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Biogeodynamics: Bridging the gap between surface and deep Earth processes

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Abstract

Life is sustained by a critical and not insubstantial set of elements, nearly all of which are contained within large rock reservoirs and cycled between Earth's surface and the mantle via subduction zone plate tectonics. Over geologic timescales, plate tectonics play a critical role in recycling subducted bioactive elements lost to the mantle back to the ocean-biosphere system, via outgassing and volcanism. Biology additionally relies on tectonic processes to supply rock-bound "nutrients" to marine and terrestrial ecosystems via uplift and erosion. Thus the development of modern-style plate tectonics and the generation of stable continents were key events in the evolution of the biosphere on Earth, and similar tectonic processes could be crucial for the development of habitability on exoplanets. Despite this vital "biogeodynamic" connection, directly testing hypotheses about feedbacks between the deep Earth and the biosphere remains challenging. Here I discuss potential avenues to bridge the biosphere-geosphere gap, focusing specifically on the global cycling and bioavailability of major nutrients (nitrogen and phosphorus) over geologic timescales.

Introduction

Primary productivity is a major driver of elemental cycling at Earth's surface, forming an important link between the geosphere and the biosphere. Autotrophic fixation of volcanically-sourced atmospheric CO_2 into organic matter, coupled to the production of molecular oxygen in its most efficient form, provides important feedbacks to climate, weathering, and the redox state of Earth's surface reservoirs. While CO_2 outgassing and silicate weathering remain the primary controls on atmospheric CO_2 levels over geologic timescales, primary productivity can effectively regulate atmospheric CO_2 in the short-term (e.g., Falkowski, 1997). In addition, long-term burial of organic carbon was a prerequisite to the buildup of oxygen in Earth's early environments (Berner, 1991).

Carbon dioxide alone is insufficient to fuel life. Organisms require greater than 20 additional major and trace elements to produce biomass and metabolic machinery (e.g., Frausto da Silva & Williams, 2001). Given the ubiquity of CO_2 at Earth's surface, it is thus the availability of these "nutrients" that dictates the success of primary producers in natural environments. Nitrogen (N) and phosphorus (P), in particular, are ubiquitous in life as we know it and are required for the formation of many essential biomolecules, including nucleic acids (DNA and RNA) and proteins. These nutrients form the basis of the canonical "Redfield ratio", which postulates that marine organic matter is produced and recycled at a nearly constant C:N:P ratio of 106:16:1 (Redfield et al., 1963), following the stoichiometry of marine phytoplankton.

Primary production in most modern aquatic environments is limited by either N or P. Large areas of the modern surface ocean appear to be limited by nitrogen (e.g., Falkowski et al., 1998). However, it is generally assumed that extended deficits in bioavailable N could be mitigated by biological fixation of atmospheric N_2, given sufficient availability of other nutrients. Notably, this scenario assumes a nearly limitless supply of volcanically-derived N_2 in the atmosphere, despite recent suggestions that atmospheric N_2 could have varied over Earth history, following changes in N burial rates and subduction over Earth history (as discussed below). Phosphorus is primarily sourced from continental weathering, without a significant atmospheric source. This dependence on riverine delivery, which is tied to tectonic processes via uplift and erosion, suggests that P is the limiting nutrient on timescales of greater than thousands of years (Tyrrell, 1999). In addition, the importance of Fe and other bioactive metals as micro-nutrients has become increasingly apparent in recent decades (e.g., Frausto da Silva & Williams, 2001; Martin, 1990). Changes in the sources and sinks of these redox-sensitive metals have been mainly tied to oxidative weathering and fluctuations in ocean redox chemistry, particularly during the Precambrian (e.g., Anbar & Knoll, 2002).

Tectonic processes can therefore exert a significant control on Earth surface redox and climate through their involvement in global nutrient cycling and primary productivity. These "biogeodynamic" controls fall under two categories: 1) A *direct control* via subduction and volcanism (e.g., for CO_2 and N_2); or, 2) An *indirect control* via burial, uplift, and erosion (e.g., for phosphorus and some bioactive trace elements). Here I examine these connections within the context of global nutrient cycling, and their possible implications for Earth system evolution over geologic history.

Biogeodynamic Controls on Atmospheric N_2

Dinitrogen gas constitutes 78% of the modern atmosphere. As the dominant atmospheric gas on Earth, the partial pressure of N_2 has an important effect on surface temperature and planetary habilitability (Goldblatt et al., 2009; Stüeken et al., 2016; Zahnle & Buick, 2016). Despite this significance, the history of pN_2 over geologic time is not well understood, and empirical constraints on past atmospheric pressure are limited. $N_2/^{36}Ar$ systematics in fluid inclusions (Nishizawa et al., 2007; Marty et al., 2013; Avice et al., 2018), fossilized raindrop imprints (Som et al., 2012; Kavanagh & Goldblatt, 2015), and gas bubbles in basaltic lavas formed at sea level (Som et al., 2016) have all been used to estimate pN_2 at $\geq$ 2.7 Ga (Figure 1A), but a consensus is lacking. Nitrogen flux estimates from modern arc systems have further complicated the picture, with some calculations suggesting a net outflux of nitrogen from the mantle or zero sum game (e.g., Fischer et al., 2002), while others suggest a net influx of nitrogen from Earth's surface to the mantle (e.g., Barry & Hilton, 2016; Busigny et al., 2011; Goldblatt et al., 2009; Mallik et al., 2018).

Determining the history of atmospheric pN_2 over time requires a detailed understanding of the processes acting to cycle nitrogen from Earth's surface to the mantle, and vice versa. The modern surficial N cycle is largely driven by biological processes. The great majority of biologically available N in the ocean-biosphere system comes from nitrogen fixation, the biological uptake of atmospheric N_2 into biomass (N_{org}) (Figure 2). Early in Earth's history, abiotic N_2 fixation reactions induced by lightning or photochemical processes could have provided small amounts of nitrogen to the biosphere (Navarro-Gonzalez et al., 2001). Hydrothermal fluids can also recycle sedimentary ammonium back into the water column at mid-ocean ridges and associated hydrothermal vent systems (Lilley et al., 1993) providing a secondary source of dissolved inorganic nitrogen (DIN). Weathering of N-rich continental rocks has additionally been proposed as a significant contribution to the terrestrial N cycle (Houlton et al., 2018), and possibly to the atmosphere (Stüeken et al., 2016). However, these inorganic sources of DIN (shown in red in Figure 2) would have constituted only a small percentage of the global supply of fixed N to surface oceans once N_2 fixation evolved very early in Earth history (Boyd & Peters, 2013; Stüeken et al., 2015; Weiss et al., 2016).

Organic N is released as ammonium (NH_4^+) during degradation of biomass, which is quickly recycled and re-assimilated. In the presence of oxygen, ammonium can also be oxidized to nitrite and nitrate, which provide an additional source of dissolved inorganic nitrogen (DIN) to the biosphere. A significant amount of this DIN is returned to the atmosphere via anaerobic processes in oxygen-minimum zones (e.g., Dalsgaard et al., 2005). Over geologic timescales, small amounts of fixed nitrogen can escape biological recycling and be buried in the sediments (Schroeder & McLain, 1998). During burial, nitrogen-bearing rocks can undergo metamorphism, which returns a significant fraction of the nitrogen back to the atmosphere (e.g., Haendel et al., 1986). The remainder of sedimentary N is subducted, along with ammonium from altered oceanic lithosphere (Busigny et al., 2011; Halama et al., 2014), forming the primary flux of N from the surface to the deep.

Once subducted, the fate of N in the mantle is less clear. Recent experimental and theoretical constraints suggest that the speciation of nitrogen is highly variable under a range of mantle redox and pH conditions, e.g., with ammonium dominating over molecular N_2 under more reducing mantle conditions (Li & Keppler, 2014; Mikhail et al., 2017; Mikhail & Sverjensky, 2014). Nitrogen speciation in the mantle is critical to the volcanic resupply of N_2 to the surface environment, because molecular N_2 is likely to be out-gassed, while ammonium could be stored in mineral phases in the deep Earth (Mikhail & Sverjensky, 2014). These constraints indicate that the storage capacity for N in the mantle could be significantly larger than previously recognized (e.g., Cartigny & Marty, 2013; Johnson & Goldblatt, 2015). For example, recent estimates suggest that silicate minerals in Earth's interior could store up to 50 times present atmospheric levels of nitrogen (Yoshioka et al., 2018).

The capacity for Earth's mantle to store large reservoirs of N in the form of ammonium-bearing silicates could provide a mechanism for changing atmospheric pN_2 over geologic timescales. As above, the drawdown of N_2 from the atmosphere into the sediments is fundamentally controlled by the operation of the biogeochemical N cycle; once subducted, the fate of sedimentary and igneous N depends on conditions in the mantle wedge, including the redox state of associated fluids. Both of these parameters have evolved over geologic time, alongside chemical and biological evolution at Earth's surface. Zerkle and Mikhail (2017) estimated that the increasing efficiency of the global biosphere could have driven the burial of organic N up to 50% of modern levels by the early Proterozoic (Figure 1B). Notably, these estimates assumed a conservative burial efficiency of 10%, similar to the modern, but burial rates could have been even higher under the anoxic depositional conditions of the Precambrian deep oceans (e.g., Kipp & Stüeken, 2017). Recent models of atmospheric N_2 dynamics suggest that large changes in N_2 fixation into biomass coupled with significantly higher overall rates of biomass burial could drawdown pN_2 to values less than 0.5 bar by 2.7 Ga (Stüeken et al., 2016).

In addition, changes in the speciation and degassing of N in Earth's mantle associated with changes in Earth surface oxygenation could have contributed to large swings in atmospheric pN_2. A significant amount of subducted rock N could have been stored as ammonium throughout the Precambrian, given that deep oceans remained largely anoxic and ferruginous until the Neoproterozoic, and perhaps even into the early Phanerozoic (Stolper & Keller, 2018). Considering only the available constraints on changes in N speciation with redox (Mikhail & Sverjensky, 2014), if the mantle wedge remained largely reducing, a net influx of N_2 from the atmosphere-biosphere system to the mantle could have been the norm for much of Earth history. Thus, N_2 levels could have started out higher than today (e.g., Goldblatt et al., 2009), and been pulled down to modern levels or even lower (as the illustrated by the upper bounds in the "Flux inversion model" in Figure 1A). In contrast, N_2 drawdown from near modern levels could have led to lower pN_2 in the Archean (as shown by the lower bounds of the "Flux inversion model") (e.g., Som et al., 2016). Following the Great Oxidation Event in the Paleoproterozoic, widespread O_2-dependent nitrogen loss from the biosphere back to the atmosphere (e.g., Zerkle et al., 2017), coupled with an enhanced N_2 release during oxidative weathering (Stüeken et al., 2016), could have somewhat eased (or at least slowed) N_2 drawdown. Once deep waters became oxygenated in the early Phanerozoic, subduction zones injected oxidizing fluids into the mantle wedge, oxidizing NH_4^+ to N_2, and promoting outgassing to modern pN_2 levels.

These theoretical scenarios for pN_2 changes through time are difficult to test given available data. In a pioneering study, Johnson and Goldblatt (Johnson & Goldblatt, 2017) provided evidence for enhanced incorporation N into continental rocks over geologic time, in the form of glacial tills and granites (Figure 1B). Additionally, the $\delta^{15}N$ ratios of these rock-bound nitrogen species support a biological origin. Intriguingly, the distribution of N in glacial tills also seems to vary with paleogeography, with total N abundance in Asian tills >> South American and African tills >> North American tills. This geographical disparity suggests some local controls on N drawdown, from variable continental growth histories, changes in local biogeochemical N cycling, and/or changes in subduction zone conditions (Johnson & Goldblatt, 2017). This sparse dataset offers a tantalizing picture of changes in the geobiological N cycle over Earth history, but additional geochemical and geodynamic data is required to tease out the mechanism(s) behind these spatial and temporal heterogeneities.

Phosphorus Burial and Continental Weathering

Phosphorus is generally believed to be the limiting nutrient for global primary productivity on $\geq$ 200 ka timescales (Tyrrell, 1999) because there is no limitless supply of phosphorus to the oceans. Instead, the input of P to the marine biosphere relies on riverine delivery from land. Once delivered to the oceans, P exists mainly as P_{org} and as P adsorbed to Fe-(oxyhydr)oxides (hereafter referred to as "Fe-oxides" for simplicity). As with nitrogen, the burial of phosphorus in deep sea sediments and subsequent subduction constitute the main flux of P to the mantle. However, P undergoes complex diagenetic cycling in marine sediments, and the extent to which P is trapped versus recycled into the water column is highly redox dependent. Under a well-oxygenated water column, phosphorus can be released during respiration of organic matter or reduction of Fe-oxides, but the released P is either efficiently scavenged by re-adsorption to Fe-oxides near the sediment-water interface, or forms authigenic carbonate fluorapatite (CFA) (e.g., Ruttenberg & Berner, 1993; Slomp & van Raaphorst, 1993). Under anoxic conditions, the Fe-oxide trap at the sediment surface is diminished, and more P is released into the water column (e.g., Ingall et al., 1993; Dellwig et al., 2010), particularly under euxinic (anoxic and sulfidic) depositional conditions when Fe-oxides are reduced by dissolved sulfide (Poulton, 2003).

The dependence of P cycling on oxygen levels implies that spatial and temporal changes in ocean redox chemistry over geologic time would also have controlled the amount of P that was buried in weatherable continental sediments and deep-sea oceanic sediments prior to subduction. In the Fe-rich oceans of the Archean, P burial rates could have been universally high due to extensive sorption onto Fe-oxides (e.g., Bjerrum & Canfield, 2002; Jones et al., 2015) and a paucity of electron donors for organic matter remineralization (Kipp & Stüeken, 2017). The redox-stratified oceans that characterized the Proterozoic (Poulton & Canfield, 2011) could have promoted high P burial in ferruginous deep-water sediments (Reinhard et al., 2017; cf, Planavsky et al., 2010), but significant recycling of P back to the water column at widespread sulfidic continental shelves (Poulton, 2017). Recent studies also suggest that Fe(II) phosphate (vivianite) could be an important sink for reactive P during early diagenesis in low-sulfide sediments or microenvironments (e.g., Jilbert & Slomp, 2013; Dijkstra et al., 2016), and vivianite has been proposed as a further important sink for phosphate in the mid-Proterozoic (Derry, 2015).

In addition to the burial-subduction controls on P cycling to the deep Earth, the flux of P to the biosphere relies on the weathering of P-bearing minerals, which is indirectly linked to tectonics via uplift and erosion. A weathering driver for P delivery relies on the availability of continental freeboard, although the net growth rate for continental crust on the early Earth is controversial (e.g., see review in Dhuime et al., 2017). For example, most estimates suggest continental freeboard could have been scarce prior to ~3.0 Ga (e.g., Cawood et al., 2013; Pons et al., 2013); alternatively, net growth of continental crust could have been complete by the end of the Hadean (e.g., Armstrong, 1981; Rosas & Koranaga, 2018). Once large continental masses appeared, enhanced P weathering could be linked to the supercontinent cycle, either by the redistribution of crustal mass to higher relief during supercontinent assembly or by the formation of continental margins during supercontinent breakup.

An enhanced flux of phosphate to the biosphere associated with tectonic activity and several extensive glaciations has been implicated in organic carbon burial and global oxygenation in the late Paleoproterozoic (e.g., Bekker & Holland, 2012; Papineau et al., 2013). Two mantle superplume events (one from ~2.45-2.48 Ga and one at around 2.2 Ga) initiated continental rifting and led to the eventual breakup of the Kenorland supercontinent at ~2.1 to 2.0 Ga (Aspler & Chiarenzelli, 1998; Barley et al., 2005; Halls et al., 2008; Heaman, 1997). The formation of epicratonic rift basins during the breakup of Kenorland could have created continental configurations that promoted the upwelling of deep P-rich waters, stimulating primary production. Increased chemical weathering fluxes of phosphorus to the oceans after major glaciations could also stimulate photosynthetic oxygen production (Lenton & Watson, 2004). In addition, generation of H_2SO_4 (sulfuric acid) during pyrite oxidation on the continents could have decreased the pH of soils and groundwaters (e.g., Holland, 2002; Konhauser et al., 2011), further promoting apatite dissolution on land and bioavailable P delivery to the oceans (Bekker & Holland, 2012; Guidry & Mackenzie, 2003).

Similarly, P fertilization from the weathering of large igneous provinces has been suggested to have contributed to the Neoproterozoic oxygenation event and ensuing radiation of macroscopic life (Planavsky et al., 2010; Horton, 2015; Laakso & Schrag, 2017). Biological colonization of the land surface could have further amplified mid- to late- Neoproterozoic weathering rates via selective weathering of P from rocks with organic acids (Lenton & Watson, 2004). As above, enhanced phosphorus scavenging in anoxic, Fe-rich oceans (Reinhard et al., 2017), coupled with global tectonic quiescence (Cawood & Hawkesworth, 2014) could also have helped to maintain the low oxygen levels that typified much of the “boring billion” years in between.

While these and other feedbacks between planetary redox, P availability and burial have received a significant amount of attention (e.g., Bekker et al., 2003; März et al., 2008), the inferred connection with tectonic processes is not well established. Cox et al. recently examined the phosphorus content of igneous rocks as a proxy for the continental P inventory (Cox et al., 2016; 2018). Notably, the average of the measured igneous P_2O_5 values are similar to P_2O_5 values measured in glacial tills (although slightly higher) (Gaschnig et al., 2016), and both show a general trend of increasing P_2O_5 through time (Figure 3). Cox et al. interpreted this trend to reflect changes in continental P content due to secular changes in mantle cooling, and linked this to atmospheric oxygenation. These researchers also identified secondary variations in crustal P_2O_5 content associated with mafic crustal production, and attributed these differences to the behavior of P during melting and fractional crystallization. This study provides a critical first step in identifying the behavior of P in igneous systems, and provides a number of interesting, and testable, hypotheses. If we further examine their dataset in the context of the supercontinent cycle (Figure 3), there also appear to be peaks in P_2O_5 roughly associated with continental breakup, at least within the given time constraints we have on the known supercontinent cycles. Notably, no systematic geochemical studies have thus far been conducted to track changes in P cycling and weathering fluxes over a supercontinental cycle, likely because of the lack of a straightforward method for estimating ancient P concentrations in seawater from the sedimentary rock record.

Conclusions and Ways Forward

The above discussion highlights some of the fundamental connections between the surface and deep Earth that contribute to global elemental cycling over geologic timescales. Sediments subducted into the mantle are highly influenced by biological activity, and their composition and abundance will vary following the evolution of life and biogeochemical cycles over Earth history. Similarly, the local environment of the mantle wedge can directly control the speciation and volatility of elements that are subducted within these sediments, with critical consequences for their storage or release from the mantle into the atmosphere. These connections extend well beyond the nitrogen and phosphorus cycles, for example, to implications for changes in the burial ratio of organic carbon to carbonate-rich sediments or in the burial of sulfur as primarily sulfide to sulfate. However, we currently lack fundamental constraints on the relevant reservoirs, in particular the speciation and the residence times of elements in the deep Earth. Similarly, uplift and erosion of continental rocks provide an important supply of nutrients to the global biosphere, but their temporal distribution and availability to weathering reactions will be dependent on their behavior and resulting mineralogy during different crustal production mechanisms.

Understanding how these mechanisms have acted in time and space has generally been a problem for geodynamicists; however, the implications for the biosphere make this of fundamental importance to biogeochemists as well. Quantifying these connections should be an important target for Earth scientists across disciplines, with priority research directions including but not limited to:

1) Experimental and theoretical examinations of the speciation and fate of bioactive elements during subduction under varying mantle conditions, along with implications for the volatilization and return of these elements to Earth's surface;
2) Development of novel tools and proxies for assessing atmospheric pressure from the rock record, and application of these (and already established) tools to more recent time periods in Earth history (particularly the mid-Proterozoic);
3) A systematic study of the distribution and weathering susceptibility of P- and micronutrient-bearing minerals under different tectonic regimes;

4) The generation of high-resolution datasets for crustal P and micronutrients across a supercontinental cycle, preferably coupled directly to weathering proxies, such as Li or Mg isotopes (e.g., Pistiner & Henderson, 2003; Teng et al., 2010); and, finally,
5) The incorporation of deep Earth reservoirs and elemental speciation in Earth system models of global nutrient cycling (e.g., Mills et al., 2014), and, as a corollary, the inclusion of geochemical and biologically-mediated sediments in geodynamic models of subduction and volatilization.

These target research areas and similar ways of thinking will allow us to gain a more holistic view of Earth system evolution over geologic timescales, and to determine the impact of biogeodynamic connections on climate, global redox, and ultimately life.

Data accessibility

All data utilized in this manuscript are available in the cited references.

Competing interests

The author declares no competing interests.

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Figure captions

Figure 1. A. Empirical constraints on pN_2 over Earth history. Constraints based on fluid inclusion data (in blue) are from Marty et al. (2013) and Nishizawa et al. (2017); fossil raindrop imprints (in green) are from Som et al. (2012) and Kavanaugh and Goldblatt (2015); gas bubbles (in red) are from Som et al. (2016). Also shown is a hypothetical scenario for the evolution of atmospheric pN_2 (in brown), based on Zerkle & Mikhail (2017), as described in the text. B. Estimates of nitrogen burial through time (based on Zerkle & Mikhail, 2017),

along with the measured N content of glacial tills and granites (from Johnson & Goldblatt, 2017).

Figure 2. The combined surface and deep Earth nitrogen cycle. Abiotic fluxes are shown in red, biological fluxes are shown in blue. N_{org} = organic nitrogen; N_{sed} = N incorporated into sediments; DIN = dissolved inorganic nitrogen.

Figure 3. Total P_2O_5 measured in glacial tills (purple diamonds; from Gaschnig et al., 2016) and in igneous rocks, including the averages (blue circles) and 95% confidence intervals (blue field; from Cox et al., 2018), compared to established supercontinent cycles.

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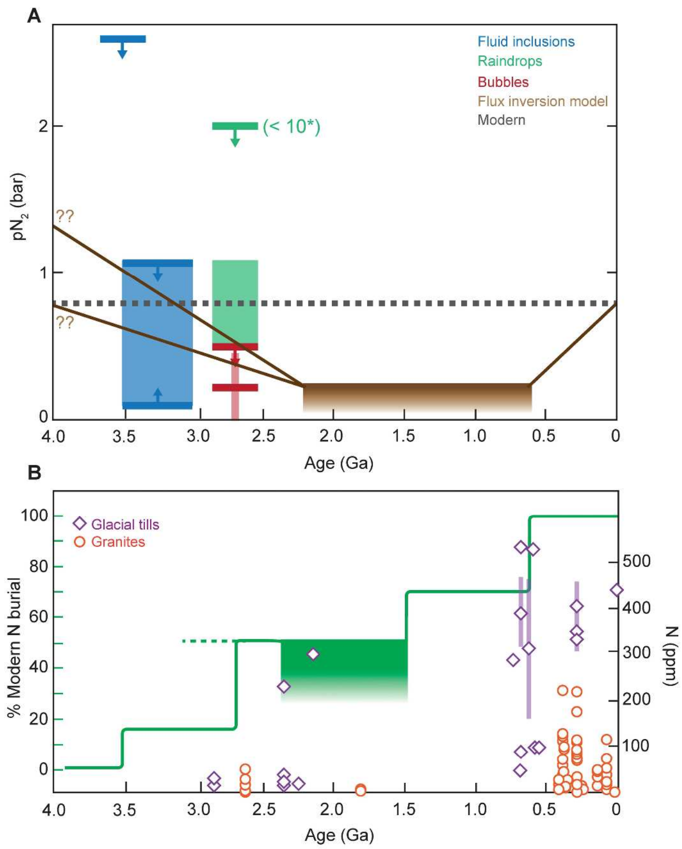

Figure 1. Figure 1. A. Empirical constraints on pN_2 over Earth history. Constraints based on fluid inclusion data (in blue) are from Marty et al. (2013) and Nishizawa et al. (2017); fossil raindrop imprints (in green) are from Som et al. (2012) and Kavanaugh and Goldblatt (2015); gas bubbles (in red) a re from Som et al. (2016). Also shown is a hypothetical scenario for the evolution of atmospheric pN_2 (in brown), based on Zerkle and Mikhail (2017), as described in the text. B. Estimates of nitrogen burial through time (based on Zerkle and Mikhail, 2017), along with the measured N content of glacial tills and granites (from Johnson and Goldblatt, 2017).

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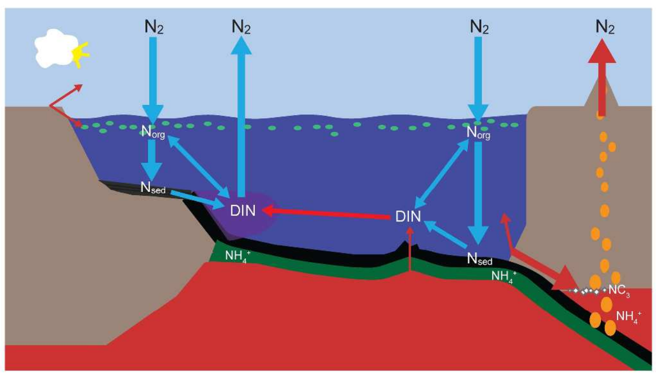

Figure 2. The combined surface and deep Earth nitrogen cycle. Abiotic fluxes are shown in red, biological fluxes are shown in blue. N_{org} = organic nitrogen; N_{sed} = N incorporated into sediments; DIN = dissolved inorganic nitrogen.

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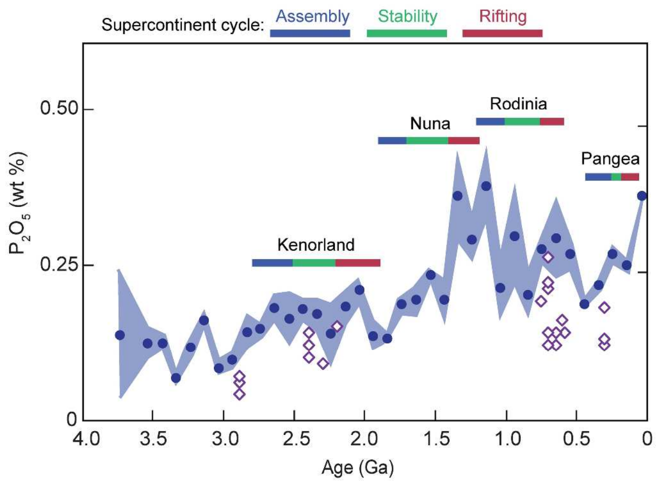

Figure 3. Total P_2O_5 measured in glacial tills (purple diamonds; from Gaschnig et al., 2016) and in igneous rocks, including the averages (blue circles) and 95% confidence intervals (blue field; from Cox et al., 2018), compared to established supercontinent cycles.

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