

The marine Pb isotope response to ice sheet growth and decay

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Northern hemisphere ice sheet growth during glacial periods caused intense physical erosion over large areal extents (~30% current land surface). The contribution of continental weathering products to the ocean associated with high latitude glaciation is poorly constrained and hampers efforts to model its impact on glacial/interglacial CO₂ cycles. During the Quaternary, early stage weathering of U+Th rich accessory phases that were freshly exposed during glacial periods is likely to have preferentially released radiogenic Pb to the subglacial, proglacial, and eventually marine system. Thus, the seawater Pb isotopic composition might act as a regional proxy for the riverine alkalinity flux to the oceans. Here we discuss the potential of this proxy at high temporal resolution for the last 45 ka at two sites from the NE and NW Atlantic, Feni Drift (ODP Site 980) and Orphan Knoll (IODP Site U1303) respectively, with additional constraints provided by glacial sediment analyses.

Pb isotope data from ferromanganese crusts [1] have been used to postulate greater weathering intensity during interglacial periods, but low temporal resolution precluded investigation of the detailed structure of the record at glacial inception and termination. We have applied a tested method of Pb extraction from authigenic Fe-Mn oxyhydroxide phases in marine sediments [2] to obtain higher resolution data from the two ocean cores. Results from both sites exhibit abrupt shifts in Pb isotope ratios to values significantly more radiogenic than obtained from Fe-Mn crust data.

Both sites show elevated ²⁰⁶Pb/²⁰⁴Pb in the early Holocene attributed to enhanced chemical weathering of terrestrial glacial deposits on initial exposure to a warmer, more humid climate. However, significant differences in the data occur during the glacial and deglacial portions of each record reflecting the different instability of the Laurentide and British ice sheets and the related delivery of ice rafted debris (IRD) to the North Atlantic. Glacial sediment and corresponding leachate Pb isotope ratios are used to explore the influence of subglacial weathering on solute composition, and hence to investigate the possible reasons for the radiogenic Pb excursions associated with IRD events.

[1] Foster, G.L., & Vance, D. (2006) *Nature* **444**, 918-921.

[2] Gutjahr, M. *et al.* (2007) *Chem Geol* **242**, 351-270.

Geochemistry of Mo in a modern Archean ocean analogue

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The aqueous geochemistry of molybdenum is typically thought of as bimodal: under oxic conditions it is largely particle-unreactive whereas, under sulphidic conditions, it is readily scavenged and sedimented [1]. Accordingly, the accumulation of Mo in marine sediments is often used as a proxy of anoxic conditions [1]. On the other hand, less is known about the reactivity of Mo under suboxic conditions and its affinity towards the (hydr)oxides of Fe. Such knowledge is critical to evaluate the Mo distribution in sediments deposited from the ferruginous Archean oceans like banded iron formations (BIFs).

The geochemical behaviour of Mo in the redox stratified, S-poor, 600-m deep, ferruginous water column of Lake Matano, Indonesia was investigated. Whereas dissolved Mo concentrations are relatively high in the oxic epilimnion (275-350 pmol l⁻¹), they decrease sharply across the chemocline between 100 and 200 m depth before increasing progressively with depth to the bottom. The profile suggests scavenging of Mo by Fe (hydr)oxides within the vicinity of the 100 m oxycline. Settling through the suboxic water column, followed by the reductive dissolution of these Fe (hydr)oxides at depth and in the sediments would explain the increase in Mo concentrations below 200 m.

[1] Anbar (2004) *Rev. Mineral Geochem.* **55**, 429-454.