

Sources and processes identification for Zn cycling in the Seine river, France

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An accurate determination of the ecological status of the Seine River (flowing through greater Paris, France) is required as it is one of the most severely damaged European rivers. However, important evaluation limitation still exists, partly because the metal cycling in this system is not fully understood, with for instance half the Seine river Zn not having clearly identified sources[1]. Along with Zn isotopic measurements, this study proposes to use XAS (X-ray Absorption Spectroscopy) to determine precisely the speciation of Zn complexes, and thus to define the proportion of water mixing vs. processes for Zn transfer in the watershed. A geographical sampling transect has been performed downstream Paris, where the contamination is maximum – 5 samples from the Seine River and 3 tributaries.

Significant isotopic signature variations are observed, varying from $\delta^{66}\text{Zn} = 0.04$ to $0.14 \pm 0.05\%$ in the particulate phase, and from $\delta^{66}\text{Zn} = -0.23$ to $0.10 \pm 0.06\%$ for the dissolved phase. These results are in line with previous work by Chen et al.[2] on the Seine River, but as we focus on the most polluted downstream part of the river, the $\delta^{66}\text{Zn}$ variation range in both dissolved and suspended loads is much narrower. The XAS analysis performed on the suspended load samples at the Zn K-edge confirmed however a real heterogeneity by showing different speciations with a major contribution of sulfides, iron oxides, amorphous silica and organic ligands.

The dissolved phase displays systematically lower isotopic signatures than the particulate phase, resulting from adsorption processes [3, 4]. A significant discrepancy was observed between summer and winter for the dissolved phase, with higher values in winter high-water stages, reflecting a bigger contribution of natural sources ($\delta^{66}\text{Zn}$ is 0.88‰ for chalk [2]) than during summer low-water stages dominated by anthropogenic sources.

The regional major wastewater treatment plant (WWTP) in Achères (shortly after Paris) brings significantly heavier Zn to the Seine River particulate material. This change in $\delta^{66}\text{Zn}$ follows a change in Zn speciation, with a strong decrease in sulfides contribution after Achères. This WWTP impacts both dissolved and particulate phases on concentration, speciation and isotopic signatures. Comparison with Chen et al.[2] indicates a significant variability of the WWTP Zn signal that needs further investigation.

[1] Thevenot et al. (2007) *Science Total Environ.* **375**, 180-203. [2] Chen et al. (2008) *Environ. Science Tech.* **42**, 6494-6501. [3] Juillot et al. (2008) *Geochim. Cosmochim. Acta.* **72**, 4886-4900. [4] Jouvin et al. (2009) *Environ. Science Tech.* **43**, 5747-5754.

Geochemical Assessment of the Metallogenic Potential of Proterozoic LIPs of Canada

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The litho-geochemistry of eight Proterozoic Large Igneous Provinces (LIPs) within Canada has been studied to determine the Ni-Cu-PGE prospectivity of these major magmatic events. Three of the LIPs discussed here, the 1.87 Ga Chukotat, 1.27 Ga Mackenzie and the 2.49-2.45 Ga Matachewan LIPs, host known magmatic Ni-Cu-PGE sulphide mineralisation; in addition, the 0.72 Ga Franklin LIP may be associated with the coeval and mineralised Dovyren intrusion in Siberia and several Franklin-related Ni-Cu-PGE prospects are known within northern Canada. The other four LIPs, the 1.14 Ga Abitibi, 0.59 Ga Grenville, ~1.25 Ga Seal Lake and 1.24 Ga Sudbury (distinct from the Sudbury impact event) LIPs, have no known Ni-Cu-PGE mineralisation.

The mineralised Chukotat, Mackenzie and Matachewan LIPs are characterised by basalts with Ti/V ratios below 50, Gd/Yb ratios close to primitive mantle values and variable La/Sm ratios. The magmas that formed these LIPs assimilated significant amounts of crustal material and samples representing both chalcophile depleted and undepleted magmas are present within these LIPs. This suggests that the magmas that formed these LIPs were fertile and S-undersaturated when they left the mantle and subsequently underwent a S-saturation event, forming immiscible magmatic sulphides. The close relationship between chalcophile element depletion and crustal contamination evident in the geochemistry of these LIPs suggests that S-saturation was caused by assimilation of crustal material, most likely by assimilation of crustal sulphides. The magmatic sulphides produced during this event were presumably segregated from silicate magmas and were deposited in cogenetic mafic-ultramafic sills and intrusives associated with these LIPs.

The Grenville and part of the Franklin LIPs have similar magma source characteristics to LIPs with known Ni-Cu-PGE mineralisation. However, although magmas from both LIPs were fertile and assimilated crustal material, the Grenville LIP did not undergo a S-saturation event prior to emplacement, whereas the Franklin LIP may have; the timing and location of this S-saturation event may be a useful guide during exploration for Ni-Cu-PGE mineralisation. The Abitibi, Sudbury and Seal Lake LIPs are alkaline, dominated by alkali basalts and are characterised by high Gd/Yb ratios, a wide range in La/Sm ratios and Ti/V ratios higher than 50. All samples from the Abitibi, Seal Lake and Sudbury LIPs are chalcophile element depleted, suggesting that these magmas left residual sulphide within the mantle during partial melting, and indicating that these LIPs are probably unprospective for Ni-Cu-PGE sulphide mineralisation.