

Coversheet

Geosphere and Biosphere coevolution: the role of trace metals availability in the evolution of biogeochemistry

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Perspective

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Abstract

Earth's geosphere and biosphere have coevolved over time, influencing each other's stability and keeping our planet habitable for most of its 4.543 billion years of history. Biogeochemical cycles play a key role in controlling this interaction, connecting long-term geological cycles and the much faster evolution of the Earth's outer biologically dominated envelopes. A small set of microbial-encoded proteins containing redox-sensitive transition metals as their core catalytic center carry out the majority of the key biogeochemical reactions. Metals such as Fe, Co, Ni, Zn, Mo, W, V, and Cu are used in these proteins to access diverse redox couples as a function of the changing planetary availability of these elements over time. Despite the importance of this process, the relationship between metal availability and metabolism evolution and diversity has not been investigated in detail. I pose that elucidating the impact of transition metal availability on microbial functional diversity holds the key to understanding the co-evolution of life and our planet, potentially unlocking a number of important discoveries at the core of diverse fields such as earth sciences, astrobiology, microbial ecology, and biotechnology.

Main

Earth's geosphere and biosphere have coevolved over time, influencing each other's stability trajectory and ultimately keeping our planet habitable for the last 4 billion years (Chopra and Lineweaver, 2016; Moore et al., 2017). Among the numerous events that have controlled the life-planet trajectory (*e.g.*, the Moon forming impact, onset of plate tectonic, evolution of land plants), the change in planetary surface redox following the Great Oxidation Event conditions has had the greatest impact, profoundly influencing the mineralogy, geochemistry, and biology of Earth (Falkowski et al., 2008; Hazen and Ferry, 2010; Jelen et al., 2016). By controlling a large portion of biogeochemical cycles, microbes significantly influence element cycling on our planet (Falkowski et al., 2008). The majority of the key reactions that control biogeochemistry are carried out by a small set of microbial-encoded proteins containing a redox-sensitive transition metal as their core catalytic center (Harel et al., 2014). Even more, life's need to exploit thermodynamic disequilibrium is intimately tied to the availability of transition metals to biologically mediated redox chemistry. A large diversity of substrates can be used by biology to conserve energy through redox reactions (Falkowski et al., 2008; Figure 1a), a task accomplished through redox proteins, known as oxidoreductases, classified by the Enzyme Commission (EC) under the EC1 group. In order to control the energy from the metabolic reactions, mainly in the form of electron flow, biology has evolved a complex system of proteins that act in a stepwise fashion transferring electrons across intermediate redox steps between the electron donor and the ultimate electron acceptor. EC1 enzymes responsible for redox chemistry are overwhelmingly metal containing proteins, also known as metalloproteins (Figure 1). To be able to transfer electrons to and from different substrates involved in energy conservation and ultimately in element cycling, life needs oxidoreductases to be precisely tuned in their midpoint electric potential (E'_0) (Figure 1b). This task is carried out evolutionarily by selecting for a wide variety of metal centers and by altering their position within the protein (Moore et al., 2017).

Elements used in metalloprotein enzymes' catalytic centers include, among others, transition metals such as Fe, Mo, W, Zn, Cu, V, Mn, Ni and Co and non-metals like S and Mg. The availability of biologically critical dissolved metals and substrates has changed over the course of Earth's history as a result of changing redox conditions, particularly global oxygenation (Anbar, 2008; Moore et al., 2017; Figure 1c). For example, metal availability might have limited nitrogen fixation and primary productivity during the mid-Proterozoic, leading to decreased organic matter production and carbon isotope fractionation observed in the geological record (Canfield, 1998; Anbar and Knoll, 2002). Changing metal availability during the Archean has probably led to the expanded biological use of new transition metals (Anbar, 2008; Dupont et al., 2010; Robbins et al., 2016), and directly influenced biological innovation with the

evolution of new metabolic pathways (Zerkle et al., 2005; Dupont et al., 2010; Jelen et al., 2016; Moore et al., 2017). This geochemical evolution has allowed biology to access a larger number of redox couples, evolutionarily tuning its protein machinery to use more oxidized compounds as they became available during the planet's evolution (Jelen et al., 2016; Moore et al., 2017). Despite these clear and pervasive geosphere-biosphere connections, we lack fundamental knowledge regarding the role of the distribution and availability of transition metals in controlling microbial functional diversity, even in extant ecosystems.

Can trace metal availability control microbial diversity?

While trace metals are recognised as important for microbial metabolism, they are not classically considered as major drivers of microbial (functional) diversity. Classic microbial ecology paradigms look at master physico-chemical variables, such as temperature and pH (Delgado-Baquerizo et al., 2018), at the availability of substrates, in the form of organic carbon (Nelson and Wear, 2014; Chen et al., 2018) and/or electron donor and acceptors (Méndez-García et al., 2015; Magnabosco et al., 2018; Ren et al., 2018), or at the thermodynamic energy landscape available to selected reactions (Akerman et al., 2011; Großkopf and Soyer, 2016) to explain the environmental distribution of different functional groups. These variables play a key role in explaining the distribution of microbial trophic groups, but alone fail to account for the large variance in microbial diversity and the apparent high functional redundancy identified in numerous environments. An additional layer of explanatory power for microbial diversity might be provided by the availability of trace metals required to synthesize key enzymes required for the different variants of each pathway.

The roles of metals in influencing biodiversity has been classically studied in the context of their toxicity, and a trove of information is available on the lowest observed adverse effect levels for different metals in diverse organisms and communities (Trevors and Cotter, 1990; Giller et al., 1998; Edgcomb et al., 2004; Macomber and Hausinger, 2011; Liu et al., 2019). Conversely, information on the minimum concentration requirements for specific trace elements are severely limited and often linked to studies on host-pathogens interactions (Hutner et al., 1950; Pandey et al., 1994; Cerasi et al., 2013; Jacquot et al., 2014; Ma et al., 2015), while very few studies have investigated their role in controlling microbial functional diversity (Morel and Price, 2003; Bertrand et al., 2007).

Early evidence for the role of transition metals in controlling biodiversity and productivity in the environment comes from studies on iron limitation on primary productivity in the oceans (Martin and

Fitzwater, 1988), although the role of trace element in biology had been investigated before (see (Hutner et al., 1950) for a detailed account of works before 1950). The role of iron as a key micronutrient controlling marine productivity is now well established (Tagliabue et al., 2017), and recent studies have investigated whether other metals, including cobalt, the key constituent of vitamin B12 and cadmium, play a part, since they are used by phytoplankton to interconvert carbon acid into CO₂ and water (Cullen et al., 1999; Saito et al., 2002; Bertrand et al., 2007; Ahlgren et al., 2014).

Other than iron limitation in marine primary productivity, most information about trace metal control in microbial functional diversity comes from empirical evidence in the field of environmental engineering, especially in the operation of anaerobic bioreactors and biogas production facilities (Feng et al., 2010; Banks et al., 2012; Schmidt et al., 2014; Carballa et al., 2015). In these systems, the selective addition of Ni, Co, W and Se in different ratios has been shown to control factors such as methane/sulfide ratio, the total methane yield of the digester, as well as the diversity of the microbial consortia in the bioreactor (Osuna et al., 2003; Demirel and Scherer, 2011; Carballa et al., 2015). These observations have been confirmed under more stringent laboratory conditions, where the availability of trace metals has been identified as one of the key factors allowing for the selective stimulation of methanogens. Methanogenesis has been shown to be strongly favored under the presence of higher concentrations of Ni and Co, since these are two key metals cofactors of the methane-producing enzymes (Schönheit et al., 1979; Kida et al., 2001) (Schönheit et al., 1979; Kida et al., 2001), and the availability of Ni and Co can directly influence growth efficiency (Jansen et al., 2007).

Despite these empirical observations, very little work has been done to understand the role of trace elements in controlling microbial diversity until recently. Two recent papers investigated the differential role of copper and iron availability in the surface ocean in controlling phytoplankton metabolism and ammonia oxidation community composition (García-Cañas et al., 2021; Shafiee et al., 2021). García-Cañas and colleagues (2021) have shown that the switch from iron containing cytochrome (iron containing) CytC6 to plastocyanin, a type I blue-copper protein, is controlled by the availability of copper in surface waters rather than by iron concentrations that are usually severely limiting. The switch from iron-dependent to copper-dependent soluble electron transporter in phototrophs might be an early adaptation evolved following the GOE and might contribute to reducing iron-competition in surface waters (García-Cañas et al., 2021). Similarly, Shafiee et al. (2021) showed differential affinities and toxicity thresholds for copper in chemolithotrophic ammonia-oxidizing bacteria compared to ammonia-oxidizing archaea. Based on this, they suggested that the niche separation in the oceanic water column among ammonia oxidizing bacteria and archaea is linked to the differential distribution of iron

and copper within the water column and thus to the evolution of efficient competition mechanisms for trace element acquisition, utilization and detoxification (Shafiee et al., 2021).

Trace metal availability, specifically the availability of cobalt, might be responsible for the differential presence of two alternative fermentation pathways within anaerobic heterotrophic bacteria. Two major pathways of glutamate fermentation are known, the 2-hydroxyglutarate and the 3-methylaspartate pathway (for a recent review, see Buckel, 2021)). The two pathways have identical stoichiometry, but differ substantially in their intermediate and cofactor requirements. The 2-hydroxyglutarate pathway relies on iron-sulfur containing proteins that are extremely oxygen sensitive so this pathway is found in strictly anaerobic bacteria. The 3-methylaspartate pathway is instead coenzyme B12-dependent, requiring 30 additional enzymes for the anaerobic biosynthesis of the coenzyme B12 (Moore and Warren, 2012), but it is more oxygen tolerant and commonly found in environmental anaerobes that can be transiently exposed to oxygen (Buckel, 2021). The different ecology of the two pathways is explained by differential sensitivity to oxygen (Buckel, 2021), and indeed oxygen is likely to play a key role in their environmental distribution. Organisms capable of switching among the two pathways suggest generally prefer to express the energy demanding coenzyme B12-dependent pathway even in the absence of oxygen, to safeguard against possible oxygen exposure during fermentation. However, data suggest that the environmental variability of cobalt (in the form of vitamin B12 or Co^{2+}) can limit the expression of the oxygen tolerant coenzyme B12-dependent 3-methylaspartate pathway, forcing the organisms to express the less energy demanding but extremely oxygen sensitive 2-hydroxyglutarate (Ramezani et al., 2011).

A few recent papers have identified the availability and distribution of trace elements in the environment as explanatory variables for the distribution of selected microbial groups or specific proteins. The distribution of microbial groups related to known iron-oxidizing bacteria has been linked to the environmental availability of iron in the subsurface communities of Costa Rica's convergent margins (Fullerton et al., 2021) and the number of copper-containing proteins has been linked to the concentrations of copper in the hot springs of South China (Srivastava et al., 2020). Taken together these observations suggest a role for trace metal availability in influencing microbial functional diversity, and addressing this relationship might unlock important discoveries that could influence diverse fields like microbial ecology, bioremediation, and biotechnology.

Changing metal availability and the emergence and evolution of metabolism

During its ca. 4.55 billion years of history, our planet has changed from having a reduced atmosphere to a whopping 21 % of oxygen during two distinct (albeit still debated) oxidation events during the late Archaean (the Great Oxidation Event, GOE, approximately 2.4 billion years ago) and in the late proterozoic (the Neoproterozoic Oxidation Event approximately 540 million years ago). Both these events, due to a complex interplay of biotic and abiotic processes, have profoundly changed the planet surface redox state influencing the diversity of minerals (Hazen and Ferry, 2010) and the solubility of trace elements (Anbar, 2008).

Considerable work has been done to understand the changes in trace metals availability in the oceans through deep time (reviewed in Robbins et al., 2016)). The historical availability of many key metals remains debated, and, with the exception of Mn and Fe, the number of studies in the proxy record for the other elements is extremely limited (Robbins et al., 2016). Despite this, a number of studies have speculated on the role of changing metal availability in influencing the evolution of metabolism. In the first edition of their seminal book “The Biological Chemistry of the Elements” Da Silva and Williams (Da Silva and Williams, 2001) proposed that a cell’s trace element inventory requirement is directly related to the conditions under which the organism evolved. For example, the current dependence of life on iron can be seen as an evolutionary relict from a time where iron was soluble and highly abundant in the archaean oceans. Da Silva and Williams' idea has shaped research on the role of trace elements in controlling evolution in recent years. Yet despite this we have limited information regarding the metal cell repertoire of often uncultured, environmentally-relevant microorganisms and their trace metal requirements.

Ongoing efforts to understand the emergence and evolution of metabolisms on our planet included the use of geochemical proxies to look for signals of metabolic innovation in the geologic record (Anbar and Knoll, 2002; Anbar, 2008; Lyons et al., 2014; Robbins et al., 2016), the use of clues hidden in the genomic makeup of ancestral microbial lineages (Zerkle et al., 2005; Weiss et al., 2016; Giovannelli et al., 2017), experimental approaches to identify early respiratory pathways in deep-branching bacteria (Giovannelli et al., 2017; Jelen et al., 2018), or combined genomic and geochemical proxies (Saito et al., 2003; Dupont et al., 2010; Harel et al., 2014; Moore et al., 2017). These attempts suggest that there is a potential link between the environmental distribution of transition metals through time and their utilization within microbially encoded proteins to access diverse redox couples (Figure 2).

Yet, direct evidence is lacking, and available information points to a much more complex interaction. The evolutionary history of nitrogenase, a key enzyme in the nitrogen cycle responsible for converting the abundant but biologically unavailable N_2 into bioavailable ammonia, can highlight these complexities. The enzyme contains a unique cofactor known as FeMoCo, that participates in the 6 electron reaction breaking the triple bond of N_2 to form NH_3 (Sickerman et al., 2019). Three different homologous variants of the enzyme exist, each containing a different metal atom in the cofactor, either a Molybdenum, a Vanadium or an Iron atom (Figure 3). Nitrogenases are believed to be ancestral enzymes and appear to have evolved very early during life's history on this planet (Canfield et al., 2010; Mus et al., 2019). Among the three metals used in nitrogenases, iron was highly abundant in the Archaean ocean and its abundance drastically decreased following GOE, while the Mo and V very scarce in the Archaean ocean, given the insolubility of their sulfide minerals, and became abundant in the ocean in their oxyanion form following GOE (Anbar, 2008). Given this information it might be tempting to conclude that the iron nitrogenase might be the ancestral form, while the Mo and V dependent might have evolved following GOE. However phylogenetic analyses of the three variants suggest that a subcluster of the Mo-dependent nitrogenase is basal to the radiation of this fundamental enzyme (Garcia et al., 2020), rendering simple inference regarding the role of trace metal availability on influencing redox enzyme evolution more complex. Diverse hypotheses can be formulated to explain this discrepancy, including yet to be characterized basal nitrogenases (Boyd et al., 2015; Garcia et al., 2020), the extinction of basal lineages predating current enzymes and cofactor promiscuities in ancestral lineages. Whatever the reason, it is clear that simplistic conclusions regarding the nature of the relationship between redox changes during planetary evolution, metal availability and the emergence and evolution of metabolism need to be carefully evaluated.

Focusing on biogeochemistry

Of all the functions carried out by life that have an impact on the environment, biogeochemically relevant reactions play a key role in controlling geosphere-biosphere interactions. Biogeochemistry, or rather geobiochemistry (*sensu* Shock and Boyd, 2015), can be defined as the set of geological and biological processes controlling the (re)cycling of matter and elements across the different spheres of our planet through time and space. Biogeochemical cycles of different elements might be more or less dependent on biological processes, meaning that steps of the cycle carried out by biology might have a more or less prominent role compared to the corresponding abiotic process. For example, the surface sulfur cycle is controlled by a combination of geological and biological processes (Sievert et al., 2007; Brimblecombe,

2013), while the surface nitrogen cycle is dominated by microbial processes (Canfield et al., 2010) and its abiotic counterpart is quantitatively negligible on extant Earth.

I argue that biogeochemically relevant enzymes, defined here as the enzymes directly acting on redox sensitive compounds that are either acquired from outside or excreted outside the cell, constitute a class of metabolic enzymes that are of particular interest for understanding the coevolution of life and our planet. Oxidoreductases represent ~70 % of total biogeochemically relevant enzymes and are dominated by metalloproteins. The majority of known biogeochemically relevant oxidoreductases use one or more of the 11 elements described in the early section of this paper for electron transfer reactions. However, the complete inventory of elements used by life is incomplete, and additional discoveries are changing our perception regarding the interaction between life and the periodic table. For example, in the last decade we have discovered variants of the well known methanol dehydrogenase, the key enzyme catalyzing the conversion of methanol to formaldehyde in aerobic methanotrophs and usually containing a calcium cofactor, that are lanthanum, cerium and neodymium dependent (Fitriyanto et al., 2011; Schmitz et al., 2021). This significantly expands the number of elements used as cofactors by life and gives a new previously unrecognized biological role to the rare earth elements. Further studies will be needed in order to clarify the nature of cofactors used by biology and their role in metabolism emergence and evolution.

The future ahead

Understanding the roles of trace metal environmental distribution and availability in influencing microbial functional diversity holds the key to understanding the co-evolution of life and our planet (Figure 2). Additionally, it might unlock numerous important discoveries at the core of diverse fields like earth sciences, astrobiology, microbial ecology, bioremediation, and biotechnology. Addressing this research area will require an innovative and interdisciplinary approach combining recent advances in microbial ecology, biochemistry and earth sciences. The number of metallomic studies, detailed repertoire of a cell metal inventory, are limited (Barton et al., 2007; Cameron et al., 2012; Galera-Laporta et al., 2021), and limit our ability to investigate the role of trace elements in controlling metabolism in diverse organisms. Additionally, several environmental studies often overlook the importance of trace elements as potential explanatory variables in controlling microbial diversity, and a rapid survey of the available rock geochemistry measurements in EarthChem (Lehnert et al., 2007) show that only 1.01 % of the samples for which trace elements have been measured have data for all 9 major biological relevant metals (603 out of 59,602 EarthChem samples, <https://www.earthchem.org/>, accessed 22 January 2022). A major gap at the

interface between geosciences and biosciences that will need to be addressed. Direct tests of the role of trace elements in controlling microbial metabolic diversity could be obtained using a combination of bottom-up and top-down approaches. For example, the experiments by Shafiee et al. (2021) can be extended to co-cultures of bacteria and archaea ammonia oxidizers used in competition experiments to test for the response to changing iron and copper availability in the growth media. Or the influence of differential copper availability could be tracked sampling soils or springs along convergent margins where the concentration of copper in the basement rocks changes following subduction parameters (Figure 3), following the large-scale approach recently proposed by Giovannelli et al. (2022).

Focusing on the role of trace metals in controlling taxonomic and functional microbial diversity has far reaching implications for our understanding of life and the role the planet has played in its evolution, and might thus provide a new framework to interpret our planet evolution (Hickman-Lewis et al., 2020) and the search for life in the universe (Kacar et al., 2021; Covone and Giovannelli, 2022).

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Competing interests

The authors declare no competing interests.

Data Availability Statement

No data have been produced for this study.

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Figures

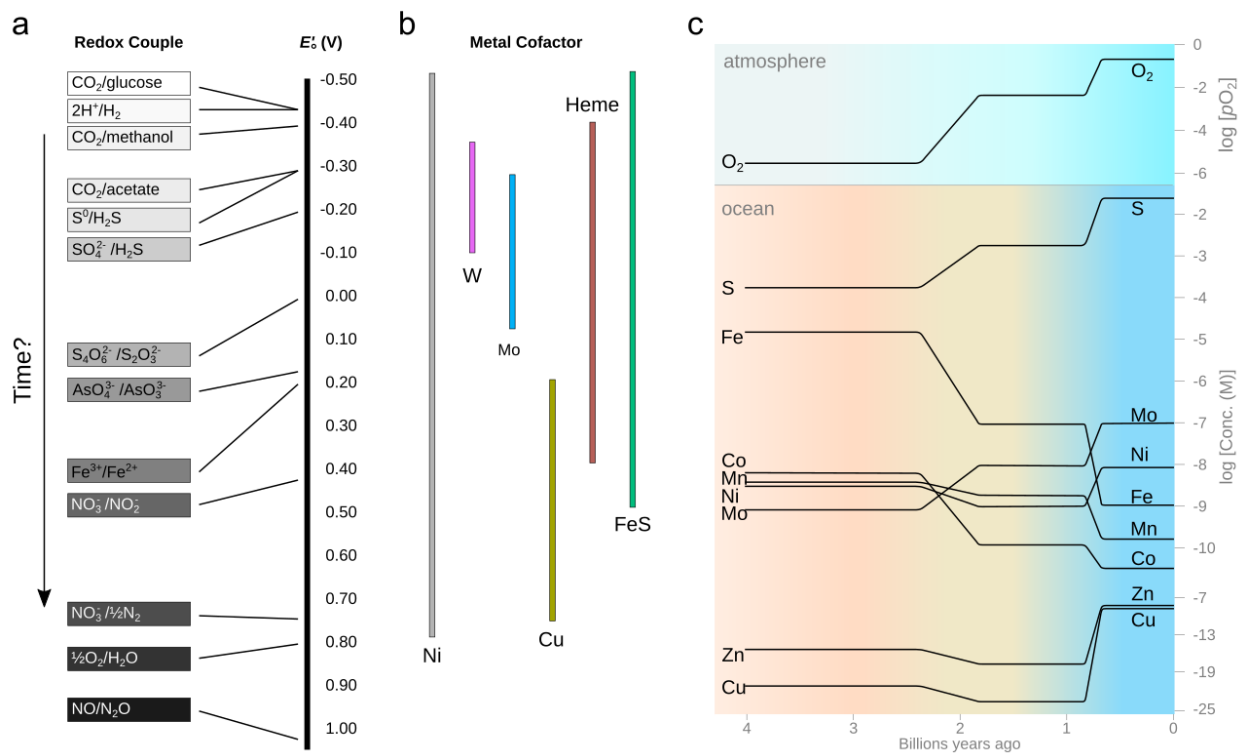


Figure 1. Microbial metabolism, transition metals midpoint potential and their abundance through time. **a)** a simplified redox tower used in microbiology to calculate the redox metabolic couples available to life. The order in which more oxidized redox couples appear in the tower coincidentally recapitulate their appearance during the planet evolution (see (Jelen et al., 2016)). **b)** Examples of metal cofactors used in metalloproteins and the extension of their midpoint potential, aligned on the E'_0 of panel a (data from (Crichton, 2019)). Variations are the result of changes in the position of the metal within the active site, coordinating amino acids and the structure of the protein. **c)** Changes in biologically relevant metal concentrations (adapted from (Anbar, 2008)) through time as a consequence of planetary surface redox change. Changing surface redox conditions changed both the availability of redox couples and the availability of transition metals used to access them.

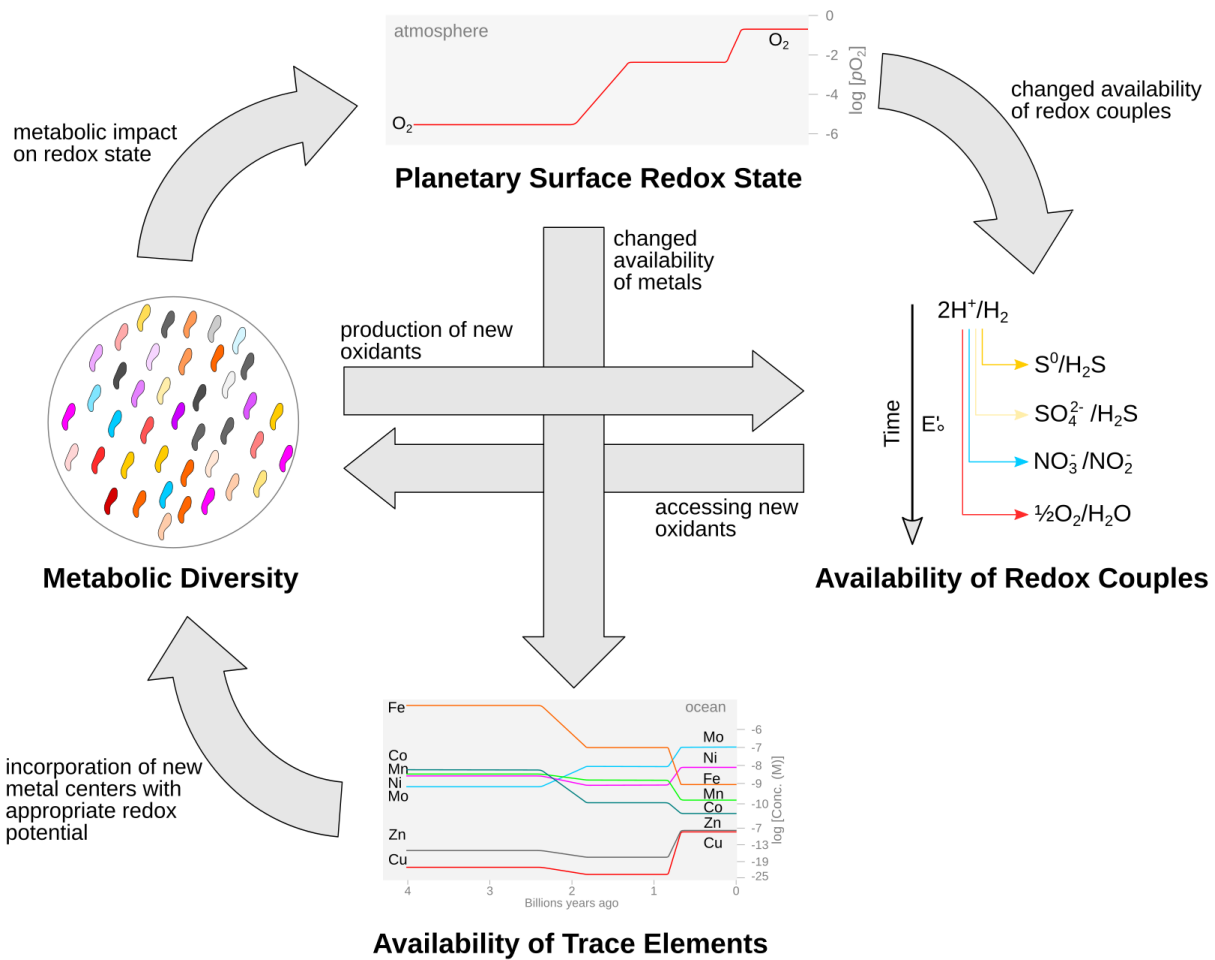


Figure 2. Overall overview of the proposed feedbacks between availability of trace elements, metabolic innovation and planetary surface redox state through deep time. The evolution of metabolic diversity is strictly linked to the availability of both diverse redox couples and appropriate metal cofactors to access them. Both are influenced by and influence the planet's surface redox state. A number of the shown feedback mechanisms might have had an outsized impact in driving the evolution of metabolism and in shaping current biogeochemistry.

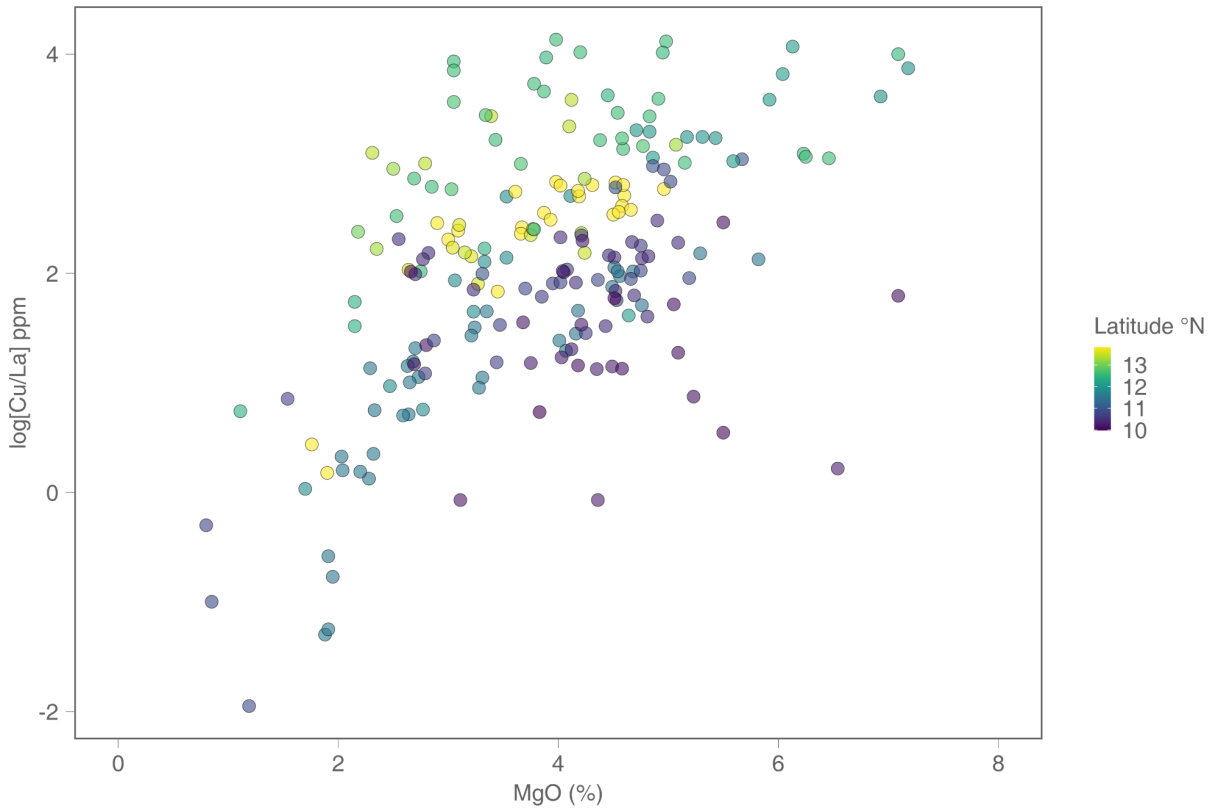


Figure 3. Variation in copper concentrations (normalized to lanthanum) as a function of MgO (wt %) in lavas from the Central America convergent margin. Latitude is plotted as color gradient. A clear trend following both magmatic evolution and latitude is present. Soil or spring samples collected in areas of similar rock types (as represented here by similar MgO concentrations) following latitudinal gradients could be used to test for the effect of varying copper concentration on the microbial functional diversity. Data from the Central American Volcanic Arc Rock Database (Carr et al., 2014).