A productivity collapse to end Earth’s Great Oxidation

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It has been hypothesized that the overall size of—or efficiency of carbon export from—the biosphere decreased at the end of the Great Oxidation Event (GOE) (ca. 2,400 to 2,050 Ma). However, the timing, tempo, and trigger for this decrease remain poorly constrained. Here we test this hypothesis by studying the isotope geochemistry of sulfate minerals from the Belcher Group, in subarctic Canada. Using insights from sulfur and barium isotope measurements, combined with radiometric ages from bracketing strata, we infer that the sulfate minerals studied here record ambient sulfate in the immediate aftermath of the GOE (ca. 2,018 Ma). These sulfate minerals captured negative triple-oxygen isotope anomalies as low as ~–0.8‰. Such negative values occurring shortly after the GOE require a rapid reduction in primary productivity of >80%, although even larger reductions are plausible. Given that these data imply a collapse in primary productivity rather than export efficiency, the trigger for this shift in the Earth system must reflect a change in the availability of nutrients, such as phosphorus. Cumulatively, these data highlight that Earth’s GOE is a tale of feast and famine: A geologically unprecedented reduction in the size of the biosphere occurred across the end-GOE transition.

Proterozoic | primary productivity | Great Oxidation Event | triple-oxygen isotopes | nutrient limitation

The rise of oxygen in Earth’s atmosphere during the early Paleoproterozoic was one of the most transformative events in all of Earth’s history. Evidence for this event can be observed through the disappearance of mass-independently fractionated sulfur isotopes (1) within reduced and oxidized forms of sulfur ca. 2,430 to 2,330 Ma (2) as well as macroscale features in the sedimentary record such as the emergence of red beds or the disappearance of detrital pyrite and uraniuminite (3). Following the initial rise in atmospheric oxygen is the largest positive shift in the carbonate carbon isotope record [–2,220 to 2,060 Ma (4, 5)] termed the Lomagundi–Jatuli Excursion (LJE). The interval between the initial rise of O2 ca. 2,430 to 2,330 Ma and the end of the LJE—marked by carbon isotope values returning to values of ~0‰—has traditionally defined Earth’s Great Oxidation Event (6) and we follow this convention here.

The LJE has widely been interpreted as a transient rise in organic carbon burial and by consequence a rise in atmospheric O2. Importantly, this rise in O2 has been suggested to exceed not only Archean, but also background Proterozoic (6, 7) and possibly Phanerozoic levels in a so-called “oxygen overshoot” (8, 9). However, this high-O2 interpretation can be tempered under different assumptions regarding changes in the isotopic value of carbon inputs to the global dissolved inorganic carbon (DIC) reservoir as well as the fractionation associated with carbon fixation by primary producers (10). Moreover, some researchers question whether these ca. 2,220- to 2,060-Ma carbonates actually record changes to global marine DIC and instead have suggested that such isotopic records may document local and/or diagenetic processes (e.g., ref. 11). This controversy surrounding the LJE has motivated independent tests of whether such an oxygen overshoot, and corresponding transition from a high-pO2 syn-Great Oxidation Event (GOE) state to a comparatively low-pO2 post-GOE state, even occurred. Numerous independent proxies, while differing in degree of severity, broadly characterize this interval as a decline in surface environment oxidant inventories (12–18). However, it is worth noting that many such records may better reflect local depositional environments and not necessarily global conditions. Moreover, almost all of these records reflect the passive response of a geochemical proxy to a change in Earth’s oxidant reservoir (i.e., the effect), rather than capturing the atmospheric signal of interest or, perhaps more importantly, the underlying cause. Cumulatively, it is clear that the application of an independent test of such models will prove useful in narrowing in on the end-GOE transition.

A critical factor in evaluating the GOE and the end-GOE transition is an understanding of the mechanism driving oxygenation. A rise in atmospheric oxygen during the GOE could have been the result of increased organic carbon production (i.e., increased gross primary production [GPP] and by consequence a larger biosphere). To sustain a larger biosphere during both the buildup to and maintenance of a high-pO2 state during the GOE, it has been proposed that high weathering rates (perhaps including siderite; ref. 9) and consequent phosphorus release would have resulted from elevated H2SO4 generation via pyrite oxidation during the GOE (although this remains debated; ref. 12). This large release of phosphorus would have then sustained the posited oxygen overshoot in a feast-like scenario (6, 8). In marked contrast to the elevated GPP hypothesized for the GOE, evidence has been presented that characterizes the mid-Proterozoic [~2,000 to 1,100 Ma (14)] as an interval of remarkably low GPP, possibly just 6% of modern levels (14, 19). Although GPP changes across this transition have been assumed (16), quantifying the degree to which the GOE deviated from the mid-Proterozoic GPP state remains largely unexplored, and how quickly such a transition in the biosphere occurred to mark the end of the GOE remains unknown. To better understand the end-GOE transition and test the hypothesis that the end-GOE was brought about by a nutrient famine, we provide new insights into the demise of increased GPP in the basin setting of the Great Oxidation Event.

Significance

The Great Oxidation Event (GOE) ca. 2,400 to 2,050 Ma caused the first significant accumulation of free oxygen in the atmosphere and potentially a dramatic growth of oxidant reservoirs on the Earth’s surface in a suggested “oxygen overshoot.” However, the termination of this event remains poorly understood. Here, we present geochemical data suggesting a drastic decline in gross primary productivity across the end-GOE transition, delineating a shift from “feast” to “famine” conditions characteristic of the next 1 billion y.

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employ a combined isotope approach utilizing triple-oxygen ($\Delta ^{17} \text{O}$), multiple-sulfur ($\delta^{34}\text{S}$, $\delta^{33}\text{S}$, $\delta^{34}\text{S}$), and Ba isotopes ($\delta^{132/124}\text{Ba}$) on barites collected from the Belcher Group, Nunavut, Canada. These samples capture the interval of time immediately after the GOE (Orosirian; ref. 20) and allow quantitative constraints to be placed on the productivity (GPP) of the biosphere at this time.

**Geological Context.** The Belcher Group is a 7- to 10-km thick sedimentary basin in subarctic Canada, largely deposited between 2,018.5 ± 1.0 Ma and 1,854.2 ± 1.6 Ma (Fig. 1 and ref. 20). The lowermost Belcher Group is composed of ∼1 km of dolomiticrite deposited in a sabkha environment (Kasegalik Formation). This is followed by several hundred meters of Eskimo Formation basalts. Overlying this are 3 km of generally supratidal to shallow subtidal carbonate sedimentary rocks with minor siliciclastic rocks (Fairweather, McLeary, Tukarak, Mavor, Costello, and Laddie formations). Progradation is recorded in the Rowatt and Mukpollo formations, followed by the deposition of granular iron formation in the Kipalu Formation. The overlying Flaherty Formation is composed of submarine basalt and is up to several kilometers thick. The Belcher Group concludes with the deposition of a flysch (Omarolluk Formation) and molasse [Loaf Formation (20 km thick]. The Belcher Group formation is concluded with the deposition of a flysch (Omarolluk Formation) and molasse [Loaf Formation (20 km thick]. No halite was observed in the McLeary Formation but it did bear small chert-replaced, twinned gypsum crystals along a single stratigraphic horizon <2 m thick. Finally, large (∼1–4 cm) barite crystals are present in the Costello Formation (22) and are the primary focus of this study. This formation is composed of some 10 to 20 m of gray to black shale, overlain by several hundred meters of rhythmically bedded, variably red, pink, gray, and cream-colored dolomiticrite with shale partings and very thinly interbedded limestone. In a small area on eastern Tukarak Island, milky-white barite crystals up to several centimeters in width occur in massive, cream-colored dolomiticrite (Fig. 1). There is no evidence for subaerial exposure or the presence of a strongly evaporitic/restricted environment associated with the Costello Formation barites; to the contrary, slumps and partial Bouma sequences have led to the interpretation that the Costello Formation was deposited in a foreslope environment (21).

**Mass-Independent Oxygen-Isotope Variations.** The $\Delta ^{17} \text{O}$ anomaly recorded within sedimentary $\text{SO}_4$ reflects both the amount of tropospheric $\text{O}_2$, which itself is driven by 3 principle variables: $p\text{CO}_2$, $p\text{O}_2$, and GPP (SI Appendix, Fig. S2). Photochemical reactions in

![Fig. 1. Location of the Belcher Islands, sampling site, and sulfate/evaporite occurrences. (A) Stratigraphic column of the Belcher Group, indicating the intervals at which gypsum pseudomorphs (gypsum pseudo.), halite casts, microbarite, and macrobarite were observed. Refer to SI Appendix, Fig. S1 for photographs of each type of occurrence. The Kasegalik Formation, deposited in a sabkha environment, was host to the largest amount of evaporite casts and $\text{SO}_4$ minerals observed in the Belcher Group. Higher in the stratigraphy, the McLeary Formation contains 1 stratigraphic horizon with a small amount of gypsum pseudomorphs. Finally, the Costello Formation contains centimeter-scale barite crystals along a single stratigraphic horizon on eastern Tukarak Island. (B) Map of North America with Belcher Islands in the black box. (C) Map of Belcher Islands. Macrobarites are indicated by a red circle. (D) Macrobarites, with Canadian penny for scale.]

![Image](https://www.pnas.org/cgi/doi/10.1073/pnas.1900325116 Hodgskiss et al.)
the stratosphere involving the production of O₃ (ozone) do so with a mass-independent partitioning of isotopes, where O₃ becomes enriched in ¹⁷O and O₂ depleted in ¹⁷O relative to a suggested definition of mass dependence [³¹⁷O/³²⁰O = 0.5305 (25, 26)]. Depletions and enrichments in ¹⁷O relative to this definition of mass-dependent fractionation are termed “triple-

oxygen isotope anomalies,” which are defined as ¹⁷O/¹⁸O = 0.5305(Δ¹⁷O) and are reported on the per mil (%ε) scale relative to Vienna Standard Mean Ocean Water (V-SMOW). The ¹⁷O depletion in O₂ (negative Δ¹⁷O values) can be made larger via isotopic exchange between O₂ and CO₂ (27) where larger depletions are observed at higher pCO₂ levels. Mass-independently depleted O₂ produced in the stratosphere is then transported to the troposphere where it is mixed with photosynthetically derived O₂ from the biosphere that carries a mass-dependently fractionated Δ¹⁷O value [i.e., Δ¹⁷O of ~0‰ (ref. 28 and SI Appendix, Fig. S2)]. Therefore, the degree of depletion from stratospheric reactions with CO₂, the rate of nonmass independent O₂ production from the biosphere, and the size of the O₂ reservoir where these fluxes compete set the Δ¹⁷O value of tropospheric O₂ (29). Provided that limited amounts of microbial cycling occur, tropospheric Δ¹⁷O values can be deposited and preserved in the sedimentary record in the form of SO₄-bearing minerals (e.g., gypsum, barite, CAS). All postatmospheric processes that fractionate toward heavier or lighter ¹⁷O in O₂ eventually to pyrite through reactions with Fe in sediments; and any isotopic effects associated with precipitation itself (14, 33). Oxidative weathering of volcanically derived sulfur produces SO₄ with a δ³⁴S value (δ³⁴S = [³⁴S/³²S]sample - [³⁴S/³²S]Standard) of ~0‰ and a δ³³S value (δ³³S = δ³⁴S - [³⁴S/³²S]⁰ = 1515) of ~0.05‰ (13) reported here relative to Vienna Canion Diablo Troilite (V-CDT) scale. Fractionation by dissimilatory SO₄ reduction or microbial sulfide oxidation (34), which likely dominated microbial S cycling across the Paleoproterozoic (35), results in sulfide species with lower δ³³S values and thus leaves residual SO₄ isotopically enriched in ¹³C (e.g., ref. 36). Minor sulfur isotopes are also sensitive to microbial cycling that will slightly increase or decrease Δ³⁴S values in residual SO₄, depending upon the dominant S metabolism (35-37). Such processes give the modern marine SO₄ reservoir a δ³⁴S value of +21.2‰ and a Δ³⁴S value of +0.05‰ (33). Therefore, multiple sulfur isotopes can aid in exploring the nature of ancient SO₄ deposits (e.g., marine or terrestrial) as well as provide insights into the degree of microbial-S cycling.

Materials and Methods
Nine “macrobarite” samples were collected from the Costello Formation for geochronological analyses. For Δ¹⁷O measurements, samples were dissolved and purified to produce pure barite, which was subsequently analyzed and measured by isotope ratio mass spectrometry (IR-MSS). δ³⁴S and Δ³⁴S measurements, S was extracted and purified using Thode solution and then fluorinated and measured by IR-MSS. Finally, S³⁴S values were carried out by sample alkaline dissolution, barium purification using column chromatography, and subsequent analysis by multicollector inductively coupled plasma mass spectrometry. Refer to SI Appendix for detailed methods.

Results
Triple-oxygen- and Ba-isotope data for microbarites from the Kasegalik Formation and macrobarites from the Costello Formation are summarized in SI Appendix, Table S1. Costello Formation macrobarite Δ¹⁷O values are closely clustered, with all analyses falling between ~0.78‰ and ~0.55‰, well below that of modern marine SO₄ [−0.09‰ (31)] and modern tropospheric O₂ (~0.51‰; ref. 30 and Fig. 2). δ³⁴S values in these samples cover a range that includes modern marine SO₄ (33) and overlap with previously published δ³⁴S CAS values from the Kasegalik Formation (Fig. 3A and ref. 42). Unlike δ³⁴S values, Δ³⁴S data significantly deviate from values for modern marine SO₄ (Δ³⁴S = +0.05‰ (33)) with predominantly negative values between ~0.11‰ and ~0.06‰ (Fig. 3B). Finally, Costello Formation macrobarite δ³⁸/S values tightly cluster between +0.08‰ and +0.12%, similar to values for modern and post-Marinoan marine barites (ref. 38 and Fig. 3B), but contrast with modern terrestrial, cold seep, or hydrothermal values (~0.49‰ to ~0.52‰, ~0.61‰ to +0.36‰, and ~0.08‰ to ~0.04‰, respectively; ref. 38).

Discussion
Genesis of Costello Formation Barites. The Costello Formation is the dominant host of barites (and Ba and SO₄) in the Beltch Group and we explore hypotheses for their genetic origin here. There is no stratigraphic, sedimentologic, mineralogic, or petrographic evidence for subaerial exposure in the Costello Formation (20-22), and thus it is unlikely that the macrobarites formed via direct precipitation of Ba- and SO₄-bearing salts in a strongly evaporitic environment. Rather, their large size, well-developed crystal habit, and lack of preferred orientation with respect to bedding strongly suggest that these barites formed postdepositionally rather than in the water column or at the sediment–water interface with coeval carbonates (Fig. 1). Since barite is an insoluble mineral (~20% Ba), significant Ba accumulation typically require the mixing of 2 separate fluids, one rich in Ba and the other in SO₄ (38, 40). The Ba- and S-isotope composition of barites thus constrains their respective source fluids and enables deduction of the significance of the Δ¹⁷O variations preserved therein.

We consider 5 possible sources of SO₄ to Costello Formation macrobarites. In stratigraphic order these are 1) remobilized SO₄ from the evaporitic and SO₄ pseudomorph-bearing horizons of the Kasegalik Formation, 2) remobilized SO₄ from the microbarite-bearing horizons of the Kasegalik Formation, 3) remobilized SO₄ from the formerly gypsum-bearing horizons of the McLeary Formation, 4) the ambient seawater SO₄ reservoir during the time of Costello Formation deposition, and 5) the downward movement of SO₄ from sediments overlying the Costello Formation. Two of these options (scenarios 2 and 3) can be ruled out on mass-balance grounds. The small stratigraphic expression of the macrobarites in...
the Kasegalik Formation and their low abundance (~1 ppm) make them a poor candidate source of SO$_4$ to the Costello Formation. Similarly, the McLeary Formation (ca. 1,945 Ma) was observed to have only a very small amount of chert-replaced gypsum. Scenario 5 is also highly unlikely because there are no known occurrences of SO$_4$-bearing minerals or their pseudomorphs in the stratigraphy overlying the Costello Formation.

The remaining 2 candidate sources of SO$_4$ set stratigraphically opposed temporal constraints on $\Delta^{17}$O signatures and, by consequence, Ba. A seawater source of SO$_4$ (scenario 4) that was penecontemporaneous with deposition of the Costello Formation would imply a more recent origin of the $\Delta^{17}$O signature, likely imparted ca. 1,930 Ma (assuming a constant sedimentation rate between age constraints), with a minimum age of 1,870 Ma $\pm$ 3 Ma from cross-cutting dykes and sills (Fig. 1 and refs. 20 and 43). A diffusive supply of seawater SO$_4$ to the barite-forming environment would also suggest that the global seawater SO$_4$ reservoir was characterized by large negative $\Delta^{17}$O values observed within the macrobarites, given that the Costello Formation bears no evidence for having formed in a strongly hydraulically restricted water mass.

While this scenario is difficult to disprove sedimentologically, it would require abnormally low rates of microbial sulfur cycling to prevent the removal of $\Delta^{17}$O-anomalous SO$_4$ and abnormally high rates of continental SO$_4$ inputs to maintain a continuous supply of SO$_4$ that carried negative $\Delta^{17}$O anomalies; such a state has been inferred only for the exceptional oceanographic case of a meltwater lens following deglaciation of the Marinoan Snowball Earth (44). The alternative “remobilization” scenario 1, in which the SO$_4$ in Costello Formation macrobarites was derived from Kasegalik Formation SO$_4$-bearing minerals, places age constraints between 2,018.5 $\pm$ 1.0 Ma and 2,015.4 $\pm$ 1.8 Ma on $\Delta^{17}$O signatures. The Kasegalik Formation contains abundant chert-replaced gypsum pseudomorphs interspersed through some 25% of the stratigraphy (Fig. 1) and therefore, on the grounds of its sheer mass of SO$_4$-bearing minerals as well as its evaporitic setting, seems a likely source of SO$_4$ to the overlying Costello Formation. The similarity of $\delta^{34}$S values of CAS measurements from the Kasegalik Formation (Fig. 3 and ref. 42) and those of the macrobarites of the
Costello Formation cannot distinguish between these 2 possibilities, and additional evidence is required to discriminate between these sources of SO4 for the Costello Formation macrobarites.

As noted previously (e.g., ref. 38), barites precipitated from large Ba reservoirs, such as seawater, generally exhibit a narrow Ba-isotope range close to the crustal average, whereas barites formed in more restricted closed-system settings show wide compositional ranges due to variable influences of inputs, diffusive transport, and precipitation–dissolution events (38). The narrow variance that was measured for δ18O Ba values for Costello Formation macrobarites (+0.10%e ± 0.02%e; ±SD, n = 7) is indicative of a large Ba reservoir (e.g., ref. 39). We contend that this reservoir was contemporaneous seawater, since the mean δ18O Ba value of Costello Formation macrobarites closely matches those of ancient and modern marine precipitates (41). Due to the insoluble nature of barite, a contemporaneous seawater source of Ba implies a nonseawater source of SO4 to the Costello Formation macrobarites. In turn, this constraint indicates that Costello Formation macrobarites record Δ17O anomalies inherited from SO4 that were tens of millions of years older than the barites themselves (10), which is possible if SO4-bearing fluids were stored in basinal or tens of millions of years older than the barites themselves (10), that is, the remobilized SO4 originated from which is possible if SO4-bearing fluids were stored in basinal or tens of millions of years older than the barites themselves (10), that is, the remobilized SO4 originated from...

A Productivity Crash to End the GOE? Δ17O values in the Costello Formation macrobarites (with sulfate that formed ca. 2,018.5 to 2,015.4 Ma) are similar to those deposited in the ca. 1,700-Ma Myrtle Shale Formation (14) and ca. 1,400-Ma Sibley Group (19), suggesting that the transition out of the GOE marks the onset of conditions that may have persisted across the >600-Ma interval separating these deposits (Fig. 2 and refs. 4, 14, 19, and 20). We set temporal constraints on this isotopic transition by comparing Costello Formation macrobarite results to the suggested youngest syn-GOE Δ17O values from the Tulomozero Formation in Russian Karelia (14, 46). The observation of highly positive δ34S values (up to +13.9‰) indicates that Tulomozero Formation sulfate was deposited during the LJE, placing an age of at least 2,108 to 2,057 Ma on these sediments and suggesting the shift in Δ17O values across the end-GOE occurred over <39 to 90 My. This illustrates the relative rapidity of the step change seen in the Δ17O record across the end-GOE.

The differences in Δ17O values between syn- and post-GOE samples could indicate a step change in the fraction of atmospheric O2 preserved within SO4 deposits (fO2), a step change in the pO2 pCO2 GPP conditions that produced the atmospheric Δ17O anomaly, or some combination of these 2 factors. If the change were only due to fO2, the shift in Δ17O values across the end-GOE transition would require a 4-fold increase in fO2 after the GOE (from >0.02 to <0.15; SI Appendix, Table S1). However, if pO2 was lower after the GOE interval (7), one would not expect more O2 incorporation into SO4 accompanying sulfide oxidation, thus placing the full burden on enhanced S cycling during the GOE to explain the Δ17O shift. Both syn- and post-GOE samples exhibit a similar range of δ34S values (~25‰; Fig. 3A) despite clear interformation variability. This is consistent with a similar degree of S cycling during both intervals and, by inference, no diminution of the syn-GOE Δ17O signal by enhanced O2 exchange with water (14, 46). Although the distinctly more positive Δ17O values in syn-GOE samples could be interpreted to reflect greater S reoxidation at this time (35, 37), another explanation is that the lack of any covariation with δ34S (cf. refs. 13 and 47) suggests that such signatures might instead reflect an isotopic shift associated with the oxidative weathering of “old” crustal sulfides (48).

In light of these considerations, we explore the Δ17O transition out of the GOE with respect to changing pO2 pCO2 GPP conditions. The spatial and isotopic consistency of the Δ17O results for the GOE (8 formations; 81 measurements; mean Δ17O = −0.18‰e ± 0.14‰e, 2σ; refs. 14 and 46), as well as for the mid-Proterozoic (3 formations; 86 measurements; mean Δ17O = −0.86‰e ± 0.25‰e, 2σ; refs. 14 and 19), is indicative of a step change in a global process as driving the transition. As a result, we use the Monte Carlo approach of ref. 19, along with independent estimates of pO2, pCO2, fO2 (24), and other atmospheric parameters (ref. 19 and SI Appendix, Table S2), to interpret the Δ17O record primarily as a monitor of a state shift in GPP. We note that the interpretations presented here are conservative, as S recycling and reoxidation—if they were greater than assumed here—would drive Δ17O values toward 0 and thus GPP estimates toward higher values.

Across a range of reported pO2 and pCO2 conditions for the syn- and post-GOE intervals (SI Appendix, Table S3), our calculations show that a dramatic shift in Δ17O values at the end of the GOE. If high pO2 levels were reached during the GOE (10% to 100% of modern pO2; ref. 9), which then fell to 0.1% to 1% of modern in the post-GOE interval (7, 49), this transition could reflect a drop in GPP of nearly 200-fold, from a median value of over 1,100% of modern to a median value of ~6% of modern (Fig. 2). This shift reflects the need to dilute a greater standing stock of tropospheric O2 during the GOE. However, it is unclear whether syn-GOE biogeochemical cycles could support an oxygenic photosynthetic biosphere that would achieve such high levels of carbon fixation and O2 production (50, 51). The Δ17O record may not require such extreme pO2 levels if their isotopic impact was tempered by some degree of enhanced S recycling and reoxidation during the GOE. A more likely scenario is a moderate transition, from initial pO2 levels of 1% to 10% of modern to 0.1% to 1% of modern, which would have instead been accompanied by a reduction in GPP of ~10-fold from a median value of ~60% modern to 6% modern (SI Appendix, Table S1). Even in the unlikely case that pO2 levels did not change across the end-GOE, the Δ17O values reported here still require over a 5-fold decrease in GPP across this transition (Fig. 2). Although the δ17O evidence presented here is not sufficient to firmly establish a Δ17O transition, it does suggest that GPP are necessary to explain the Δ17O results, there is still a considerable range of possible Earth system states, underscoring the need for additional investigations of how biogeochemical cycles reorganized across the end-GOE transition.

Multiple studies have suggested a larger ocean–atmosphere oxidant inventory over the GOE interval compared with the following 1 billion y of Earth’s history (8, 12–18, 52). Interpretations of this decline in oxidant inventory are typified by falling marine SO4 levels (12–14), as well as a potential decrease in organic carbon burial (50). The Δ17O evidence presented here suggests that a reduction in GPP may be a common underlying cause of the biogeochemical changes across this interval. This shift in GPP could reflect a change in the availability of critical nutrients, most likely phosphorus (50, 51, 53, 54), to sustain photautotrophic growth. The switch from a nutrient feast to famine may have resulted from different Fe-P dynamics across this interval (51, 53), perhaps due to the exhaustion of weatherable apatite- and pyrite-rich sediments (8) as well as less P regeneration from biomass that had built up large nutrient reservoirs before the GOE (55). While the most conservative geological constraints limit the duration of this Earth system “tipping point” to ~200 My, the geochemical, geochronological, and sedimentological observations reported here point toward a much quicker timescale (~39 to 90 My; Fig. 2) for the end-GOE transition. Cumulatively these findings suggest the end-GOE transition was potentially one of the largest sustained shifts in the productivity of the biosphere, rivaling the colonization of the terrestrial realm by land plants [>2-fold (56)] and the Permo-Triassic mass extinction [>2-fold (52)] and perhaps even approaching the advent of oxygenic photosynthesis [~1,000-fold (57)] in magnitude.

Conclusion. We present data suggesting that the end-GOE transition marks one of the most pronounced sustained changes in the productivity of the biosphere across all of Earth’s history. Moreover, our results strengthen the inextricable link between...
the ultimate source of oxygen production (the marine biosphere) and the oxidation of the Earth’s surface environment. We find a drop in GPP >5-fold, but possibly as much as 2 orders of magnitude across the end-GOE transition using a Monte Carlo approach to published estimates of pO2 and pCO2. This drop was likely brought about by a large decrease in nutrients supplied to the biosphere that, in turn, marked the conclusion of the GOE and ushered in the subsequent 1-billion-y interval characterized by markedly low and stable GPP compared with the modern Earth. Although the end-GOE is not considered a major biotic event, our results show that the decrease in gross primary productivity across this transition eclipses even the largest extinction events in all of Earth’s history.