Nutrient Supply to Planetary Biospheres From Anoxic Weathering of Mafic Oceanic Crust

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Abstract Phosphorus is an essential element for life, and the phosphorous cycle is widely believed to be a key factor limiting the extent of Earth’s biosphere and its impact on remotely detectable features of Earth’s atmospheric chemistry. Continental weathering is conventionally considered to be the only source of bioavailable phosphorus to the marine biosphere, with submarine hydrothermal processes acting as a phosphorus sink. Here, we use a novel 29Si tracer technique to demonstrate that alteration of submarine basalt under anoxic conditions leads to significant soluble phosphorus release, with an estimated ratio between phosphorus release and CO2 consumption (∑PO43−/∑CO2) of 3.99 ± 1.03 µmol mmol−1. This ratio is comparable to that of modern rivers, suggesting that submarine weathering under anoxic conditions is potentially a significant source of bioavailable phosphorus to planetary oceans and that volatile-rich Earth-like planets lacking exposed continents could develop robust biospheres capable of sustaining remotely detectable atmospheric biosignatures.

Plain Language Summary It is conventionally thought that continents above sea level are required in order for habitable planets to support a robust biosphere. We use experimental geochemistry and a simple model of biological cycling to show that this is incorrect, significantly expanding the possible range of planets that may host surface biospheres that would be detectable through telescope observations.

1. Introduction

Phosphorus (P) is a critical component of the genetic and energetic machinery of all life and plays key structural roles in most organisms. Indeed, recent debate has bolstered the case that P is not only essential for life on Earth but is also likely central for recognizable biochemistry more broadly (Erb et al., 2012; Reaves et al., 2012). Recent biogeochemical modeling and reconstructions of the evolution of marine phosphate (PO43−) concentrations from Earth’s rock record indicate that P has been the ultimate limiting nutrient for the biosphere throughout Earth’s history (Derry, 2015; Laakso & Schrag, 2014, 2018), and it has also been argued that P would be expected to limit the extent of life on exoplanets where oxygenic photosynthesis has evolved (Reinhard et al., 2017). Therefore, a mechanistic understanding of how the global P cycle has changed through time is crucial both for a basic understanding of the history of life on our planet and in the development of predictive frameworks for the production and maintenance of exoplanet biosignatures (Meadows et al., 2018).

Marine PO43− concentrations are controlled through time by the interplay between the magnitude of P source(s) into the ocean and the efficiency of P burial. Continental weathering, an important long-term CO2 sink that acts to regulate planetary climate, is also the only significant source of P to the modern oceans (Ruttenberg, 2003). Submarine weathering of basaltic oceanic crust, while also serving as a long-term CO2 sink, currently acts a significant removal process of P from marine systems (L. A. Coogan & Gillis, 2013; McManus et al., 2019; Wheat et al., 2003, 2017). For example, roughly 20% of the P sourced to the oceans today is removed through seafloor weathering of basalt (Ruttenberg, 2003; Wheat et al., 2003). The remainder is removed in association with the burial of authigenic apatite and carbonate minerals, organic P, and...
iron oxides in marine sediments. It has also been proposed that anoxic and iron-rich (ferruginous) oceans, which were widespread on the early Earth (Poulton & Canfield, 2011; Song et al., 2017), lead to enhanced P scavenging through adsorption onto iron oxide minerals formed near the oxygenated ocean-atmosphere interface, through the precipitation of reduced iron-phosphate minerals, such as vivianite, directly from seawater, or through scavenging onto a range of other reduced Fe-bearing mineral phases (Bjerrum & Canfield, 2002; Derry, 2015; Johnson et al., 2020; Reinhart et al., 2017).

Phosphorus removal during seafloor weathering may have been enhanced in Earth’s past, given that it is likely that oceanic crust weathering played a more significant role in weathering and CO₂ sequestration prior to the emergence of continents above sea level and the proliferation of land plants in terrestrial ecosystems (Krissansen-Totton et al., 2018; Mills et al., 2014). However, previous work has neglected the possibility that dissolved P may become liberated into seawater during marine weathering of oceanic crust in the absence of dissolved O₂ — as a natural result of limited Fe²⁺ oxidation and subsequent P scavenging. Although mid-ocean ridge basalts (MORB) typically do not contain igneous apatite, P⁵⁺ substitutes for Si⁴⁺ in primary silicate minerals (Koritnig, 1965; Watson, 1980), and this P could potentially be released during submarine basalt weathering. If operative, this process would reshape our view of the evolution of the P cycle on Earth (Mills et al., 2014; Reinhart et al., 2017) and would become an important component of attempts to predict planetary P cycling on habitable exoplanets. Here, we provide direct experimental support for the idea that seafloor weathering of oceanic crust under anoxic marine conditions can be a significant source of bioavailable P to aqueous systems, compare our observations with modern seafloor weathering systems, and provide initial estimates of the potential global biogeochemical impacts of this process.

2. Materials and Methods

We use an enriched dissolved ²⁶SiO₄²⁻ tracer to directly and accurately correlate the extent of primary silicate mineral dissolution with the amount of PO₄³⁻ mobilized into seawater upon reaction with natural submarine basalt. We focus here on two sets of experiments, one utilizing fresh submarine basalt and one in which the fresh submarine basalt was treated with the citrate-bicarbonate-dithionite (CBD) reductive dissolution procedure designed to remove pre-existing Fe³⁺-oxides associated with the partial oxidation during recovery from the seafloor (Mehra & Jackson, 1958) along with associated elements, in particular P, that have a high affinity toward adsorption onto Fe³⁺-oxides. We combine extensive mineral characterization of the reactant basalt with time-series changes in solution chemistry and thermodynamic modeling to evaluate the efficacy of seafloor weathering of basalt as a potential source of soluble, bioavailable phosphorus under the anoxic conditions characteristic of the early Earth and reducing habitable exoplanets lacking continents above sea level (see Supporting Information S1). Oxygenated basalt weathering experiments were also conducted in order to demonstrate the removal and retention of dissolved PO₄³⁻ as a consequence of the formation of Fe³⁺-oxide minerals upon reaction, providing a comparative analysis of PO₄³⁻ mobility with the anoxic experiments (see Supporting Information S1).

Reactant basalt was extensively characterized before and after reaction using scanning electron microscopy (SEM), electron microprobe (EMPA) with wavelength-dispersive X-ray spectroscopy (WDS), coupled with synchrotron X-ray fluorescence mapping (SXRF), and Fe K-edge (7.112 keV) X-ray absorption near-edge spectroscopy (XANES) imaging (see Supporting Information S1). Time-series measurements of solution chemistry from experiments were performed using a Thermo Scientific™ Orion™ PerpHeCT™ ROSS™ Combination pH Micro Electrode and Thermo Scientific™ Element™ XR inductively coupled plasma mass spectrometer (ICP-MS). The relative standard deviation (2σ) of the ICP-MS measurements ranges between 6% and 10% for P, 1%–5% for Fe, Mn, and Ni, 1%–3% for ²⁶Si, ²⁸Si, and ²⁹Si, and 1%–2% for the major cations, Ca²⁺ and Mg²⁺. The range in temperatures prescribed for the basalt weathering experiments, 15–75°C, is similar to temperatures associated with modern low-temperature seafloor springs and is within the range estimated through oxygen isotope composition of carbonate minerals formed within altered oceanic crust (Coogan & Gillis, 2013; Coogan et al., 2019; Gillis & Coogan, 2011; Wheat et al., 2017). The Geochemist’s Workbench v. 12.0.4 (Bethke et al., 2018), outfitted with a custom database produced using the DBCreate software package (Kong et al., 2013), was used to calculate the speciation of the time-series solution samples.
3. Results and Discussion

Mineralogy and element distributions in reactant basalt are shown in Figure 1a and Figures S3 and S4, while detailed time-series solution and CBD extraction chemistry are given in Figure 2, Tables S1–S4 and Figures S6–S11. Analysis by EMPA demonstrates that primary PO$_4^{3-}$ occurs principally as a trace phase within silicates (rather than a more concentrated P-bearing mineral such as apatite), present between 0.01 and 0.4 wt% as P$_2$O$_5$ (Figure 1a). Prior to reductive CBD treatment, some P is also concentrated on altered surfaces in association with secondary Fe-oxides and clay mineral phases (Figure 1a), as confirmed by SXRF and XANES imaging (Figure S4). Thermodynamic analysis suggests that the soluble P produced under our experimental conditions is present exclusively as P$_5^{+}$ (Figure 1b), consistent with release of trace substituted P in the silicate lattice during basalt dissolution into a protonated PO$_4^{3-}$ pool (predominantly H$_2$PO$_4^{-}$). These observations, together with results from the oxygenated experiments, indicate that the lack

![Figure 1](image1.png)

**Figure 1.** (a) Representative electron microscopy maps of Al, Fe, and P from grains derived from ground basalt sampled from the Juan de Fuca Ridge used in the seafloor weathering experiments. Phosphorus is concentrated along areas of altered grains that are concentrated in Fe, attributable to a mixture of secondary Fe$^{3+}$-oxide minerals and clays formed upon interaction with seawater at the sampling location. (b) Activity diagram showing the speciation of phosphorus in solution as a function of pH and solution redox state (Eh) at 25°C. The open circle shows the conditions of our seafloor weathering experiments, while the gray lines show the stability limits of water. Hot colors toward red represent high concentrations of the element of interest.

![Figure 2](image2.png)

**Figure 2.** Time-series solution chemistry for the anoxic seafloor weathering experiments (BA-1 and BA-2). (a) Dissolved $^{29}$Si/$^{28}$Si ratio of experimental solutions, showing a rapid drop accompanying the dilution of $^{29}$SiO$_2$-enriched synthetic seawater by dissolved Si derived from basalt dissolution with a natural abundance $^{29}$Si/$^{28}$Si ratio. (b) Calculated dissolved SiO$_2$ derived from dissolution of basalt. (c) Dissolved Fe$^{2+}$ and PO$_4^{3-}$ concentrations in experimental solutions, showing progressive increase in both species with continued reaction progress. Black line in (c) shows the P/Fe ratio expected for dissolution of fresh mid-ocean ridge basalt (MORB).
of Fe-oxide precipitation during seafloor weathering of basalt under anoxic conditions leads to efficient release of soluble reactive P into percolating fluids during silicate dissolution.

Time-series solution chemistry also provide strong evidence for effective mobilization of bioavailable P during basalt dissolution under anoxic conditions (Figures 2, S6 and S8). The rapid decrease in the bulk $^{28}$Si/$^{29}$Si ratio of the experimental seawater solutions, together with the roughly constant total dissolved SiO$_2$ concentrations, reflects the dissolution of reactant basalt, mixing of isotopically natural SiO$_2$ with $^{28}$SiO$_2$-enriched synthetic seawater, and precipitation of Si-bearing secondary minerals (Tables S1 and S4, Figure 2a). Our tracer results, which allow us to estimate the contribution of basalt-derived Si to the overall SiO$_2$ budget of the system (see Supporting Information S1), demonstrate a sharp increase in basalt-derived aqueous Si with reaction progress, asymptotically reaching concentrations of ~35 µmol kg$^{-1}$ after ~1,300 hr (Figure 2b). As silicate dissolution progresses, we observe significant mobility of both dissolved Fe$^{3+}$ and PO$_4^{3-}$ with continued reaction progress (Figure 2c). These results are in stark contrast to the oxygenated basalt weathering experiments, in which dissolved Fe derived from the dissolution of primary silicate minerals remained below the detection limit while P was either removed from solution (despite high initial dissolved P levels) or remained at steady state levels throughout reaction progress as a consequence of adsorption onto pre-existing and incipiently formed Fe$^{3+}$-oxide minerals (see Table S2 and Figure S7). We can further evaluate the potential of submarine basalt weathering under anoxic conditions to serve as a source of bioavailable PO$_4^{3-}$ to the deep ocean by using the time-series $^{28}$Si/$^{29}$Si data to quantify the total amount of atmospheric CO$_2$ that would be consumed upon alteration of primary basalt by seawater. We assume a SiO$_2$/Alkalinity ratio (Si/Alk) indicative of the composition of tholeiitic basalt, represented here for simplicity as enstatite (e.g., with Si/Alk = 1.0):

$$\text{MgSiO}_3 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{SiO}_2(aq)$$

(1)

By combining the time-series changes in $^{28}$Si/$^{29}$Si with the total dissolved SiO$_2$ of the experimental solution, we can use mass balance to quantify the total CO$_2$ consumed throughout the reaction progress ($\Sigma$CO$_2$). We can then compare $\Sigma$CO$_2$ with the total PO$_4^{3-}$ released during basalt dissolution ($\Sigma$PO$_4^{3-}$), which yields the “mobility ratio” of bioavailable P released per mol of CO$_2$ consumed during anoxic submarine basalt weathering ($\Sigma$PO$_4^{3-}$/\Sigma$CO$_2$; Figure 3). The experiment including the CBD reductive dissolution pretreatment provides the most precise estimate of the $\Sigma$PO$_4^{3-}$/\Sigma$CO$_2$ ratio during submarine basalt weathering under anoxic conditions, yielding a $\Sigma$PO$_4^{3-}$/\Sigma$CO$_2$ value of 3.99 ± 1.03 µmol mmol$^{-1}$ (Figure 3). Combining estimated ranges for modern CO$_2$ outgassing fluxes and riverine PO$_4^{3-}$ fluxes of 5–20 TmolC y$^{-1}$ (Coogan & Gillis, 2020; Isson et al., 2018; Wallmann & Aloisi, 2012) and 0.032–0.058 TmolP y$^{-1}$ (Ruttenberg, 2014), respectively, and stochastically resampling 10$^6$ times from uniform priors yields a median estimated mobility ratio for the modern Earth system of 3.6 µmol mmol$^{-1}$ with a 95% credible interval of 2.26–6.95 µmol mmol$^{-1}$ (Figure 4a). Our experimental results thus indicate that the $\Sigma$PO$_4^{3-}$/\Sigma$CO$_2$ value characteristic of submarine basalt weathering under anoxic conditions is of similar magnitude to that estimated for modern weathering of the continental crust (Figure 4a). This suggests that submarine basalt weathering under anoxic conditions off-axis of the mid-ocean ridge (MOR) should in many cases be roughly similar in its effectiveness at exporting bioavailable P during CO$_2$ consumption as the weathering of continental crust above sea level. Further, these experimental results suggest that PO$_4^{3-}$ may be sourced to the biosphere under anoxic seawater conditions from ridge-flank and on-axis MOR hydrothermal systems, in contrast to modern MOR systems, which...
demonstrate significant scavenging of dissolved PO$_4^{3-}$ onto Fe$^{3+}$-oxide minerals formed during seawater-rock interaction and hydrothermal plume formation (Wheat et al., 1996, 2003).

The $\Sigma PO_4^{3-}/\Sigma CO_2$ value obtained by our experiments can be used to illustrate the potential importance of submarine basalt weathering under anoxic conditions for a hypothetical water-rich silicate planet on which seafloor weathering of basalt is the primary CO$_2$ sink (Abbot et al., 2012; Kite & Ford, 2018). We envision this scenario as being applicable to portions of Earth’s earliest history and to Earth-like volatile-rich exoplanet “waterworlds” on which oxygenic photosynthesis has evolved. Conceptually, PO$_4^{3-}$ is released to the ocean as volcanic/metamorphic CO$_2$ is consumed during submarine basalt weathering, and some fraction of this bioavailable P passes through the biosphere while the remainder is scavenged. This in turn leads to organic C burial and a release of O$_2$ to the ocean-atmosphere system. The rate of O$_2$ release associated with this process ($J_{O_2}$) is given by:

$$J_{O_2} = J_{volc} \cdot f_{weath} \cdot \left(\frac{\Sigma PO_4}{\Sigma CO_2}\right) \cdot (1 - \epsilon_P) \cdot r_{CP}$$

where $J_{volc}$ represents the rate of volcanic CO$_2$ outgassing, $f_{weath}$ represents the fraction of CO$_2$ removal that is balanced by seafloor basalt alteration, $\epsilon_P$ represents a global scavenging efficiency, $r_{CP}$ gives the global net C/P ratio for material buried from the oceans, and $\Sigma PO_4/\Sigma CO_2$ is the mobility ratio as described above. We note that for planets in which the inorganic carbon cycle is balanced by seafloor weathering, the set point of the silicate weathering thermostat (e.g., steady state atmospheric CO$_2$) will ultimately balance rates of volcanic CO$_2$ outgassing regardless of the available area of reactive seafloor. For example, if available reactive surface area is small, atmospheric CO$_2$ will rise until the resultant temperature and seawater chemistry are sufficient for seafloor weathering to balance volcanic outgassing. Because the values of many of these parameters are uncertain even for the Earth system, these estimates are meant only to provide a conceptual framework that allows us to broadly illustrate the potential large-scale impacts of anoxic submarine P release.

Our results indicate that fluxes of PO$_4^{3-}$ from oceanic crust weathering can potentially support significant biospheric O$_2$ release rates (Figure 4b). For example, at a volcanic CO$_2$ flux of 20 Tmol y$^{-1}$, a global C/P burial ratio of 300, and a P scavenging efficiency of 50% our mobility ratio results indicate a biospheric O$_2$ flux of ~10 Tmol y$^{-1}$. For comparison, the total net biospheric O$_2$ flux on the modern Earth is on the order of ~10–20 Tmol O$_2$ y$^{-1}$ (Catling & Kasting, 2017), while biospheric O$_2$ fluxes during the Proterozoic following the initial oxygenation of Earth’s atmosphere have been estimated to be roughly 2–5 Tmol O$_2$ y$^{-1}$ (Ozaki et al., 2019). Although the precise values of P scavenging efficiency and global burial C/P ratio are not fully known through Earth’s history or across a wide range of planetary scenarios, they are likely to operate inversely to one another (e.g., Reinhard et al., 2017), such that our simple estimate, though non-unique, is likely to be broadly representative.

4. Conclusions

Studies of Earth system evolution and conceptual models used to forecast the emergence and maintenance of biosignatures on volatile-rich exoplanets have neglected the differences in hydrothermal P cycling between oxic and anoxic systems, and have instead implicitly invoked conditions under which P is effectively scavenged through adsorption onto Fe$^{3+}$-oxide minerals formed from the hydration and oxidation of primary silicates in submarine basalt (Korenaga et al., 2017; Unterborn et al., 2018). Our results stand in strong contrast to this prevailing conceptual model, and thus provide impetus to revisit mechanistic
models for Earth's early oxygen cycle (e.g., Mills et al., 2014) and the factors regulating the oxygen cycles of volatile-rich silicate planets more generally. In particular, it will be important for future work to establish the ocean-atmosphere $O_2$ “threshold” above which oxygenation of the deep oceans attenuates bioavailable P fluxes by initiating widespread Fe$^{2+}$ oxidation within the ocean interior, and the dynamics of P scavenging and global C/P/O stoichiometry across a wider range of planetary boundary conditions. Nevertheless, our results clearly suggest that biospheres sustained entirely by bioavailable P released during submarine basalt weathering under anoxic conditions, including that of the earliest Earth, are potentially capable of generating extremely high biogenic gas fluxes that rival or exceed even those of the modern Earth. Anoxic submarine weathering should thus be considered an important component of the large-scale redox balance of terrestrial planets.

Data Availability Statement

All datasets for this research are included in this study (and its Supporting Information S1). The geochemical speciation database, solution chemistry, and rock characterization data used in the study are also available at Mendeley Data (https://doi.org/10.17632/mdg28kxpdh.2). The simple P-C-O$_2$ mass balance model is determined through Equation 2 and parameters explicitly described in the Supporting Information S1.

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