



RESEARCH ARTICLE

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Did phosphorus derived from the weathering of large igneous provinces fertilize the Neoproterozoic ocean?

Forrest Horton¹¹Earth Science Department, University of California, Santa Barbara, Santa Barbara, California, USA

Key Points:

- Weathering of Neoproterozoic flood basalts increased the phosphorus flux to the ocean
- Phosphorus fertilization may explain Neoproterozoic ocean-atmosphere oxidation

Supporting Information:

- Table S1

Correspondence to:

F. Horton,
fhorton@umail.ucsb.edu

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Abstract Primary productivity and organic carbon burial rates in the Precambrian were highly sensitive to fluxes of phosphorus (P) from the weathering of continental crust. Large igneous provinces (LIPs)—containing substantial P and highly susceptible to chemical weathering—occurred regularly during the breakup of the Rodinia supercontinent, and flood basalts probably covered $3.7\text{--}7.4 \times 10^6 \text{ km}^2$ at a time when a low-latitude continental configuration expedited weathering. Assuming chemical weathering liberated much of the P contained in the flood basalts, an estimated $1\text{--}4 \times 10^{17}$ mol of biologically available P entered the ocean from LIPs between 900 and 500 Ma. Especially, voluminous LIP magmatism began at ~ 850 Ma and culminated with the Franklin Province at 720 Ma, after which an estimated bioavailable P flux from flood basalts of $1\text{--}5 \times 10^9$ mol/yr may have been sustained for millions of years, elevating primary production and organic carbon burial rates. P enrichment of LIP magmas prior to eruption could have contributed to efficient reactive P delivery to the ocean: liquid-crystal fractionation beneath thick cratonic lithosphere and the incorporation of metasomatic P potentially enriched Neoproterozoic LIP magmas more than anytime previously. Thus, a unique convergence of tectonic conditions—supercontinent breakup, voluminous mafic volcanism containing abundant P, and a low-latitude continental configuration—may have facilitated an unprecedented flux of bioavailable P to the ocean that was capable of triggering oxidation of the ocean-atmosphere system and enabling accelerated biologic diversification.

1. Introduction

The Neoproterozoic era was punctuated by profound tectonic, evolutionary, and environmental change; the feedbacks among the breakup of the Rodinia supercontinent, “Snowball Earth” glaciations, atmospheric oxygenation, and rapid biologic diversification remain controversial. Biologic and climatic conditions may have been especially sensitive to fluctuations in seawater phosphorus (P), believed to have been the biolimiting nutrient at the time [e.g., *Van Cappellen and Ingall*, 1996; *Papineau*, 2010; *Laakso and Schrag*, 2014; *Lenton et al.*, 2014]. During the Archean and early Proterozoic, the limited bioavailability of P [*Bjerrum and Canfield*, 2002; *Jones et al.*, 2015] and trace metals [*Anbar and Knoll*, 2002; *Konhauser et al.*, 2009] may have severely restricted the rate of photosynthesis and therefore the rise of atmospheric oxygen. High seawater phosphate levels during the Neoproterozoic would have increased the burial of organic carbon, triggering a marine redox shift— O_2 in the ocean and atmosphere increased from $<0.1\%$ [*Lyons et al.*, 2014; *Planavsky et al.*, 2014] to $>10\%$ [*Canfield*, 2005] of present atmospheric levels—correlated with the rise of metazoans [*Van Cappellen and Ingall*, 1996; *Planavsky et al.*, 2010]. The increase of O_2 in the oceans may have removed an environmental barrier preventing the evolution of larger, more complex life [e.g., *Nursall*, 1959; *Canfield and Teske*, 1996], although the ways in which photosynthetic oxygen production influenced biologic diversification remain uncertain [*Knoll and Sperling*, 2014; *Mills and Canfield*, 2014].

Complex feedbacks govern the ocean-atmosphere P cycle. For example, weathering rates for P-bearing minerals are temperature dependent [e.g., *Guidry and Mackenzie*, 2000] and recycling of P from the seafloor is redox dependent [e.g., *Van Cappellen and Ingall*, 1996]. Further complicating matters, our chronologic resolution for the Neoproterozoic cannot resolve climate fluctuations on 1000 to 10,000 year time scales, making it difficult to distinguish the causes of oxygenation from the effects. There is, however, general consensus among modelers that P (and possibly nitrogen) [*Anbar and Knoll*, 2002; *Fennel et al.*, 2005] was the limiting control on primary production and thus oxygenation over million year time scales [e.g., *Van Cappellen and Ingall*, 1996; *Schrag et al.*, 2002], and that the Neoproterozoic oxygenation event involved an increased rate

of bioavailable P delivery to the ocean [e.g., *Lenton and Watson, 2004; Laakso and Schrag, 2014; Mills et al., 2014*]. Such changes in the P cycle are recorded in Neoproterozoic sediments: significantly elevated marine phosphate concentrations have been postulated for the Sturtian deglaciation [*Planavsky et al., 2010*] at ~660 Ma [*Rooney et al., 2015*], and carbonates with high distributed phosphorus contents were formed during the Ediacaran and early Cambrian periods [*Shimura et al., 2014*]. Furthermore, microfossils with phosphate scales have been identified in pre-Sturtian sediments [*Cohen et al., 2011*]; surplus dissolved phosphate in the ocean could explain why protists utilized P at that time [*Cohen and Knoll, 2012*].

Because P in the ocean derives from weathering of continental crust, proposed mechanisms for elevated P fluxes to the Neoproterozoic ocean have included enhanced weathering of P during biologic colonization of the continents [*Lenton and Watson, 2004*], accelerated glacial weathering [*Planavsky et al., 2010*], and high surface topography [*Campbell and Squire, 2010*]. I propose an alternative hypothesis: that the weathering of voluminous large igneous provinces (LIPs) associated with the breakup of the Rodinia supercontinent increased the bioavailable P flux to the ocean. If indeed LIP magmatism periodically fertilized the Precambrian ocean, tectonic processes may have played a central role in fostering complex life in the oceans. To evaluate this hypothesis, I review the major controls on the global marine P flux, examine evidence for LIP magmatism in the Neoproterozoic, and present simple models to assess the effects of LIP weathering. Based on these results, I discuss the tectonic factors that favor efficient transfer of igneous P to the oceans and postulate that complementary tectonic conditions aligned in the Neoproterozoic to facilitate an unprecedented and sustained P flux to the ocean. If so, LIP magmatism may help explain why the Neoproterozoic era was conducive to the evolution of complex life.

2. The Phosphorus Cycle

Phosphorus is a biolimiting nutrient that influences the production of organic matter in marine environments. Most P was incorporated into Earth's core during early differentiation, so the bulk silicate Earth contains only trace concentrations (90 ppm) [*McDonough and Sun, 1995*]. Because P behaves as an incompatible element during mantle melting and during early stages of mafic magma crystallization [*Watson, 1980*], continental crust contains higher P concentrations (~570 ppm) [*Rudnick and Gao, 2003*] than the primitive mantle, although mantle xenoliths reveal that metasomatized mantle locally reaches >4000 ppm P [*O'Reilly and Griffin, 2000*]. The concentration in the ocean depends on the relative rates of P input (i.e., continental weathering and subaqueous sedimentary P remobilization) and the sequestration of P (i.e., bioaccumulation, burial of sediments, and hydrothermal activity). Although P in the ocean today derives from terrestrial weathering of both igneous fluorapatite and marine sedimentary carbonate fluorapatite, nearly all the P that cycles through sedimentary and biologic systems must have initially derived from continental weathering of igneous rocks.

The reactive P flux to the ocean may be modulated by changes in continental silicate weathering rates [e.g., *Föllmi, 1996; Schrag et al., 2002*] but can also be influenced by the rate of P liberation during weathering [e.g., *Lenton and Watson, 2004*]. Only a fraction of riverine P enters the oceans in a biologically reactive form, so changes in the fraction of nonreactive P bound in Fe-oxides will influence primary productivity [e.g., *Laakso and Schrag, 2014*]. An increased flux of bioavailable P to the ocean, as proposed for the Neoproterozoic, requires some combination of (i) an increase in overall silicate weathering rate, (ii) an increase in P weathering relative to the total silicate weathering rate, and/or (iii) a greater fraction of weathering-derived P that became bioavailable. Factors that potentially influence the reactive P flux include high continental surface topography, land colonization, and the composition of continental surfaces.

2.1. Topographic Relief

Continental weathering rates are highly sensitive to topographic relief. The extensive Gondwanan continent-continent collisions that occurred in the late Neoproterozoic were expressed on Earth's surface as thousands of kilometers of high mountains and likely resulted in large fluxes of nutrients to the ocean [*Squire et al., 2006*]. A secular shift to cooler metamorphic gradients in the Neoproterozoic [e.g., *Maruyama and Iou, 1998; Brown, 2006*] suggests that surface topography reached unprecedented heights at that time. Rapid erosion of the mountain belts would have increased global sediment flux; this may have accelerated carbon burial and increased the flux of P and Fe to the ocean, and induced atmospheric oxygenation [*Campbell and Squire, 2010*]. The steady increase in $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 1) in carbonates from 850 to 500 Ma probably reflects an

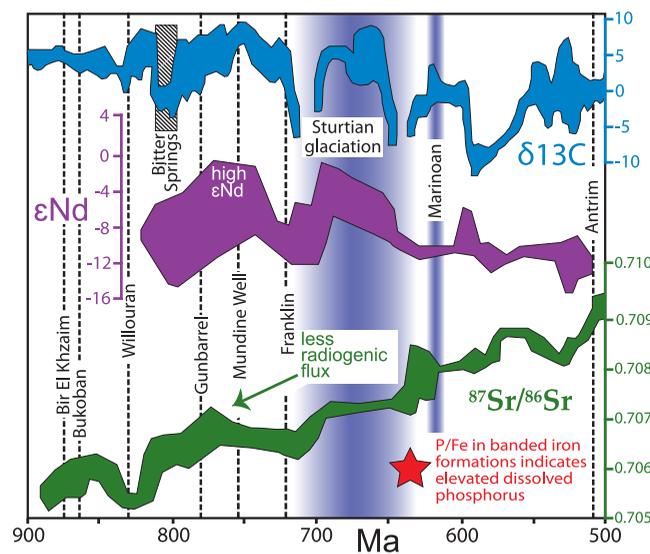


Figure 1. $\delta^{13}\text{C}$ [Macdonald *et al.*, 2010], ϵNd [Halverson *et al.*, 2010], and $^{87}\text{Sr}/^{86}\text{Sr}$ [Asmerom *et al.*, 1991; Halverson *et al.*, 2010] records for Neoproterozoic marine sedimentary rock. Elevated marine dissolved P concentrations have been inferred from P/Fe ratios of banded iron formations associated with the Sturtian deglaciation [Planavsky *et al.*, 2010]. Large igneous provinces (LIPs) with mafic dike swarms that cover an area greater than $2 \times 10^5 \text{ km}^2$ (dotted lines) are based on Ernst and Buchan [2001], and coincide with high ϵNd and a less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ flux—indicators of young mantle-derived rock entering the ocean. “Snowball Earth” glaciations [Rooney *et al.*, 2015] are shown as dark blue bands.

caused by the colonizing biota could have fertilized the oceans, increasing organic carbon burial and O_2 production [Lenton and Watson, 2004]. Although highly controversial, $\delta^{13}\text{C}$ fractionation trends in carbonates may suggest that simple land biota propagated sometime after 850 Ma [Knauth and Kennedy, 2009], and molecular clock estimations correspondingly indicate that land plants may have existed by 700 Ma [Heckman *et al.*, 2001]. An increase in clays relative to quartz in shaly sediments has also been attributed to an expansion in land biota; in response, organic carbon burial rates—proportional to clay content in ocean margins—may have increased by 600–700% sometime between 800 and 500 Ma [Kennedy *et al.*, 2006]. However, the modal increase in clay is apparently due to micaceous rather than weathering-derived clays inputs, suggesting that accelerated physical erosion rather than land colonization is responsible for the trend [Tosca *et al.*, 2010]. Unfortunately, the timing and overall impacts of land colonization remain poorly understood.

2.3. Surface Lithology

Phosphorus behaves as an incompatible element in most igneous environments: low degrees of partial melting (or fractional crystallization and segregation of a P-poor phase) in the crust or mantle generally produces magmas with elevated P concentrations. In arcs, granitic and intermediate rocks typically have low P concentrations due to apatite saturation and crystal-liquid segregation (Figure 2) [Lee and Bachmann, 2014]. Likewise, S-type granites become P saturated at low concentrations, so P minerals are commonly retained in the restite. Apatite saturation occurs at higher P concentrations when magmas have lower silica and water contents, and when temperatures are higher [Lee and Bachmann, 2014], which explains why mafic rocks typically contain more P. Mid-ocean ridge basalt (MORB) derived from depleted mantle has ~ 800 ppm P [Gale *et al.*, 2013], but alkali basalts and nephelinites can contain 2000–9000 ppm P when apatite exists in the source region [Beswick and Carmichael, 1978]. Despite having higher P concentrations than upper continental crust and covering $>70\%$ of solid Earth’s surface, submarine basalt acts as a P sink because hydrothermal processes at spreading ridges sequester P in Fe-oxides [Wheat *et al.*, 1996]. On the other hand, the weathering of subaerial basalt can release P into the oceans.

Silicate minerals in mafic igneous rocks can contain up to 25% of bulk rock P because P^{5+} readily substitutes for Si^{4+} [Koritnig, 1965]. Olivine, for instance, can contain $>0.4 \text{ wt } \%$ P, but such high-P contents only

increase in silicate weathering rate on continents during that period [e.g., Shields, 2007]. However, this hypothesis fails to explain the pronounced increase in primary productivity in the Cryogenian and the Sturtian glaciation, both of which occurred during a rift-dominated period of the Wilson Cycle. High topographic relief associated with the Neoproterozoic continental assembly—widespread orogenesis began at ~ 650 Ma [e.g., Meert and Lieberman, 2008]—cannot explain the elevated primary productivity inferred from $\delta^{13}\text{C}_{\text{carbonate}} > 5\text{‰}$ [Halverson *et al.*, 2005; Och and Shields-Zhou, 2012] that preceded Gondwana assembly by >100 Myr. Instead, high weathering rates during the breakup of Rodinia were likely due to the dispersion of continents and a low-latitude continental configuration [e.g., Donnadieu *et al.*, 2004].

2.2. Land Colonization

An increase in overall silicate weathering rate and/or P weathering efficiency

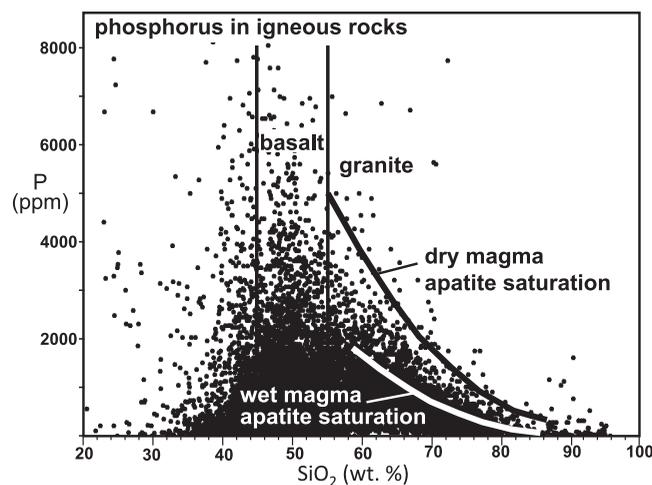


Figure 2. P versus silica content for all igneous rocks >500 Ma (Phanerozoic data are similar) in the EarthChem database (<http://www.earthchem.org/>). Apatite saturation in felsic magmas limits the P concentration in granitic rocks. P concentrations can be much higher in basalts.

occurs when crystal growth outpaces P^{5+} diffusion in the magma because P preferentially partitions into residual melt [Milman-Barris *et al.*, 2008]. Instead, P is incorporated into fluorapatite or, if quenched before apatite precipitates, preserved in basaltic glass [e.g., Brunet and Chazot, 2001]. Experiments indicate that fluorapatite dissolution in aqueous solutions is pH dependent, increasing from 10^{-11} to 10^{-10} mol/m²/s at pH 6–8 to 10^{-7} mol/m²/s at pH 2 [Guidry and Mackenzie, 2003; Chairat *et al.*, 2007]; dissolution rates for quartz and feldspars (major constituents of felsic rocks) are more than an order of magnitude slower across the same pH range [Bandstra and Brantley, 2008]. At pH lower than 6, basalt also dissolves slower than fluorapatite, but at pH 6–8

the dissolution rates of basalt and fluorapatite are comparable [Guidry and Mackenzie, 2003; Bandstra and Brantley, 2008]. Depending on composition, sedimentary carbonate fluorapatite dissolution is probably slower than for fluorapatite at moderate pH [Guidry and Mackenzie, 2003]. The crystallinity of the basalt strongly influences dissolution rate: basaltic glass can weather an order of magnitude faster than crystalline basalt [Gislason and Hans, 1987]. Similarly, the dissolution rate for apatite is influenced by surface area, so larger grains will release dissolved P slower. These observations suggest that weathering of fluorapatite and basaltic glass will typically release P at higher rates than weathering of mafic and felsic rocks at moderate to low pH. In general, basaltic volcanic rocks probably release P efficiently during weathering because they are, on average, richer in P than felsic rocks, prone to rapid chemical weathering [e.g., Desert *et al.*, 2001], and more likely to host P in basaltic glass or fine-grained fluorapatite that can dissolve quickly.

3. Large Igneous Provinces

LIPs are typically defined as volumetrically large (>0.1 Mkm²) magmatic provinces erupted or emplaced rapidly, commonly in less than 5 Myr [e.g., Ernst, 2007]. LIPs are dominantly composed of tholeiitic basalt and occur in both oceanic and continental settings. No pre-Mesozoic intraoceanic LIPs (i.e., ocean plateaus) still exist and only the “plumbing system” of feeder dikes are well preserved for Precambrian LIPs [Ernst, 2007]. Pulses of geographically isolated LIPs are associated with every supercontinent breakup of the Wilson Cycle [Ernst and Bleeker, 2010]. The breakup of Rodinia was no exception: rifting may have initiated with a superplume at ~825 Ma [Li *et al.*, 2013] and was punctuated by major LIPs until ~720 Ma [Ernst *et al.*, 2008]. As discussed below, a significant fraction of Earth’s land surface may have been covered by flood basalts—enriched in P relative to average continental crust—during the breakup of the Rodinia supercontinent.

3.1. Timing of LIP Events

LIP magmatism has occurred since ~3.5 Ga with an average frequency of 20 Myr [Ernst, 2007], with above-average rates of LIP magmatism during periods of supercontinent breakup. In particular, there were frequent LIP events associated with the breakup of Nuna (1600–1200 Ma) and Rodinia (825–750), but less-frequent (yet still large) LIP events during the intervening period of Rodinia assembly [Ernst *et al.*, 2008]. This could have been due to intracontinental rifting that occurred even during periods of prevailing collisional tectonics. The updated LIP database (<http://www.largeigneousprovinces.org/>) based on Ernst and Buchan [2001] lists 26 large mafic magmatic events between 900 and 500 Ma (unless noted, the age and volume of LIPs are from their database). Of these, this study excludes 12 LIPs without size constraints and five LIPs that have imprecise age constraints (uncertainty >100 Myr).

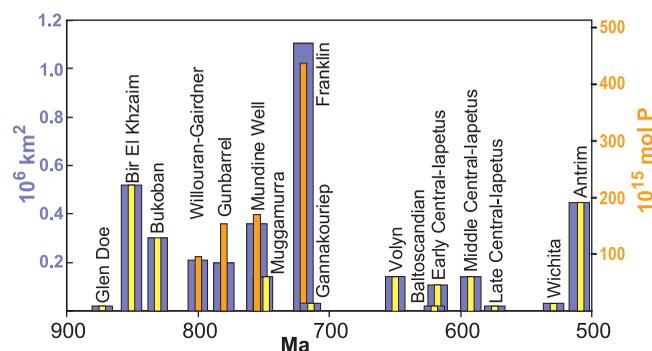


Figure 3. Area of mafic dike swarms (purple) and estimated P content (yellow/orange) for Neoproterozoic and early Cambrian LIPs. Orange bars are based on median P concentrations for LIPs (supporting information Table S1). Yellow bars are based on P concentration of average MORB (802 ppm) [Gale et al., 2013].

3.2. Volume of LIP Events

Due to the susceptibility of mafic volcanic rock to subaerial weathering, Precambrian LIPs have largely been eroded, and their eruptive volumes must be estimated from dike swarms. Mafic dike swarms that occurred between 900 and 500 Ma cover $3.7 \times 10^6 \text{ km}^2$ (Figure 3), or $\sim 4\%$ of the total Neoproterozoic land surface (assumed to be $90 \times 10^6 \text{ km}^2$) [Goddéris et al., 2003]. However, length-based and width-based estimates of dike swarm area are generally conservative [Ernst and Buchan, 2001] because portions of LIPs may be missing or not exposed.

And because flood basalts can flow great distances, the areas of LIP flood basalts were presumably greater than the area of mafic feeder dike swarms; Abbott and Isley [2002] found that the feeder dikes of the Columbia River basalt province represent 52% of the total flood basalt province. Thus, assuming that flood basalts cover areas twice as large as LIP feeder dikes, flood basalts in the Neoproterozoic may have collectively covered $7.4 \times 10^6 \text{ km}^2$, or $\sim 8\%$ of the land surface. This estimate is consistent with models of Neoproterozoic climate [Goddéris et al., 2003; Donnadieu et al., 2004] that use basalt flow areas of $4\text{--}8 \times 10^6 \text{ km}^2$. For comparison, a single Mesozoic LIP, the Central Atlantic Magmatic Province, spanned a similar area [Marzoli et al., 1999], so Neoproterozoic continental flood basalts could have, conceivably, covered an even greater area. (Note that although submarine LIPs can be much larger than continental LIPs, only extrusive continental volcanic rocks would have been immediately exposed to subaerial chemical weathering that transported reactive P into the ocean.)

The original thicknesses of LIP flood basalts are unknown. Better-preserved Phanerozoic LIPs provide some insight: the Cretaceous-Tertiary Deccan traps originally covered an area of $1.8 \times 10^6 \text{ km}^2$ and had a volume of $8.6 \times 10^6 \text{ km}^3$ [Eldholm and Coffin, 2000], implying a thickness of $>4 \text{ km}$. On the other hand, the Jurassic Karoo province averages 2.5 km thick ($2.5 \times 10^6 \text{ km}^3$ over 10^6 km^2) and the preserved extrusive portion of the Permian-Triassic Siberian traps is $\sim 1 \text{ km}$ thick over an area of $0.34 \times 10^6 \text{ km}^2$ [Sharma, 1997]. Based on such analogues, it seems reasonable to assume that Neoproterozoic LIPs were 1–4 km thick.

Evidence of extensive Neoproterozoic continental flood basalt weathering is preserved in the marine sedimentary record. Although $^{87}\text{Sr}/^{86}\text{Sr}$ systematically increases from ~ 830 to 550 Ma, with sharp inflections during glaciation events, there is an apparent decline between ~ 775 and 720 Ma (Figure 1) that is consistent with intense weathering of flood basalts with an unradiogenic mantle signature [Halverson and Hurtgen, 2007]. Sediments from ~ 750 to 720 Ma also have distinctly unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ that can be explained by weathering of voluminous juvenile basalt [Rooney et al., 2015]. A coincident increase in $^{143}\text{Nd}/^{144}\text{Nd}$ at $\sim 740 \text{ Ma}$ has also been attributed to the weathering of flood basalts (Figure 1) [Barovich and Foden, 2000], but the two records are from disjunct sedimentary successions that are difficult to correlate [Halverson et al., 2010]. Most notably, the ϵNd value of -12 at 800 Ma increased to an ϵNd of ~ 0 at 750 Ma (Figure 1), and these high values were presumably sustained until $\sim 600 \text{ Ma}$ [Barovich and Foden, 2000]. The biggest LIPs were emplaced during this time interval: of the 17 considered in this study, LIPs emplaced from 850 to 700 Ma constitute $\sim 75\%$ of the overall LIP area, and the 720 Ma Franklin Province alone makes up 29% of the total area.

3.3. Phosphorus Content of LIPs

Median P concentrations for mafic rocks related to the rifting of Rodinia range from 741 ppm (Franklin Province) to $>1000 \text{ ppm}$ (Glen Doe and Gunbarrel events). Most LIPs exhibit considerable compositional variability, so median values may not be representative. Notably, the largest LIP (Franklin Province) has the lowest P—lower even than average MORB. Neoproterozoic median P concentrations are comparable to other major LIPs, but the Gunbarrel ($\sim 2200 \text{ ppm}$) event may have had elevated P concentrations. All LIP flood basalts, however, likely had higher P concentrations than average Neoproterozoic upper continental

crust. For comparison, the Archean Baltic Shield and Superior Province both have median P less than 500 ppm, which is less than typical granite concentrations of ~ 650 ppm P. Thus, assuming that P-rich sedimentary rocks constituted a negligible fraction of the land surface in the Neoproterozoic, LIP basalts that covered a significant fraction of continents had higher P concentrations than other land surfaces by a factor of 1.5 to >2 .

4. Weathering Models

Numerous factors—many of which are poorly understood for the Neoproterozoic—influence the rate of bioavailable P production by the chemical weathering of LIPs, but simple models can provide basic constraints. The models presented here are based on (i) the geologic record of LIP magmatism, including the P concentrations and areal extents of mafic dike swarms; (ii) Phanerozoic LIPs that are well preserved; and (iii) modern weathering and erosion rates. In the model, flood basalts are emplaced instantaneously and are proportional in size to the preserved mafic dike swarms. P is released from the flood basalts at a constant rate until the basalt has been fully denuded by chemical weathering and physical erosion; the total P released to the ocean is the sum of the P fluxes from the exposed LIP basalts. The model spans the Neoproterozoic to early Cambrian period of interest from 900 to 500 Ma. The approach is to use reasonable values from the rock record and previous studies as inputs and then conduct sensitivity tests for each variable. Given the interdependence and natural variability of many input parameters, these models are extreme simplifications; the results are approximations.

4.1. Input Parameters

For each LIP with basalt geochemical data, the median P concentration (supporting information Table S1) is assumed to be representative of the entire LIP. All other LIPs are assigned a MORB-like P concentration of 802 ppm [Gale *et al.*, 2013]. The total flood basalt area is assumed to be twice (see rationale in Abbott and Isley [2002]) that of mafic dike swarm areas [Ernst and Buchan, 2001]. An average chemical weathering rate of 40 t/km²/yr is assumed based on modern weathering rates for basaltic watersheds in temperate regions with moderate runoff [Millot *et al.*, 2002; Dessert *et al.*, 2003]. This is considerably lower than rates observed in high-runoff areas; Reunion Island, for example, has chemical weathering rates of 63–170 t/km²/yr [Louvat and Allègre, 1997]. Physical denudation rates in modern settings can be many times greater than chemical weathering rates [e.g., Millot *et al.*, 2002], but a default physical erosion rate equal to the chemical weathering rate has been adopted here to evaluate the maximum potential P extraction from LIP flood basalts.

Weathering fluxes from Neoproterozoic flood basalts are compared to weathering fluxes from granitic crust: assuming a continental area of 9×10^7 km² [Goddéris *et al.*, 2003], an average chemical weathering rate of 2 t/km²/yr (reasonable for granitic catchments: Millot *et al.*, 2002), that 40% weathered P became bioavailable, and an average granitic P concentration of 650 ppm (although Archean shield samples are on average much lower), the total reactive P flux would have been $\sim 1.5 \times 10^9$ mol P/yr, or less than a percent of the modern flux ($\sim 25\text{--}30 \times 10^{10}$ mol P/yr) [Ruttenberg, 2003]. Considering that a low-reactive P flux of $<10\%$ of the modern preagricultural flux may have been necessary to stabilize low Proterozoic pO₂ [Laakso and Schrag, 2014], such a low pre-LIP flux seems reasonable. Although the weathering of sediments could have also contributed to the pre-LIP flux, 1.5×10^9 mol P/yr is used as a background flux for the models to highlight the role of flood basalt weathering relative to average crust.

4.2. Sensitivity Tests

Several parameters affect the calculated P flux independent of flux duration (Figure 4). Doubling the flood basalt area, for example, will double the P flux. Likewise, higher P concentrations in the basalt and greater fractions of reactive P will proportionally increase the P flux. Input ranges for each variable with otherwise default parameters (Table 1) produce maximum P fluxes at ~ 720 Ma of $1\text{--}3 \times 10^9$ mol P/yr, or roughly twice the background Proterozoic P flux. Compounded increases in areal extent, P concentrations, and higher bioavailable fractions of weathered P cause much higher fluxes.

P fluxes are especially sensitive to parameters that affect the duration and magnitude of P transfer from individual LIPs. Thicker flood basalts provide a longer and more consistent P flux to the ocean, and increase the total P transferred to the ocean. Tripling the LIP thickness from 1 to 3 km creates a sustained rather than punctuated P flux for ~ 200 Myr and doubles the peak flux, which is reached for all the models at

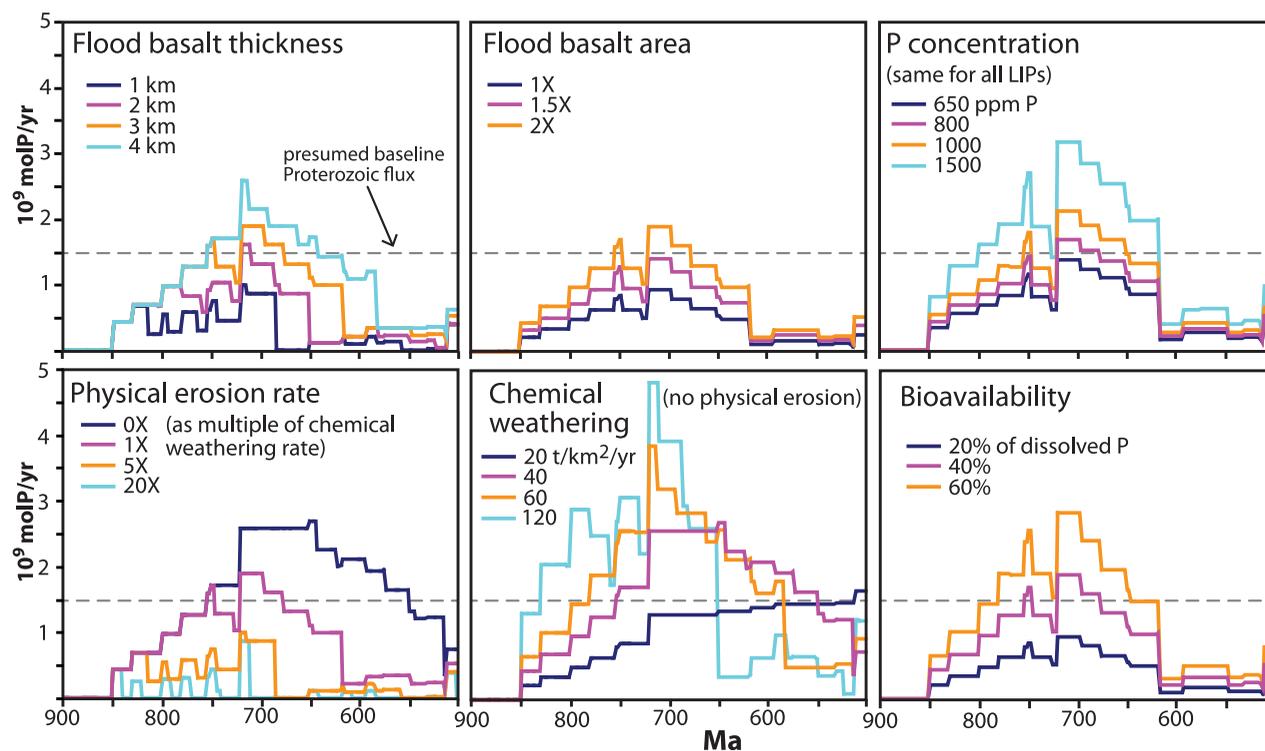


Figure 4. Sensitivity tests for P flux models. Unless noted, default parameters in Table 1 are used. See text for details.

~720 Ma when the Franklin Province is emplaced. The relative rates of chemical weathering and physical erosion have similar effects: high rates of physical erosion increase the fraction of P retained in detrital particulate matter and therefore decrease the overall reactive P flux while hastening the denudation of the basalt. Conversely, increasing chemical weathering relative to physical erosion not only increases the total dissolved P flux but also hastens denudation. A physical erosion rate 20 times that of the chemical weathering rate releases P in short 10 Myr bursts that never exceed the background Proterozoic P flux. Model runs with 100% chemical weathering, however, reach peak P fluxes 4 times as high as the background flux.

5. Discussion

Neoproterozoic P fluxes are difficult to assess due to poor constraints for LIP volumes, physical erosion rates, and the fraction of Fe-bound P that remains nonreactive. Nevertheless, the models presented here provide a basis for evaluating the effects of Neoproterozoic LIP weathering. Below, I discuss complex feedbacks that complicate the interpretation of these results and hypothesize that geochemical enrichment of LIP magmas prior to eruption contributed to the reactive P flux.

5.1. The Timing of LIP-Related P Fluxes

Although LIP events occurred regularly throughout the Neoproterozoic, LIP sizes vary from 2000 km² (Glen Doe) to 1,100,000 km² (Franklin). Sizeable LIPs that were emplaced from 850 to 720 Ma include the Bir El Khazaim (520,000 km²), Bukoban (300,000 km²), Willouran-Gairdner (210,000 km²), Gunbarrel (200,000 km²), Mundine Well (360,000 km²), Muggamurra (140,000 km²), and Gannakourie (180,000 km²) events and culminated with the

Parameter	Default Value	Units
P concentration	802	ppm
Flood basalt thickness	3	km
Flood basalt area	2	Multiple of mafic dike swarm area
Basalt density	2.75	g/cm ³
Chemical weathering rate	4 × 10 ⁷	g/km ² /yr
Physical erosion rate	4 × 10 ⁷	g/km ² /yr
Bioavailable fraction	0.4	
Background Proterozoic P flux	1.5 × 10 ⁹	mol/yr

enormous Franklin Province. During this 130 Myr period, continental surfaces were repeatedly covered with abnormally large volumes of mantle-derived magma. Considering that Phanerozoic traps such as the Siberian, Karroo-Ferrar, and Deccan still exist after tens to hundreds of Myr, multiple LIP flood basalts most likely coexisted for much of the late Neoproterozoic. The ϵNd anomaly in the Neoproterozoic indicates that juvenile (i.e., mantle-derived) material entered the ocean over a prolonged period from ~ 750 to ~ 600 (Figure 1) [Barovich and Foden, 2000]. This is inconsistent with physical erosion rates fast enough to have denuded LIPs in less than 10 Myr. Rather, the ϵNd sedimentary record points to protracted chemical weathering of LIPs. If so, and unless denudation rates were exceedingly slow, the surface area covered by flood basalts likely peaked at ~ 720 Ma with the emplacement of the Franklin Province, before steadily declining. Increasingly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ in sediments from 660 to 630 Ma [Rooney *et al.*, 2015] may reflect this decline. Magmatism associated with the opening of the Iapetus contributed relatively minor volumes of basalt from 620 to 575 Ma, and the next sizable LIP event occurred at ~ 510 Ma, on the tail end of Gondwana assembly.

5.2. P Fluxes Prior to Neoproterozoic LIP Volcanism

The degree to which LIP-derived P perturbed oxygen and carbon cycles in the Neoproterozoic depends on the background Proterozoic P flux. In modern rivers, greater than 90% of the P is bound to suspended particulate matter; dissolved P in river water ($3.2\text{--}5.8 \times 10^{10}$ mol P/yr) and aerosol P ($2\text{--}5 \times 10^{10}$ mol P/yr) make up the rest of the flux to the ocean [Froelich, 1988; Ruttenberg, 2003]. Of the suspended particulate-bound P, roughly 20–40% is organic and the rest is mostly oxyhydroxides and detrital apatite [Ruttenberg, 2003]. An estimated 25–45% ($15\text{--}29 \times 10^{10}$ mol/yr) [Ruttenberg, 2003] of the total particulate flux is mobilized upon reaching the ocean, such that the combined dissolved riverine, particulate-bound, and aerosol P fluxes contribute $12\text{--}40 \times 10^{10}$ mol P/yr—and most likely $25\text{--}30 \times 10^{10}$ mol P/yr [Ruttenberg, 2003]—of bioavailable P to the ocean. The global marine burial flux of reactive P—roughly half of which occurs in marine shelf environments with high productivity [Filippelli, 1997]—is nearly as large ($18\text{--}24 \times 10^{10}$ mol P/yr) [Ruttenberg, 2003]. The majority of reactive P is buried as authigenic carbonate fluorapatite ($2\text{--}9 \times 10^{10}$ mol/yr) [Ruttenberg, 1993]; most of the remainder is removed from seawater by hydrothermal activity at mid-ocean ridges (1.4×10^{10} mol/yr) [Wheat *et al.*, 1996] and the burial organic matter ($1\text{--}4 \times 10^{10}$ mol/yr), nonhydrothermal Fe-oxides ($0.4\text{--}4 \times 10^{10}$ mol/yr), and minerals with loosely bound P on their surfaces (1.3×10^{10} mol/yr) [Ruttenberg, 1993, 2003].

Prior to Neoproterozoic LIP volcanism, the flux of reactive P from the continents was probably much less than the preagricultural modern flux. Laakso and Schrag [2014] produced models to evaluate steady state low atmospheric pO_2 , concluding that 10% modern preagricultural reactive P flux could have stabilized pO_2 at $\sim 1\%$ of modern atmospheric levels. But atmospheric pO_2 in the middle Proterozoic may have been $\leq 0.1\%$ of present levels [Planavsky *et al.*, 2014], which could imply an even smaller middle Proterozoic P flux to the ocean. Assuming weathering of granitic continental surfaces was the dominant source of P, an unrealistically high chemical weathering rate of ~ 20 t/km²/yr of rock with 650 ppm P over modern continental land surface areas would have been necessary (assuming 40% of weathered P became bioavailable) to sustain $>10^{10}$ mol P/yr flux. Thus, the background reactive P flux to the ocean may have been low enough that the weathering of LIPs (possibly reaching $1\text{--}5 \times 10^9$ mol P/yr) would have constituted a major nutrient source.

5.3. Iron-Bound P

Most of the bioavailable P entering the ocean is released from Fe-oxides [e.g., Froelich, 1988; Benitez-Nelson, 2000]. Experiments show that Fe-oxides derived from Fe^{2+} in the presence of modest amounts of dissolved Si can incorporate up to 0.2 mol P/mol Fe in freshwater [Mayer and Jarrell, 2000], but that dissolved Si limits P incorporation into oxides when present in higher concentrations in seawater [Jones *et al.*, 2015]. Lattice-bound P in Fe-oxides generally remains biologically unavailable for as long as the oxide remains insoluble, whereas P bound to Fe-oxide surfaces is susceptible to desorption [Froelich, 1988; Ruttenberg and Sulak, 2011]. When Fe-oxides are buried, terrestrial weathering-derived P that coprecipitated with the oxides or sorbed to oxide surfaces can bypass the biologic cycle. However, Fe-oxides that enter the ocean can rapidly release surface-sorbed P (over the course of minutes) because seawater phosphate concentrations are lower than in rivers and because seawater contains anions that compete for surface sites [Froelich, 1988]. After the removal of loosely bound surface P, additional P is slowly released (on the order of days) from the interior

of Fe-oxide particles [Ruttenberg and Sulak, 2011]. If Fe-oxides reach a reducing environment—such as settling into anoxic waters—oxides can dissolve, releasing any remaining P into the water column.

Laakso and Schrag [2014] propose that the low pO_2 Proterozoic environment slowed the oxidation of iron enough that Fe^{2+} could be transported from the subsurface to rivers and estuaries, where Fe-oxides precipitated in the presence of higher dissolved P concentrations. If so, and assuming that the Fe-bound P was permanently buried, the fraction of weathered P that became incorporated into Fe-oxides—and, thus the fraction that bypassed the biologic cycle—would have been greater. If, on the other hand, Proterozoic atmospheric oxygen levels were low enough that not all weathering-derived Fe was oxidized before reaching the ocean, a higher fraction of the weathered P would be expected to enter the ocean in solution. Also, if anoxic conditions were common below the storm wave base in the Neoproterozoic ocean [Canfield *et al.*, 2008], a greater fraction of settling Fe-oxides may have dissolved and released bioavailable P. These uncertainties regarding the oxidation state of various Neoproterozoic environments make it difficult to estimate the fraction LIP-derived P that became bioavailable.

In addition to having higher average P concentrations than granitic rocks, basalts also contain more Fe. Therefore, compared to granite weathering, basalt weathering releases more Fe into groundwater and rivers that can be precipitated as oxides. However, average P/Fe in mafic and felsic rocks are comparable: molar P/Fe of Karoo-Ferrar (0.014) and Deccan Traps (0.021) rocks compare closely with that of upper continental crust (0.017 [Rudnick and Gao, 2003]) and andesite (~ 0.018 [GeoRoc Database, <http://georoc.mpch-mainz.gwdg.de/georoc/>]). And, because Fe oxyhydroxides have high sorption capacities (P/Fe of ~ 0.5 [Gunnars *et al.*, 2002]), the Fe contents of most crustal rocks do not limit the capacity of Fe-oxides to fix dissolved P during weathering. Thus, the weathering of LIPs would not have necessarily yielded a greater or lesser fraction of Fe-bound P compared to average crust.

5.4. P Enrichment Beneath Thick Lithosphere

Subaerial tholeiitic basalt provides more P to the ocean than average crust. Basalts with higher P concentrations—which some Neoproterozoic LIP rocks contained—yield even more reactive P. Geochemical enrichment can explain the elevated P concentrations observed in LIP basalts and the correspondingly high reactive P fluxes that may have resulted from their weathering.

Lithosphere thickness can influence the composition of asthenosphere-derived magmas. Upwelling asthenosphere undergoes higher degrees of decompression melting at shallower depths, so thick lithosphere that inhibits the ascent of asthenosphere will limit the degree of melting [Kerr, 1994]. In addition, asthenosphere plumes that pond beneath or within thick lithosphere incubate for longer periods of time [e.g., Kent *et al.*, 1992], which can lead to higher degrees of liquid-crystal segregation. P concentration in high degree/shallow (low P) and low degree/deep (higher P) melts probably do not differ by more than a factor of 2–3, but these differences can become exaggerated by fractional crystallization and liquid-crystal segregation, which occurs for longer periods beneath or within thick lithosphere. Such trends are apparent in Karoo samples: high-Ti and high-P concentrations are restricted to areas above thick lithosphere and can be explained by low degrees of partial melting beneath thick lithosphere and fractional crystallization [Jourdan *et al.*, 2007]. P-enriching fractional crystallization trends are observed for the Karoo-Ferrar, Deccan Traps, and North Atlantic Igneous Province (Figure 5) and are characteristic of LIPs generated beneath thick lithosphere. In contrast, the Central Atlantic Magmatic Province magmas probably formed with lower initial P concentrations due to high degrees of partial melting and underwent less P enrichment during fractional crystallization. Interestingly, the Karoo-Ferrar samples have both a high-P and a low-P enrichment trend, reflecting generation beneath thick and thin lithosphere, respectively [Jourdan *et al.*, 2007].

Thick (>180 km) lithosphere is believed to have existed since the Archean because the removal of heavy elements during high degrees of melting in the hot Archean mantle produced buoyant residue [Djoman *et al.*, 2001]. It is unclear why pre-Neoproterozoic LIPs were apparently less enriched in P by fractional crystallization than the strongly fractionated Phanerozoic LIPs. Perhaps higher mantle temperatures in the pre-Neoproterozoic mantle caused higher degrees of melting and thus lower P concentrations in primary magmas. Limited fractional crystallization for pre-Neoproterozoic LIPs may simply reflect the fact that the LIPs for which we have data were emplaced through thinner lithosphere. Data (albeit relatively sparse) from Neoproterozoic LIPs exhibit a liquid-crystal segregation enrichment trend analogous to that of Phanerozoic LIPs (Figure 5). Higher degrees of liquid-crystal segregation decrease melt volume, so fractional crystallization may not

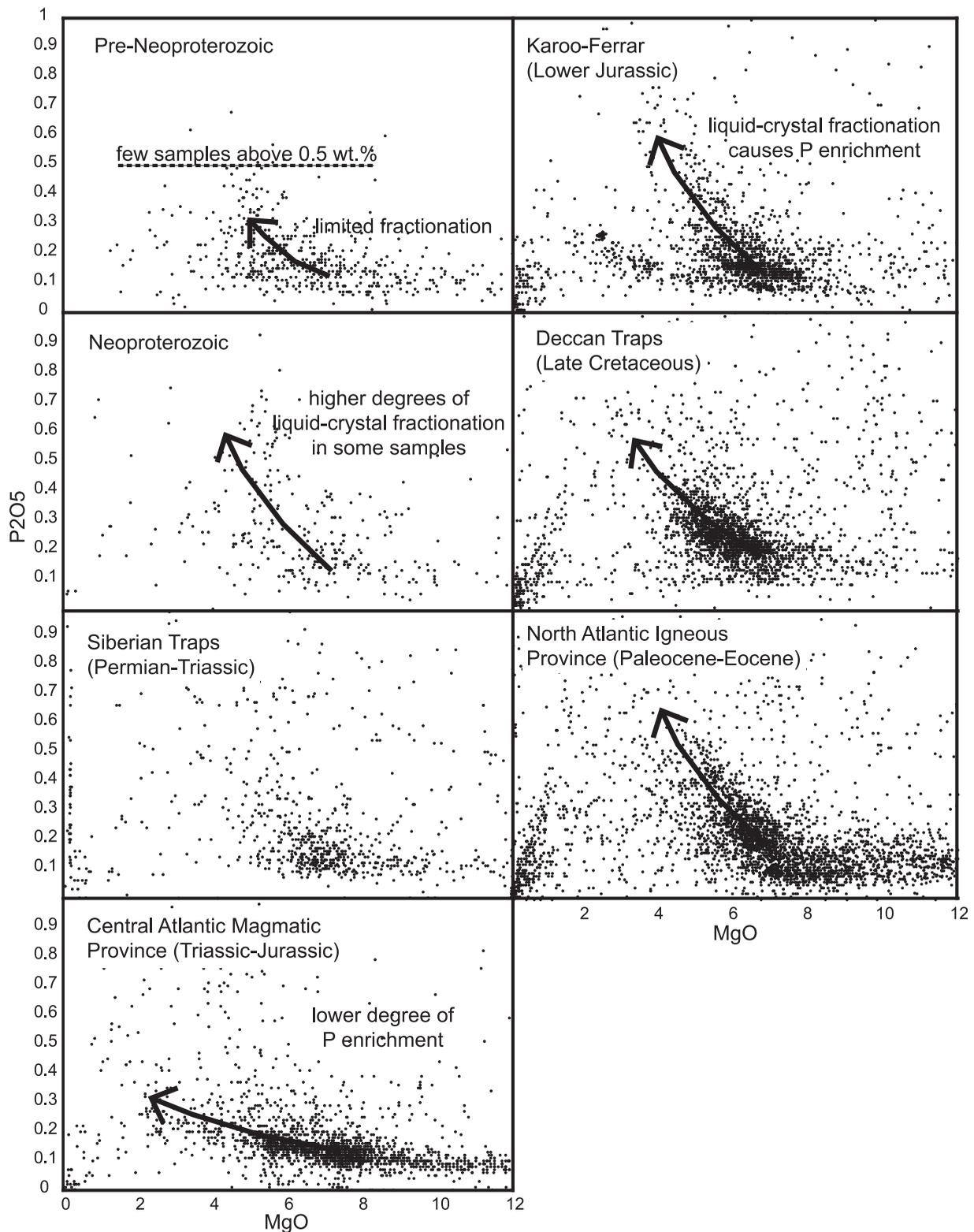


Figure 5. MgO versus P₂O₅ for LIPs (Pre-Neoproterozoic and Neoproterozoic data in supporting information Table S1). Siberian Traps, Central Atlantic Magmatic Province, Karoo-Ferrar, Deccan Traps, and North Atlantic Igneous Province data are from the GeoRoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). Pre-Neoproterozoic LIPs exhibit limited liquid-crystal fraction that increases P concentrations. Some Neoproterozoic and Phanerozoic LIPs, however, show strong enrichment trends.

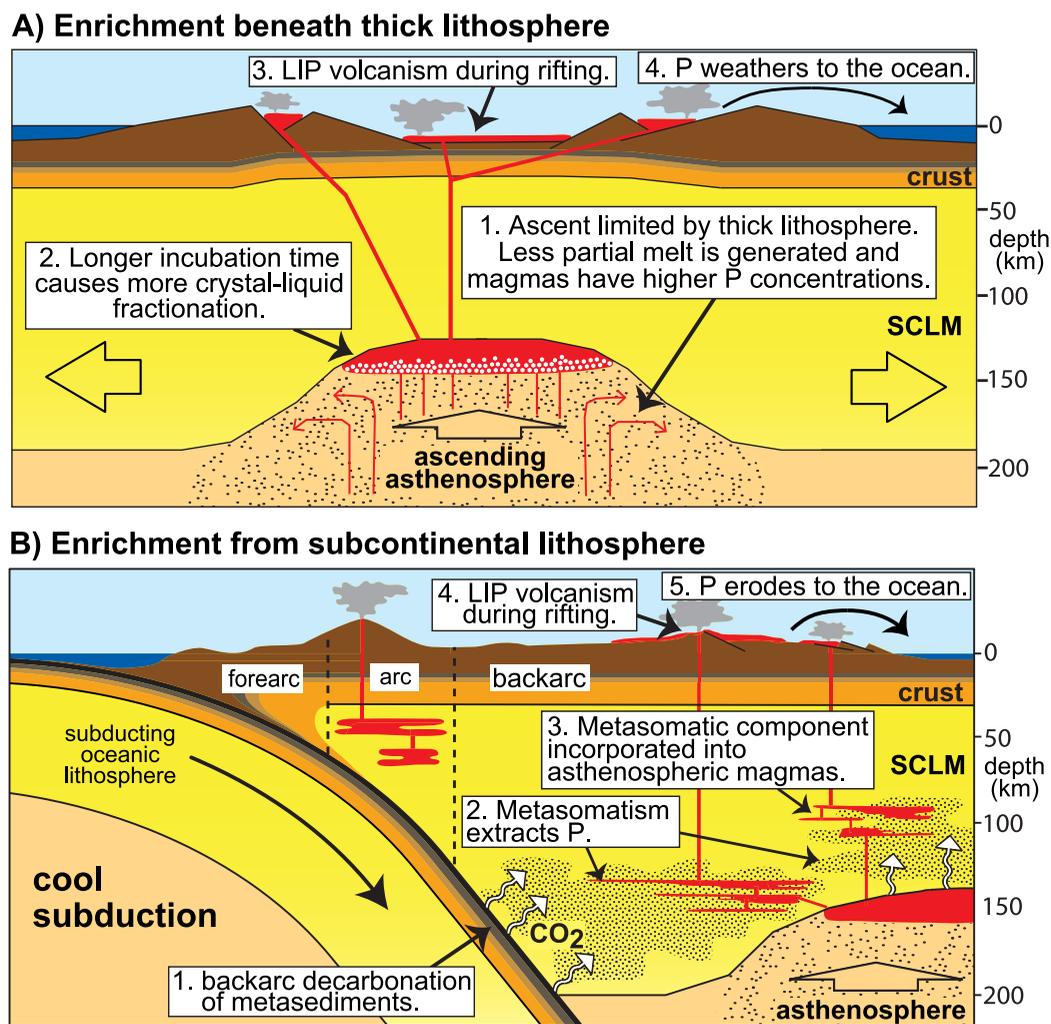


Figure 6. Magmatic and metasomatic processes that cause P enrichment in LIP basalts. (a) When thick lithosphere inhibits the ascent of asthenosphere, less decompression melting occurs and longer incubation allows for more crystal-liquid fractionation. (b) Metasomatic fluids from subducting ocean crust and/or rising asthenosphere extract P from subcontinental lithosphere (SCLM) and metasomatic components become incorporated into tholeiitic magmas from the asthenosphere.

ultimately yield more total P; this may explain why the largest Neoproterozoic LIP (Franklin Province) has the lowest median P concentration. P concentrations in some Neoproterozoic LIP basalts may have increased by a factor of 2–3 during liquid-crystal segregation, but most samples were not enriched to that extent. Fe also becomes enriched during liquid-crystal segregation, so P/Fe of LIP magmas does not systematically increase.

5.5. P Enrichment Via Incorporation of Subcontinental Mantle

LIP magmas are not exclusively derived from the asthenosphere. Phanerozoic plume-related continental flood basalts are mixtures of asthenosphere and metasomatically enriched subcontinental lithosphere melts [Zhang and O'Reilly, 1997; Jourdan et al., 2007; Song et al., 2008], suggesting that rising asthenosphere incorporates lithosphere. At least six major flood basalt eruptions since the Mesoproterozoic are temporally and spatially associated with metasomatism-related carbonatite, lamproite, and kimberlite magmas [Rao and Lehmann, 2011, and references therein] that were partially engulfed by the voluminous tholeiitic magmas. Metasomatism by K-rich brines and CO₂ readily partitions and redistributes P from common mantle minerals: although P in the primitive mantle range from 60 to 100 ppm, mantle xenoliths from metasomatized mantle can have >4000 ppm [O'Reilly and Griffin, 2000]. LIP magmas can be enriched in P when rising asthenosphere melts preexisting metasomatized mantle, or by releasing and then reincorporating metasomatic fluids.

Volatile-rich, highly potassic magmatism is only associated with LIPs younger than ~1 Ga [e.g., Rao and Lehmann, 2011] and, in general, few alkaline silica-undersaturated rocks exist in the Precambrian rock record [e.g.,

Gupta, 2015]. Neither of these observations is adequately explained by poor preservation. Rather, the widespread appearance of these rocks may reflect a secular change in the thermal structure of continents [e.g., Brown, 2007] and subduction zones in particular [e.g., Dasgupta, 2013]. Little evidence exists of crust having subducted to depths greater than 150 km—e.g., blueschists and eclogites—and returning to continental depths prior to ~750 Ma [Jahn *et al.*, 2001; Maruyama and Liou, 2005]. This suggests that there was a Neoproterozoic transition to a cooler subduction regime. In hot subduction zones, metasediment and metabasalt release most CO₂ at crustal depths [Kerrick and Connolly, 2001] and any slab disintegration would have further limited transport of CO₂ to the mantle. In contrast, metasediments in cooler subduction zones retain CO₂ beyond subarc depths (~140 km) unless external H₂O infiltrates the slab [Kerrick and Connolly, 2001; Gorman *et al.*, 2006]. Pre-Neoproterozoic warmer subduction presumably caused carbonate to decompose at shallow depths, but in cooler Neoproterozoic-Phanerozoic subduction zones, the release of CO₂ from metasedimentary rock caused widespread carbonate metasomatism in mantle wedges behind the arc [Dasgupta and Hirschmann, 2010; Dasgupta, 2013]. Thus, metasomatized P-rich subcontinental mantle—which provides a fertile P source for rising asthenosphere during LIP magmatism—may have only existed since ~1 Ga.

Quantifying the fraction of metasomatic P in modern LIPs is difficult due to sampling bias (for example, kimberlites are disproportionately analyzed compared to tholeiitic basalts), and even more difficult for Neoproterozoic LIPs that have been largely eroded. Many high-P LIP rocks that are not associated fractional crystallization trends (scatter in the upper right corners of MgO versus P₂O₅ plots; Figure 5) may contain a metasomatic component. Rocks that were enriched beyond P/Fe >0.2 would have been especially fertile sources of P because Fe-oxides derived from them during weathering could have become saturated with P. Even though volatile-rich magmas can contain multiple weight percent P₂O₅, metasomatic melt components probably contribute less than half of the total P of any given LIP. Nevertheless, metasomatic P enrichment of LIPs—a process that became widespread in the Neoproterozoic—provides another link between tectonic processes and the flux of bioavailable P to the ocean.

5.6. Consequences of an Elevated Neoproterozoic P Flux

If Neoproterozoic flood basalts covered twice the areas of preserved mafic dike swarms (7.4×10^6 km²) and were 3 km thick, the basalt provinces are estimated to have contained 1.7×10^{18} mol P. Despite high dissolution rates at moderate to high pH, some fluorapatite resisted weathering and bypassed the biologic cycle as detritus; this fraction is assumed to be 50% of the total P. Of the P released during over the course of LIP weathering and transported to the ocean, probably <10% was dissolved and >90% was Fe bound. If modern preagricultural conditions are representative, 25–45% [e.g., Ruttenberg, 2003] of the particulate-bound P may have become bioavailable upon reaching the ocean. Thus, assuming 40% of the combined Fe-bound and dissolved fractions became reactive in the ocean, only ~20% of the total P in the LIPs could have reached the ocean in a bioavailable form. Even so, the calculations summarized in Table 2 and Figure 4 suggest that $1\text{--}4 \times 10^{17}$ mol P from LIPs could have fertilized the ocean between 900 and 500 Ma, approximately the same amount of P that would have been derived from the total silicate weathering of the continents (of presumed average granitic composition) for the same period. Up to 5 times as much could have been released if none of the LIP-derived P was buried in Fe-oxides or detrital apatite.

Modeling by Laakso and Schrag [2014] suggests that organic carbon burial rates were very sensitive to the P supply in the low oxygen Proterozoic environment. If so, modest increases in reactive P may have caused pronounced increases in atmospheric oxygen. Weathering of Neoproterozoic LIPs could have more than doubled the reactive P flux and sustained an elevated flux for tens of millions of years but fails to explain the 10-fold increase reactive P deemed necessary by Laakso and Schrag [2014] to stabilize an atmosphere with present-day pO₂. They propose that the reactive P supply was oxygen dependent and that slower oxidation of Fe in ground waters caused more uptake of P into Fe-oxides; if this mechanism produces two biogeochemical steady states (i.e., low pO₂ Proterozoic and high pO₂ Phanerozoic), then LIP weathering may have raised pO₂ enough to prompt a switch to the higher pO₂ state. Alternatively, modest oxygenation caused by the weathering of LIP basalts may have permitted the colonization of continental surfaces by microorganisms that expedite P release from rocks and soils [e.g., Lenton and Watson, 2004], irreversibly increasing the reactive P supply to the ocean.

The consumption of CO₂ during basalt weathering and the resulting burial of calcium carbonate can cool the global climate [e.g., Dessert *et al.*, 2001], and it has been postulated that the weathering of LIP basalts triggered the Sturtian glaciation [Godd ris *et al.*, 2003]. The model presented in this study reaches a maximum

Table 2. LIP Age and Size [After Ernst and Buchan, 2001], As Well As Calculated P Contents

Large Igneous Province	Approx. Age (Ma)	Dike Swarm Area (10^3 km^2)	Median P Concentration (ppm)	Estimated P Content (10^{15} mol)	Estimated P Flux (Including Iron-Bound P) (10^6 mol/yr)
Glen Doe	873	2	1264	1	7
Bir El Khzaim	850	520		222	1077
Bukoban	830	300		128	622
Willouran-Gairdner	800	210	828	93	449
Gunbarrel	780	200	2254	153	743
Mundine Well	755	360	872	167	811
Muggamurra	750	140		60	290
Franklin	720	1100	741	434	2106
Gannakourie	720	30		13	62
Volyn	650	140		60	290
Baltoscandian	619	10		4	21
Early Central-Iapetus	617	105		45	218
Middle Central-Iapetus	592	140		60	290
Late Central-Iapetus	575	7		3	15
Wichita	530	30		13	62
Antrim	510	450		192	932
Total		3744		1648	7995

flood basalt area of $3.66 \times 10^6 \text{ km}^2$ —roughly half of the area of current exposed subaerial basalt [Dessert *et al.*, 2003]—when the Franklin Province was erupted at $\sim 720 \text{ Ma}$; if Neoproterozoic CO_2 consumption rates were similar to modern rates, we might expect that the weathering of LIPs to consume CO_2 at half the rate of modern basalts, or $\sim 1.5 \times 10^{12} \text{ mol CO}_2/\text{yr}$ [Dessert *et al.*, 2003]. The burial of organic carbon would have also consumed atmospheric CO_2 : assuming that the reactive P flux from LIPs reached $1\text{--}5 \times 10^9 \text{ mol/yr}$, and that all that reactive P was buried with a C:P ratio between 106 and 170 [Shaffer, 1996], then LIP-induced organic carbon burial could account for an additional $0.1\text{--}0.9 \times 10^{12} \text{ mol CO}_2/\text{yr}$. This first-order approximation may explain high pre-Sturtian $\delta^{13}\text{C}_{\text{carbonate}}$ values that suggest organic carbon made up $>32\%$ of total carbon burial [Hayes *et al.*, 1999]. Although organic carbon burial would have declined precipitously at the outset of glaciation, the reactive P flux from LIPs likely contributed to the destabilization of the climate prior to glaciation.

6. Conclusions

Tectonic conditions converged in the Neoproterozoic such that mantle-derived P could fertilize the ocean at an unprecedented rate. Voluminous flood basalts associated with the breakup of the Rodinia supercontinent covered a significant fraction of continental surfaces, and the low-latitude continental configuration facilitated chemical weathering. Some Neoproterozoic LIPs had elevated P concentrations due to fractional crystallization beneath thick cratonic lithosphere and by the incorporation of metasomatic P from lithospheric mantle. The large uncertainties regarding the P content of flood basalts, weathering rates, and the fraction of Fe-bound P in continental runoff make it difficult to assess the overall effects of LIP-derived P fluxes. Preliminary results presented here suggest that LIP-derived P fluxes were high enough to boost primary productivity and organic carbon burial rates. If so, the weathering of LIPs may have initiated the Neoproterozoic oxygenation of the ocean-atmosphere system, destabilized the climate, and set the stage for accelerated evolutionary developments.

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