

Mercury isotope fractionation during aqueous photo-reduction of methylmercury in presence of dissolved organic matter

PRIYANKA CHANDAN¹, SANGHAMITRA GHOSH¹ AND BRIDGET A. BERGQUIST^{1*}

¹Department of Geology, University of Toronto, 22 Russell Street, Toronto, Ontario, M5S 3B1, Canada
(*correspondence: bergquist@geology.utoronto.ca)

Monomethylmercury (MMHg) is a globally persistent toxin that bioaccumulates in aquatic ecosystems. The photo-degradation of MMHg in freshwater systems is a significant pathway for the destruction of MMHg from surface waters and is considered an important sink in aqueous systems, which limits MMHg availability to biota. Quantifying this sink for MMHg is challenging, and it was suggested that natural fractionation of Hg isotopes might be useful in both understanding and quantifying this pathway [1]. In order to use this new tool, the isotopic fractionation factors associated with MMHg photo-degradation need to be characterized along with the variability that might be induced by environmental factors (i.e. type and amount of organic matter, light intensity and wavelength).

In a previous study, aqueous photo-reduction of MMHg in the presence of dissolved organic matter (DOM) was shown to display both mass dependent (MDF) and mass-independent (MIF) fractionation of Hg isotopes with the odd isotopes (¹⁹⁹Hg and ²⁰¹Hg) being preferentially retained in the reactant [1]. The observation of large MIF signatures (>0.5‰) is likely due to magnetic isotope effect (MIE), which is expressed during radical pair photochemistry. It was also observed that the magnitude and extent of MIF was different for two concentrations of DOM. Since these experiments were carried out on different days in natural sunlight, which likely had different solar intensity and frequency, it was unclear whether the variability in MIF was due to varying DOM concentrations or the variability in solar radiation.

We investigated the effects of different types and amounts of DOM on the isotope fractionation of Hg isotopes during aqueous photo-reduction of MMHg to assess if MIF signatures can be used to track photo-degradation of MMHg in natural waters. From experiments conducted with different amounts of reduced organic sulfur (S_{red}-DOM), it appears that MIF during photo-reduction may be dependent on whether MMHg is dominantly bound to S_{red}-DOM. Similar fractionation factors were observed for experiments where S_{red}-DOM was in far excess of MMHg, while significantly lower fractionation factors were observed with lower S_{red}-DOM. We also characterized the signature of MIF (i.e. $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$) during MMHg photo-degradation to assess if it was similar in different matrices. The experimental $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio for all the MMHg-DOM experiments was 1.39 ± 0.06 (2SE). However, we observed that the experimental slope is slightly but statistically different than the slope observed in freshwater fish.

[1] Bergquist & Blum (2007) *Science* **318**, 417-420.

Anomalous zircon Ce⁴⁺/Ce³⁺ ratios from early Jurassic plutons in Yukon: implications for porphyry exploration

JOHN B. CHAPMAN^{1*}, SIMON E. JACKSON¹ AND JAMES J. RYAN²

¹Geological Survey of Canada, Ottawa, Ontario, Canada,
john.chapman@nrcan-mcan.gc.ca (* presenting author);
simon.jackson@nrcan-mcan.gc.ca

²Geological Survey of Canada, Vancouver, British Columbia, Canada, jim.ryan@nrcan-mcan.gc.ca

Studies suggest that a genetic link exists between oxidized magmas and porphyry-style Cu ($\pm\text{Au}\pm\text{Mo}$) mineralization.[1] However, many indicators of magmatic redox state – such as whole-rock Fe³⁺/Fe²⁺ ratio – can be reset during both hydrothermal alteration and surficial weathering. Zircon (ZrSiO₄) is an abundant accessory mineral in granitoids, and is both refractory and resistant to alteration. Cerium commonly shows anomalously high concentrations within zircon, due to its stable +4 oxidation state and preferential incorporation of the Ce⁴⁺ ion over Ce³⁺. The magnitude of this substitution should correlate with the Ce⁴⁺/Ce³⁺ ratio in the parent magma, and as such can be used as a qualitative proxy for oxidation state.[2] In this study, we determined zircon Ce⁴⁺/Ce³⁺ ratios for a suite of late Triassic to Jurassic granitoid intrusions from southern and western Yukon, Canada, including mineralised and host rocks of the Minto Cu-Au mine, and for mid- to late-Cretaceous intrusive phases associated with the Casino Cu-Mo-Au deposit.

Results for the Casino samples show that the major mineralising intrusive breccia phases have average zircon Ce⁴⁺/Ce³⁺ values of 200-350, and peak values approaching 500, in contrast to mid-Cretaceous host granitoid rocks which have average values of 50-100 and peak values <250. Both sets of observations fit previously published models for the identification of Cu prospective intrusive rocks.[2,3] Hence, it appears possible to use zircon Ce⁴⁺/Ce³⁺ ratios for exploration fingerprinting within the Cretaceous of the Yukon.

The 'Carmacks Copper Belt' (CCB) of western central Yukon includes the Minto Cu-Au mine, the Carmacks Copper deposit, and several smaller Cu \pm Au occurrences and showings. Both the Minto and Carmacks Copper deposits are hosted within the Triassic-Jurassic plutonic rocks of the Granite Mountain batholith, part of a regionally extensive suite of plutonic rocks of similar age and composition. The Triassic-Jurassic samples appear to fall into two distinct groupings: those with modal zircon Ce⁴⁺/Ce³⁺ values >700, and those with values <600. The regionally extensive nature of these elevated Ce⁴⁺/Ce³⁺ values may reflect the petrogenesis of these plutonic rocks, and as such need to be better understood before reliable prospectivity indicators can be defined. In contrast to the Cretaceous suite, all early CCB samples analysed have zircon Ce⁴⁺/Ce³⁺ ratios greater than the previously published prospectivity threshold values.[2,3] However, Granite Mountain samples have higher apparent oxidation state, so the broad relationship to mineralisation established for the Cretaceous suite is maintained.

[1] Richards (2011) *Economic Geology* **106**, 1075-1081. [2] Ballard et al. (2002) *Contributions to Mineralogy and Petrology* **144**, 347-364. [3] Liang et al. (2006) *Mineralium Deposita* **41**(2), 152-159.