# Identification of trace metal speciation in environment using Z-contrast imaging

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A major challenge to understanding the fate of contaminants in environment is the direct identification of trace concentrations (ppm to ppb) at the nano-scale. In order to efficiently characterize the trace metals, we have utilized high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). In general, the image contrast in the HAADF-STEM is correlated to the atomic mass.

(i) Fine- and ultra-fine particles in urban aerosols from Detroit were examined to investigate metal concentrations and speciation. The trace element speciation: Pb, As, Sb, La, Ce, Sr, Zn, Cr, Se, Sn, Y, Zr, Au, Ag and U have been characterized. We have identified nanocrystals of uraninite encapsulated in carbonaceous matter (~50 nm). The "carbon-caged" nanocrystals of uraninite are protected from the immediate oxidation that would lead to increased mobility of uranium in the environment. Still, the presence of uranium in the very fine-fraction ($PM_{2.5}$) of atmospheric particulates provides another pathway for radiation exposure [1].

(ii) A direct, near atomic-scale characterization of Pb is demonstrated in zircon (3.3-4.4 Ga). Two forms of Pb have been identified: Pb concentrated at ~3 atom% as a nanoscale patch in zircon structure, and Pb concentrated within the amorphous domain created by fission fragment damage. The first result suggests that the Pb atoms directly substitute for $Zr^{4+}$ in the zircon structure, and the latter observation demonstrates that Pb diffusion can occur through amorphous regions created by radiation damage, although volume diffusion is typically considered to be the dominant diffusion mechanism for Pb [2].

These examples illustrate the value of HAADF-STEM as a powerful technique for the direct characterization of trace elements. This is a particularly useful technique for the heavy metals that occur at low bulk concentrations in a lighter element matrix [3].

## References

[1] Utsunomiya S., Jensen K.A., Keeler G.J., Ewing R.C., *Environ. Sci. Technol.* **36,** 4943-4947.

[2] Utsunomiya S., Palenik C.S., Valley J.W., Cavosie, A.J., Wilde, S.A., Ewing R.C., *Geochim.Comochim Acta.* **68,** 4679-4686.

[3] Utsunomiya S., Ewing R.C., *Environ. Sci. Technol.* **37,** 786-791.

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# Hydrogeochemical signature of various amorphous $As^{V}$-$Fe^{III}$ phases

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The precipitation of amorphous $As^{V}$-$Fe^{III}$ phases is widely used as a remediation method for As-contaminated effluents from mining and processing industries. A better description of these phases (and of water/mineral interactions during ageing) is needed for the modeling of their long-term stability in tailing ponds. The hydrogeochemical signature of a synthetic "coprecipitate" (CPT) and of its equivalent "adsorbed ferrihydrite" (ADS) were the subject of a recent investigation the results of which are presented here.

The CPT and ADS amorphous $Fe^{III}$-$As^{V}$ precipitates were synthesized, under the following specific conditions: 21°C, a sulphate medium, a final pH=4, a molar ratio As/Fe=0.28. Duplicates of CPT and ADS were aged for 6 months at 21±1°C, following a self-drift method, with a liquid to dry solid ratio of L/S=15±1. The aqueous matrix was composed of pure water oversaturated with respect to gypsum and calcite. This water (filtered at 0.025 µm poresize) in contact with ADS and CPT was analysed during ageing. The initial solids showed some significant chemical and morphological differences.

Hydrogeochemical signatures were representative of major differences between ADS and CPT: both of these showed a fast decrease of pH values from 7.5 (buffered in the blank matrix over 6 months) to pH 5.6 and pH 3.6 for ADS and CPT respectively. Dissolved iron was released from CPT (up to 1.3 mg/l), whereas arsenic remained on the solid. Arsenic was released from ADS until its equilibrium concentration to reach [As] = 2.5 mg/l. This behaviour was interpreted as resulting from initial different $Fe^{III}$-$As^{V}$-$H_2O$ binding mechanisms between ADS and CPT.

This study demonstrates the distinct nature of the "coprecipitate" when compared to "As-adsorbed ferrihydrite". It sheds new light on the ageing behaviour of these nanomaterials, with implications for the quality of porewater in tailings ponds and for long-term stability modeling of $Fe^{III}$-$As^{V}$ phases.

## Acknowledgments

This research was supported by NSERC, Hatch, COGEMA, Barrick Gold and Placer Dome.