

# Nickel Speciation in Serpentine Soils using Synchrotron Radiation Techniques

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## Abstract

We examined nickel in serpentine soils from Southwest Oregon to determine metal speciation and co-localization. Serpentine soils naturally contain elevated concentrations of nickel, manganese, chromium, and cobalt and are the media on which many Ni hyperaccumulating plants evolved. Hyperaccumulators are effective at removing extraordinary amounts of nickel from serpentine soils and are considered excellent candidates for phytoremediation of Ni contaminated soils. Nickel contaminated soil results from nickel refining and steel production. Nickel has been identified in over 800 hazardous waste sites in the US and is a common soil contaminant near nickel refineries in Canada and Russia. Our results will help to elucidate metal uptake mechanisms used by hyperaccumulating plants by identifying soil Ni species. X-Ray Absorption Spectroscopy (XAS) yields a more accurate picture of metal speciation in mineralized or contaminated soils than traditional, sequential chemical extractions. We employed synchrotron-based X-Ray Fluorescence (SXRF) mapping, bulk- and micro- Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS), and micro-X-Ray Diffraction ( $\mu$ -XRD). From these techniques, we determined that Ni co-localizes with iron and manganese in serpentine soils, and the major species contributing to the Ni EXAFS spectra include Ni-containing Fe and Mn minerals and Layered Double Hydroxide (LDH) phase minerals.

## Key Words

Nickel speciation, serpentine soil, X-ray absorption spectroscopy, phytoremediation

## Introduction

The fate of trace metals (e.g., Ni) in soil systems is a significant issue in environmental science and health. Metal enriched soils are prevalent in nature, originating from both anthropogenic and geogenic sources. Anthropogenic inputs include waste from municipal incineration, stainless steel production, coal combustion, and nickel refinery emissions. Geogenic sources of Ni include magmatic sulfide ores and lateritic silicates found in serpentine soils. Anthropogenic Ni in soil poses significant health risks to communities neighboring nickel emission sources. A Ni refinery in Port Colborne, Ontario, Canada enriched 345 km<sup>2</sup> of land with Ni, and farms in the immediate vicinity of the refinery demonstrated reduced vegetable crop yields (McNear *et al.*, 2007). Ni refinery emissions have been underestimated in parts of northwestern and central Russia (Boyd *et al.*, 2009). Soil contaminated from smelter emissions on the Kola Peninsula, Russia, contained 9000 ppm Ni, which is 450 times higher than background concentrations. Native plants like berries and mushrooms growing 3000 km<sup>2</sup> around the smelter complex contain elevated nickel concentration, making the food unsuitable for human consumption (Barcan *et al.*, 1998). Complete Ni leaching from the A<sub>o</sub> layer of the soil was calculated to be 160–270 years (Barcan, 2002). One may be exposed to nickel by air, skin contact with soil, or metals containing nickel; however, the major source of exposure to nickel is food. Nickel refinery dust is carcinogenic to humans (ATSDR, 2005). Although Ni is an essential micronutrient for plant growth, elevated Ni concentrations in soils are toxic to crops.

While serpentine soils have been studied extensively, to our knowledge no study has appeared on the direct speciation of nickel naturally present in serpentine soils using synchrotron-based XAS. Traditionally, sequential chemical extractions were used to ascertain soil metal speciation and involved repeated extractions with increasingly aggressive reagents. These techniques were effective in determining that nickel accumulates partly in magnesium silicates but mostly with manganese and iron oxides (Alexander *et al.*, 2007). However, these techniques are limited by the possibility of sample alteration. XAS is capable of determining *in-situ* metal speciation with minimal chemical sample treatment.

## Methods

Basic soil characterization was performed. Soil pH was determined by mixing the soil with distilled water in a 1:1 ratio and measuring the pH. Percent organic matter was determined by the loss-on-ignition method. Elemental compositions were determined via microwave digestion with nitric acid followed by ICP-OES. For synchrotron studies, soil samples were ground to a powder and dusted on kapton tape, removing excess

dust. Sufficient incident energy to simultaneously excite fluorescence from Ni, Co, Fe, and Mn for mapping was used to enable determination of local metal associations and co-occurrence. Multi-element fluorescence data were collected with a Ge multi-element detector positioned 90° to the incident beam (45° to the sample). Because of the well-defined energy resolution of the multi-element detector, special attention was paid to selecting the fluorescence of the Ni K-alpha peak so that the resulting spectra did not include fluorescence from the Fe K-beta peak. Course XRF maps (1-3 mm<sup>2</sup> using an X-ray beam spot of ~60µm<sup>2</sup>) were used to observe distinct metal correlations and to identify regions of interest (i.e., “hotspots”) for µ-EXAFS and µ-XRD analysis. Fine XRF maps (200µm<sup>2</sup>) were generated using shorter dwell times. With the monochromator calibrated for nickel, µ-EXAFS spectra were collected from approximately 50eV below the absorption edge energy to k values of 10 Å<sup>-1</sup> in the EXAFS region, and µ-XRD data were collected with a CCD detector. Multiple scans were collected until satisfactory signal to noise ratios were achieved. For each sample, depending on the number of hotspots and concentration, XRF mapping required a total of 2 to 4 hours and EXAFS scans required 4 to 6 hours. Micro-XRD spectra were collected for 60 seconds per scan. EXAFS spectra collected from heterogeneous systems were analyzed by principle component analysis, target transformation, and linear least squares fitting to extract structural information for the coordination shells and the most dominant Ni species contributing to the spectra.

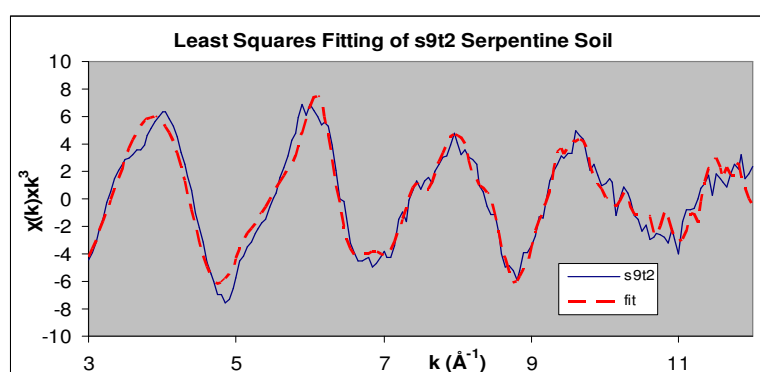
## Results and Discussion

Table 1 presents the basic soil characterization data. For serpentine soils, the pH is considered slightly low. Elevated Ni concentrations are evident. Samples also contained elevated amounts of Cr and Mn.

pH	Texture	OM (%)	Co	Cr	Mn	Fe	Ni
5.9-6.9	loamy sand to clay loam	2.7 -6.5	63 - 310	500 - 3080	350 - 3300	32000 - 190000	560 - 7500

**Table 1. Soil characterization data, elemental concentrations given in parts per million (ppm)**

Figure 1 presents the results of least squares fitting (LSF) of the Ni EXAFS spectra from serpentine soil (s9t2) from Oregon. LSF shows some of the major contributing Ni species. Figure 1 was deduced from a suite of over 25 Ni EXAFS standard spectra. This spectrum was collected at beamline 11-2 at the Stanford Synchrotron Radiation Laboratory. Multiple sweeps were calibrated using a Ni internal reference foil, averaged, and background subtracted using SixPack software. From the spectra, it is evident that manganese and iron minerals, as well as Ni/Al-LDH phases, play a large role in Ni speciation in the serpentine soil. From the fitted data, Ni hydroxides, oxides, and pure phyllosilicate phases do not appear to be important components in this serpentine soil.

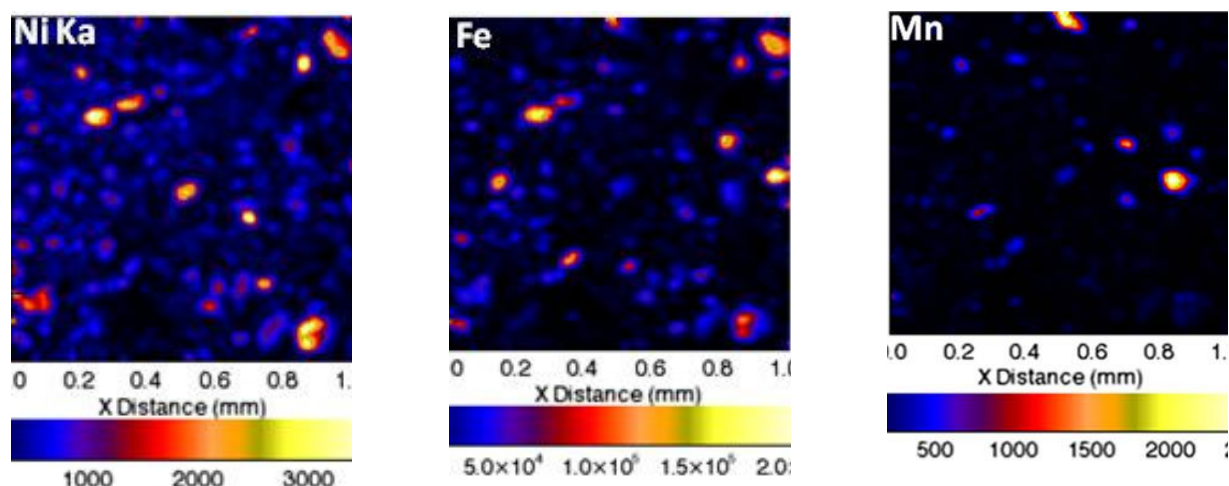


Component	%
Ni/Al-LDH	34.1
Gaspetite (Ni,Mg,Fe)CO <sub>3</sub>	25.9
Ni-Mn-Oxide	60.3

**Figure 1. Least Squares Fitting of a Ni EXAFS spectrum for serpentine soil s9t2.**

Figure 2 presents the XRF maps of nickel, iron, and manganese for the s18t2 serpentine soil sample. These maps were generated at beam-line X26A at the National Synchrotron Light Source at Brookhaven National Laboratory. Incident X-Ray energy was 11000eV. Each map describes the same 1x1mm area of sample. Ni fluorescence coordinates highly with the fluorescence of iron, indicating that these two elements are highly coordinated within the sample. It is important to distinguish from the scale bars that the sample contains much more Fe than Ni, which denotes that Ni is partitioned into iron-containing minerals. This specific soil contains approximately 20% iron. Although to a lesser degree, Ni is also associated with Mn, indicated by

the white circles. From this 1x1mm sample area, two  $\mu$ -EXAFS spectra were obtained to assess the heterogeneity of Ni-speciation on the micron-scale.



**Figure 2. Multi-element fluorescence mapping from the s18t2 serpentine soil sample. Map intensities are independent of each other. The scale bar for each element is specific for its map, and its unit is in number of fluorescence photons counted per second by the multi-element detector.**

### Conclusion

We have provided spectroscopic evidence and confirmation that Ni accumulates largely with iron and manganese in serpentine soils from southwest Oregon. These data provide the first spectroscopic evidence confirming Ni association with Fe and Mn. The LSF of sample s9t2 provides convincing evidence that Ni is associated with both Fe and Mn because Ni-Fe and Ni-Mn reference spectra contribute significantly to the Ni EXAFS serpentine soil spectrum. Additionally, LDH phases are known to develop with Ni at higher pH. Because serpentine soils generally have slightly alkaline pH it is reasonable to conclude that their formation is possible. Because hyperaccumulator plants are native to this type of soil, they must employ a mechanism that can either remove Ni from Fe/Mn compounds or dissolve those compounds to effectively liberate nickel into the soil solution where it can be taken up into the above ground biomass.

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