

Nickel isotopes, BIFs and the Archean oceans

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Trace metal isotopes provide vital clues to the Earth's biogeochemical evolution. Key to these efforts is the development and application of new isotopic systems of bioessential elements important to specific organisms or metabolisms or, as recorders of changing environmental conditions through time. Nickel (Ni) is primarily restricted to microorganisms and metabolisms that might have evolved in a much different Archean environment [1-3]. Methanogens and their particular metabolism, methanogenesis, purportedly fit the criteria for an ancient origin of evolution and many studies have shown the absolute requirement that these microorganisms have for Ni.

Recently, we published the first measurements of nickel stable isotopes from abiotic terrestrial materials and pure cultures of methanogens [4]. Terrestrial samples representing the mantle and crust displayed very little isotopic variability (average $\delta^{60}\text{Ni}$ of $0.15 \pm 0.24\%$, 2σ). In contrast, Ni isotopes were significantly fractionated by pure cultures of methanogens. The largest fractionation, $\delta^{60}\text{Ni}$ of $-1.46 \pm 0.08\%$, was achieved by a methanogenic hyperthermophile. Our data suggest the biological cycling of Ni may be an important contributor of Ni isotopic variations in the rock record. Furthermore, biological fractionation of Ni has the potential to be a powerful new biomarker particularly in regards to the nature and impact of early life.

We have started evaluating our new Ni isotopic tool by applying it to the measurement of Ni stable isotopes in banded iron formations (BIFs). In order to characterize the Ni isotopic composition of the geochemical and biological environment of the primitive Earth, it is essential to first understand the state and changing conditions of the Archean oceans. Such information recorded within BIFs and other terrestrial materials is necessary to support our continued efforts to establish Ni stable isotopes as a functional and detectable biosignature.

[1] Bapteste *et al.* (2005) *Archaea* **1**, 353-363. [2] Fraústo da Silva & Williams (2001) in *The Biological Chemistry of the Elements: The Inorganic Chemistry of Life* (Oxford University Press, Oxford), pp. 436-449. [3] Tice & Lowe (2006) *Earth Sci Rev* **76**, 259-300. [4] Cameron *et al.* (2009) *Proc Natl Acad Sci USA* **106**, 10944-10948.

The weathering of platinum from nuggets and platinum immobilisation by *Cupriavidus metallidurans*

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Platinum nuggets, collected from a platiniferous and auriferous site near Fifield, New South Wales, Australia were examined to evaluate mineral dissolution-precipitation processes occurring at the nugget-'soil solution' interface. Nuggets possessed striations indicating mechanical transport with the soil environment and micrometer-scale dissolution pits corresponding to regions possessing soil materials (quartz, clays and organics) and acicular, iron oxides suggesting an oxidising weathering environment. The occurrence of 100 nm-scale, cubic minerals at the soil solution interface and comparably sized cubic dissolution 'pits' suggest that platinum weathering occurs via preferential dissolution of the 'bulk' platinum nugget (an Fe-Pt alloy). Examination of these cubic minerals using scanning electron microscopy in secondary electron and back-scattered electron (BSE) imaging modes, and using energy dispersive spectroscopy indicated that they are enriched with copper (i.e., a Cu-Pt alloy). Growth of platinum nuggets via secondary platinum mineral formation was not observed. *Cupriavidus metallidurans* cultures reacted with 0.5 and 5 mM platinum (IV) chloride, immobilised platinum from solution rapidly i.e., within minutes. EXAFS/XANES analysis of these reaction systems demonstrated that most of the Pt(IV) chloride complex was reduced to Pt(II) and that platinum binding shifted from chloride to primarily, amino functional groups. Using transmission electron microscopy, *C. metallidurans* was also found to precipitate nm-scale colloidal platinum when exposed to 5 mM platinum (IV) chloride; the formation of these colloids occurred within the bacterial cell envelope. Understanding the biogeochemistry of platinum, in particular weathering and formation of colloids has important implications within geologic settings, i.e., for platinum dispersal in relation to exploration geochemistry programs.