

Tight coupling of life and metals throughout evolution

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The chemistry of the environment is intimately tied to the chemistry of life in a feedback system. The original reductive chemistry of life inexorably drove oxidation of Earth's surface. The contrast in solubility products between hydroxides and sulfides lead to a predictable sequence of altered environmental concentrations of metals. Some metals increased in availability: notably the latecomers, Cu and Zn, but others decreased e.g. Fe. Such changes are charted in the chemistry of ancient sediments.

Signals of the changing metal environment can also be found in the genomes of extant life. A rise in the number of Cu and Zn metal domains in proteins, fundamental to the advancement of life towards complexity and multicellularity, parallels the increasing Cu and Zn in the environment. This implies that the initial rise of oxidative products, and newly available metals, at first toxic to life, could be turned to advantage by leading to the emergence *de novo* of catalysts allowing increased complexity to evolve [1].

By contrast, a decrease in environmental availability of metals already exploited by enzymes, can drive substitution by new metals to perform old functions, at least in labile enzymes. An example is the change in metalcentre found in "cytochrome-c oxidase". The original protein was likely based on Fe only but later it became the copper-dependent, O₂-reducing enzyme cytochrome oxidase, seen today.

The recent identification of an unusual Cd/Zn carbonic anhydrase from the marine diatom *Thalassiosira weissflogii* [2] has revealed a biochemical function for Cd, substituting for Zn. This discovery holds the potential to explain the long-standing mystery as to why Cd, regarded as toxic to life, displays a nutrient-like profile in the modern ocean and isotopic (¹¹⁴Cd/¹¹⁰Cd) compositions which indicate removal into phytoplankton. We investigate whether this single known biological role for Cd can account for its apparent nutrient like behaviour by analysing the isotopic fractionation of Cd in the model bacteria, *Escherichia coli*, which have been transformed to express the CDCA1 gene. Our results demonstrate that whole cells accumulate and fractionate Cd regardless of CDCA1 expression. Our analysis of different cellular components suggest that, rather than direct use of Cd, it is detoxification in response to inadvertent Cd acquisition which is responsible for the fractionation of Cd isotopes. Such detoxification mechanisms are highly conserved across the diversity of life, and we conclude that detoxification acts as the driving force of the observed seawater Cd concentration and isotopic variations. In order to explain the negligible response of Cd uptake to expression of CDCA1, we shall explore if this unusual enzyme is a labile form of the conventional, non-exchanging carbonic anhydrases.

[1] Williams and Rickaby, *Evolution's Destiny*, in press, [2] Xu, *et al.*, (2008) *Nature* **452**, 56-61.

Interrogating >1Myr Time-Scale Controls On Ocean Chemistry In A 3D Model?!

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Marine archives of paleo environments, particularly when encoded in deep-sea sediments, can be highly spatially heterogeneous. Whilst box models have had success in interpreting environmental heterogeneity on a basin-scale, fully 3D ocean-based models are required to resolve the geological record at any finer spatial resolution than this. However, the extreme scale contrast between the typical time-step required by dynamical ocean models – order days (or considerably shorter), and the 100 kyr time-scale of weathering feedback to >1 Myr residence time of many trace metal and isotope systems of interest, presents a seemingly insurmountable barrier (unless one is prepared to wait the best part of a year for a model experiment to finish).

I will present a new methodology applied to a 3D Earth system model ('cGENIE') that involves alternating its behavior between fully 3D climate+carbon cycle and mass balance 'box' model modes. In so doing, solving the silicate weathering feedback can, for example, be accelerated by a factor of 10-100 compared to a fully dynamical calculation but with a virtually identical end result. To avoid boring you stupid with a discourse of pure technical model details, I will illustrate how the $\delta^7\text{Li}$ composition of the ocean responds to massive CO₂ release and warming and how the encoding of this emerging weathering proxy in marine carbonates relates to more established proxies (e.g. wt% CaCO₃, $\delta^{13}\text{C}$) for tracking changes in global carbon cycling.