

Microspectroscopic study of cobalt speciation and localization in hyperaccumulator *Alyssum murale*

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Abstract (Summary)

A vast amount of research on phytoremediation has been conducted over the past several decades since Chaney (1983) first proposed the idea of using accumulator plants to extract metals from anthropogenically-contaminated soils (phytoextraction) or metalliferous soils (phytomining), and noted the opportunity to recover metals of economic value by ashing the shoot biomass. Substantial research on metalliferous soils existed previously, and the use of metallophytes as geobotanical indicators for mineral prospecting had been well-established (Tkalic 1938; Brundin 1939; Cannon, 1960). The first three Ni hyperaccumulators discovered were of the genus *Alyssum* in the family *Brassicaceae* (*A. bertolonii* in 1948, *A. murale* Waldst. & Kit. in 1961, and *A. serpyllifolium* Desf. in 1969), although discoveries of other genera of accumulator plants rapidly added to the list of accumulators (Morrison, 1980). R.R. Brooks and co-workers conducted the majority of pioneering research to identify metal accumulators by large-scale surveys of metalliferous flora and analysis of metal concentrations in field specimens (plants and soils) as well as analysis of herbarium specimens (Brooks et al., 1974; Brooks 1977; Brooks et al., 1977a,b,c; Wither and Brooks, 1977; Brooks and Radford, 1978; Jaffré et al., 1979a,b; Morrison, 1980; Reeves et al., 1981, 1983). In time, research focus shifted from field-based observations of metalliferous flora to laboratory-scale investigations of metal-specific "hyperaccumulators" with emphasis largely on metal phytoextraction from artificially-contaminated (single-metal) media. Encouraging results from laboratory investigations obtained under ideal conditions quickly fueled implementation of field-scale remediation. However, early efforts to apply phytoextraction in the field were marginally successful because a fundamental understanding of the mechanisms underlying metal accumulation and tolerance was lacking as was the necessary information regarding agronomic practices for cultivation of hyperaccumulator plants.

In the last decade, major advances in biotechnology and plant molecular biology offered new opportunities to gain fundamental insight to the mechanisms underlying metal homeostasis in accumulators, and provided the necessary tools for investigating *in vivo* the complex physiological and biochemical processes regulating metal tolerance and hyperaccumulation. Many early biogeochemical and phytochemical studies of hyperaccumulators that reported on plant-soil relationships, metal distributions in plants, and metal-ligand complex formation were conducted with *ex situ* analytical techniques. Recent advances in analytical techniques for *in situ* chemical measurements (e.g. synchrotron-based spectroscopic methods) have created new opportunities to relate knowledge of the biochemical pathways mediating plant metal homeostasis with molecular-scale information of the localization, associations, and speciation of the metals in plants. A more comprehensive understanding of the mechanisms involved in metal uptake by plants will lead to enhanced phytoextraction through breeding programs or transgenic developments, and provide a greater potential to produce nutrient-fortified foods and to improve crop production on nutrient-poor soils.

In this investigation, a combination of novel *in situ* techniques (e.g. synchrotron-based spectroscopies), advanced *ex situ* analytical methods (e.g. electron microprobe analysis), and wet-chemical procedures (e.g. high performance liquid chromatography) were used to investigate the localization and speciation of cobalt in the Ni/Co hyperaccumulator plant (*Alyssum murale*). Synchrotron-based microspectroscopic tools were applied to gain (sub)micrometer-scale

information regarding the *in situ* chemical form (i.e. molecular speciation), spatial location, and elemental associations of the plant-accumulated metals (Co and Ni). The first research objective was to investigate aspects of Co accumulation and storage in *A. murale* and to determine the influence of simultaneous hyperaccumulation (i.e. Ni and Co) on metal localization. The second objective was to examine the molecular speciation of Co in various *A. murale* tissues (e.g. roots, stems, shoots, leaf tips) in an effort to improve our understanding of the biochemical mechanisms regulating Co transport and tolerance (i.e. metal homeostasis). The research findings presented in Chapter 2 revealed a novel metal sequestration mechanism for accumulated Co (exocellular sequestration) that is potentially involved with Co tolerance in *A. murale*. Furthermore, the sequestration mechanism for Co is completely different from the intracellular mechanism used to sequester Ni in *A. murale* (i.e. vacuolar compartmentalization) and other *Alyssum* hyperaccumulators; compartmentalization of metals in the epidermal cell vacuoles of leaves has been established as a key component of the (hyper)tolerance mechanism used by the majority of hyperaccumulator plants.

The research findings presented in Chapter 3 represent the first report on the occurrence of Co/Si-rich biogenic nanoparticles (e.g. Phytoliths with two-dimensional hydrous cobalt silicate domains) and other Cobaltian mineral precipitates (e.g. Widgiemoolthalite, Co-analogue) and polymers (e.g. Cobalt hydroxide fumarate coordination polymer, $[\text{Co}_3\text{C}_4\text{H}_2\text{O}_4]_2 \cdot x\text{H}_2\text{O}$) sequestered on the leaf surface of a metal hyperaccumulator plant.

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