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Uncovering the Ediacaran phosphorus cycle

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Abstract

Phosphorus is a limiting nutrient that is thought to control oceanic oxygen levels to a large extent [1-3]. A possible increase in marine phosphorus concentrations during the Ediacaran Period (~635-539 Myr) has been proposed as a driver for increasing oxygen levels [4-6]. Little is known, however, about the nature and evolution of phosphorus cycling during this time [4]. Here we use carbonate-associated phosphate (CAP) from six globally-distributed sections to reconstruct oceanic phosphorous concentrations during a large negative carbon isotope excursion – the Shuram Excursion (SE), which co-occurred with global oceanic oxygenation [7-9]. Our data suggest pulsed increases in oceanic phosphorus concentrations during the falling and rising limbs of the SE. Using a quantitative biogeochemical model, we propose that this observation could be explained by carbon dioxide and phosphorus release from marine organic matter oxidation primarily by sulphate, with additional phosphorus release from carbon dioxide-driven weathering on land. Collectively, this may have resulted in elevated organic-pyrite burial and ocean oxygenation. Our CAP data also seem to suggest equivalent ocean phosphorus concentrations under maximum and minimum extents of ocean anoxia across the SE. This observation may reflect decoupled phosphorus and ocean anoxia cycles, as opposed to their coupled nature in the modern ocean. Our findings point to external stimuli such as sulphate weathering rather than internal oceanic phosphorus-oxygen cycling alone as a possible control on oceanic oxygenation in the Ediacaran, and in turn this may help explain the prolonged rise of atmospheric oxygen levels.

Phosphorus (P) is considered the primary limiting nutrient for marine productivity on geological timescales [1]. Consequently, it has been proposed that the coupled cycling of P and oxygen (O_2) maintains oxygen availability over million-year timescales, preventing runaway ocean anoxia in the Phanerozoic (<539 Myr ago) [1-3] and, whereby sustaining oxygen-demanding eukaryotic life. This relationship exists because dissolved P and O_2 follow negative feedback cycles, where higher oceanic P concentrations under ocean anoxia enhance photosynthetic production of oxygen, which oxygenates previously anoxic water masses [1,2]. This feedback arises due to release of P from both the decomposition of organic matter and iron (Fe) (oxyhydr)oxides in anoxic sediments [10]. Under oxygenated bottom waters, this released P generally becomes trapped in the sediment via a variety of pathways, including uptake by Fe (oxyhydr)oxides, biological sequestration of polyphosphates [2,10], or formation of authigenic phosphate minerals, all of which prevent the return of P to the oceans [10]. Under anoxic bottom waters, a proportion of the mobilised P can diffuse out of the sediment [11], however, enhanced organic matter preservation [11] and iron mineral formation under ferruginous (anoxic and Fe^{2+}-containing) conditions [12] can aid P retention in the sediments. Consequently, euxinic conditions (anoxic and sulphidic) are particularly conducive to sedimentary P release because of uptake of dissolved iron as sulphide minerals, thereby limiting P sequestration by iron minerals [12].

The coupled cycling of P and O_2 may have supported high levels of ocean P in the largely anoxic Precambrian oceans (>539 Myr ago) [13], as interpreted from P/Fe ratios in iron-formations [14]. Conversely, alternative interpretations of this P/Fe record suggest low oceanic P [15,16], due to effective drawdown of P by iron minerals and sequestration under ferruginous conditions [15,17]. Alternatively, low P Precambrian oceans may have arisen due to a lack of oxidants, such as oxygen and sulphate, which suppressed P release from organic matter [4,5]. Some researchers have speculated that these low marine P levels substantially increased during the Ediacaran in conjunction with extensive deep ocean oxygenation, giving rise to modern-like oceanic P levels [4-6]. The Ediacaran P cycle is thus key to any understanding of how the interaction of P and O_2 cycles evolved from the Precambrian to the modern world and its potential role in the co-evolution of atmospheric O_2 and complex life. However, little is known about the nature and evolution of the Ediacaran P cycle. To shed light on the Ediacaran P cycle, we use the newly developed Carbonate Associated Phosphate (CAP) proxy to directly document variability in oceanic phosphate concentrations during a major Ediacaran ocean oxygenation event [7-9,18]. This episode witnessed major diversification of multicellular eukaryotic and metazoan life [18,19] and the largest known negative carbonate-carbon isotope ($\delta^{13}C_{carb}$) excursion in Earth's history, referred to here as the Shuram Excursion (SE).

We analysed six globally distributed and well-preserved carbonate sections (Fig. 1a; see Methods) to capture oceanic phosphate variability during the SE: the Jiulongwan and Sishang sections of the Doushantuo and Dengying formations from South China, the Mochia-Khutuk section of the Shuiquan formation in North-western China, the Cerro Rajón section of the Clemente, Pitiquito and Gamuza formations of northern Mexico, the Death Valley section of the Johnnie Formation of South-western USA, and the Parachilna Gorge section of the Wonoka Formation of South Australia. All sections preserve >10‰ shifts in $\delta^{13}C_{carb}$ values characteristic of the SE (Fig. 1b-g) [20-27]. The six sections reported here are taken to represent global expressions of the SE and are temporally correlated via a combination of chemostratigraphy, fossil assemblages, lithological correlation and palaeomagnetism (see Supplementary Information 2).

Among all the measured sections, CAP shows a similar "M-shape" pattern, which is broadly coincident with four stages in the temporal evolution of the $\delta^{13}C_{carb}$ trend at each section (Stage I-IV; Fig. 1b-g). Note, that the Death Valley and Parachilna Gorge sections do not preserve the final recovery and initial drop in $\delta^{13}C_{carb}$ of the SE, respectively, and the Sishang section is faulted in the middle (Fig. 1d-e, g); however, the sections capture three out of the four CAP shifts identified in other global sections. In Stage I (falling limb of the SE), there is a large increase in CAP ("P-1st" in Fig. 1) at the onset of declining $\delta^{13}C_{carb}$ values, with CAP values reaching between 0.39 and 1.33 mmol/mol [CAP/(Ca+Mg)]. This increase is followed by an equally large decrease in CAP to a minimum during the mid-SE (Stage II; the plateau in SE $\delta^{13}C_{carb}$ values), with CAP values ranging between 0.03 and 0.24 mmol/mol. A rebound in CAP begins in the mid-SE (Stage II) and continues to increase as $\delta^{13}C_{carb}$ values increase toward the termination of the SE, reaching values of 0.32 to 2.18 mmol/mol (Stage III; rising limb of the SE; "P-2nd" in Fig. 1)), which is then followed by a gradual decline in CAP values to between 0.07 and 0.20 mmol/mol following the termination of the SE (Stage IV; a return to pre-SE $\delta^{13}C_{carb}$ values). Given that the CAP trends in all sections are connected to the $\delta^{13}C_{carb}$ excursion, and since the SE is approximately synchronous [28], a broadly contemporaneous shift in global oceanic P levels is implied.

CAP can be used to produce direct estimates of relative changes in palaeoceanic phosphate levels at the time of carbonate precipitation, if contamination, diagenetic alteration and other potential changes in oceanic chemistry can be evaluated [29]. Our CAP extractions show no signs of contamination by other sources of sedimentary P, as there is little to no correlation between CAP and bulk rock P, total organic carbon (TOC) or La (an element used for tracking phosphate mineral dissolution [29,30]) (Extended Data Table 1; see Supplementary Information 3). Encouragingly, an independent methodology using in-situ analysis of CAP in carbonate preserving primary textures gives trends consistent with our bulk CAP data from the Dengying Fm. in the Jiulongwan section of South China (Fig. 1b) [30].

While the global occurrence of our CAP trends is difficult to reconcile with diagenetic alteration, globally synched diagenetic alteration of carbonate has been purported to result after marine regression exposes platforms to meteoric waters [31]. The SE, however, is recognised as a marine transgression event, which is unlikely to expose carbonate sediments to meteoric alteration [32]. Nevertheless, in order to assess the potential effects of diagenetic alteration on CAP we utilise an open-system diagenetic model to evaluate chemical signals of alteration (Extended Data Fig. 1). Our diagenetic model shows that CAP is altered at similar or greater fluid-to-rock ratios than a number of carbonate proxies, such as $\delta^{13}C_{carb}$, $\delta^{18}O$, $\delta^{44/40}Ca$ or Mn/Sr. Therefore, CAP could correlate with these proxies across the SE if altered, but this is not observed in our samples (Extended Data Table 1; Fig. 1) [29,30]. Furthermore, coexisting $\delta^{34}S$ values in Carbonate-Associated Sulphate ($\delta^{34}S_{CAS}$) decline throughout the SE [20-22,24] (Fig. 1b-d), which is inconsistent with known diagenetic pore water chemistry and the increasingly elevated $\delta^{34}S_{CAS}$ values that commonly occur in diagenetic carbonates due to microbial sulphate reduction [33]. In addition, local redox proxies (e.g., I/(Ca+Mg), Ce/Ce*, Fe-speciation) measured among globally distributed SE sections record differing local redox conditions [34-36], which is also inconsistent with a global diagenetic pathway (see Supplementary Information 3). Finally, $^{87}Sr/^{86}Sr$ values and trends in the Cerro Rajón and Death Valley sections reflect local diagenetic alteration (see Supplementary Information 2) yet preserve similar CAP trends to other SE sections (Fig. 1).

Importantly, calcite and dolomite minerals in the study sections have undergone different diagenetic pathways and may have differences in distribution coefficients for CAP [28]. Despite this, CAP trends remain consistent among sections regardless of whether they are hosted in calcite or dolomite minerals (Fig. 1b-g). This strongly argues against a dominant diagenetic and mineralogical control on the CAP trends, and therefore we conclude that the CAP trends observed in this study most likely represent primary changes in seawater chemistry although diagenetic alteration of local CAP values may have exerted a minor influence. However, we note that in addition to diagenetic processes, changes in ocean pH, alkalinity, temperature and carbonate precipitation can all impact CAP values without concomitant changes in oceanic phosphate concentrations. We consider all of these potentially impacting factors on our CAP data in Supplementary Information 3, 4 and 9, and find that changes in oceanic phosphate concentration is the most plausible overarching control on the global CAP trends that we observed, albeit with possible minor overprints from changes in seawater chemistry.

Given the lower-than-mantle $\delta^{13}C_{carb}$ values of the SE, some models which report the SE as a primary-seawater-signal have centred on oxidation of an organic matter reservoir, such as dissolved organic matter (DOM) [37,38], fossil kerogen [23], or methane [39], all of which contain ^{13}C-depleted carbon, and with the exception of methane, also contain P. Assuming oxidant supply exceeds demand, these models are supported by many redox studies which suggest a transient global oceanic oxidation event during the SE, as supported by potential global-scale redox proxies such as $\delta^{238}U_{carb}$ (Fig. 1b-d). Other models have invoked a diagenetic origin or air-sea exchange of CO_2 [32] for the low $\delta^{13}C_{carb}$ values of the SE [31,40], but it is difficult to envisage how these models could reconcile the co-evolving trends of our new CAP data with the $\delta^{13}C_{carb}$ and redox proxy trends of the SE (see Supplementary Information 3 and 7).

Here we entertain a number of primary seawater signal hypotheses for the SE (see Supplementary Information 7 and Extended Data Fig. 2 for details). As discussed below, we find that a best-fit solution is achieved when rising oceanic sulphate levels (driven by enhanced weathering) stimulates sulphate-limited microbial sulphate reduction and oxidation of a DOM reservoir [37] (Fig. 2). This mechanism is supported by higher values of Carbonate-Associated Sulphate (CAS) concentration and lower values of $\delta^{34}S_{CAS}$ during the SE (Fig. 1b-d) [20-24], which are indicative of a growing oceanic sulphate reservoir [37]. Enhanced weathering (and accordingly sulphate supply) during the SE is supported by elevated $^{87}Sr/^{86}Sr$ [41] (Fig. 1b-e) and εNd(t) records [42]. We quantitatively explore this scenario and its impact on ocean P using the COPSE biogeochemical model (Fig. 3; Extended Data Figs. 2-7).

It is well documented that the Ediacaran oceans were dominated by deeper anoxic waters [43,44], and therefore free oxygen would have been in contact with a small fraction of the deep-ocean DOM pool. Consequently, sulphate is the primary oxidant in our model. Indeed, if a DOM reservoir was oxidised by free oxygen, our modeling indicates that ocean anoxia would not significantly decrease during the SE, which would allow for sustained high ocean P levels resulting from elevated weathering and DOM oxidation (Extended Data Fig. 3). However, this contrasts with coexisting $\delta^{238}U_{carb}$ data showing a substantial decrease in ocean anoxia, as well as the CAP records showing a drop in oceanic P levels during the SE [8,35] (Fig. 1b-g). Similarly, models for DOM oxidation by a combination of sulphate and free oxygen are also inconsistent with the observed $\delta^{238}U_{carb}$-CAP records (Extended Data Fig. 3).

The sizes of the modelled DOM reservoir and sulphate pulse to the oceans were adjusted to produce a SE with a duration of 15 Myr (see Supplementary Information 5), while also reproducing the two observed CAP peaks (Extended Data Figs. 4-6; P-1st and P-2nd in Fig. 1). Varying the magnitude of the additional sulphate pulse to the oceans has little effect on modelled CAP trends, while burying all additional sulphate as pyrite creates a pO_2 trend inconsistent with redox proxies from the SE (Extended Data Fig. 5). Similarly, if gypsum is assumed not to covary with seawater sulphate levels, increasing sulphate levels prevent a return to anoxia after the SE, which is inconsistent with coexisting $\delta^{238}U_{carb}$ and $\delta^{34}S_{CAS}$ records (Extended Data Fig. 5) . Finally, to best fit our CAP data, we suppressed oceanic P levels in COSPE under anoxia by assuming that P is also buried in association with Fe^{2+}, rather than only with Fe^{3+} (Fig. 3; also see Extended Data Fig. 7 for model results with no Fe^{2+}-associated P burial). This choice is based on the predominantly ferruginous ocean conditions in the late Neoproterozoic and previous suggestions that ferruginous oceans may have drawn down ocean P through uptake via a variety of Fe mineral precipitates [6,15,17]. The relative magnitudes of the modelled ocean P peaks were varied by changing the onset and waning of Fe^{2+}-P burial and whether HCO_3^- is released alongside CO_2 during sulphate reduction of DOM (Fig. 3). Details and rationale for the model choices are provided in the Methods section and Supplementary Information 6-8.

Our quantitative modelling indicates that the SE CAP profiles may have recorded feedbacks in weathering, organic matter burial/oxidation, and the extent of marine anoxia that bridges previously elusive $\delta^{13}C$ and palaeoredox proxy relationships. We detail the scenario below: (1) Additional sulphate input to the oceans from weathering triggers the oxidation of a DOM reservoir by sulphate at the beginning of the SE (Fig. 2a). This released organic-bound C and P, which led to declining oceanic $\delta^{13}C$ and increased oceanic P as well as atmospheric pCO_2, thereby elevating P input to the oceans via silicate weathering (Stage I and P-1st in Figs. 1b-g, 3b). CO_2-driven weathering also resulted in an elevated $^{87}Sr/^{86}Sr$ curve across the SE (Figs. 1b-e, 3d) [41]. (2) Greater P availability would then elevate primary productivity and concomitant organic matter and pyrite burial, which increased pO_2 (Fig. 2a) and decreased the extent of ocean anoxia (Fig. 2b), as suggested by the observed global shift to more positive $\delta^{238}U$ values (Figs. 1b-d; 3c). (3) A decrease in ocean anoxia would increase P burial and lead to a decrease in the oceanic P reservoir (Fig. 2b), consistent with declining CAP values, and coincident maximum $\delta^{238}U$ values (Stage II in Figs. 1b-g, 3b-c). (4) As the size of the DOM reservoir dwindled, oceanic $\delta^{13}C$ would start to return to pre-SE values (Stage III in Figs. 1b-g, 3a). Simultaneously, decreasing organic and pyrite burial drove atmospheric oxygen lower, which supported by a reduced P reservoir and consequently lower rates of oxygenic photosynthesis, resulted in lower pO_2 levels and increasing marine anoxia (Fig. 2c), which may be recorded by a transition to increasingly negative $\delta^{238}U$ values (Stage III in Figs. 1b-d and 3c) [8,45]. Other independent carbonate- and siliclastic-hosted redox proxies (e.g., Tl and Mo isotopes [46,47], carbonate-bound iodate [35] and Fe-speciation [36]), corroborate the increase after a prior decrease in ocean anoxia across the SE. Increasing ocean anoxia would decrease P burial, which, when coupled to continued P release from DOM and weathering, would lead to another increase in the P reservoir (Fig. 2c), as observed in the CAP data (P-2nd in Figs. 1b-g, 3b). (5) Finally, cessation of massive DOM oxidation and reduced continental weathering led to a waning P input from DOM and continental weathering, which in turn decreased organic and pyrite burial supporting a return of elevated anoxia, as evidenced by negative $\delta^{238}U$ values during the terminal SE in multiple global carbonate sections[7,9] and a return to pre-SE $\delta^{13}C_{carb}$ values and coexisting low CAP values (Stage IV in Figs. 1b-g and 3a-c).

An alternative to DOM oxidation could be methane oxidation [23] by sulphate. However, anaerobic oxidation of methane is less likely because methane oxidation will not release P directly and is unlikely to lead to pCO$_2$ increases (and thus elevated P weathering) —favouring alkalinity increases instead. The possibility of small temporal differences in our δ^{13}C$_{carb}$ and CAP trends among globally distributed sections (Fig. 1) may have resulted from heterogeneous redox conditions in the Ediacaran which led to variable spatiotemporal rates of DOM oxidation, continental weathering and element cycling [22]. Consequently, we conclude that our CAP data in cohort with coexisting C, S, and U isotopic data, as well as other redox proxies, are best explained by the oxidation of an organic matter reservoir (DOM or fossil organic matter) by sulphate and resulting organic and pyrite burial, which facilitated ocean oxygenation and perhaps the coeval diversification of complex life in the Ediacaran (Fig. 3e) [18,19].

The CAP proxy predominantly records local seawater P levels, reflecting P fluxes from surrounding sediments, riverine input, ocean upwelling etc. Whether local seawater P levels are controlled by local or global processes will depend on the magnitude of fluxes involved at different timescales. Observations of long-term oceanic P cycling suggest that upwelling of deep ocean P onto continental shelves is quantitatively larger than local continental shelf P fluxes [10]. This can be demonstrated using a quantitative four-box ocean P cycle model which predicts that continental shelf P concentrations, aside from the most proximal areas and mixed layer, track deep ocean P levels over geological timescales, due to the supply from upwelling [3,13] (Extended Data Fig. 8). Given the relatively homogenous concentration of deep ocean P, and a residence time greater than the oceanic mixing time [10], upwelling of deep ocean P is expected to result in continental shelf P concentrations that capture overall P levels in the global ocean when viewed over geological timescales. Consequently, our CAP trends from continental shelves are expected to represent global changes in the average ocean P concentration over geological timescales, and their global relationships are thus preserved despite the potential for local overprints that include redox controls on continental shelf P concentrations (see Supplementary Information 8). This view is supported by similar CAP trends among our global sections, despite having been deposited under differing local redox conditions [34,35].

Given that CAP and $\delta^{238}U_{carb}$ trends may reflect relative changes in the average global ocean P concentration and extent of ocean floor anoxia respectively, our study provides a unique opportunity to explore dynamics in the Ediacaran P and O_2 cycles. As predicted by observations of modern aquatic environments, expansion of oxygenated bottom waters during the SE (evidenced by $\delta^{238}U_{carb}$) should be accompanied by declines in marine P concentration (as seen in CAP). Surprisingly, however, minimal extents of ocean floor anoxia (i.e., the most positive $\delta^{238}U_{carb}$ values in Stage II of the SE) are associated with CAP values of equal magnitude to those CAP values during periods of maximum ocean floor anoxia before/ after the SE (i.e., the most negative $\delta^{238}U_{carb}$ values in the early Stage I and Stage IV) at all studied sections (Fig. 1b-d). This observation is in stark contrast to modern P and O_2 cycling where widespread ocean floor anoxia supports higher ocean P levels relative to periods with limited ocean floor anoxia. Similarly, $\delta^{238}U_{carb}$ and CAP co-vary, increasing and decreasing at the start and end of the SE, respectively (Fig. 1b-e), which also contrasts with canonical models of modern P and O_2 cycles. This difference indicates that the Ediacaran P and O_2 cycles may have been fundamentally differed to the modern (Fig. 3b-c; Extended Data Fig. 7) [1-3,11]. Note that, this conclusion is based on the comparison of CAP values from discrete intervals when $\delta^{238}U_{carb}$ data are at their maximum and minimum, and therefore a precise temporal correlation of CAP trends among the studied sections does not affect the conclusions. Moreover, CAP and $\delta^{238}U_{carb}$ were measured in identical sample powders and minerals, ruling out effects of temporal or mineralogical differences.

One may argue that P fluxes from continental weathering and organic matter oxidation could have maintained high ocean P levels during the SE, effectively balancing the increased P sinks under oxygenated bottom waters. However, current quantitative models of P and O_2 cycling, indicate that even under the most extreme P input fluxes, oceanic P levels are still expected to be lower during minimal oceanic anoxia during the SE, relative to before or after the SE when the extent of seafloor anoxia was greater (see Extended Data Fig. 4 and Supplementary Information 9). Additionally, modeling and experimental results suggest that changes in pH, alkalinity or carbonate precipitation rate resulting from shifts in surface weathering, $p\mathrm{CO}_2$ and organic remineralisation are unlikely to have decoupled the CAP and $\delta^{238}U_{carb}$ values (see Extended Data Fig. 9 and Supplementary Information 4 and 9).

The roughly equivalent oceanic P levels under maximum and minimum extents of ocean floor anoxia across the SE provides the first direct observation for a decoupling of the modern-style negative feedback cycles between oceanic P and O_2. Currently there are no other coupled datasets of CAP and $\delta^{238}U_{carb}$ which capture a modern-style P and O_2 cycle that we can compare our dataset to. However, chemical traits of redox-dependant phosphorus burial are frequently observed in Phanerozoic sediments [2,11,12], but largely absent in Ediacaran sediments deposited under ferruginous conditions [48], which may support our conclusion of decoupled P and O_2 cycles in Ediacaran oceans. For example, C_{org}/ P_{Tot} (total sediment organic carbon/ total sediment P) values are roughly invariant among siliciclastic sediments deposited under variable redox conditions in the

Ediacaran Doushantuo Formation [48], whereas C_{org}/ P_{Tot} commonly covaries with local redox conditions in Phanerozoic sediments [2,11,12].

While we favour a primary seawater signal as described above, and cannot entirely rule out an early diagenetic interpretation of the CAP trends, such a scenario is unlikely to change our conclusion of decoupled P and O_2 cycling in the Ediacaran Ocean. This is because in modern marine sediments, increasingly ^{13}C-depleted pore waters carry increasingly higher P concentrations following the remineralisation of organic matter. Therefore, if carbonate deposited during the SE indeed captured diagenetic porewater chemistry, the more ^{13}C-depleted fluids (down to −12‰) should have carried higher solution P concentrations relative to fluids surrounding carbonate deposited before or after the SE with high $\delta^{13}C_{carb}$ values (up to +5‰). However, carbonates with these endmember $\delta^{13}C_{carb}$ values across the SE carry equable CAP values (Fig. 1b-g). According to our early diagenetic model (Supplementary Information 3), in order to achieve a $\delta^{13}C_{carb}$ shift from +5 to −12‰ in diagenetic carbonates, CAP is expected to increase by at least a factor of four yet plots of our $\delta^{13}C_{carb}$ and CAP data show no such trend (Extended Data Fig. 1d). This decoupling between $\delta^{13}C_{carb}$ and CAP required substantial sequestration of P released from diagenetic organic remineralisation in reducing Ediacaran pore waters (directly evidenced by bottom-water redox proxies, e.g., Fe speciation data across the interval of highly depleted $\delta^{13}C$ values in the Jiulongwan section [43]). This P sequestration in anoxic porewaters (and Ediacaran water columns) [43,44] is also in stark contrast to modern P and O_2 cycling, thus supporting a decoupled P and O_2 cycle in the Ediacaran (see more detailed discussion in Supplementary Information 3). Moreover, purported models for the SE which achieve low $\delta^{13}C$ in seawater via non-DOM-oxidation mechanisms [32] still advocate for carbonate deposited during the SE to have captured seawater chemistry. Consequently, the observed CAP and $\delta^{238}U_{carb}$ trends would be faithful recorders of seawater chemistry and therefore support the conclusion of decoupled P and O_2 cycles in the Ediacaran.

The decoupling of ocean P recycling and anoxia observed here likely results from persistent P removal by organic or iron mineral phases under widespread oxidant-depleted, ferruginous conditions in Ediacaran Oceans [16]. Given similar redox conditions and potentially a small P reservoir in Precambrian oceans preceding the Ediacaran [49], it is reasonable to infer that such a decoupling of the P and O_2 cycles may have existed throughout most of the Precambrian [50]. Importantly, a weakening of the oceanic P and O_2 feedbacks as suggested here would have locked the Precambrian oceans and atmosphere into a largely anoxic state, because ocean anoxia would not have resulted in elevated marine P availability, oxygenic photosynthesis and organic matter burial relative to periods of lower marine anoxia. Consequently, Precambrian oceanic oxygenation events, such as the SE and maybe others (e.g., the Great Oxygenation Event [50]), may have relied on external stimuli such as sulphate weathering inputs rather than internal oceanic P-O_2 cycling alone [4,5]. This may explain the prolonged rise of oxygen and complex life over Earth history until the removal of widespread ferruginous conditions or increases in sulphate/oxidant availability in the Phanerozoic which shifted the Ediacaran P and O_2 cycles into a modern-style, negative feedback cycle [1]. In turn this transition may explain the prolonged oxygenation and metazoan habitation of the Phanerozoic oceans [1].

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Author Contributions

C.L led the research. C.L and M.S.D designed the research. M.S.D, Z.Z, M.C and H.G performed analyses. W.S and B.J.W.M conducted modelling work. C.L, T.W.L, D.S.H, S.J.L, M.W.W, A.vS.H, K.L, M.C, H.G provided samples and assistance in the field. S.W.P provided analytical assistance. M.S.D, C.L, and W.S wrote the manuscript with important discussion and contributions from all authors.

Data Availability Statement

All data generated or analysed during this study are available at https://figshare.com/articles/dataset/Dodd_et_al_2023_xlsx/22274293 and included with the published article (and its supplementary information files).

Materials Availability

All samples were collected and exported in a responsible manner and in accordance with relevant permits and local laws. Global coordinates and/ or location information and drill core names are given for all samples collected in the supplementary information files. Requests for materials should be addressed to C.L.

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Methods

Bulk-rock Phosphorus analysis

Although altered material could not be completely avoided, fresh pieces of only fine-grained carbonate rock were selected and crushed to a powder. Phosphorus measurements were conducted by dissolving ~50 mg of sample powder using a standard HNO_3–HF digestion protocol, in which HNO_3–HF (1:1) and HNO_3 were sequentially added to a 15-mL Teflon bomb at 190°C until complete digestion was achieved. Distilled HNO_3 and trace metal-grade HF reagents were used for all samples. The leachates were then measured by ICP-MS using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS). Analytical errors were better than ±7% for phosphorus based on duplicate analyses of two USGS standards (BCR-2, BHVO-2) and two Chinese national standards (GSR1, GSR5).

Carbon analysis

Total carbon (TC) and total organic carbon (TOC) were measured using a CS-900 Carbon Analyser. TC was measured directly by weighing out ~0.1g of rock powder with iron shavings and tungsten pellets to aid combustion in the analyser. A calcium carbonate carbon standard (AR1034) was analysed after every 10 samples to check reproducibility (± 0.1 wt% C; n = 30). To measure TOC, an aliquot of sample powder (~1 g) was reacted with 6 M HCl to decarbonate the sample, rinsed with deionised water to neutral pH, then centrifuged and dried, and finally measured in the analyser as for TC. Total inorganic carbon (TIC) was then calculated by the difference between TC and TOC.

Carbonate carbon isotope analysis

About 60 to 300 μg of sample powder was loaded into a vial after drying at 70°C for 24 hr in an argon atmosphere. The samples were then reacted with 100% phosphoric acid under a vacuum at 70°C for 220 s using a Kiel IV device. The resulting CO_2 was subsequently introduced into a MAT 253 isotope ratio mass spectrometer (IRMS) for isotopic measurements. Delta values were calibrated relative to international reference standard NBS-19 (δ13C = +1.95‰; δ18O = −2.20‰)

and Chinese national standard GBW04416 ($\delta^{13}C$ = +1.61 ± 0.03‰; $\delta^{18}O$ = = 1.59 ± 0.11‰). Carbon and oxygen isotope data for carbonates are reported relative to Vienna Pee Dee Belemnite (VPDB) with a precision of better than ±0.1‰ based on duplicate analyses of GBW04416 and the study samples.

Carbonate-Associated Phosphate (CAP) analysis

CAP was measured following previously established protocols [29]. Only samples comprising >50% carbonate were chosen for analysis. Based on sample TIC and carbonate mineralogy, sufficient sample powder was weighed out to yield ~1 mmol of carbonate. An appropriate amount of 2% vol/vol acetic acid was then added to the powder to dissolve up to 70% of the carbonate. After 30 minutes the sample was centrifuged, and the leachate was extracted. An aliquot of leachate was taken for major and trace element analyses and measured using an Expec 6000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for Ca and Mg and an Agilent 7700x ICP-MS for trace elements. Analytical errors were better than ±2% for all studied elements based on duplicate analyses of two USGS standards (BCR-2, BHVO-2) and two Chinese national standards (GSR1, GSR5). Another aliquot was taken and mixed with H_2SO_4 to achieve a 1 M H_2SO_4 concentration and left for 1 hour to remove Ca as $CaSO_4$. Then P was measured by spectrophotometry using the molybdenum-blue method at a wavelength of 880 nm, with a relative standard deviation of better than ±5%. The sample residue was then washed with 50ml of 10% NaCl solution buffered to pH 8 with $NaHCO_3$ for 24 hours, and P was measured by the molybdenum-blue method. This sequence was repeated until P in the wash was below detection limit (0.05 ppm). The P in the leach and washes were then summed together to give CAP, which was then normalised to the Ca and Mg concentrations in the leach. Three Ediacaran dolomite sediments of varying TIC and TOC were run alongside unknown samples to check reproducibility for quality assurance, repeat CAP measurements were within ±5%.

Strontium isotope analysis

The extraction method for strontium isotope analysis was based on previous works [51-53]. Around 0.1g of sample was weighed out and then washed for 24 hours in 10ml of 1M ammonium acetate buffered to pH 8 in order to remove exchangeable strontium. The sample was then centrifuged, and the wash discarded and the sample rinsed with Milli-Q water. Subsequently the sample was partially leached in 2% acetic acid to dissolve 30% of the sample carbonate and left to react overnight. The sample was then centrifuged, and the acetic leach discarded and the sample rinsed with Milli-Q water. Following this a further aliquot of 2% acetic acid was added to dissolve 40% of the sample carbonate and left to react for 30 minutes. The sample was then centrifuged, and the leachate collected for Sr isotope analysis.

The leachate collected was then centrifuged to remove insoluble residues and then decanted, dried, and subsequently dissolved in HNO_3. Strontium separation by cation exchange was carried out using automatic column chromatography separation device, see Zhou et al., (2021) [55] for details. Approximately 200–300 ng of the dried sample was transferred onto a degassed and pre-baked high purity Re filament with Ta_2O_5 activator. The prepared filaments were measured using the VG Sector 54 thermal ionisation mass spectrometer in the Thermal Ionisation Mass Spectrometry facility of China University of Geoscience (Wuhan). Filaments were transferred to a sample carousel, heated under vacuum to a temperature between 1450 and 1650 °C, and analysed when a stable signal was detected on the mass 88 ion beam. Approximately 100 $^{87}Sr/^{86}Sr$ ratio data points were collected for each sample. Final data have been corrected for fractionation using the standard value $^{86}Sr/^{88}Sr = 0.1194$. The fraction of ^{87}Sr resulting from in situ decay from ^{87}Rb was removed by measurement of rubidium abundance at mass 85. Repeated analysis of the BCR-2 and BHVO-2 standards yields an average value of $^{87}Sr/^{86}Sr = 0.70498$ and 0.70347 ± 0.00001 (2σ) during the analytical window.

Carbonate precipitation experiments

The precipitation of carbonate and uptake of CAP from seawater solutions followed previous methodologies [29]. In brief, a peristaltic pump was used to add solutions of 1M $CaCl_2$ and 1M Na_2CO_3 with KH_2PO_4 to 1L solutions of synthetic seawater made to emulate modern day seawater chemistry. Solutions were constantly stirred, and an air pump was used to bubble air through the solution in order to maintain a stable pH. For precipitation rate experiments variable amounts of carbonate seeds were used to vary the precipitation rate in conjunction with varying the pump rates of $CaCl_2$ and Na_2CO_3. Solution chemistry was checked periodically for pH, alkalinity, calcium and phosphorus concentrations. A Thermofisher pH electrode was used to check pH with an accuracy better than ± 0.1 units, alkalinity was measured by titration of seawater aliquots with 0.1M HCl, phosphorus and calcium were measured as outlined above in CAP analysis. At the end of the experimental run, carbonate was collected by filtration through 0.2 μm PES filters and the carbonate washed with 1M $NaHCO_3$ until phosphorus concentrations in the washes were below detection. Once the carbonate samples were clean of adsorbed phosphorus, 0.1g was completely dissolved in 2M HCl and solutions subsequently analysed for P, Ca, and Mg as outlined above in CAP analysis. Carbonate precipitation rates were calculated as mole/m^2/s following Barkan et al. (2020) [54].

COPSE biogeochemical modelling

The COPSE model was used to calculate biogeochemical feedbacks between P cycle and DOM oxidation during the Shuram Excursion (SE). This model follows the work of ref. [55] and is solved in MATLAB using the Ordinary Differential Equation (ODE) suite. Here, we provide a key description of our model work, and the full description of our model work is given in the Supplementary Information.

Steady-state calculation for low background phosphorus concentration under high ocean anoxia in Ediacaran oceans. Based on the observed CAP and redox proxy trends across the SE we can infer that a mechanism(s) was maintaining P at lower levels during the early Stage I and Stage IV of the SE under high ocean anoxia. While it is ambiguous what mechanism(s) could maintain a lower P reservoir under anoxia during the Ediacaran [4-6,15], we chose to modify the iron-bound P burial (Equation 1) to maintain a low oceanic P reservoir during high ocean anoxia because Fe^{2+}-P burial is being recently recognized as an important P sink in Precambrian ferruginous-dominated oceans (see Supplementary Information 6 for rationale) [11, 14-16], but also allow for an increase in oceanic P burial with decreasing ocean anoxia as modern P cycle. We stress that this modification of the COPSE model is a qualitative change, as there are no current quantitative relationships for Fe^{2+}-P burial. Importantly, this modification does not significantly change the model results between model runs with and without Fe^{2+}-P burial; except for lowering ocean P levels under high ocean anoxia (Extended Data Fig. 7). Therefore, this modification is appropriate for this study, however future modelling work will require field relationships linking enhanced P burial under anoxia to produce more meaningful results. Thus, we modified the flux of iron-bound P burial in the standard COPSE model and include a ferrous iron scavenging flux that has a positive relationship with the degree of anoxia (ANOX) as below:

$$\mathrm{fepb}_{sws} = \frac{k_1}{k_2} \cdot \frac{P_t}{P_0} \tag{1}$$

$$\mathrm{fepb}_{fe3} = \mathrm{fepb}_{sws} \cdot (1 - ANOX) = \frac{k_1}{k_2} \cdot \frac{P_t}{P_0} \cdot (1 - ANOX) \tag{2}$$

$$\mathrm{fepb}_{fe2} = \left(\mathrm{fepb}_{sws} - \mathrm{fepb}_{fe3}\right) \cdot ANOX = \frac{k_1}{k_2} \cdot \frac{P_t}{P_0} \cdot ANOX^2 \tag{3}$$

$$\mathrm{fepb}_{tot} = \mathrm{fepb}_{fe3} + \mathrm{fepb}_{fe2} = \frac{k_1}{k_2} \cdot \frac{P_t}{P_0} \cdot (ANOX^2 - ANOX + 1) \tag{4}$$

Here fepb_{sws} is the flux of iron-bound P burial reaching the seawater-sediment interface, and fepb_{fe3} is the final flux of P that is buried with Fe^{3+}, while fepb_{fe2} is the Fe^{2+} scavenging flux including vivianite burial, and fepb_{tot} is the total flux of iron-bound P burial. P_t and P_0 are the mass of the marine P reservoir at time t and present day, respectively. $k_1 = 10^9\ \mathrm{mol\ P\ yr^{-1}}$ and $k_2 = 0.997527$ are constants, and $0 < ANOX < 0.997527$. This modification changes the original definition of the total iron-bound P burial which is negatively correlated with anoxia in the standard COPSE model. In practice, this allows for a low ocean P concentration in anoxic-ferruginous Precambrian oceans given a $p\mathrm{O}_2$ = 0.01 PAL (see Supplementary Information for details of Fe-scavenging). We chose this modelling approach because the simplistic separation of Fe-P burial into Fe^{2+}- and Fe^{3+}-P burial allowed us to increase P burial under high ANOX (per the CAP and redox data) while also keeping the original COPSE model P and O_2 cycle in effect.

Weathering sulphate input. We run the COPSE model to steady state, forcing the model conditions to represent the expected geochemical conditions for Ediacaran period. We included a DOM reservoir that responds to a weathering sulphate pulse ($sulfate_{pulse}$), which uses a simple step-forcing that follows previous work [37]. The time-dependent forcing function for the sulphate pulse is:

$$sulfate_{pulse} = interp1([-10\ 0\ 1\ 15\ 16\ 30], [0\ 0\ x\ x\ 0\ 0])$$

where the first vector is time (m.y.) and the second vector is the additional sulphate input relative to the background weathering flux (x = 3, 4, or 5). The sulphate pulse is set to last for ~15 million years, which follows the geological $^{87}Sr/^{86}Sr$ and εNd(t) records for elevated weathering input during the SE [43], as well as the rough time-taken for the duration of the SE (see Supplementary Information 5 for details on the age framework of the SE). For the model runs in the manuscript, both normal steady-state 'background' flux (subscript 'background') and additional weathering pulse input (subscript 'pulse') are working together and respond to changing geochemical conditions:

$$gypw_{background} = k_{gypw} \cdot U \cdot R \cdot \frac{carbw}{k_{carbw}} \tag{5}$$

$$gypw_{pulse} = gypw_{background} \cdot sulfate_{pulse} \tag{6}$$

$$pyrw_{background} = k_{pyrw} \cdot U \cdot R \cdot \frac{carbw}{k_{carbw}} \tag{7}$$

$$pyrw_{pulse} = pyrw_{background} \cdot sulfate_{pulse} \tag{8}$$

Here the k_{gypw} and k_{pyrw} are the present-day weathering rates of gypsum and pyrite, U and R are the normalised uplift and river runoff forcing, and the $\frac{carbw}{k_{carbw}}$ is a climate dependence representing the effect of pCO_2 on global carbonate weathering. For this study, the test case of x = 5 is used for our idealised ('best fit') scenario (Extended Data Fig. 6), which maintains a negative $\delta^{13}C_{carb}$ excursion of ca. –10 ‰ for million years.

DOM oxidation. The size of the DOM reservoir (model term DOC) is set at the beginning of the model run. This reservoir has an output flux via DOM oxidation, which is driven by sulphate reduction

[37]:

$$\frac{dDOC}{dt} = \begin{cases} 0, & DOC < 10^{12}\ mol \\ 2 \cdot \left(gypw_{pulse} + pyrw_{pulse}\right) \cdot \frac{S_t}{S_0} \cdot \frac{DOC_t}{DOC_0}, & DOC \geq 10^{12}\ mol \end{cases} \quad (9)$$

Here S_t and S_0 are the mass of the marine sulphate reservoirs at time t and present day, DOC_t and DOC_0 are the mass of DOM reservoir at t time and pre-SE, respectively. The $DOC_0 = 30$ times the mass of the modern DIC reservoir following previous estimation, in order to maintain a $\delta^{13}C_{carb}$ excursion of ~15 million years and reaching values of –10 ‰. We consider sulphate as the only direct oxidant for DOM oxidation, and its additional pulses set the rate of DOM consumption. The normal background sulphate fluxes are set not to be involved in DOM oxidation, but instead balance the oxidation of fresh organic carbon. In nature, free oxygen can also oxidise DOM once its local concentration crosses over a certain threshold (e.g., ~4 μM[58]. We also test this possibility of DOM oxidation by free oxygen using two output fluxes via both sulphate and oxygen, which is given in the Extended Data Fig. 3 and Supplementary Information 7. We follow previous models that set DOM oxidation to terminate when the DOM reservoir becomes smaller than 10^{12} moles, rather than zero, to prevent system instability [37].

Sulphate burial. The COPSE model assumes that marine sulphate is removed via the burial of gypsum and pyrite, which are linearly proportional to the total oceanic sulphate concentration [55]. In order to balance the additional sulphate input, we add additional fluxes of both gypsum ($mgsb_{additional}$) and pyrite ($mpsb_{additional}$) burial, among which the pyrite burial is equal to half the DOM oxidation rate. The remaining sulphate pulse that is not consumed by DOM is assumed to be buried as gypsum:

$$mgsb_{additional} = (gypw_{pulse} + pyrw_{pulse} - \frac{dDOC}{2 \cdot dt}) \cdot \frac{S_t}{S_0} \quad (10)$$

$$mpsb_{additional} = \frac{dDOC}{2 \cdot dt} \tag{11}$$

Phosphorus mass balance. In this study, elevated sulphate supply to the Ediacaran Ocean, following previous proposals [24], is proposed to create a large long-term oxidant source. This input of oxidising power oxidised a large marine DOM pool, releasing DIC and P. The P released by DOM oxidation ($pdoc$) is assumed to be a net source for the marine P reservoir, which is calculated using the rate of DOM oxidation ($\frac{dDOC}{dt}$) and the C/P_{DOC} ratio. The new P mass is estimated with the following equations, adapted from ref. [55]:

$$\frac{dP}{dt} = psea + pdoc - mopb - capb - fepb_{tot} \tag{12}$$

Here $psea$ is the weathering flux of reactive P to the ocean, $mopb$ and $capb$ is P burial with organic carbon and calcium, respectively. We chose a fixed ratio of $C/P_{DOC} = 1000$ as the default, but also tested the influence of changing C/P_{DOC} (250, 1000, 3500, and no P release) on the marine P concentration (see Extend Data Fig. 4).

Full model description. See Supplementary Information for full modified COPSE model equations and parameters.

Code availability.

MATLAB code for COPSE is freely available at https://github.com/sjdaines/COPSE/releases.

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Main text figure captions

Figure 1. Carbonate-Associated Phosphate (CAP; given as CAP/(Ca+Mg)) and accompanying key geochemical records in six globally distributed sections which recorded the Shuram Excursion (SE), the largest known negative C-isotope excursion in carbonate ($\delta^{13}C_{carb}$) from the geological record. a) Global palaeogeographic map showing the locations of study regions (red stars) at ~560 Ma, modified after ref. [25]. b) Jiulongwan section (South China); c) Cerro Rajón section (Mexico), inset graph shows entire Ediacaran section; d) Death Valley section (USA), e) Parachilna Gorge section (Australia). f) Mochia-Khutuk section (North-western China), g) Sishang section (South China). Geochemical data sources: CAP and $^{87}Sr/^{86}Sr$ data are from this study, also $\delta^{13}C_{carb}$ of the Sishang and Parachilna Gorge sections are data from this study; other C-, U- and S-isotope data from refs.[7,8,21,22,23,24,26,27]. P-1st = first CAP peak; P-2nd = second CAP peak. PQ Fm., Pitiquito Formation; Gm Fm., Gamuza Formation; DY Fm., Dengying Formation; VPDB, Vienna Pee Dee Belemnite; VCDT, Vienna Canyon Diablo Troilite. Stratigraphic heights are meters above the first exposed outcrops of Ediacaran strata, except in the Death Valley, Parachilna and Mochia-Khutuk sections which are meters above the lower boundary of the measured geological formation and Sishang metres below Dengying Formation. Light blue circles are CAP in calcite and dark blue circles CAP in dolomite. White circles are $\delta^{13}C_{carb}$ and CAP outliers and error bars show a 5% error

margin. Black line through CAP data = LOESS smoothing. Stages I to IV are defined as follows: Stage I (falling limb of $\delta^{13}C_{carb}$), Stage II (plateau of $\delta^{13}C_{carb}$ values), Stage III (rising limb of $\delta^{13}C_{carb}$) and Stage IV (return to pre-SE $\delta^{13}C_{carb}$ values). See Supplementary Information 2 for correlation between sections and published data.

Figure 2. Conceptual model illustrating the co-evolution of the phosphorus cycle and dissolved organic matter (DOM) oxidation during the Shuram Excursion (SE) (see text for detailed description of the panels). a) Increasing weathering sulphate oxidises oceanic DOM increasing oceanic P and atmospheric O_2 and CO_2; b) elevated atmospheric O_2 decreases ocean anoxia and increases sedimentary P burial; c) cessation of DOM oxidation and pyrite burial leads to a decrease in atmospheric O_2 and the return of ocean anoxia. Stage I-IV refers to SE stages I-IV in Figure 1. Arrows from Fe^{2+} and Fe^{3+} signify the burial of P with Fe under anoxic and oxic conditions, respectively.

Figure 3. Biogeochemical model results which best replicate the observed Carbonate-Associated Phosphate (CAP) and C- and U-isotope records in Figure 1. a) Ocean carbonate C-isotopic composition ($\delta^{13}C_{carb}$); b) ocean P concentration ($[P]_{sw}$); c) ocean carbonate uranium isotopic composition ($\delta^{238}U_{carb}$); d) ocean sulphate sulphur isotopic composition ($\delta^{34}S_{CAS}$); e) ocean carbonate strontium isotopic composition ($^{87}Sr/^{86}Sr$); f) Ediacaran fossil record (adopted after ref [19]). Note the different time axes of panels a-e from panel f. Stage I-IV and P-1st and P-2nd refer to Shuram Excursion (SE) $\delta^{13}C_{carb}$ profile and CAP peaks in Figure 1, respectively. Turquoise lines represent model run with continuous Fe^{2+}-P burial and no HCO_3^- release from DOM oxidation; blue

lines represent Fe^{2+}-P burial stops during SE and no HCO_3^- release from DOM oxidation; dark blue lines represent Fe^{2+}-P burial stops during SE and HCO_3^- released during DOM oxidation, which halves CO_2 release from DOM (see Supplementary Information 4 and 6 for details).

Extended Data Table and Figure Captions

Extended Data Table 1. Statistics for Carbonate-Associated Phosphate (CAP) extraction and diagenetic measures. The strong, statistically significant correlation between bulk rock La and bulk rock P in the Jiulongwan section derives from the dissolution of phosphate minerals. Yet, no statically significant correlations are seen between La and CAP in the partial leach, implying minimal contamination from phosphate minerals for bulk rock P. Unless otherwise stated all elemental data is derived from CAP partial leach extraction. Isotopic data is obtained for the bulk rock. Note, when removing < 10% of data points as outliers, significant levels [$P(\alpha)$] all increase above 0.01 for all sections, indicating statistically insignificant correlations. All trendlines are linear fits. TOC = Total Organic Carbon.

Extended Data Figure 1. Open system diagenetic evolution fluid-rock interaction model. (a-c) Fluid -rock alteration models showing the relative order of alteration for CAP, CAS, Fe, Mn, IO_3, $\delta^{13}C$, $\delta^{34}S_{CAS}$, $\delta^{238}U$, $\delta^{44/40}Ca$, $^{87}Sr/^{86}Sr$. Multiple curves are presented for $\delta^{13}C$ and $\delta^{34}S_{CAS}$ under varying dissolved inorganic carbon (DIC) and sulphate concentrations in the diagenetic fluid. (d) Fluid-rock alteration model showing the predicted trends between CAP and $\delta^{13}C$, grey points are CAP and $\delta^{13}C$ data from all study sections. Solid and dashed lines represent different pore water DIC concentration and $\delta^{13}C$ compositions. Dotted line is trendline through datapoints with R value. See Supplementary Information for model description. Yellow stars mark the point at which 50% of the CAP value has been altered, the red/ grey stars mark the point at which 50% of the element of interest has been altered. CAP = Carbonate-Associated Phosphate, CAS = Carbonate-Associated Sulphate.

Extended Data Figure 2. COPSE model results comparing different hypotheses (dissolved organic matter (DOM) oxidation by sulphate only, elevated organic matter recycling, elevated weathering by uplift, elevated weathering by volcanism) for the observed changes in ocean P during the Shuram Excursion. a, A, I, i. Relative increase in sulphate addition versus background flux. **b, B, II, ii**. Phosphorus concentration in seawater ($[P]_{sw}$). **c, C, III, iii**. Relative atmospheric oxygen concentration (pO_2). **d, D, IV, iv**. Degree of ocean anoxia (Anoxia). **e, E, V, v**. Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). Note in panel E, the $\delta^{13}C_{carb}$ reflects the $\delta^{13}C$ of porewater dissolved inorganic carbon (DIC), not oceanic $\delta^{13}C$. **f, F, VI, vi**. Modelled marine sulphate sulphur isotope composition ($\delta^{34}S_{sulphate}$). **g, G, VII, vii**. Modelled marine carbonate uranium isotope composition ($\delta^{238}U_{carb}$). For the DOM oxidation hypothesis, we run the COPSE model with a DOM reservoir 30 times the size of the modern marine DIC reservoir and the C:P of the DOM reservoir is 1000, while the C:P of organic matter in the organic matter recycle model is 250 (see Supplementary Information 6 for more details). PAL = Present Atmospheric Level.

Extended Data Figure 3. COPSE model results comparing the oxidation of a dissolve organic matter (DOM) reservoir using sulphate, free oxygen (Shields et al., 2019) and sulphate + free

oxygen, respectively. a, A, I Relative increase in sulphate addition versus background flux (the varying colour shades of the model lines reflect the varying magnitude of the sulphate pulse for different model runs). **b, B, II**. Phosphorus concentration in seawater ($[P]_{sw}$). **c, C, III**. Relative atmospheric oxygen concentration (pO_2). **d, D, IV**. Degree of ocean anoxia (Anoxia). **e, E, V**. Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). **f, F, VI**. Modelled marine sulphate sulphur isotope composition ($\delta^{34}S_{sulphate}$). The C:P of the DOM reservoir is set to 1000 in all model runs. The magnitude of the sulphate pulses for each model is variable because higher additional sulphate fluxes are required for models where DOM is oxidised by O_2 resulting from pyrite burial, in comparison to models where DOM is oxidised only by sulphate (see Supplementary Information 7 for details).

Extended Data Figure 4. COPSE model results with varying sizes (sub-figures A-F) and variable P content (a-d) of an initial dissolved organic matter (DOM) reservoir and higher initial steady-state pO_2 of 20% present atmospheric level (PAL), with C:P of DOM = 250 (sub-figures a-d) (no Fe^{2+}-P burial) (sub-figures I-IV). A. Size of DOM reservoir in moles of carbon. **B**. Phosphorus concentration in seawater ($[P]_{sw}$). **C**. Relative atmospheric oxygen concentration (pO_2). **D**. Degree of ocean anoxia (Anoxia). **E**. Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). **F**. Modelled marine carbonate uranium isotope composition ($\delta^{238}U_{carb}$).. In panels A-F, we choose an additional sulphate pulse of 4 times that of the background flux and the C:P of the DOM reservoir is 1000. **a, I**. Size of DOM reservoir in moles of carbon. **b, II**. Phosphorus concentration in seawater ($[P]_{sw}$). **c, III**. Relative atmospheric oxygen concentration (pO_2). **d, IV**. Degree of ocean anoxia. In panels a-d, we choose a sulphate input of 4 times the background flux and the size of the

DOM reservoir is 30 times that of the size of the modern marine dissolved inorganic carbon (DIC) reservoir. For panels I-IV, the DOM reservoir is 30 times that of the size of the modern marine dissolved inorganic carbon (DIC). Higher steady-state pO_2 was achieved by adjusting the model terrestrial P input flux and gypsum burial.

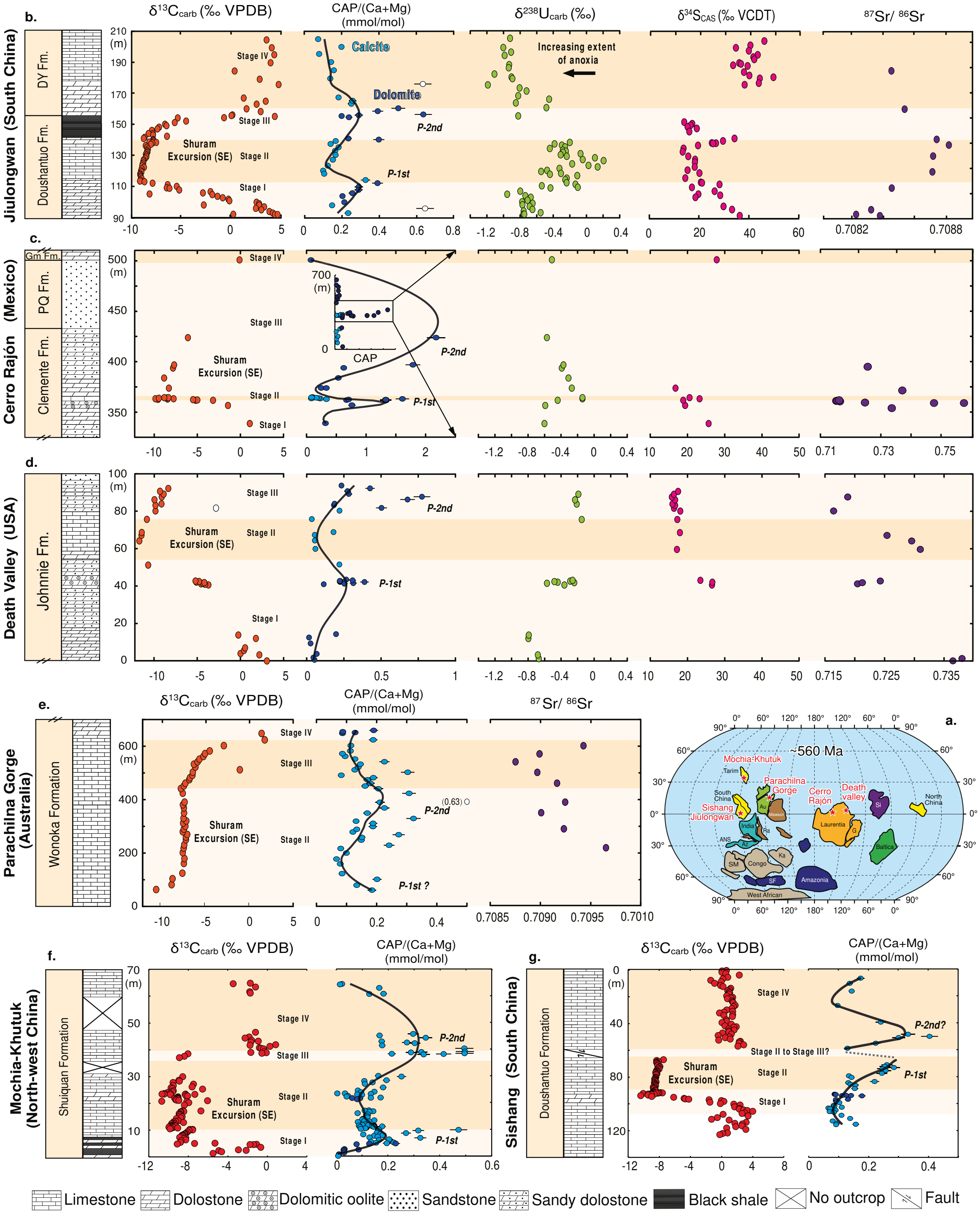
Extended Data Figure 5. COPSE model results varying the magnitude of an additional sulphate pulse for dissolved organic matter (DOM) oxidation by sulphate only (no Fe^{2+}-P burial) (a-h), burying all additional sulphate pulse as pyrite (I-VIII) and setting gypsum burial to a constant rate (i-viii). **a**. Size of DOM reservoir in moles of carbon. **b**. Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). **c**. Phosphorus concentration in seawater ($[P]_{sw}$). **d**. Modelled marine carbonate uranium isotope composition ($\delta^{238}U_{carb}$). **e**. Relative atmospheric oxygen concentration (pO_2). **f**. Degree of ocean anoxia. **g**. Modelled marine sulphate sulphur isotope composition ($\delta^{34}S_{sulphate}$). **h**. Modelled marine carbonate strontium isotope composition ($^{87}Sr/^{86}Sr$). The blue line, the grey line, and the dashed grey line are additional sulphate pulses of 3, 4 and 5 times the background flux respectively. **I, i.** Relative atmospheric oxygen concentration (pO_2). **II, ii.** Phosphorus concentration in seawater ($[P]_{sw}$). **III, iii.** Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). **VI, vi.** evolution of ocean anoxia. **V, v.** Modelled marine carbonate uranium isotope composition ($\delta^{238}U_{carb}$). **VI, vi.** Modelled marine sulphate sulphur isotope composition ($\delta^{34}S_{sulphate}$). **VII, vii.** Sulphate concentration in seawater ($[SO_4]_{sw}$). **VIII, viii.** Oceanic gypsum burial rate (mgsb). Here we used a DOM reservoir size that is 30 times that of the size of the modern marine dissolved inorganic carbon (DIC) reservoir. PAL = present atmospheric level, POL = present oceanic level.

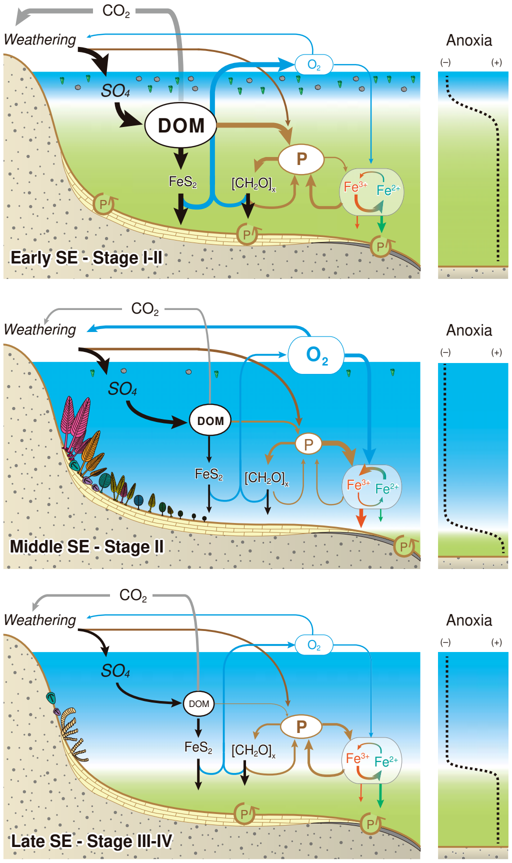
Extended Data Figure 6. Full COPSE model outputs for dissolved organic matter (DOM) oxidation by sulphate with constant (Fe^{2+}) -bound phosphorus burial, using a sulphate pulse of 4 times background flux, DOM C:P of 1000, and the size of the DOM reservoir is 30 times the size of the modern marine dissolved inorganic carbon (DIC) reservoir. a. Weathering sulphate pulse versus background flux. **b.** DOM oxidation flux (DOM_{ox}) in moles of carbon per year. **c.** DOM reservoir (DOM_{pool}) in moles of carbon. **d.** P concentration in sea water ($[P]_{sw}$). **e.** Relative atmospheric oxygen concentration (pO_2) to present atmospheric level (PAL). **f.** Degree of marine anoxia (Anoxia). **g.** Modelled marine carbonate carbon isotope composition ($\delta^{13}C_{carb}$). **h.** Modelled marine sulphate sulphur isotope composition ($\delta^{34}S_{sulphate}$). **i.** Silicate weathering flux (silw) in moles of carbon per year. **j.** Modelled marine carbonate strontium isotope composition ($^{87}Sr/^{86}Sr$). **k.** Relative marine sulphate concentration ($[SO_4^{2-}]_{sw}$) to present oceanic level (POL). **l.** Relative marine new primary productivity (newp) to POL. **m.** Relative atmospheric carbon dioxide concentration (pCO_2) to PAL. **n.** Average global temperature (Temp) in ℃. **o.** Organic carbon weathering flux (oxidw) in moles of carbon per year. **p.** Marine organic carbon burial flux (mocb) in moles of carbon. **q.** Gypsum sulfur weathering flux (gypw) in moles of sulfur. **r.** Pyrite sulfur weathering flux (pyrw) in moles of sulfur. **s.** Marine pyrite sulphur burial flux (mpsb) in moles of sulphur. **t.** Marine gypsum sulphur burial flux (mgsb) in moles of sulphur. **u.** Phosphorus releasing flux from DOM oxidation (DOM_{OX}_P) in moles of phosphorus. **v.** Flux of weathered phosphorus reaching the sea (psea) in moles of phosphorus. **w.** Total iron-bound phosphorus burial flux (fepb) in moles of phosphorus. **x.** Carbonate-bound phosphorus burial flux (capb) in moles of phosphorus. **y.** Marine organic phosphorus burial flux (mopb) in moles of phosphorus. **z.** Ferric iron (Fe^{3+}) -bound phosphorus burial [fepb(Fe^{3+})] in moles of phosphorus. **aa.** Ferrous iron (Fe^{2+}) -bound phosphorus burial [fepb(Fe^{2+})] in moles of phosphorus.

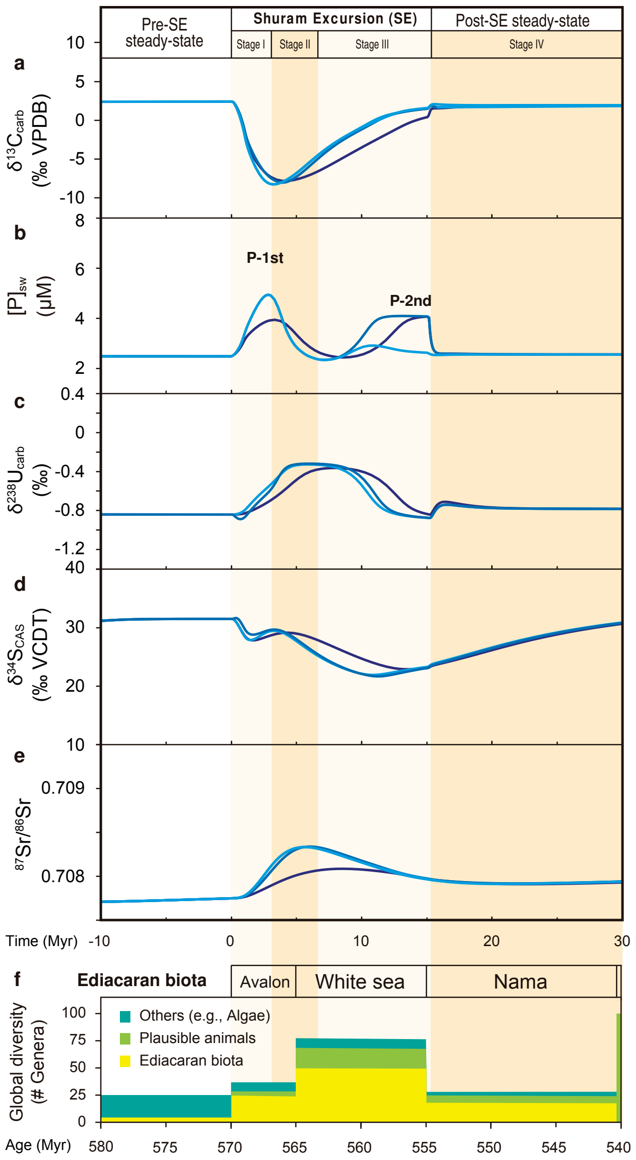
Extended Data Figure 7. Comparison of COPSE model results for ocean P cycling with and without P burial by Fe^{2+} scavenging. a. Ocean inorganic carbon isotopic composition ($\delta^{13}C_{carb}$). **b.** Ocean P concentration ($[P]_{sw}$); red shaded areas represent uncertainty windows in Fig. 3. **c.** Ocean uranium isotopic composition recorded in carbonates ($\delta^{238}U_{carb}$). **d.** Ocean sulphur isotopic composition recorded in carbonate-associated sulphate ($\delta^{34}S_{CAS}$). **e.** Ocean strontium isotopic composition ($^{87}Sr/^{86}Sr$). **f.** Ediacaran fossil record adapted after Darroch et al. (2018). Stages I to IV are defined as the SE intervals of falling limb, plateau, rising limb and post-SE, respectively, as in Figure 1 which are matched with modelled ocean P reservoir shifts. Model parameters for outputs are the same as detailed in Fig. 3 and Extended Data Fig. 6 except for the red line which excludes P burial by Fe^{2+}-scavenging (i.e., a modern-style P and O_2 cycle). P-1st and P-2nd refers to carbonate-associated phosphate (CAP) peaks in Figure 1.

Extended Data Figure 8. Model output of a quantitative 4-box ocean P cycle model. Output from Figures 4a and 5a in Alcott et al. (2019) with the P concentrations in the respective boxes (proximal shelf, distal shelf, deep ocean) plotted. This shows the relative concentration of soluble reactive phosphorus in each ocean box during a model solution in which P levels are oscillating on a large scale. These results show that even under substantial changes in P concentration, the distal shelf (i.e., the area of the shelf that is not dominated by riverine input) is expected to be strongly linked to the deep ocean P concentration. See Alcott et al. (2019) for full model details.

Extended data Figure 9. Experimental constraints on the effects of alkalinity (a) and precipitation rate (b) on carbonate-associated phosphate (CAP) values in carbonate. a. CAP uptake increases with progressively lower $[CO_3^{2-}]$ and alkalinity concentrations. **b.** CAP uptake decreases with increasing precipitation rate. The changes in CAP over the observed ranges in alkalinity and precipitation rate are small compared to the effects of phosphate concentration and solution pH (Dodd et al., 2021). All trendlines are linear fits. Error bars are ± 5% for CAP and ± 0.1 for Ca/ ALK.


b.
Jiulongwan (South China)
DY Fm.
Doushantuo Fm.
δ13Ccarb (‰ VPDB)
CAP/(Ca+Mg) (mmol/mol)
δ238Ucarb (‰)
δ34SCAS (‰ VCDT)
87Sr/86Sr
Stage IV
Stage III
Stage II
Stage I
Shuram Excursion (SE)
Calcite
Dolomite
P-2nd
P-1st
Increasing extent of anoxia
c.
Cerro Rajón (Mexico)
Gm Fm.
PQ Fm.
Clemente Fm.
CAP
d.
Death Valley (USA)
Johnnie Fm.
e.
Parachilina Gorge (Australia)
Wonoka Formation
P-1st ?
(0.63)
a.
~560 Ma
Mochia-Khutuk
Tarim
Parachilina Gorge
Cerro Rajón
Death valley
South China
Sishang
Jiulongwan
North China
Laurentia
Baltica
Amazonia
Congo
West African
India
SM
SF
Ka
Si
ANS
f.
Mochia-Khutuk (North-west China)
Shuiquan Formation
g.
Sishang (South China)
Doushantuo Formation
P-2nd?
Stage II to Stage III?
Limestone
Dolostone
Dolomitic oolite
Sandstone
Sandy dolostone
Black shale
No outcrop
Fault


CO$_2$
Weathering
SO$_4$
DOM
O$_2$
P
FeS$_2$
[CH$_2$O]$_x$
Fe^{3+}
Fe^{2+}
P
P
P
Early SE - Stage I-II
Anoxia
(–)
(+)
CO$_2$
Weathering
O$_2$
SO$_4$
DOM
P
FeS$_2$
[CH$_2$O]$_x$
Fe^{3+}
Fe^{2+}
P
Middle SE - Stage II
Anoxia
(–)
(+)
CO$_2$
Weathering
O$_2$
SO$_4$
DOM
P
FeS$_2$
[CH$_2$O]$_x$
Fe^{3+}
Fe^{2+}
P
P
Late SE - Stage III-IV
Anoxia
(–)
(+)


Pre-SE steady-state
Shuram Excursion (SE)
Post-SE steady-state
Stage I
Stage II
Stage III
Stage IV
a
$\delta^{13}C_{carb}$ (‰ VPDB)
10
5
0
-5
-10
b
$[P]_{sw}$ (μM)
8
6
4
2
P-1st
P-2nd
c
$\delta^{238}U_{carb}$ (‰)
0.4
0
-0.4
-0.8
-1.2
d
$\delta^{34}S_{CAS}$ (‰ VCDT)
40
30
20
10
e
$^{87}Sr/^{86}Sr$
0.709
0.708
Time (Myr)
-10
0
10
20
30
f
Ediacaran biota
Avalon
White sea
Nama
Global diversity (# Genera)
100
75
50
25
0
🟩 Others (e.g., Algae)
🟩 Plausible animals
🟨 Ediacaran biota
Age (Myr)
580
575
570
565
560
555
550
545
540