## A multi-proxy study of the Mackenzie Shelf waters

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The Arctic Ocean is one of the most intense  $CO_2$  sinks of the oceanic realm due to the low temperature and relatively high primary productivity of its waters [1]. Nevertheless, the Arctic Ocean is prone to rapid transformations in response to climate change, such as changes in sea-ice melt and freezing rates, increased freshwater, nutrient, and particulate input due to higher riverine discharge, as well as changing carbon and sediment fluxes caused by coastal erosion and permafrost thawing. Given the complex interplay between these factors, predicting how the strength of the Arctic Ocean atmospheric  $CO_2$  sink will vary in the future is still a matter of debate [2]. In this context, we address how  $CO_2$  in the surface mixed layer (SML) of the Arctic Ocean may change in response to increased sea-ice melt and riverine inputs.

During the summer of 2009, we conducted high resolution water column sampling on the Mackenzie and Beaufort Shelves (Canadian Arctic) to examine the impact of sea-ice melt and river runoff on surface ocean CO<sub>2</sub> chemistry. We used a combination of natural tracers (salinity, total alkalinity (TA) and stable oxygen isotopic composition ( $\delta^{18}$ O-H<sub>2</sub>O)) to distinguish between sea-ice melt (SIM) and meteoric water (MW) [3]. SIM is characterised by a low TA (415 ± 35 µmol kg<sup>-1</sup>), a relatively high  $\delta^{18}$ O-H<sub>2</sub>O (-2.0 ± 0.5‰) and relatively low CO<sub>2</sub> partial pressure (pCO<sub>2</sub>≈300 µatm). MW is characterised by a high TA (1618 ± 55 µmol kg<sup>-1</sup>), low  $\delta^{18}$ O-H<sub>2</sub>O (-18.9 ± 0.1‰), and relatively high pCO<sub>2</sub> (>450 µatm). In addition, we analysed the stable carbon isotopic composition ( $\delta^{13}$ C) of dissolved inorganic carbon (DIC) to determine the origin of the CO<sub>2</sub>, i.e. metabolic or atmospheric.

During the study period, significant contributions of MW (>50%) to the SML were only observed on the inner Mackenzie Shelf. In contrast, SIM contribution to the SML reached 30% close to the ice pack, located beyond the shelf break. The admixture of SIM to the SML may therefore allow for the absorption of atmospheric CO<sub>2</sub>. A preliminary analysis of the  $\delta^{13}$ C-DIC data reveals two distinct patterns indicating that CO<sub>2</sub> was either taken up from the atmosphere or produced *in situ* by microbial respiration.

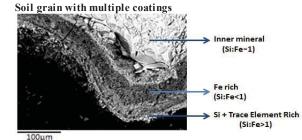
[1] Takahashi et *al.* (2009) Deep-Sea Research II **56**, 554–577. [2] Cai et *al.* (2010) Science **329**, 556-559. [3] Lansard et *al.* (in press) Journal of Geophysical Research

## Trace element interactions with altered surfaces in smelter affected acidic soils; Sudbury, Canada Sonia Lanteigne<sup>1\*</sup>, Michael Schindler<sup>1</sup>, Andrew McDonald<sup>1</sup>

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Elevated concentrations of metal(loids) in silica rich alteration layers has recently been described for altered surfaces at the solidwater and solid-atmospheric interfaces in tailings, and in the vicinity of smelters, respectively. To determine if similar coatings occur in acidic soils, samples were taken from unlimed areas around three major smelting centers in Sudbury, Ontario, Canada. Coated grains were extracted from these samples and individually mounted to be analysed with SEM, Micro-raman spectroscopy, Laser Ablation ICP-MS and XPS. Preliminary results indicate that coatings are mainly composed of Fe and Si, and that trace elements seem to be associated primarily with coatings having Si : Fe ratios greater than 1, whereas coatings with Si : Fe ratios less than 1 have lower concentrations of associated trace elements. The silica-rich coatings were most likely formed through the precipitation of amorphous silica in iron hydroxide. Their higher metal concentrations with respect to Fe-rich coatings can be explained either by the promoted growth and encapsulation of jarosite group minerals by a silica matrix, or by higher sorption of metal(loids) by iron hydroxide minerals with high silica content which have a lower positive surface charge, lower crystallinity and number of polymerized polyhedra, as well as a higher reactivity than Si-depleted Fe-hydroxides. In conclusion, micro-coatings are capable of taking up and in some cases preserving metal(loid)s such as As,Pb,Se,Cu and Zn among others, and therefore play an important role in the interaction of trace elements with soils, and may affect their behaviour within the soil environment.



**Figure 1.** SEM backscatter image of a grain with multiple coatings; a bright Si-rich coating with associated trace elements and a darker Fe-rich coating.

[1] Durocher et al. (2011) *Applied Geochemistry*, pp.1-16 [2] Mantha et al. (2012) *Geochimica Cosmogeochimica Acta* (in press)

[3]Dyer et al. (2010) J. Colloid Interface Science, 348, pp.65-70