

# Sulfur, trace metals, microbial community structure, and the evolution of atmospheric oxygen

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## Introduction

Major changes over geologic time occurred in biologically-important trace metal concentrations in the oceans such as Ni (Konhauser et al., 2009), but this list also includes Co, Cr, Cu, Zn, Mo, Mg, Mn (e.g. Williams and Fraústo da Silva, 1997). Previous studies have explored ferro-ferric-oxides for trace metals in Precambrian banded iron-formations (BIFs), but another robust time-dependent record of such signals in the ancient marine system is sulfide minerals. Enrichment of seawater in ferrous iron and the transformation to abundant  $\text{Fe}_3\text{O}_4$  in marine sediments was the signature style of sedimentation under anoxic conditions on the early Earth when oceanic Fe(II) concentrations were high. Sulfides incorporated into BIFs probably sample sulfur to the water column from atmospheric or magmatic exhalative sources at time of deposition, and the chemical interaction of metal-sulfides with seawater prior to diagenesis. BIF sulfides carry the added dimension that in the case of sediments older than about 2.4 Ga – and prior to the ‘Great Oxidation Event’ (GOE) – they can host sulfur isotope signatures that track  $p\text{O}_2$  rise from the demise of mass-independent sulfur isotope fractionations (MIF; e.g. Papineau et al., 2007; Guo et al., 2009). Here, two ideas (trace metals and MIF sulfur) are combined together into a singular metric to explore changes to global surface redox and to draw some conclusions about gross changes to marine microbial community structure over geologic time.

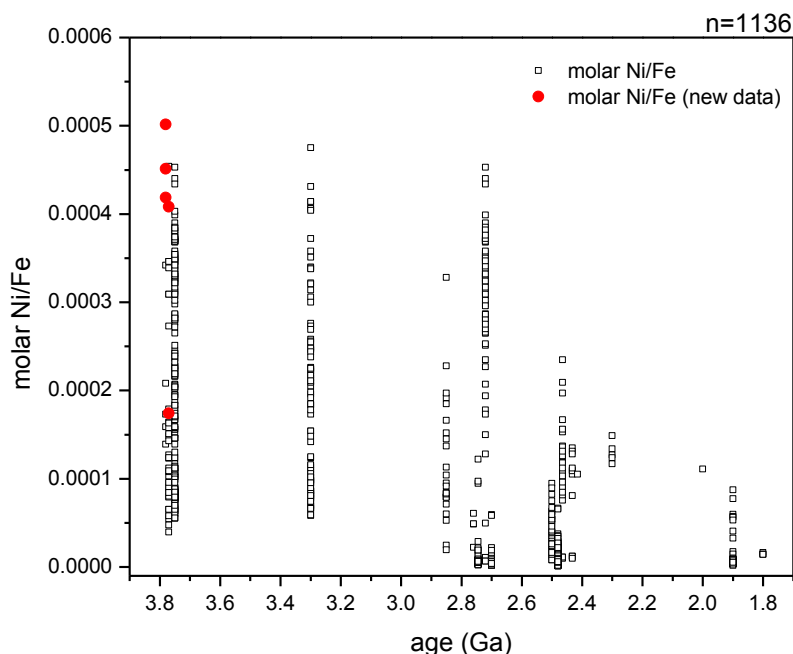
## Theory

The structure and composition of microbial populations have modulated the geochemical cycles and seawater concentrations of the bio-essential elements (S, P, O, N, C, H, Fe, S, etc.) and those trace metals (e.g. Ni, Co, Cr, Zn, Mo, Mg, Mn and others) which figure prominently in life (see review by Saito et al., 2003). Concentrations of these seawater trace metals had to have changed in response to changes in the Earth System, such as the rise of oxygen. Increase in the oxidation state of the Earth’s atmosphere/hydrosphere system is reasonably well documented, but the reasons why are not. Acute  $p\text{O}_2$  increases that accompanied the GOE (whether stepwise, catastrophic, oscillatory or gradual/asymptotic; this has yet to be determined, see Anbar et al., 2007) governed changes in nutrient abundances of the oceans, such as N and P availability (Bjerrum and Canfield, 2002). But how? The timing and trajectory of atmospheric oxygen evolution could also have been dictated by the combined effects of (oxygenic) photosynthesis and the composition of volcanic gases (Holland, 2002). However, changes in mantle  $f\text{O}_2$  over the past 3.8 Gyr were slight (Li and Lee, 2004). Paleoarchean microfossils regarded as oxygenic photosynthetical microbes (‘cyanobacteria-like structures’) as old as 3.49 Ga (e.g. Schopf, 1994), are ambiguous (Brasier et al., 2002). Stromatolites are not exclusive to cyanobacteria (Papineau et al., 2005); and molecular biomarkers considered as good evidence for cyanobacteria by ~2.8 Ga (Brocks et al., 1999) are likely younger than that (ca. 2.3 Ga; Rasmussen et al., 2008).

The question reduces to: Do we know when oxygenic photosynthesis appeared? If cyanobacteria emerged slightly **before** the time of the rise of  $\text{O}_2$  recorded in the geologic record it might be possible to track this appearance in trace metal concentrations in banded iron-formations.

## Trace metals and banded iron-formations: case studies in Ni and Co

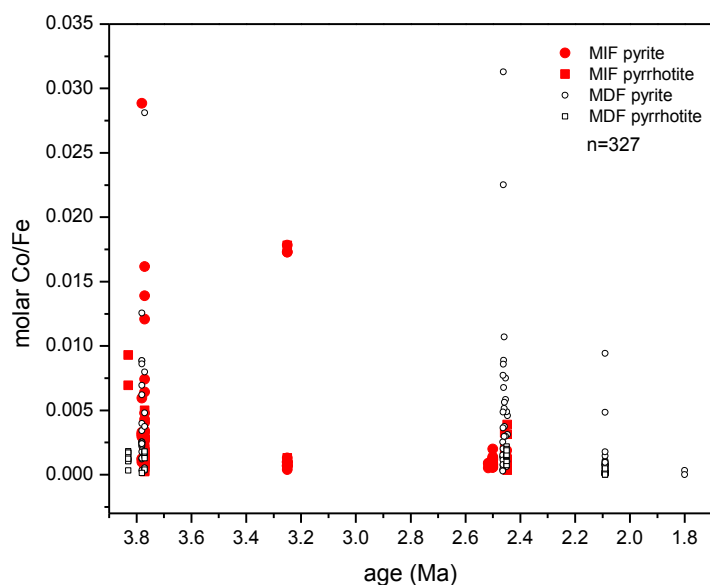
The rise of free O<sub>2</sub> in the Paleoproterozoic probably led to the ultimate demise of the 'classic' finely laminated banded iron-formations by about 1.7 Ga, but not before they reached their 'peak' in abundance in the Paleoproterozoic (Klein, 2005). Since BIFs are the principal sedimentary rock of the (early) Precambrian and because they are marine sedimentary precipitates, they are the sole repositories of data about the nature of surface environments which include the establishment of the biogeochemical cycles, changes in atmosphere/ocean redox and the evolution of hydrothermal and ocean chemistry from the earliest times.



**Figure 1.** Molar Ni/Fe for BIFs vs. age in 10<sup>9</sup> years (Ga). The 1,136 data points reported here include literature data in Konhauser et al., 2009, and other published bulk (red) analyses for Eoarchean BIFs (Mojzsis, 2007). These data were previously used to argue that a 'Ni famine' after ~2.7 Ga was responsible (at least in part) for the collapse of atmospheric methane that facilitated the rise of atmospheric oxygen at ~2.4 Ga.

Konhauser et al (2009) documented systematic changes in molar Ni/Fe ratios in BIF Fe-oxide phases (magnetite, hematite) which was attributed to changes in ocean chemistry, effective mantle temperature (and thereby degree of partial melts that determine metal content such as Ni, but also Co and Cr), and oxidation state of the atmosphere-hydrosphere system (**Figure 1**). These authors interpreted their trace-metal data to mean that a decline in the molar Ni/Fe in BIFs starting about 2.7 Ga is attributable to a reduced flux of Ni to the oceans. Since Ni is a key metal cofactor in several enzymes of methanogens (Juan and Thauer, 2007) it could mean that Ni decline would have stifled methanogenesis and led to a decline in biogenic methane production even before oxygen began to appear in the environment. What is unique about the Konhauser et al. (2009) study is how they showed that enzymatic reliance of methanogens on a diminishing supply of volcanic Ni links mantle evolution to the redox state of the atmosphere. Importantly, it is entirely likely that photoferrotrophs (Crowe et al., 2008) shared dominance of the marine microbial system with the methanogens prior to the appearance of cyanobacteria. If changes in seawater trace metal (Ni) concentrations (and in supply of nutrients such as N and P) influenced the evolution of methanogens, it likely did this to methanotrophs, photoferrotrophs, and cyanobacteria. Hydrogenases from purple bacteria contain nickel and a Fe-S cluster (Zorin, 1986) and aside from the necessary Ni for methanogenesis (see Hausinger, 1987) Cobalt is also important since it occurs in vitamin B<sub>12</sub>, the tetrahydrofolate pathway (which is very ancient), and in CO and N utilization by methanogens.

Cobalt, like Ni, shows major changes relative to Fe around the time of the GOE (**Figure 2**).



**Figure 2.** Molar Co/Fe for BIF sulfides vs. age (Ga). The 327 measurements include literature reported in Mojzsis (2007), and new unpublished data. The results show a change over time in Co/Fe similar to that observed in **Figure 1** for Ni/Fe.

## Tempo of oxidation associated with major changes in global marine microbial community structure

Data still leave unexplained the tempo of oxygenation of the surface zone. If cyanobacteria were present ~2.7 Ga or earlier (Brocks et al., 1999; cf. Rasmussen et al., 2008), why did it take so long to see their effects on the global environment?

Hypothetically, a cyanobacterium growing exponentially with a doubling time of 24h and given an ocean volume of  $1.5 \times 10^9$  km<sup>3</sup> could populate Earth's oceans to a density of  $10^9$  cells/mL in a little over a week.

Diffusion time for cells, and dispersal considerations probably

limit this to 12-18 months. Leveling-off of microbial growth after a period of exponential increase usually involves poisoning of the growth medium with waste, consumption of metabolites, and limitation of essential nutrients. Cyanobacteria have an unlimited supply of an electron donor (H<sub>2</sub>O), and energy to drive chemical reactions (light). Waste is easily dealt with as O<sub>2</sub> is relatively insoluble in water and will partition to the gas phase, diffusing away. Another sink for waste O<sub>2</sub> from cyanobacteria would be through the rapid abiotic oxidation of Fe(II) that was abundant in the ancient oceans, as well as methane in the atmosphere and oxidative weathering of land surfaces. Conceivable limits to growth would be the volume of ocean exposed to the appropriate photon flux, essential nutrients (N, P), trace metals needed to arm enzymatic centers, and dispersion of cells to new habitats by wind and currents.

However, a relatively late (~2.5 Ga) emergence of cyanobacteria could plausibly explain the rise in oxygen in the Paleoproterozoic around 2.4 -2.3 Ga and major changes in the Fe, Ni and Co cycle (**Figure 2**), and the "Whiff" of oxygen in the Neoproterozoic (ca. 2.5 Ga; Anbar et al., 2007). If photoferrotrophs (Crowe et al., 2008) shared dominance of the marine microbial system with the methanotrophs prior to the appearance of cyanobacteria, it is eminently conceivable that changes in seawater trace metal concentrations (and in supply of nutrients such as N and P) stymied cyanobacteria. Did cyanobacteria appear about the time of the "Whiff" and were suppressed by N and P limitation until they could evolve adaptive strategies to cope with these limitations in P (Van Mooy et al., 2006; Ji and Sherrell, 2008) and N (Madigan et al., 2000)?

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