Assessing sea ice algal productivity in the Western Arctic: A combined biomarker and GCIRMS approach

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The Western Arctic Ocean is an area undergoing significant climatic changes, the affects of which on the carbon cycle are not yet well understood. Decreased sea ice cover may lead to increased primary productivity in the photic zone in the absence of light attenuation from sea ice. However, overall primary productivity could be diminished by ice loss, by removing the contribution made by algae embedded in sea ice in the Chukchi and Beaufort seas. Recent studies by Belicka *et al*. [1] and Gradinger [2] have used a molecular biomarker approach to estimate the extent of marine and terrestrial inputs to the Chukchi and Western Beaufort Seas. Gradinger [2] suggested that the proportion of sea ice algal productivity to the marine primary productivity in the region may be as high as 4-26% in seasonally sea ice covered areas. However, the sources of a number of biomarkers are unclear, as certain biomarkers used to identify terrestrial and phytoplankton sources have also been isolated from sea ice algae. It is therefore important that the source of these compounds to sediments be determined in order for unambiguous interpretation of the biomarker data to be possible.

Through compound specific analyses performed on a series of cores from the Western Arctic and of the sea-ice algae *Melosira arctica*, origins of the carbon are able to be determined. We have established through bulk carbon isotope analysis that *Melosira arctica* sourced compounds will have the most enriched signature, with a bulk carbon value of -18‰, with local peat and riverine POM sources being most depleted at -28‰, whilst water column phytoplankton are characterized by a variable, but intermediate value around -22‰. Compound specific isotope analysis will then be corroborated with bulk carbon, nitrogen and sulfur data to assess the contribution of sea ice algal input to the carbon cycle in the western Arctic Ocean.

[1] Belicka, LL, Harvey, HR (2009) *Geochimica et Cosmochimica Acta,* **73**, 6231–6248. [2] Gradinger, R (2009) *Deep Sea Research II*, **56**, 1201–1212

The interactions of neptunium with Fe(II) bearing biogenic mineral phases

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Neptunium is a long-lived, redox active, radionuclide that is significant in the global radioactive waste legacy. Under oxic conditions, Np (V) is predicted to be relatively mobile as NpO_2^+. In contrast, under reducing conditions, highly insoluble Np (IV) dominates. Biogenic Fe (II) bearing phases are likely to be significant in controlling the redox chemistry of the sub-surface in both contaminated land and geo-disposal scenarios. Here we describe a highly select series of X-ray absorption characterisation experiments to understand the redox cycling behaviour of neptunium during exposure to key biogenic Fe (II) bearing phases, and on reoxidation of these phases. For reduction experiments, Np sorption to biogenic Fe (II) bearing minerals including magnetite, vivianite and Fe (II) media was variable. Furthermore, for the sorbed Np component XANES analysis showed clear evidence for abiotic reduction to Np (IV). For air reoxidation systems, remobilisation of Np to solution was dependent on Np (IV) reoxidation to Np (V). Reoxidation of Np (IV) was retarded compared to oxidation of Fe (II). Similarly, with microbially mediated nitrate mediated oxidation in the Fe (II) media sample, Fe (II) was readily oxidised to Fe (III) but Np (IV) was recalcitrant to reoxidation and remobilisation. Overall these results highlight the complexity of Np redox cycling in key biogenic Fe bearing minerals and indicate the importance of biogeochemical cycling to transuranic element behaviour in materials relevant to the global nuclear waste legacy.