

## Natural organic matter roles in floc/sediment Pb dynamics

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### Introduction

Natural organic matter (NOM) is a fundamental component of freshwater ecosystems and a geochemically significant substrate for lead (Pb) transport, retention and fate in watersheds. Although Pb release into the environment by atmospheric deposition has declined in recent decades, concern remains whether Pb remobilization from sediments (e.g. pH driven Pb solid-solution partitioning) and subsequent transport by soluble organic-Pb complexes and floc-aggregates may continue to pose risk to freshwater ecosystems. As such, the objectives of this study were to: (1) investigate Pb and NOM distributions among suspended floc, surficial bed sediment and water-column compartments; (2) identify the important solid phases for Pb sequestration in floc and surficial bed sediments; and (3) establish the role of pH (pH 5-8) impacting dissolved organic carbon (DOC) and Pb solid-solution partitioning from natural limnetic floc, as well as lake, stream and wetland sediments both *in situ* and under controlled laboratory settings.

### Results and Conclusions

Water, floc and sediments were collected for aqueous Pb and NOM analysis across nine highly variable freshwater (wetland, stream, lake) ecosystems of Ontario, Canada. Results indicate soluble organic-Pb complexes dominated Pb aqueous species in NOM-rich environments. Surficial sediments and floc showed distinct Pb sequestration and solid-solution partitioning patterns across sites driven by differential roles of living versus refractory NOM within each compartment. Stable organo-Pb complexes dominated sediment Pb solid-solution partitioning, as mobilization of DOC and Pb occurred with increasing pH from NOM-rich sediments, while Pb release was inhibited from NOM-poor sediment. In contrast, amorphous Fe oxyhydroxides, collected by microbes and extracellular polymeric substances, were the best predictor of floc Pb solid-solution partitioning and the key floc Pb sequestration phase across sites. These results and their implications for Pb mobility in freshwater catchments from upstream NOM-rich wetlands through to downstream NOM-poor littoral lake environments will be presented.

## Significance of sulfidic organic-rich Archean shales

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In the past few years multi-proxy studies of black shales have transformed our view of the evolution of Precambrian Earth system processes<sup>1-4</sup>. Part of the utility of black shale studies lies with our ability to tie them to well-understood modern and Phanerozoic analogs. Geochemical signatures in black shales have the potential to hold information about concentrations of key trace nutrients, the emergence of an oxidative biosphere, and the onset of significant oxidative weathering. However, there have been relatively few truly comprehensive, multi-proxy studies of Precambrian units, which has made it difficult to delineate temporal trends from the black shale record and to evaluate the significance of emerging geochemical results. This problem is particularly acute for the Archean. To fill this gap, we have conducted a multielement (C-S-Fe-trace metal) biogeochemical study in black shales from several (ca. 2.7 Ga) drill cores within the Abitibi Greenstone belt in Ontario. We are particularly interested in the Abitibi since it was a strongly hydrothermally influenced basin.

The shales are marked by variable but in some cases extremely high organic carbon concentrations (up to 32% TOC). C-S-Fe systematics and simple sediment dilution calculations suggest that oxygenic photosynthesis was the primary source of organic carbon in the basin. Further, our data reveal a sustained and spatially widespread episode of Fe-limited pyrite formation under an anoxic water column. The Abitibi work, therefore, supports the emerging view that euxinic conditions were a common feature in productive Archean settings. Trace metal systematics allow us to tease apart the influence of hydrothermal systems on abundances of bio-essential metals in Archean anoxic oceans. We will focus on Mo, Zn, Cu, and U systematics and co-variation.

[1] Anbar *et al.* (2007) *Science*, **317**, 1903-1906

[2] Scott *et al.* (2008) *Nature*, **452**, 456-459

[3] Reinhard *et al.* (2009) *Science*, **326**, 713-716

[4] Scott *et al.* (2011) *Geology*, **39**, 119-122.