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Title: Earth's Great Oxidation Event facilitated by the rise of sedimentary phosphorus recycling

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Abstract

The rise of atmospheric oxygen during the Great Oxidation Event some 2.4 billion years ago was a defining transition in the evolution of global biogeochemical cycles and life on Earth. However, mild oxidative continental weathering and the development of ocean oxygen oases occurred several hundred million years prior to the Great Oxidation Event. The Great Oxidation Event thus represents a tipping point, whereby primary productivity and O_2 production overwhelmed the input of reduced species that consume O_2, and its timing is determined by the input of phosphate, the major limiting nutrient, and the dynamics of the solid Earth. Here, we determine the phase partitioning of phosphorus in 2.65 to 2.43 billion year old drill core samples from the Transvaal Supergroup, South Africa, to investigate the sequence of events that facilitated persistent atmospheric oxygenation. Based on the elevated C:P ratios found within sulfidic sediments, relative to the Redfield ratio, we suggest that, as oxidative continental weathering increased the influx of dissolved sulfate and hence dissolved sulfide in the oceans, bioavailable phosphorus became more abundant due to anoxic recycling of sedimentary phosphorus phases. Biogeochemical modelling indicates that this initiated a positive feedback on primary productivity and shows that the evolution of phosphorus recycling may have been a critical step that enabled Earth's transition to a persistently oxygenated atmosphere.

Main text

The evolution of oxygenic photosynthesis resulted in the first development of locally oxygenated surface waters in continental margin settings during the late Archean[1,2]. These "oxygen oases" apparently became more expansive between ~2.9 and ~2.5 Ga[3,4], prior to the start of the Great Oxidation Event (GOE) at ~2.4 Ga. This progressive surface ocean oxygenation occurred against a backdrop of persistently anoxic, ferruginous (iron-rich) deep-ocean conditions[5], but enhanced oxidative continental weathering also increased the delivery of sulfate to the ocean system, thus increasing the microbial production of dissolved sulfide[6]. In addition to an expansion of sulfidic pore waters, this led to spatially and temporally restricted episodes of ocean euxinia (sulfidic water-column conditions) in some Neoarchean continental margin settings[2,7,8].

These progressive changes in ocean and sediment redox conditions prior to the GOE would be expected to exert a major control on the bioavailability of phosphorus (P)[9]. Phosphorus is generally considered to have been the major limiting nutrient throughout Earth history[10], but was likely scarce during the Archean due to extensive drawdown and fixation in association with iron minerals under widespread ferruginous conditions[4,11-13]. This "iron-trap" is thought to have limited primary productivity and organic carbon burial, such that the global sinks for oxygen (continental weathering and oxidation of reduced species delivered by hydrothermal and volcanic volcanism) exceeded its production, maintaining an anoxic atmosphere[6,12]. However, the rise of sulfidic environments would have limited drawdown and fixation of P in association with reactive Fe minerals, due to the transformation of such minerals to pyrite, to which P does not significantly adsorb[14]. In addition, organic-bound P is preferentially released from organic matter (C_{org}) via anaerobic remineralisation, particularly during the production of sulfide via microbial sulfate reduction, which results in high molar C_{org}/P_{org} ratios relative to the Redfield Ratio (106:1)[15,16].

These processes result in the release of bioavailable P, either directly to the water column under euxinic conditions or to pore waters in sulfidic sediments. A proportion of the P released to pore waters may undergo "sink switching" to authigenic phases such as carbonate fluorapatite[17] or vivianite[18,19]. Nevertheless, a substantial proportion of the P released may be recycled back to the water column, ultimately driving further surface ocean primary productivity and carbon burial, and hence increasing O_2 production[20]. However, the rise of P recycling has not previously been considered in relation to either the GOE or the gradual oxygenation of Earth's surface during the late Archean. Instead, studies of early Earth oxygenation have tended to focus on increases in the weathering input of phosphate, leading to enhanced oxygenic photosynthesis and aerobic heterotrophy, or on mechanisms that directly consume or produce free O_2, such as the nature of the hydrothermal influx, oxidation of reduced gases, or escape of hydrogen to space[21-24]. Given the >10 fold increase in sedimentary P release that commonly occurs under anoxic, sulfidic conditions[20], the impact of P recycling has the potential to overwhelm other Earth system controls on oxygenation[25].

Redox Conditions in the Water Column and Sediments

To investigate the role of anaerobic P recycling as sulfide became more abundant in the ocean system prior to the GOE, we analysed four cores through the ~2.65 to 2.43 Ga Campbellrand and overlying Koegas subgroups, South Africa (Fig. 1; see Supplementary Information for full details on the geologic setting and all data; Fig. S1; Fig. S2). Existing[2,26] and new geochemical data (see Methods) for the older part of the stratigraphic succession from the GKF01 (proximal) and GKP01 (distal) drill cores demonstrate a complex redox history across the continental shelf-slope transect (Fig. 1). Samples from below the ~2650 Ma Lokammona Formation show evidence of deposition under fluctuating oxic (Fe_{HR}/Fe_T <0.22; Fe/Al <0.66) to ferruginous (Fe_{HR}/Fe_T >0.22; Fe/Al >0.66; Fe_{py}/Fe_{HR} <0.7) bottom waters. However, Fe_{py}/Fe_{HR} ratios are relatively high, including for samples deposited under oxic water-column conditions, demonstrating that pore waters were sulfidic during early diagenesis[27]. The Lokammona and Monteville formations also show evidence for deposition beneath oxic bottom waters, but some samples have higher Fe_{HR}/Fe_{T} (>0.38) and Fe_{py}/Fe_{HR} (>0.7) ratios, consistent with conventional criteria for identifying euxinic depositional conditions[5]. However, pyrite textures in these samples are more consistent with intense sulfide production during very early diagenesis beneath a ferruginous water column (see Supplementary Information; Fig. S8), which was likely stimulated by a higher rate of organic matter burial (Fig. 1).

The lower and upper Nauga formations contain intervals deposited beneath partially oxic surface waters, based on Fe speciation and trace metal systematics[2], but other horizons in these units with elevated Fe_{HR}/Fe_{T} (>0.38) and low Fe_{py}/Fe_{HR} (<0.7) suggest redox fluctuations between oxic and ferruginous conditions. The lower part of the Klein Naute Formation dominantly shows evidence of anoxic deposition (elevated Fe_{HR}/Fe_{T} and/or high Fe/Al), with some intervals of high Fe_{py}/Fe_{HR} (>0.7). These latter intervals are consistent with well-established criteria for recognition of water-column euxinia[2,5,26], which, in contrast to the Lokammona and Monteville formations, is also supported by conventional interpretation of pyrite textures in these samples (see Supplementary Information). The overlying Kuruman Iron Formation documents an extensive interval of iron formation deposition, which persisted during deposition of most of the overlying sediments in the GTF01 and GEC01 cores. Here, the iron mineralogy is characterised by high concentrations of Fe-rich silicates, giving relatively low Fe_{HR}/Fe_{T} ratios (Fig. 1). However, elevated Fe/Al and low Fe_{py}/Fe_{HR} ratios support persistent deposition under anoxic, ferruginous conditions.

Redox Controls on the Phosphorus Cycle

Phosphorus concentrations are generally below the average shale value throughout the succession, although normalisation to Al suggests that the majority of samples are similar to average shale (Fig. 1). There are exceptions, however, and the high P concentrations that occur in the Monteville and Klein Naute formations (drill cores GKF01 and GKP01) are likely due to the elevated organic content in these samples. Notably, high P concentrations and P/Al ratios also occur in the Kuruman Iron Formation, which contrasts with the generally much lower P content of the overlying iron formations of the Koegas Subgroup (GTF01 and GEC01 drill cores; Fig. 1).

To evaluate the potential for phosphorus recycling, we determined the phase partitioning of P via a sequential extraction scheme[28] (Fig. 2; Fig. S3; Fig. S6). All data for the two drill cores that represent the older part of the succession (GKP01 and GKF01) have C_{org}/P_{org} ratios that are highly elevated, relative to both the Redfield Ratio of 106:1, and the predicted ratio of ~300:1 for organic matter buried under the P-limited conditions inferred for the early Precambrian[12]. This suggests extensive preferential release of P during anaerobic organic matter remineralisation[15]. Indeed, the molar C_{org}/P_{org} ratios we observe (up to ~8,000) are up to two orders of magnitude higher than primary depositional ratios expected under P-limited conditions[12], and the only known process capable of generating C_{org}/P_{org} ratios of this magnitude is via preferential release of P during organic matter remineralization.

To determine whether this P was recycled to the water column or fixed as authigenic phases in the sediment, we define a reactive P pool (P_{reac}), which, in addition to P_{org}, includes the phases that may sequester dissolved P (e.g., authigenic P, P_{aut}, and iron-bound P, P_{Fe}). With the exception of some ferruginous shale and iron formation samples (where in addition to the organic P sink, drawdown would also have occurred in association with Fe minerals, giving low initial C_{org}/P_{reac} ratios), most samples continue to plot well above the Redfield Ratio, demonstrating extensive recycling of P back to the water column[16]. Phosphorus recycling is evident in all samples that are conventionally interpreted as being deposited under euxinic or oxic conditions, as well as in a large proportion of ferruginous samples (Fig. 2). This highlights that the development of sulfidic porewaters close to the sediment-water interface was sufficient to promote extensive P recycling. Thus, our identification of P recycling is not contingent on our reconstruction of water column euxinia during deposition of the lower part of the Klein Naute Formation.

The overlying interval of ~2.48 to 2.43 Ga iron formation deposition (Fig. 1) records a secular event driven by the emplacement of Large Igneous Provinces (LIPs) and an exceptionally high submarine hydrothermal flux[29,30]. High concentrations of P are apparent during the earliest stages of Kuruman Iron Formation deposition (Fig. 1), supporting extensive P drawdown in association with Fe minerals from a water column that was initially enriched in recycled P. Subsequently, generally muted P concentrations (drill cores GTF01 and GEC01) reflect the maintenance of decreased water-column P concentrations during the prolonged period of iron formation deposition. Indeed, a significant proportion of samples have C_{org}/P_{reac} ratios that fall below the Redfield Ratio (Fig. 2D), consistent with drawdown of P in association with Fe minerals. However, some samples (particularly shales) have C_{org}/P_{org} and C_{org}/P_{reac} ratios that fall above the Redfield Ratio (and above the predicted ratio of ~300:1 for organic matter buried under P-limited conditions), likely reflecting significant P recycling back to the water column during early diagenesis, as a result of P release from both organic matter and Fe-mineral transformations. Furthermore, while P recycling and organic carbon burial was clearly less extensive when BIFs were deposited, the riverine input of P was likely high due to enhanced chemical weathering in association with LIP emplacement at this time[30], and thus water-column P concentrations may locally have remained relatively high. This is supported by an array of samples that have C_{org}/P_{org} ratios close to the Redfield Ratio (Fig. 2B), suggesting that productivity was not strongly limited by P bioavailability during BIF deposition.

Progressive Oxygenation of the Earth System

We note that the Transvaal Supergroup contains an unconformity at the top of the Koegas Subgroup beneath the oldest glacial diamictite (Makganyene Formation) of the GOE (Fig. 1). Therefore, the behaviour of the P cycle immediately prior to the onset of the GOE is unclear. Thus, to provide global context, we also consider the longer-term pyrite sulphur isotope record (Fig. 3A), which demonstrates a clear and consistent increase in the range of $\delta^{34}S$ values from the Mesoarchean (which we define as Stage 1 in Earth's early oxygenation history) through the more expansive, but still localized, continental margin oxygenation of the Neoarchean (which we term Stage 2). This likely represents a gradual increase in seawater sulfate concentration driven by oxidative continental weathering[6,31], thus leading to an increase in sulfide availability in the ocean system. More extensive anaerobic recycling of P from Stage 1 to Stage 2 would be a natural consequence of this increase in sulfide availability, and, consistent with this, the longer-term P record (Fig. 3B) documents elevated P content at times in Stage 2 when P was drawn down and fixed in the sediment (e.g., during some shorter-term intervals of iron-formation deposition).

Our data imply that long-term oxygenation in the run up to the GOE was dependent on increased recycling of P from the sediments. This mechanism would have operated in addition to any changes in weathering-related input of P (i.e., via the emergence of appreciable subaerial landmasses[32], a secular increase in the continental phosphorus inventory[22,33], or the emplacement of LIPs[30]). To evaluate how changes in sulfide availability, P recycling and P input may have influenced planetary oxygenation we utilise a modified biogeochemical model of the C-O-P cycles[25] (see Methods; Fig. S4). We run the model to steady state under variable continental P weathering inputs and sedimentary P recycling rates, while maintaining the global rate of reductant input fixed at a level inferred for the Paleoproterozoic (15×10^{12} mol O_2 equiv. yr^{-1})[34,35]. The range in P recycling rates encompasses the primary molar C:P ratio of organic matter (106:1) through to the uppermost values found in our data (~8,000:1). This range reflects the C_{org}:P_{org} ratios of samples deposited under ferruginous conditions, as well as the significantly elevated ratios we commonly observe under highly sulfidic conditions, and is used to evaluate the model's response to sulfide availability, as the sulfur cycle is not explicitly included. We use C_{org}:P_{org} to drive the model because C_{org}:$P_{reactive}$ forms part of the model internal calculations.

We find that both recycling and changes to the continental weathering influx of P can cause substantial changes to the atmospheric O_2 reservoir. With elevated sedimentary molar C_{org}:P_{org} ratios, as measured in the majority of our ferruginous and euxinic shale samples (~5000 ± 3000), the GOE transition could have occurred with only limited continental weathering, at around 0.3 times the present-day P input rate (Fig. 4), which is consistent with recent calculations for apatite weathering rates on the early Earth[36]. When sedimentary molar C_{org}:P_{org} ratios are instead assumed to be ~300, the GOE transition requires a much larger, and highly unlikely[36], P weathering influx of around 2-3 times the present day (Fig. S9). Indeed, our data indicates at least a 10 fold increase in P recycling during the study interval, which far exceeds any apparent change in either weathering rates or reductant input[36,37].

We note here that our proposed increase in primary production might be expected to result in a positive shift in the δ^{13}C record, which has not yet been recognized. However, previous models[38,39] have demonstrated that the resulting oxidation of isotopically light carbon (e.g., marine dissolved organic carbon, methane, or recycled sedimentary organic carbon from the upper continental crust) in the surface system would act to stabilise the isotopic signal at a long-term average of 0‰ (Extended Data Fig 1). Thus, taken together, our new geochemical data and model results are consistent with the rise of sedimentary P recycling being a necessary prerequisite factor in paving the way for the GOE on Earth, and, indeed, the GOE was likely not possible without it.

Reconstructions of the bioavailability of P, based on both the shale and iron formation records, have suggested that P concentrations were persistently very low throughout the Archean, thus maintaining organic carbon burial and oxygen production at a low level[11,12]. By contrast, we demonstrate here that the rise of sulfide in the ocean system, which was initiated by the onset of mild oxidative continental weathering, led to progressively enhanced anoxic recycling of P, thus initiating a positive productivity feedback. This initially led to an intermediate oxygenation state in the Earth System, characterised by more pervasive oxygenation of continental margin settings during the Neoarchean, but with the atmosphere maintained in an anoxic state. Subsequently, extensive phosphorus recycling, possibly combined with a general increase in the continental weathering P influx[30,32], led to a major turning point in Earth history, whereby rates of oxygen production became sufficient to result in the first persistent oxygenation of the atmosphere.

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Author contributions

S.W.P., L.J.A., B.J.W.M., and A.B. designed the research and collected the samples. L.J.A. and S.W.P. performed geochemical analyses and interpreted the data. B.J.W.M. guided the biogeochemical modelling, and A.B. provided geological context. All authors contributed to writing the manuscript.

Competing Interests Statement

The authors declare no competing interests.

Figure Legends

Figure 1. *Stratigraphy and geochemistry of the studied drill cores*[30,40-44]*. Grainsize divisions are mudstone, siltstone, sandstone, and breccia for the two Koegas Subgroup drill cores, and mudstone, sandstone, and boundstone for the two Campbellrand Subgroup drill cores. Dashed lines on the* Fe_{HR}/Fe_T *plots represent the defined boundaries for identifying oxic and anoxic deposition, with equivocal samples falling between these lines. Dashed line on* Fe_{Py}/Fe_{HR} *plots distinguishes euxinic from ferruginous deposition for grey circles (representing samples clearly deposited from an anoxic water-column), whereas red open circles likely represent deposition under oxic conditions, and hence* Fe_{py}/Fe_{HR} *ratios for these samples reflect production of sulphide during early diagenesis. Dashed lines on Fe/Al plots represent the normal range for oxic deposition. Dashed lines on the P and P/Al plots represent the average shale. Fe/Al and P/Al ratios are reported as wt%/wt%. Ong. – Ongeluk Formation; Mak. – Makganyene Formation; Roo. – Rooinekke Formation; Dore. – Doredale Formation; Pann. – Pannetjie Formation; Griq. – Griquatown Iron Formation; Nel. – Nelani Formation; Kur. – Kuruman Iron Formation; Kl. Na. – Klein Naute Formation; K. – Kamden Member; Mont. – Monteville Formation; Loka. – Lokamonna Formation; Boom. – Boompaas Formation; Vryb. – Vryburg Formation; Vent. – Ventersdorp Group.*

Figure 2. *Relationships between organic carbon and different phosphorus pools. (A)* C_{org}:P_{org} *for the Ghaap Group drill cores (GKF01 and GKP01); (B)* C_{org}:P_{org} *for the Koegas Subgroup drill cores (GTF01 and GEC01); (C)* C_{org}:P_{reac} *for the Ghaap Group drill cores; (D)* C_{org}:P_{reac} *for the Koegas Subgroup drill cores. Dashed lines represent the Redfield Ratio (106:1) and the inferred* C_{org}/P_{org} *ratio for the early Precambrian sediments deposited under highly oligotrophic P-limited conditions (300:1*[12]*).*

Figure 3. *Long-term trends in the phosphorus content and the sulphur isotope composition of marine sediments, highlighting Stages 1 to 3 in the progressive oxygenation of the early Earth. Stage 1: approximately 3.2 – 2.7 Ga; Stage 2: approximately 2.7 – 2.43 Ga. Stage 3: approximately 2.43 to 2.0 Ga. (A) Whole-rock* δ^{34}S *compilation, including data for the GKF01 and GKP01 drill cores, which demonstrates a progressively increasing range in* δ^{34}S *data through the three stages*[45]*. The Koegas Subgroup sulfur isotope data is from Johnson et al., 2013*[46]*. (B) An expanded dataset showing published P/Al ratios*[12] *and P/Al ratios for the GTF01, GEC01, GKF01, and GKP01 drill cores (see Supplementary Information).*

Figure 4. *Steady-state model solutions for a fixed reduced gas flux. (A) Total primary organic carbon production (moles C/year). (B) Total organic carbon burial (moles C/year). (C) Atmospheric oxygen concentration in PAL units.* C_{org}/P_{org} *ratios for Phanerozoic shales commonly exceed several thousand*[21]*, consistent with the average value of ~5000 ± 3000 for shales in the GKP01 and GKF01 drill cores. Model runs that produce non-steady state results have been interpolated with respect to neighbouring results and are indicated by crosses.*

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Methods

Iron Speciation

We utilised Fe-S systematics to evaluate local redox conditions[47,48]. A highly-reactive fraction (Fe_{HR}) was determined as the sum of carbonate-associated iron (Fe_{Carb}), ferric oxides (Fe_{Ox}), mixed-valence iron oxides (principally magnetite; Fe_{Mag}), and pyrite-associated Fe (Fe_{py}). Iron concentrations (Fe_{Carb}, Fe_{Ox}, and Fe_{Mag}) were determined via AAS, while Fe_{py} was determined gravimetrically following precipitation of pyrite sulphur as Ag_2S. Whole-rock elemental concentrations (Fe, Al, and P) were measured by ICP-OES following a HNO_3-HF-$HClO_4$-H_3BO_3 whole-rock digest. Ratios of Fe_{HR} to total Fe (Fe_T) above 0.38 suggest deposition from anoxic bottom waters[5]. By contrast, Fe_{HR}/Fe_T ratios below 0.22 suggest deposition from oxic bottom waters, while intermediate values are considered equivocal[5]. Shales and iron formation samples deposited in ferruginous settings can be impacted by transfer of non-sulphidized Fe_{HR} to poorly reactive sheet silicates during early diagenesis, which lowers Fe_{HR}/Fe_T ratios[49-51]. To account for this possibility, we also considered Fe/Al ratios, whereby values >0.66 provide a robust indication of anoxic depositional conditions[52], and thus we identify anoxic water column deposition by a combination of Fe_{HR}/Fe_T >0.38 and/or Fe/Al >0.66 (Fig. 1).

Phosphorus Speciation

A sequential extraction for ancient Fe-rich rocks was applied to determine phosphorus speciation[28]. The method targets four operationally defined phosphorus pools, including iron-bound phosphorus (P_{Fe}), authigenic P (P_{aut}), organic-bound P (P_{org}), and crystalline apatite P (dominantly detrital P; P_{cryst}). Phosphorus concentrations were either determined spectrophotometrically using the molybdate-blue method at 880 nm[53], or via ICP-OES for extracts containing chemicals that interfere with colour development via the molybdate-blue method[28]. Reactive P (P_{reac}) was calculated as the sum of P_{Fe}, P_{aut}, and P_{org}[16].

Biogeochemical Modelling

Our biogeochemical model[25] comprises the carbon, oxygen, and phosphorus cycles, integrated over a four-box representation of the global hydrosphere that includes the atmosphere, shelf seas, open ocean, and deep ocean. The model considers P-driven primary production, export, remineralization, sedimentation and early diagenesis, including a redox-dependent P-cycle (see Supplementary Information). We fix the input of reduced gases at 15 x 10^{12} moles/year O_2 equiv., representative of estimates for 2.4 Ga[25], and explore changing the net C_{org}:P_{org} ratio of buried material, which reflects the extent of phosphorus regeneration from sediments. The GOE is achieved in the model once oxygen production from net organic carbon burial overwhelms oxygen consumption by the reduced gas flux[25] and the main control on atmospheric oxygen switches to being maintained by oxidative weathering. This is a simplification of the process and other atmospheric feedbacks are likely involved[54]. The values considered for the C_{org}:P_{org} ratio of organic matter are constrained by the minimum value, as defined by the organic matter formation ratio (Redfield Ratio; 106:1), and the maximum value of the range found in the studied shales (~5000 ± 3000). This range is broadly consistent with other ancient C:P ratios from anoxic settings through time (up to ~3500[15]) and more recent Mediterranean sapropel sediments (up to ~4000[55]). We utilise our measured C_{org}:P_{org} ratios, rather than C_{org}:P_{reac} ratios, to drive the model. This was chosen to simplify the model which calculates each P sink individually.

References only found in the methods

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Data Availability

The geochemical dataset is available at https://doi.org/10.6084/m9.figshare.14186114.

Code availability

Model code and output data are available from the corresponding author on reasonable request.

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