silicate oxidation. Following the same logic, the stoichiometry of the second reaction is such that for every mol of siderite oxidized, $6/7$ mol of carbonate are acidified and $13/7$ mol of organic carbon are buried, inducing the following...
isotopic mass balance:

\[(1 - \alpha)F_{\text{sid}}^w \delta_{\text{sid}}^w + \frac{6}{7}(1 - \alpha)F_{\text{sid}}^w \delta_{\text{carb}}^w = \frac{13}{7}(1 - \alpha)F_{\text{sid}}^w \delta_{\text{org}}^b\]  

(S32)

Adding the above expressions to the mass balance of the pre-Lomagundi carbon cycle,

\[F_{\text{in}}^{w,0} \delta_{\text{in}}^w = F_{\text{carb}}^{b,0} \delta_{\text{carb}}^b + F_{\text{org}}^{b,0} \delta_{\text{org}}^b\]  

(S33)

gives:

\[F_{\text{in}}^{w,0} \delta_{\text{in}}^{w,0} + \alpha F_{\text{sid}}^w \delta_{\text{sid}}^w + (1 - \alpha)F_{\text{sid}}^w \delta_{\text{carb}}^w + \frac{6}{7}(1 - \alpha)F_{\text{sid}}^w \delta_{\text{carb}}^b = F_{\text{carb}}^{b,0} \delta_{\text{carb}}^b + F_{\text{org}}^{b,0} \delta_{\text{org}}^b + \alpha F_{\text{sid}}^w \delta_{\text{org}}^b + \frac{13}{7}(1 - \alpha)F_{\text{sid}}^w \delta_{\text{org}}^b\]

We assume that the isotopic composition of all the organic carbon burial is fractionated by a constant amount relative to seawater, so given by \((\delta_{\text{carb}}^b - \epsilon)\), where \(\epsilon\) is the photosynthetic fractionation. Collecting terms gives the following mass balance equation:

\[F_{\text{in}}^{w,0} \delta_{\text{in}}^{w,0} + F_{\text{sid}}^w \left[\delta_{\text{sid}}^w + \frac{6}{7}(1 - \alpha)\delta_{\text{carb}}^w\right] = F_{\text{carb}}^{b,0} \delta_{\text{carb}}^b + \left[F_{\text{org}}^{b,0} + \left(\frac{13}{7} - \frac{6}{7}\alpha\right)F_{\text{sid}}^w\right] (\delta_{\text{carb}}^b - \epsilon)\]  

(S34)

Rearranging so that it is given for \(\delta^{13}\text{C}\) of the ocean-atmosphere system:

\[\delta_{\text{carb}}^b = \frac{F_{\text{in}}^{w,0} \delta_{\text{in}}^{w,0} + F_{\text{sid}}^w \left[\delta_{\text{sid}}^w + \frac{6}{7}(1 - \alpha)\delta_{\text{carb}}^w\right] + \epsilon \left[F_{\text{org}}^{b,0} + \left(\frac{13}{7} - \frac{6}{7}\alpha\right)F_{\text{sid}}^w\right]}{F_{\text{carb}}^{b,0} + F_{\text{org}}^{b,0} + \left(\frac{13}{7} - \frac{6}{7}\alpha\right)F_{\text{sid}}^w}\]  

(S35)

Note that:

\[F_{\text{in}}^{w,0} = F_{\text{org}}^{b,0} + F_{\text{carb}}^{b,0}\]  

(S36)

and

\[F_{\text{in}}^{w,0} \delta_{\text{in}}^{w,0} = F_{\text{org}}^{b,0} (\delta_{\text{carb}} - \epsilon) + F_{\text{carb}}^{b,0} \delta_{\text{carb}}\]  

(S37)

so that assuming \(\delta_{\text{carb}}^{w,0} = 0\%_0\) gives:

\[F_{\text{in}}^{w} \delta_{\text{in}} + F_{\text{org}}^{b} \epsilon = 0\]  

(S38)
Thus:

\[
\delta^{b}_{\text{carb}} = \frac{F^{w,0}_{\text{in}} \delta^{w,0}_{\text{in}} + \epsilon F^{b,0}_{\text{org}} + F^{w}_{\text{sid}} \left[ \delta^{w}_{\text{sid}} + \left( \frac{13}{7} - \frac{6}{7} \alpha \right) \epsilon \right]}{F^{w}_{\text{in}} + \left( \frac{13}{7} - \frac{6}{7} \alpha \right) F^{w}_{\text{sid}}}
\]  

(S39)

and finally:

\[
\delta^{b}_{\text{carb}} = \frac{F^{w}_{\text{sid}} \left[ \delta^{w}_{\text{sid}} + \epsilon \left( \frac{13}{7} - \frac{6}{7} \alpha \right) \right]}{F^{w}_{\text{in}} + \left( \frac{13}{7} - \frac{6}{7} \alpha \right) F^{w}_{\text{sid}}}
\]  

(S40)

To make the expression more compact we define an alpha prime:

\[
\alpha' = \frac{13}{7} - \frac{6}{7} \alpha
\]  

(S41)

So the final expression is:

\[
\delta^{b}_{\text{carb}} = \frac{F^{w}_{\text{sid}} \left[ \delta^{w}_{\text{sid}} + \epsilon \alpha' \right]}{F^{w}_{\text{in}} + \alpha' F^{w}_{\text{sid}}}
\]  

(S42)

Equation 10 in the main text (or Equation S42 above) has a Michaelis-Menten form (as is borne out in Figure 2: as the value of \(F^{w}_{\text{sid}}\) increases, \(\delta^{b}_{\text{carb}}\) asymptotically approaches the value of \(\frac{\delta^{w}_{\text{sid}}}{\alpha} + \epsilon\), which is approximately 24 %o. When the siderite flux is zero, the carbon isotopic composition of the ocean-atmosphere system returns to its long-term steady-state value of 0%o.

### S6 Global mass balance

Using Equation S42 it is further possible to calculate the siderite oxidation flux required by a Gaussian shaped positive excursion of up to +10 %o of a given duration (Figure S3). The total siderite flux is then given by the area under the \(F^{w}_{\text{sid}}\) curve.

To calculate an alpha, we use a constrained optimization algorithm (fmincon, Matlab (3)), such that a minimum amount of siderite is used, coupled to the constraint that the total integrated oxidation of pyrite not exceed the total exogenic sulfur pool of 534 Emol of sulfur. The logic behind this choice is that the total amount of exogenic sulfur, which is currently partitioned
Figure S3: A. Gaussian shaped positive $\delta^{13}$C$_{\text{carb}}$ excursions up to +10 % with durations of 100, 130, 190, and 250 m.y. B. The resulting siderite oxidation flux according to Equation S42, with the values of alpha set to keep the total sulfate production below 534 Emol. Area under curves given in Table S3. Different colored curves in both plots correspond to different durations.

between the ocean, continental sulfide, and continental sulfate, likely existed entirely as continental sulfide prior to the Lomagundi event, and was thus available for oxidation during the event. We do not claim that all the sulfur was oxidized and precipitated as gypsum. Rather, we utilize this constraint as an upper theoretical bound on the extent of siderite oxidation via Equation S31.

The results are given in Table S3 for four durations (100, 130, 190, and 250 m.y.) and three input fluxes (25, 50, and 75 Tmol/yr). The code to produce the figure and table is given in the supplementary files. We also include the cumulative amounts of reactants consumed and products produced during our dynamic model runs, which are discussed in Section S7. The three runs (Model 1–3) given are the same model runs that are presented in Figure S7. Positive values for CaCO$_3$ in the first two runs indicate that carbonate dissolution was lower in the perturbed state than in steady-state. This is due to the lower than baseline $p$CO$_2$ which occurs
in those two runs.

<table>
<thead>
<tr>
<th>$F_{\text{in}}$</th>
<th>Duration</th>
<th>FeS$_2$</th>
<th>CaCO$_3$</th>
<th>FeSiO$_3$</th>
<th>FeCO$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaSO$_4$</th>
<th>CH$_2$O</th>
<th>$\alpha$</th>
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Table S3: Top: total amounts in Emol ($10^{18}$) of reactants consumed and products generated during a Gaussian shaped $\delta^{13}C$ excursion of up to $+10\%$, obtained via two different calculations. First, by utilizing Equation 10 (Figure S3), together with the constraint that the amount of pyrite oxidized together with siderite (Reaction 9) did not generate sulfate in excess of the modern CaSO$_4$ + FeS$_2$ reservoirs (534 Emol); siderite oxidation accompanied by iron silicate oxidation (Reaction 8) was presumed to make up the remainder. Second, using the dynamic model runs, in which case runs with non-physical atmospheric chemistries ($pO_2 \gg 1$ atm and $pCO_2 \ll 0$ atm) were rejected. The three runs (Model 1–3) are the same model runs presented in Figure S7. Positive values for CaCO$_3$ in the first two runs indicate that carbonate dissolution was lower in those runs than in steady-state. In all cases the fraction of siderite accompanied by FeSiO$_3$ oxidation (Reaction 8) is given by $\alpha$. Bottom: estimated reservoir sizes. All are given for the present, except for siderite which is given for 2.2 Ga. Higher Fe$_2$O$_3$ estimate includes oxidized iron in crystalline silicate rocks.

To compare the results of our calculations to measured values, we compiled estimates of relevant sedimentary reservoirs sizes. First, we give some comments on the estimates culled from the literature which are presented at the bottom of Table S3. We then discuss the degree of correspondence between our calculations and the estimates. The most detailed inventory of the
sizes of the crustal reservoirs of CaCO$_3$, C$_{org}$, FeS$_2$, and CaSO$_4$ can be found in Holser et al. (6), which also summarizes previous estimates from Holser and Kaplan (10), Li (11), Garrels and Perry (4), Schidlowski and Eichmann (12), Nielsen (13), and Garrels and Lerman (14). The reported values fall in the range of 84 – 294 Emol S for the sulfide reservoir; 81 – 240 Emol S for the sulfate reservoir; 3505 – 6460 Emol for CaCO$_3$; and 930 – 1300 Emol for C$_{org}$. Hayes and Waldbauer (7) give an updated and in-depth discussion, which, in addition to the values given by Holser et al., summarizes more recent values for sedimentary compilations given by Wedepohl (15), Hunt (16), Des Marais (17), Berner (18), and Arvidson et al. (19), which fall within the range of 2800 – 6500 Emol of CaCO$_3$ and 675 – 1300 Emol of C$_{org}$. They also cite mass-age data on carbonates from Wilkinson and Walker (20), which suggest a somewhat larger carbonate reservoir size (7900 – 9600 Emol), and thus a correspondingly larger C$_{org}$ reservoir size (1400 – 1700).

Estimates for crustal iron are given by Yaroshevsky (8), who summarizes previous results from Vinogradov (21) and Ronov et al. (22): the sedimentary shell is estimated to contain 393.75 Emol of oxidized iron and 1018.5 Emol of reduced iron, with another 888 Emol of oxidized iron and 1867 Emol of reduced iron in the upper crust (granitic-metamorphic shell), totaling 1280 Emol of oxidized iron and 2886 of reduced iron. For oxidized iron, Garrels and Perry estimate the excess oxidized iron in sedimentary rocks at 263 Emol Fe$_2$O$_3$. Sleep (5) gives a lower estimate for sedimentary oxidized iron: 50 Emol of sedimentary Fe$_2$O$_3$, requiring 100 Emol of Fe and 25 Emol of O$_2$ to have been produced, but a higher estimate for oxidized crustal iron (including hard rocks) of 4000 Emol of Fe$_2$O$_3$, requiring 8000 Emol Fe and 2000 Emol O$_2$, though he does acknowledge that the uncertainties in composition of the lower continental crust could lead to the lower, but still very large, estimate of 2000 Emol Fe$_2$O$_3$, requiring 1000 Emol of O$_2$ to have been produced. Hayes and Waldbauer (7) cite Ronov and Yaroshevsky (23) for an estimate of 1020 O$_2$ equivalents, or 2040 Emol of Fe$_2$O$_3$, and a higher estimate.
from Goldschmidt of 1860 Emol O₂ equivalents, or 3720 Emol Fe₂O₃—near the estimate of Sleep. Altogether, the estimates converge on oxidized crustal iron as being the most substantial reservoir of O₂ equivalents.

For siderite, other than the anecdotal descriptions of its relative abundance given in Ohmoto et al. (24), the only quantitative estimate is by Ronov et al. (9) based on observations of the Russian platform. At 2.3 Ga, they estimate that Jasperlites (which, as stated in the text, are considered to be altered siderites) to constitute 14% of the sedimentary shell of 25,000x10²⁰ gr, or 3.0x10²¹ mol FeCO₃. Incorporating models for sediment recycling results in an even larger estimate of 22%, as discussed by Garrels and Mackenzie (25). In fact, the large increase in Jasperlites followed by their total disappearance in the phanerozoic is perhaps one of the most remarkable features of Ronov et al’s data, as already pointed out by Garrels and Mackenzie (25). Garrels and Perry (4) give a value of 350 Emol of sedimentary FeCO₃, though this estimate is based on the amounts required to balance oxidized sedimentary iron rather than by rock data. Nonetheless, their logic holds, and the much larger estimates for oxidized iron which include iron in crystalline silicate rocks correspond very well to the total estimated the mass of siderite available for oxidation at 2.3 Ga.

How did such large amounts of oxidized iron accumulate in the crust? During the Archean iron was likely delivered in reduced form from the weathering of silicate rocks and the dissolution of pyrite and siderite in sedimentary rocks. It likely exited the ocean in equally reduced form as pyrite and siderite. Ferric to total iron ratios in shales are not much different from mantle values until the Great Oxidation Event (38) and it is only following during it that the ferric iron content of shales rises substantially. During the Lomagundi Event pO₂ rose to significant levels for the first time and reduced iron delivered from weathering became oxidized on land for the first time. The weathered iron accumulated as oxidized iron in shales and as redbeds on the con-
tinents (redbeds make their first appearance following the Great Oxidation Event). In addition, diagenetic alteration of reduced iron as oxidizing fluids flowed through sedimentary basins for the first time likely also led to substantial accumulation of iron oxides (39). Oxidation of iron in mid-ocean ridge basalts by oceanic sulfate (which likely rose from very low Archean levels for the first time) likely also contributed to growth of the oxidized iron reservoir. The iron in oceanic basalts undergoing subduction would have been particularly likely to be incorporated into crystalline rocks of the continental crust. During the remainder of the Proterozoic, following the Lomagundi Event, weathering would have delivered both oxidized iron and reduced iron. The fraction of iron that in reduced form was likely oxidized subaerially. Some of that iron accumulated as redbeds while some of it was delivered to the marine realm where it was likely reduced and exited as pyrite. This situation likely persisted until oxidation of the deep ocean, much later, during the Phanerozoic, which led to an additional loci of iron oxide deposition in deep sea.

Comparing the values computed according to Equation 10, and the estimated sizes of the crustal reservoirs, in particular of organic carbon, oxidized iron, and sulfate, given in Table S3, shows that the lower estimates (corresponding to a lower duration of the Lomagundi Event and/or lower estimates for total carbon input) match reasonably well to the existing crustal reservoirs. Moreover, the larger estimates for organic carbon, though they exceed the estimates for the current reservoirs, do not invalidate the conclusions, as material could have been lost since the Lomagundi Event. For instance, subduction of organic carbon or its oxidation subsequently to the Lomagundi Event could have led to a smaller fraction of the produced organic carbon being preserved. In particular, the hypothesis that subduction of organic carbon as well as its oxidation to methane were accelerated during and immediately following the Lomagundi Event is an attractive one, as it would explain the unidirectional and permanent nature of the Earth surface oxidation that occurred in association with it.
Many workers have highlighted the fact that Earth has an excessively oxidized atmosphere and crust. In particular, Lovelock (27, 28) pointed out that while Mars and Venus are at the equilibrium redox potential appropriate to their stations in the solar system, that of Earth is far more oxidized than its position would suggest. The implication is that Earth’s unique features, plate tectonics and life, are likely responsible for its current redox state (see also Hayes and Waldbauer, 7). This process was very likely aided by a methane “hydrogen balloon” (Lovelock and Lodge (27), Catling et al. (29)) which transported hydrogen to the upper atmosphere. We suggest that the processes of hydrogen loss to space and to the mantle may have been pulsed as well, and tightly coupled to episodes of organic carbon production (and burial). Thus, the oxidized products accumulated in the crust and atmosphere, while the reducing power was transferred to organic carbon, and then subsequently subducted into the mantle and lost to space.

It is worth emphasizing the main difference between our own interpretation of the carbon cycle and that of Hayes and Waldbauer, and others before them, is that while they postulate that the accumulation of oxidants ($\text{Fe}^{3+}$, $\text{SO}_{4}^{2-}$, $\text{O}_2$) and reductants ($\text{C}_{\text{org}}$, $\text{FeS}_2$) occurred gradually throughout the Geozoic, we acknowledge the possibility that large portions of these reservoirs could have been accumulated, and destroyed, in shorter periods of geologic time (on the order of tens to hundreds of millions of years).

**S7 Model Description**

The model includes mass boxes for the oceanic concentrations of carbon, calcium, sulfur, phosphate, oxygen, and alkalinity, as well as isotopic mass for carbon, calcium and sulfate (Figure S4). The sedimentary reservoirs included in the model are organic carbon, carbonate carbon, sulfide sulfur, sulfate sulfur, reduced iron, and siderite. A carbonate system solver, modified from Emerson and Hedges (30) and Zeebe and Wolf-Gladrow (31), is used to calculate $p\text{CO}_2$, ...
pH, and the carbonate saturation state ($\Omega$) from values of alkalinity and DIC at every model
timestep. Complete list of constitutive equations and flux relations is given in Section S8. The
full code is supplied in supplemental files.

The first numerical experiment we perform is a simple sanity test: we force the model with
weathering fluxes of siderite, sulfide, and carbonate, and burial of organic carbon and sulfate,
in stochiometric relations according to Equation 9 in the main text, such that a +10 permil
excursion results. This perturbation is a “Goldilocks” solution with the reactants and products
exactly balanced so should incur no changes in $pO_2$ or $pCO_2$. Results are shown in Figure
S5. In Table S4 we give the values produced by the model, calculated in two ways: firstly,
by integrating the relevant fluxes with respect to time, and secondly by subtracting the initial
Table S4: Table comparing model output to analytical calculations. First row (Model Int) is obtained by integrating the time-varying fluxes in the model. The second row is obtained by subtracting initial and final sedimentary reservoir sizes. The third row (Calc) are the same values given in Table S3 (5th row: 50 Tmol/yr, 100 m.y.) but without rounding. Nearly identical solutions between the first and second rows indicate that the model conserves mass. Nearly identical solutions of the semi-analytical calculation and numerical model indicate that the model is accurate.

and final sedimentary reservoir masses. The differences between the first row (integration) and second row (subtraction) are in the second decimal point, indicating that the model preserves mass. The differences between the model and the calculation arise due to truncation error, as well as the maximal $\delta^{13}$C in the model, which is 10.001%, as opposed to an exact 10% in the calculation. The differences are on the order of 0.15% of the analytical solution, indicating that the model is reasonably accurate.

The next numerical experiment we perform is to incorporate parameterizations for the weathering and burial fluxes, and force a pulse of organic carbon burial. We first force the model without any pyrite oxidation, and we then add two different parameterizations of the pyrite oxidation flux. We show the model outputs for $\delta^{13}$C, $p$CO$_2$, and $p$O$_2$ in Figure S6.

The model results are that under the scenario of pyrite oxidation according to the Williamson and Rimstidt parameterization (green dashed line) $p$CO$_2$ falls to 46.6 ppm. Under the scenario where the pyrite and gypsum weathering fluxes are set to the modern ones with modification for the reservoir size (blue solid line), $p$CO$_2$ falls the least, but still reaches very low values of 108.3 ppm. The decline in $p$CO$_2$ is driven by the burial of organic carbon: the removal of DIC from ocean water, with little accompanying alkalinity, drives the carbonate system from neutrality and towards a zone of higher pH and lower $p$CO$_2$. The weathering fluxes, which are
Figure S5: Model outputs for a pulse of carbon burial coupled to carbonate carbon acidification, sulfide oxidation, and siderite oxidation in accordance with Equation 9 in the main text, such that a +10 permil excursion results. This perturbation does not result in changes in pO$_2$ or pCO$_2$ since it follows a stoichiometrically balanced reaction for both species. A. The concentration of inorganic carbon in the ocean (C$\text{C}$) and its isotopic composition ($\delta_{\text{Carb}}$). B. Atmospheric oxygen and carbon dioxide concentrations (pO$_2$, pCO$_2$) C. Mass of sedimentary organic carbon and carbonate carbon reservoirs (M$^{\text{sed}}_{\text{Corg}}$ and M$^{\text{sed}}_{\text{Ccarb}}$). D. Mass of siderite and the siderite oxidation flux (M$^{\text{sed}}_{\text{FeCO3}}$ and F$^W_{\text{FeCO3}}$).
Figure S6: Model outputs for a pulse of carbon burial unaccompanied by increased carbon input. All simulations show a drop in $pCO_2$ to extremely low levels. Under the scenario of no pyrite oxidation (red dash-dotted line) $pCO_2$ falls to 3.76 ppm, close to the theoretical value calculated in Table S1. Under the scenario of pyrite oxidation according to the Williamson and Rimstidt parameterization (green dashed line) $pCO_2$ falls to 46.6 ppm. Under the scenario where the pyrite and gypsum weathering fluxes are set to the modern ones with modification for the reservoir size (blue solid line), $pCO_2$ falls the least, but still reaches very low values of 108.3 ppm. The inclusion of pyrite oxidation impacts the $pO_2$ response as well. Without pyrite oxidation, oxygen accumulates and remains high, whereas with pyrite oxidation, $pO_2$ returns to baseline after the perturbation. The peak values for $pO_2$ are 0.46 atm (2.1 PAL) under the Williamson and Rimstidt parameterization, and $3 \times 10^{-5}$ (3x baseline) under the alternative parameterization. Note log scale on y axes in B. and C.
set to be proportional to $pCO_2^{0.3}$, respond by declining, thus lowering the input of carbon and alkalinity from weathering. The carbonate burial flux, which is proportional to the carbonate saturation state, declines as well, even as pH increases, because of the reduction in the input of Ca$^{2+}$. The system thus approaches a new equilibrium, one in which the inputs of alkalinity are equal to the much reduced outputs of alkalinity. When sulfide oxidation is added to the model weathering fluxes, the contribution of sulfate helps mitigate the imbalance in alkalinity, thus resulting in higher $pCO_2$ levels. The oxidation of pyrite also leads to a more realistic behavior of O$_2$, whereby instead of accumulating in the atmosphere and remaining constant after the perturbation, O$_2$ returns to steady-state after the perturbation (compare dash-dotted curve to the dashed and solid lines in Figure S6.B).

Since the parameterization of the pyrite oxidation flux exerts such a strong control on the $pCO_2$ and $pO_2$ response of the model during the positive excursion, a brief description of the available choices is in order. The first, simpler yet probably less appropriate parameterization, is one that takes the current modern estimates and scales them to the size of the Late Archean - Early Proterozoic sulfate and sulfide sedimentary reservoirs, which were likely much smaller and much larger, respectively. Thus, if the Phanerozoic estimates for the sulfide and sulfate sedimentary reservoirs are 294 and 240 Emol (a ratio of 0.55), and associated fluxes are 0.93 and 0.76 Tmol S /yr (using the values from Garrels and Perry, 4), then assuming a 0.99 ratio of sedimentary reservoir masses in favor of sulfide gives fluxes of 1.72 and 0.01 Tmol S /yr for the Late Archean - Early Proterozoic. We allow the sulfide oxidation flux to scale as the square root of the ratio of $pO_2$ to its initial value, and linearly with the size of the remaining pyrite reservoir:

$$F_{FeS2}^w = F_{FeS2}^{w,i} \left[ \frac{pO_2}{pO_2,i} \right]^{0.5} \left[ \frac{M_{FeS2}^{sed}}{M_{FeS2,i}^{sed}} \right]$$  \hspace{1cm} (S43)

The alternative formulation takes into account the kinetics of pyrite oxidation as experimentally
constrained by Williamson and Rimstidt (32) (see also Bolton et al., 33):

\[
R_{FeS_2} = \frac{10^{-8.19} \left[ pO_2 \ast K_{H2O}^O \right]^{0.5}}{[H^+]^{0.11}} \ast 31536000;
\]  \hspace{1cm} (S44)

where \( R_{FeS_2} \) is the rate at which pyrite is oxidized with units of \( \frac{mol}{m^2 \text{ yr}} \) (the factor of 31536000 converts from seconds to years). It is observed to scale with the square root of the dissolved aqueous \( O_2 \) concentration (which is given by atmospheric \( O_2 \) multiplied by Henry’s constant for oxygen, 0.00126 [mol/L/Atm at 25C]), and to be weakly inversely proportional (0.11 power) to the concentration of protons in the weathering solution, which we calculate as pH of pristine rainwater in equilibrium with atmospheric \( CO_2 \), which is given as the roots of a cubic equation in \([H^+]\) (Harte (34), Stumm and Morgan (35)):

\[
[H^+]^3 - [pCO_2 \ast k_1 \ast k_H + k_w] \ast [H^+] - 2 \ast (pCO_2 \ast k_2 \ast k_1 \ast k_H) = 0
\]  \hspace{1cm} (S45)

with the appropriate rate constants: \( k_H = 10^{-1.47}, k_1 = 10^{-6.35}, k_2 = 10^{-10.33}, k_w = 10^{-14} \).

Once the oxidation rate is known, a scaling relationship between the calculated rate of pyrite oxidation under modern \( pCO_2 \) and \( pO_2 \) conditions \( (R_{FeS_2}^{mod}) \), and the estimated modern pyrite oxidation flux \( (F_{FeS_2}^{w,mod}) \) and reservoir size \( (M_{FeS_2}^{sed,mod}) \) can be obtained:

\[
K_{Pyr}^{ox} = \frac{F_{FeS_2}^{w,mod}}{R_{FeS_2}^{mod} \ast M_{FeS_2}^{sed,mod}}
\]  \hspace{1cm} (S46)

This constant \( K_{Pyr}^{ox} \) can then by used to calculate the pyrite oxidation flux under different boundary conditions of reservoir size and oxidation rate (as a function of \( pO_2 \) and \( pCO_2 \)):

\[
F_{FeS_2}^w = K_{Pyr}^{ox} \ast R_{FeS_2} \ast M_{FeS_2}^{sed};
\]  \hspace{1cm} (S47)

The result of scaling to a higher \( pCO_2 \), lower \( pO_2 \), and larger reservoir size, is that pyrite oxidation is calculated to be substantially smaller in the low-\( O_2 \) Archean (approximately \( 1x10^9 \) Tmol/yr versus \( 1x10^{11} \) Tmol/yr in the present). The initial magnitude of the sulfide oxidation flux under the different parameterizations (\( 4.47x10^9 \) or \( 1.67x10^{12} \) Tmol/yr) makes a difference
for how high $pO_2$ needs to go up to increase the flux such that it balances the accumulation of alkalinity due to organic carbon burial. The higher the initial value, the less $pO_2$ has to increase in order to balance the input and outputs of carbon and alkalinity. Nonetheless, because of the inherent imbalances associated with pyrite oxidation, which lead to a shortage of carbon, $pCO_2$ falls to low levels, irrespective of the parameterization used.

Next, we perturb the model with a Gaussian shaped excess organic carbon burial flux, and allow for siderite and iron silicate oxidation, in addition to pyrite oxidation. The results are shown in Figure S7. With increasing siderite contribution the $pO_2$ peak increases, the $pCO_2$ minimum rises, and the $pCO_2$ maximum becomes more pronounced. In the first case (red dash-dotted line) with 813 Emol of FeCO$_3$ consumed $pCO_2$ falls to 2800 ppm and then rises 13,600 ppm. In the second case (green dashed line) with 1118 Emol of FeCO$_3$ consumed $pCO_2$ falls to 7600 ppm and then rises 16,500 ppm. In the third case (blue solid line) with 1424 Emol of FeCO$_3$ consumed $pCO_2$ is not reduced at all and then rises 21,150 ppm. Perhaps counter-intuitively, the increasing amount of siderite causes the $pCO_2$ peak associated with the declining limb of the $\delta^{13}C$ excursion to be smaller. This is because the oxidation of siderite (and iron silicates) diverts O$_2$ from sulfide oxidation, and it is the sulfide oxidation flux which drives the increase in $pCO_2$ through its effects on alkalinity and thus carbonate burial. A higher sulfide oxidation flux leads to a smaller carbonate burial flux because of the sulfide oxidation’s contribution of acidity, and hence a larger imbalance which then is required to correct itself, leading to a $pCO_2$ overshoot.

We show the changes in [SO$_4$] and $\delta^{34}S$ of the oceanic sulfate box associated with each of these three model runs in Figure S8 and Figure S9. The resulting trends in $\delta^{34}S$, as stated in the main text, arise mainly due to two effects. The sharp rise and decline in $\delta^{34}S$ are a result of increased fractionation associated with increased availability of sulfate. We use the
Figure S7: Model outputs for a pulse of carbon burial accompanied by siderite, pyrite, and iron silicate oxidation. With increasing siderite contribution the \( pO_2 \) peak increases, the \( pCO_2 \) minimum rises, and the \( pCO_2 \) maximum becomes more pronounced. In the first case with a low amount of siderite oxidized (red dash-dotted line) \( pCO_2 \) falls to 2800 ppm and then rises 13600 ppm, and \( pO_2 \) rises to 0.14 Atm. In the second case with an intermediate amount of siderite oxidized (green dashed line) \( pCO_2 \) falls to 7600 ppm and then rises 16500 ppm, and \( O_2 \) rises to 0.23 Atm. In the third case with a large amount of siderite oxidized (blue solid line) \( pCO_2 \) is not reduced at all and then rises 21150 ppm, while \( pO_2 \) rises to 0.34 Atm.
Figure S8: Variation in the $[\text{SO}_4]$ and $\delta^{34}\text{S}$ of the oceanic sulfate box, same model runs as in Figure S7 above.

Parameterization suggested by Habicht et al. (36), with a fractionation factor of 1.029 above a threshold of 190 $\mu$M and a linear decrease to 1.000 as sulfate decreases towards zero. Since all model runs include a rise in $\text{SO}_4$ above 190 $\mu$M there is little variation in the response with varying pyrite oxidation rates. In contrast, the drop in $\delta^{34}\text{S}$ in the middle is a result of the influx of light sulfide to the sulfate box from pyrite oxidation, and some variation is apparent: lower $\delta^{34}\text{S}$ result from increased sulfate input. As shown in Figure S9 and in the main text these results fit the data from Planavsky et al. (37) quite well, lending support to our interpretation of the events which occurred during Lomagundi times.
Figure S9: Plot of modeled $\delta^{34}$S variation overlaying data from Planavsky et al. (37). In the model the sharp rise and fall in $\delta^{34}$S are a result of increased fractionation associated with increased availability of sulfate, while the drop in $\delta^{34}$S in the middle is a result of the influx of light sulfide to the sulfate box from pyrite oxidation. Lines are the same model runs as in Figures S7 and S8.
S8 Model Equations
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<td>pH</td>
<td>ph</td>
<td>8.03</td>
<td>-</td>
</tr>
<tr>
<td>Steady-state volcanic input</td>
<td>$F_{\text{volc}}$</td>
<td>$5 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Weathering input of organic carbon</td>
<td>$F_{\text{org}}$</td>
<td>$9 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Weathering input of CaCO$_3$</td>
<td>$F_{\text{carb}}$</td>
<td>$36 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Silicate weathering input of calcium</td>
<td>$F_{\text{sil}}$</td>
<td>$4 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Weathering input of phosphate</td>
<td>$F_{\text{p}}$</td>
<td>$9.3 \cdot 10^{10}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Burial of organic carbon</td>
<td>$F_{\text{org}}^b$</td>
<td>$10 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Burial of CaCO$_3$</td>
<td>$F_{\text{carb}}^b$</td>
<td>$40 \cdot 10^{12}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>Burial of phosphate</td>
<td>$F_{\text{p}}^b$</td>
<td>$9.3 \cdot 10^{10}$</td>
<td>mol/yr</td>
</tr>
<tr>
<td>C:P burial ratio</td>
<td>CP</td>
<td>106</td>
<td>-</td>
</tr>
<tr>
<td>$\delta^{13}$C of volcanic flux</td>
<td>$\delta_{\text{volc}}$</td>
<td>-5</td>
<td>permil</td>
</tr>
<tr>
<td>$\delta^{13}$C of carbonate weathering</td>
<td>$\delta_{\text{carb}}$</td>
<td>0</td>
<td>permil</td>
</tr>
<tr>
<td>$\delta^{13}$C of organic carbon weathering</td>
<td>$\delta_{\text{org}}$</td>
<td>-25</td>
<td>permil</td>
</tr>
<tr>
<td>$\delta^{13}$C of carbonate burial</td>
<td>$\delta^b$</td>
<td>0</td>
<td>permil</td>
</tr>
<tr>
<td>$\delta^{13}$C of organic carbon weathering</td>
<td>$\delta_{\text{org}}^b$</td>
<td>-25</td>
<td>permil</td>
</tr>
<tr>
<td>Photosynthetic fractionation</td>
<td>$\epsilon$</td>
<td>25</td>
<td>permil</td>
</tr>
</tbody>
</table>

Flux values after DePaolo (40) and Kump and Arthur (1). Magnitude of photosynthetic fractionation from Hayes et al. (41). Concentrations of carbon, calcium, and phosphate converted to masses using an ocean volume of $1.32 \cdot 10^{21}$ L and salinity of 1.035 kg/L.
Table S6: Isotopic mass equations for oceanic reservoirs

\[
\frac{dM_C}{dt} = F_{C_{volc}}^w + F_{CaCO_3}^w + F_{C_{org}}^w - F_{C_{org}}^b - F_{C_{carb}}^b
\] (S48)

\[
\frac{dM_{Ca}}{dt} = F_{Ca_silt}^w + F_{CaCO_3}^w + F_{CaSO_4}^w - F_{CaCO_3}^b - F_{CaSO_4}^b
\] (S49)

\[
\frac{dM_{PO_4}}{dt} = F_{PO_4}^w - F_{PO_4}^b
\] (S50)

\[
\frac{dM_S}{dt} = F_{S_{volc}}^w + F_{CaSO_4}^w + F_{Pyr}^w - F_{CaSO_4}^b - F_{Pyr}^b
\] (S51)

\[
\frac{dO_2}{dt} = F_{C_{org}}^b + 1.875 F_{Pyr}^b - F_{C_{org}}^w - 1.875 F_{Pyr}^w - f_{\text{redox}} F_{C_{volc}}^w
\] (S52)

\[
- 1.875 f_{\text{redox}} F_{S_{volc}}^w
\] (S53)

\[
\frac{d\delta_C}{dt} = \left[ F_{C_{volc}}^w (\delta_{C_{volc}} - \delta_C) + F_{CaCO_3}^w (\delta_{CaCO_3} - \delta_C) + F_{C_{org}}^w (\delta_{C_{org}} - \delta_C) - (F_{C_{org}}^b)(-\epsilon_C) \right] \frac{1}{M_C}
\] (S54)

\[
\frac{d\delta_{Ca}}{dt} = \left[ F_{Ca_silt}^w (\delta_{Ca_silt} - \delta_C) + F_{CaCO_3}^w (\delta_{CaCO_3} - \delta_C) + F_{CaSO_4}^w (\delta_{CaSO_4} - \delta_C) - (F_{CaSO_4}^b + F_{CaSO_4}^b)(-\epsilon_C) \right] \frac{1}{M_{Ca}}
\] (S55)

\[
\frac{d\delta_S}{dt} = \left[ F_{S_{volc}}^w (\delta_{S_{volc}} - \delta_S) + F_{CaSO_4}^w (\delta_{CaSO_4} - \delta_S) + F_{Pyr}^w (\delta_{Pyr} - \delta_S) - F_{Pyr}^b(-\epsilon_S) \right] \frac{1}{M_S}
\] (S56)
Table S7: Mass and isotopic mass equations for sedimentary reservoirs

\[
\frac{dM_{\text{sed,pyr}}}{dt} = F_{\text{pyr}}^b - F_{\text{pyr}}^w - F_{\text{subd}}^{\text{S,pyr}} \quad (S57)
\]

\[
\frac{dM_{\text{sed,sulf}}}{dt} = F_{\text{CaCO}_3}^b + F_{\text{CaSO}_4}^b - F_{\text{CaSO}_4}^w - F_{\text{subd}}^{\text{S,sulf}} \quad (S58)
\]

\[
\frac{dM_{\text{sed,org}}}{dt} = F_{\text{org}}^b - F_{\text{org}}^w - F_{\text{subd}}^{\text{org}} \quad (S59)
\]

\[
\frac{dM_{\text{CaCO}_3}}{dt} = F_{\text{CaCO}_3}^b - F_{\text{CaCO}_3}^w - F_{\text{subd}}^{\text{CaCO}_3} \quad (S60)
\]

Table S8: Weathering feedbacks

\[
F_{\text{Ca}_\text{sil}}^w = F_{\text{Ca}_\text{sil}}^w \cdot (R_{\text{CO}_2})^{0.3} \quad (S61)
\]

\[
F_{\text{CaCO}_3}^w = F_{\text{CaCO}_3,i}^w \cdot (R_{\text{CO}_2})^{0.3} \quad (S62)
\]

\[
F_{\text{org}}^w = F_{\text{org},i}^w \cdot (R_{\text{CO}_2})^{0.3} \quad (S63)
\]

\[
F_{\text{PO}_4}^w = F_{\text{PO}_4,i}^w \cdot (R_{\text{CO}_2})^{0.3} \quad (S64)
\]
Table S9: Sulfide oxidation feedbacks

\[ [H^+] = \text{roots}([H^+]^3 - [pCO_2 * k_1 * k_H + k_w] *[H^+] - 2 * (pCO_2 * k_2 * k_1 * k_H)) \]  \hspace{1cm} (S65)

\[ k_H = 10^{-1.47}, \ k_1 = 10^{-6.35}, \ k_2 = 10^{-10.33}, \ k_w = 10^{-14} \]  \hspace{1cm} (S66)

\[ R_{FeS_2} = \frac{10^{-8.19} (pO_2 * K_{O2}^{0.5})}{[H^+]^{0.11}} * 31536000; \]  \hspace{1cm} (S67)

\[ K_{Pyt}^{ox} = \frac{F_{w,mod}^{FeS_2}}{R_{FeS_2}^{mod} * M_{FeS_2}^{sed,mod}} \]  \hspace{1cm} (S68)

\[ F_{FeS_2}^w = K_{Pyt}^{ox} * R_{FeS_2} * M_{FeS_2}^{sed}; \]  \hspace{1cm} (S69)

Table S10: Burial feedbacks

\[ F_{CaCO_3}^b = F_{CaCO_3,i}^b \cdot \left( \frac{\Omega_{CaCO_3}}{\Omega_{CaCO_3,i}} \right) \]  \hspace{1cm} (S70)

\[ F_{CaSO_4}^b = F_{CaSO_4}^b \cdot \left( \frac{ICP_{CaSO_4}}{ICP_{CaSO_4,i}} \right) \]  \hspace{1cm} (S71)

\[ F_{PO_4}^b = F_{PO_4,i}^b \cdot \left( \frac{M_{PO_4}}{M_{PO_4,i}} \right) \]  \hspace{1cm} (S72)

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Table S11: Auxiliary definitions

\[ \Omega_{\text{CaCO}_3} = \frac{[\text{Ca}] \cdot [\text{CO}_3^{\text{2-}}]}{K_{\text{sat \text{calcite}}}} \]  \hspace{1cm} (S73)

\[ \text{ICP}_{\text{CaSO}_4} = [\text{Ca}] \cdot [\text{SO}_4] \]  \hspace{1cm} (S74)

\[ [\text{ALK}] = 2[\text{Ca}] - 2[\text{SO}_4] + 2[\text{Mg}] + [\text{K}] + [\text{Na}] - [\text{Cl}] \]  \hspace{1cm} (S75)

\[ R_{\text{CO}_2} = \frac{p\text{CO}_2}{p\text{CO}_2,i} \]  \hspace{1cm} (S76)

\[ R_{\text{CO}_2} = \frac{p\text{CO}_2}{p\text{CO}_2,i} \]  \hspace{1cm} (S77)
References


