Deep Sea Metalliferous Deposits as Modern Analogues for Ancient Marine Environments

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Modern seafloor metalliferous deposits provide unique analogues of ancient deposits currently mined on land. Their study is crucial for the establishment of genesis models and their relationships to oceanic and crustal evolution through time. Trace metal concentrations and isotopic compositions of laminated, organic matter-rich sediments (i.e. black shales) and iron formations are now widely used to draw inferences concerning paleoredox conditions as well as metal inventories in ancient oceans. Transition metal isotope geochemistry (e.g. Fe and Mo isotopes) is of special interest due to its potential to provide information about the biogeochemical cycling of bio-reactive metals, which allows both quantitative and qualitative estimates of their sources and sinks in the oceans. However, despite the increasing number of investigations, it is still unclear whether ancient metalliferous deposits and organic matter-rich rocks faithfully record ocean-scale processes, considering the importance of diagenetic and hydrothermal overprinting.

Here, we will focus on "calibrating" and "proving" a range of proxies - in particular Fe-isotopes - by undertaking a comparison between ancient metal deposits and modern seafloor metalliferous deposits. We will present geochemical and Fe-isotope signatures of (1) exhalative metalliferous sulfide and oxide deposits from the Atlantis II Deep, Red Sea which offers a unique modern analogue of laterally extensive metalliferous deposits such as ancient SEDEX deposits and possibly banded iron formation; (2) organic matter-rich sediments from the Guaymas Basin seafloor hydrothermal field as modern analogue of Precambrian black shales that are considered to be affected by hydrothermal metal input and reworking; (3) hydrothermal Fe-oxide deposits and microbial mats from the Loihi Seamount hydrothermal field which provides an ideal system in which to test hypotheses on biotic vs. abiotic origin of iron formation and Fe-isotope biosignatures.

This comparative approach should provide better constraints on the effects and signatures of hydrothermal overprinting on the ancient ocean rock record, ultimately leading to a better understanding of mechanisms of metal redox-cycling and microbiological interactions in ancient oceans.

Individual organic compounds in oil sands process-affected waters: identification and toxicity

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Introduction

The toxicity of oil sands process-affected water (OSPW) has often been at least partially attributed to compounds given the uninformative term 'naphthenic acids' (NA). Until our studies in 2011, no-one knew what any of these NA in OSPWwere, or how toxic they were [1-4]. Even now, many compounds remain to be identified and the concentrations remain to be accurately measured with isotopically-labelled analogues.

The present study therefore describes use of gas chromatography x gas chromatography-mass spectrometry (so-called' 2D GCMS'or GCxGC-MS) with both nominal and accurate mass resolution, 'normal' and 'reversed' phase GC column couplings and synthesised isotopically labelled authentic standard compounds, to identify and measure the individual NA components of OSPW. The distributions of the acids can be used to profile and distinguish different sources of NA in the environment.

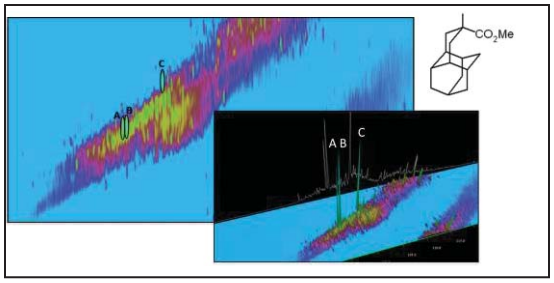

Figure 1: GCxGC-MS mass chromatogram of some of the individual isomers of tetracyclic acids (methyl esters) in OSPW.

Results and Conclusion

Use of trideuterated analogues of diamondoid acids (e.g. esters of adamantane carboxylic acids) and measurement of electron ionisation response factors for the analytes and for the deuterated internal standards, allowed the cocntrations of individual NA in OSPW from different industrial processors of oil sands ore, to be measured for the first time. GCxGC-MS with high accuracy mass resolution and reversed phase GCxGC columns allowed novel acids to be identified with greater certainty. Synthesis of novel acids allowed the toxicity to a number of biological endpoints to be determined. Such studies remove some of the need for speculation about the actual toxicants in OSPW.

[1] Rowland *et al*. (2011)*Environ. Sci. Technol.* **45,** 3154-3159. [2] Rowland *et al*. (2011) *Rapid Commun. Mass Spec.* **25,** 1198-1204.
[3 Rowland *et al*. (2011) *Environ. Sci. Technol.* **45,** 9806-9815.
[4] Jones *et al*. (2011) *Environ. Sci. Technol.* **45,** 9776-9782.