Inorganic geobiochemical implications of the oxic-anoxic transition in ancient Earth oceans

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The development of free dioxygen in the Earth's atmosphere around 2.2Ga led to considerable biological changes. In particular, the early Earth biota was dominated by anaerobic prokaryotes including archaebacteria, possibly the most primitive life forms. Subsequent to the development of an oxic environment, aerobic bacteria and eventually prokaryotes developed. The inorganic biochemistry of the two groups are characterized in part by the relative dominance of nickel and cobalt proteins in the primitive anoxic group and the appearance of copper proteins in aerobic bacteria and multicellular organisms (Frausto di Silva and Williams 1996). Nickel and cobalt proteins are less important in aerobic organisms and copper is insignificant in the primitive anaerobes. Iron and zinc appear equally important throughout, although their dominant biochemical functions change.

It is well established that base metal concentrations constitute limiting growth factors for present-day aerobic and anaerobic communities. For example, increasing oceanic iron concentrations enhances the growth of planktonic algae (Martin et al 1991). Iron has long been known as a limiting factor for the development of anaerobic sulphate reducing bacteria because of its importance to cytochrome c_3. (Postgate 1965). The present paper presents the results of a study of thermodynamic of oxic and anoxic ocean models based on the recent definition and discovery of a large number of base metal sulphide and polysulphide complexes (Luther et al. 1996; Chadwell et al. in prep). I assume that biological availability potentially embraces any soluble metal species and not only free metal aquo ions.

The chemical models were made using Geochemists' Workbench® version 3.4 (GWB). The GWB seawater model has been discussed by Bethke (1996). The input thermodynamic database is a modified selection of the Lawrence Livermore National Laboratory thermodynamic dataset THERMO.COM.V8.R6.FULL. based on a compilation by Thomas Wolery and co-workers which is in turn largely based on Helgeson et al.(1978). The composition of early Earth oceans is not rigorously constrained and both acid and alkaline oceans have been proposed. I take a conservative view in this study, assuming that ocean composition is currently buffered by reaction with oceanic lithosphere and that this effect is likely to have been enhanced in the higher heat flow regimes of the ancient Earth. As a starting point, I therefore take the composition of the modern oxic oceans, which is fairly well defined. I then reduce it through the GWB reaction progress algorithm, basically by titrating electrons. During this process, the total major element concentration (excluding dioxygen) of the oceans remains constant. The pH remains around 8.0.

In *oxic oceans*, inorganic base metal chemistry is dominated by free metal aquo ions, hydroxide, oxyhydroxide and chloride complexes. The database includes a number of simple base metal organic complexes, but these do not appear to affect the model and their stability constants may not be well-constrained.

In *anoxic oceans*, base metal speciation is simplified and their chemistry is largely controlled by sulphide and bisulphide complexes. The introduction of base metals (bi)sulphide complexes into the anoxic ocean model increases the relative dissolved concentrations of all base metals except Mn. The enhancement is approximately 2 magnitudes or more. This relative enhancement is independent of the sulphide mineral substrate. The total dissolved metal concentrations decrease markedly with peak concentrations around $-200mV$. The concentrations increase from around $-300mV$ through $-400mV$. A feature of the anoxic ocean is the diminution of the free metal aquo ion concentrations.

I took a computed dissolved metal concentration of 10^{-15} M as being a limiting value for the presence of the metal in solution. The absolute concentrations of base metals in anoxic systems is not well constrained because of the lack of information about the nature of the metastable mineral sulphides. The increase in solubility of metastable compared with stable iron sulphides is better known . The first precipitated FeS

is some 13 magnitudes more soluble than stable pyrite and dissolved Fe was present in nanomolar concentrations in the anoxic ocean . By analogy, Co and Ni bisulphide complexes probably led to similar dissolved metal concentrations The results suggest that the Mn, Fe, Co, Ni and Zn were biologically available in primitive anoxic ocean but that Cu was not. In oxic oceans, Cu becomes available at concentrations $> 10^{-15}$ M . However, the low concentrations of dissolved metals implies that they constituted limiting factors for biological development in the early anoxic ocean as in the present oxic oceans. Suggestions that the life originally evolved in base-metal rich environments, such as hydrothermal vents, are consistent with this conclusion.

In *suboxic oceans,* which must have occurred during transitional period(s) during the development of oxic oceans, polysulphide complexes of the base metals become potentially significant. Interestingly, Cu polysulphide complexes have surprising stabilities and $Cu_2(S_4)_2$, for example, is stable down to pH>2 with $b_1 \sim 17.8$.

The results are consistent with the relative importance of base metals in different evolutionary groups of organisms. In particular, methanogen (archaebacteria), cultivation requires an initial Eh of -400 mV, coincident with the enhanced solubility of Ni (and Co) bisulphide complexes. Likewise, sulphate-reducers (anaerobic bacteria) require an initial Eh of -200mV for cultivation. Cu is widely toxic to organisms and was virtually absent from these primitive anoxic systems. The increase in copper bioavailability through polysulphide complexing in the sub-oxic ocean would have provided an ecological niche for organisms able to handle significantly enhanced dissolved copper concentrations. Organisms seem to manage this at present through periplasmic and membrane-situated, thiol-rich proteins. Frausta da Silva and Williams (1991) note that copper enzymes are used during extra-cellular oxidative, free-radical coupling involved in the development of the connective tissues necessary for the development of multi-cellular life.

References

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