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## 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 sub-micron scale. In order to efficiently characterize the trace metals in various environmental and geological samples, we have utilized high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with conventional TEM techniques. In general, the image contrast observed in the HAADF-STEM is correlated to the atomic mass: heavier elements contribute to a brighter contrast. Additionally, the contrast in HAADF-STEM is characteristically independent of focus, because the image is formed by incoherent scattering. Remarkable results obtained using the advanced TEM technique are shown as an example.

(i) Fine- and ultra-fine particles with heavy metals in urban aerosols from various locations 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<sub>2.5</sub>) 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<sup>4+</sup> 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. Beyond the first percolation point, i.e., when the amorphous domains overlap and form a fully interconnected network, there is a new fast pathway for the diffusion of Pb [2].

These examples illustrate the value of HAADF-STEM as a powerful technique for the direct investigation and identification of trace elements in nano-scale particles. This is a particularly useful technique for the relatively heavy metals that occur at extremely low bulk concentrations (ppb to ppm) 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.
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- [3] Utsunomiya S., Ewing R.C., *Environ. Sci. Technol.* **37**, 786-791.