

Biogeochemistry as a regional mineral exploration tool: Northeast Yilgarn Craton, Western Australia

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Regional biogeochemical surveys can potentially be of great use for mineral exploration where access problems and the hindrance of transported overburden make other techniques problematic. A large area of the north Yilgarn Craton hosting numerous Ni, Au, U and VMS deposits was selected for this proof of concept study. *Acacia aneura* (mulga) was sampled approximately every 8 km in this region as it is one of the most widespread plant species across Australia. Mulga samples were collected at water wells and bores corresponding to a regional hydrogeochemistry sampling program. Vegetation samples were dried, split, milled, digested in aqua regia then analysed using ICP-MS/OES. A large, robust, statistically verified geochemical data set was generated which provides the ability to detect lithological signatures using geochemical indices and multivariate statistics (with around 20% error of prediction). Uranium in mulga was the only distinct target element for secondary U deposits, and was successful for most known prospects. Gold exploration potential was improved by the use of multi-element indices. Nickel prospects were identified where the samples were close to the prospects (<2 km) or where supergene mineralisation was dispersed. The Leinster and Murrin Murrin areas were highlighted by elevated Ni, Co, Cr and Fe concentrations compared to background with haloes up to 20 km wide. Detection of VMS style deposits is hampered by Zn and Cu being essential plant nutrients however, high Zn values seen on the regional scale may warrant further investigation. Little correlation exists between hydrogeochemistry and biogeochemistry, meaning one cannot be used as a surrogate for the other; however, both are useful tools in detecting mineralisation and lithological signatures using different chemical properties for a regional setting. Also, mulga can be sampled without the need for drilling to access groundwater.

Sensitivity and feedback in the oceanic molybdenum cycle

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The oceanic inventories of trace elements have fluctuated markedly during Earth's history as a function of prevailing Earth surface redox conditions. Given the importance of many trace elements in a wide variety of enzymatic processes, such changes may have had significant downstream effects on the global biogeochemical cycling of carbon, nitrogen, and oxygen [1]. Molybdenum (Mo) is particularly important in this regard, being a crucial catalytic component of enzymes involved in biological N₂ fixation, assimilation of NO₃⁻, and oxygen atom transfer reactions.

Here, we explore the response of the oceanic Mo reservoir to perturbations in marine redox in a one-box ocean model in which Mo enrichment and burial are first-order with respect to the ambient Mo reservoir. Despite imposing this negative feedback, we find that relatively small changes in ocean redox can have significant effects on the concentration of Mo in seawater ([Mo]_{sw}) at steady state, and that relaxation to steady state following perturbation occurs relatively quickly. In addition, although it is possible to draw down [Mo]_{sw} to levels that would have been likely to exert negative effects on some biological processes, the muted enrichments seen in many Proterozoic black shales [2] are likely not compatible with global-scale sulfidic conditions.

In order to further explore the feasibility of attaining varying degrees of expanded anoxia we employ a simple oxygen budget for the modern North Atlantic. This exercise corroborates that of [3], and suggests that the redox state of the deep ocean could have been severely impacted purely by air-sea gas exchange limitations at presumed Proterozoic atmospheric oxygen levels. Further, a simple regional budget of sulfide and highly reactive iron (Fe_{HR}) fluxes to marine sediments suggests that were the ocean to become anoxic due to limited O₂ supply (as in the Proterozoic) the deep ocean would most likely have become ferruginous (anoxic and Fe-rich) [4] while marginal environments would likely have been prone to sulfidic conditions.

[1] Anbar & Knoll (2002) *Science* **297**, 1137–1142. [2] Scott *et al.* (2008) *Nature* **452**, 456–459. [3] Canfield (1998) *Nature* **396**, 450–453. [4] Poulton & Canfield (2011) *Elements* **7**, 107–112.