

# Root-induced Changes in Metal Speciation in the Rhizosphere and Metal Homeostasis in a Ni/Co Hyperaccumulator: A Spectromicroscopic Investigation

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Hyperaccumulator plants concentrate trace metals in aerial biomass, and thereby offer sustainable treatment of metal-contaminated sites and an opportunity to mine metal-rich soils (phytomining). Synchrotron-based techniques such as microfocused X-ray absorption (XAS), X-ray micro-fluorescence (XRF), and micro-tomography (CMT) enable the investigation of metals in natural systems at the micron scale. XAS and XRF were used to study root-induced changes in rhizosphere of *Alyssum murale*. Changes in speciation were not observed for unplanted model soil or for grains lacking intimate association with roots (outer-rhizosphere), but were observed in the rhizosheath (100  $\mu\text{m}$ ). Model soils initially consisted of a single metal species, but mixtures of species were observed following two weeks growth. Dissolution and re-precipitation occurred due to fluctuations in rhizosphere chemistry, and metal complexation with organic acids affected re-precipitation products. Spectromicroscopy was used to study *in planta* metal speciation. CMT cross-sectional images (tomograms) of roots revealed unique metal localization patterns as a function of distance from root tips (tissue age and function). Leaf tomograms revealed Ni enrichment in epidermal and vascular tissue, while Co was limited to the vasculature. XRF images revealed a uniform Ni distribution in leaves and preferential localization of Co at leaf tips/margins. Primary species in leaves and roots were aqueous metal-ligand complexes with malate and histidine. Cobalt deposited at leaf tips formed a  $\text{Co}(\text{OH})_2$  precipitate. Results suggest *Alyssum* relies on a different tolerance mechanism for Co than for Ni to maintain metal homeostasis.

