Nickel Speciation in Several Serpentine (Ultramafic) Topsoils via Bulk Synchrotron-Based Techniques

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ABSTRACT

Serpentine soils have elevated concentrations of trace metals including nickel, cobalt, and chromium compared to non-serpentine soils. Identifying the nickel bearing minerals allows for prediction of potential mobility of nickel. Synchrotron-based techniques can identify the solid-phase chemical forms of nickel with minimal sample treatment. Element concentrations are known to vary among soil particle sizes in serpentine soils. Sonication is a useful method to physically disperse sand, silt and clay particles in soils. Synchrotron-based techniques and sonication were employed to identify nickel species in discrete particle size fractions in several serpentine (ultramafic) topsoils to better understand solid-phase nickel geochemistry. Nickel commonly resided in primary serpentine parent material such as layered-phylllosilicate and chain-inosilicate minerals and was associated with iron oxides. In the clay fractions, nickel was associated with iron oxides and primary serpentine minerals, such as lizardite. Linear

combination fitting (LCF) was used to characterize nickel species. Total metal concentration did not correlate with nickel speciation and is not an indicator of the major nickel species in the soil. Differences in soil texture were related to different nickel speciation for several particle size fractionated samples. A discussion on LCF illustrates the importance of choosing standards based not only on statistical methods such as Target Transformation but also on sample mineralogy and particle size. Results from the F-test (Hamilton test), which is an underutilized tool in the literature for LCF in soils, highlight its usefulness to determine the appropriate number of standards to for LCF. EXAFS shell fitting illustrates that destructive interference commonly found for light and heavy elements in layered double hydroxides and in phyllosilicates also can occur in inosilicate minerals, causing similar structural features and leading to false positive results in LCF.

KEY WORDS: *nickel, serpentine, speciation, ultramafic, sonication, EXAFS, F-test, Hamilton test*

1. INTRODUCTION

Serpentine soils have elevated amounts of trace metals, such as nickel, cobalt, and chromium versus non-serpentine soils. Identifying the nickel bearing minerals during soil weathering will allow for prediction of the potential mobility of nickel over the long term. These minerals strongly affect nickel solubility and mobility (Echevarria et al., 2006; Massoura et al., 2006).

Traditionally, sequential chemical extractions with increasingly aggressive reagents were used to identify soil metal species. Sequential extractions were effective in determining that nickel can accumulate partly in magnesium silicates and also with manganese and iron oxides (Cheng et al., 2011). However, sequential extractions are limited by the possibility of sample alteration, and it is difficult to compare studies on nickel solubility because often different sequential extraction procedures are used (Antic-Mladenovic et al., 2011). X-ray Absorption Spectroscopy (XAS) is capable of determining *in situ* metal speciation with minimal chemical sample treatment and was used in this study.

Because nickel is geogenic in serpentine soils and not anthropogenic (i.e., it is not from deposited aerosols emitted by smelters), apart from being sorbed to clay mineral surfaces and organic matter, nickel is commonly incorporated into the crystal lattices of clay, silt and sand-sized particles of the parent material and secondary minerals (Alexander et al., 2007a). Minerals common in serpentine soils, serpentinized peridotites, and ultramafic lateritic deposits that associate with nickel include those such as lizardite, antigorite, smectite, vermiculite, goethite and hematite (Cheng et al., 2011; Colin et al., 1990; Echevarria et al., 2006; Gaudin et al., 2005; Hotz, 1964; Massoura et al., 2006). Other studies have also shown nickel incorporation in silicate minerals (Decarreau et al., 1987; Hseu, 2006; Manceau and Calas, 1985). For XAS data,

this means that nickel fluorescence emits from nickel sorbed to clay surfaces (e.g., iron and manganese oxides) and also from bulk parent material and larger-sized minerals still present in the whole soil fraction (e.g., lizardite). In order to discern between sorbed nickel phases and nickel incorporated into larger mineral phases, a sonication method was developed to remove clay coatings from the silt and sand fractions of the soils.

Several serpentine topsoils from Oregon, California and Maryland, USA were analyzed with the objective of characterizing the nickel species that naturally occur. Nickel species were identified in the sand, silt, and clay fractions using physical separation methods, sonication, bulk X-ray Diffraction (XRD), chemical digestion, and synchrotron radiation methods [e.g., Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy]. Problems with the Linear Combination Fitting (LCF), a technique commonly used for EXAFS data analysis of soils, are presented and solutions are suggested by utilizing the F-test [Hamilton test, (Hamilton, 1965)] and employing shell fitting of Fourier-transformed EXAFS data. LCF of EXAFS data is commonly problematic in soils because of similar standards that can be used to fit the sample data. Substitution of similar standards and increasing or decreasing the number of standards by just one can have large impacts on the calculated percentage of each component. An averaged-based approach to determining percentage of components found from LCF is presented, which buffers LCF results from these large impacts.

2. MATERIALS AND METHODS

2.1. Physicochemical and mineralogical analysis

Soil samples from three sites were obtained for this study. The first and largest set of samples is from the Klamath Mountains, specifically the Cave Junction area of Josephine County

in Southwest Oregon. The second set of samples is from the Jasper Ridge Biological Preserve in San Mateo County, CA and has been previously characterized (Oze et al., 2004). The third is a serpentine soil from Soldiers Delight Natural Environment Area near Baltimore, Maryland. The soils from Cave Junction and Soldiers Delight were sampled from field sites used for testing of nickel agromining and phytoremediation. They are all from the Ap horizon (0-15 cm). Initially they were partially dried and sieved to 4 mm. Then they were air dried and sieved to 2 mm. Further particle size fractionation is discussed in Section 2.2.

Soil elemental compositions were determined by a combination of digestion procedures including: microwave digestion with nitric acid (EPA method 3051), EPA method 3050B hot nitric, and an Aqua Regia method, all followed by ICP-OES. Particle size analysis was carried out by the hydrometer method. Citrate-dithionite extractions of the soils and soil fractions were also carried out to remove iron and manganese oxides and to determine nickel concentrations in the iron and manganese oxide fraction of the clay (Holmgren, 1967; Loeppert and Inskeep, 1996). Soil pH was determined by mixing the soil with distilled water in a 1:1 ratio and measuring the pH. Organic matter was determined by the loss-on-ignition (LOI) method. Elemental concentrations of the serpentine mineral standards were determined by complete dissolution of the mineral by a Katanax® Fusion machine with a mix of lithium tetraborate, metaborate, and bromide.

X-ray diffraction (XRD) was carried out on a Philips/Norelco powder diffraction system using Bragg-Brentano parafocusing optics with a graphite monochromator. Copper k-alpha radiation (8.04 keV) was used, operating at 35 kV and 20 mA. XRD was carried out on serpentine mineral standards obtained from the University of Delaware's mineralogical supply (serpentine mineral sample numbers 96, 185, and 5811). XRD was also carried out on the coarse

sand, silt, clay and citrate-dithionite treated clay fractions of samples from Oregon and Maryland. Samples were powdered in mortar and pestle prior to XRD analysis. Additional XRD was carried out on synthetic nickel standards prepared in the laboratory and of bedrock (br) from the California soils (JR3br and COIIbr). Synthetic, nickel-doped mineral standards [magnetite, hematite, goethite, and ferrihydrite, and Ni-Fe layered double hydroxide (LDH) (2:1)] were made in the laboratory and characterized by XRD, EXAFS, and chemical digestion. Preparation methods of synthetic standards can be found in the Supplementary Materials. Mineral identification of diffraction data from the soils and soil fractions was carried out using Match!® software (Crystal-Impact, 2012).

2.2. Particle size fractionation via sonication method

Particle size fractionation was used to separate the whole soil fraction, to allow for identification of discrete nickel species located in the sand, silt, and clay size fractions. Other studies have shown nickel concentrations increase in the clay fraction (Oze et al., 2004) where particle sizes range from two micrometers to the nano-scale. This method, modified from published methods, served to disperse the clay fraction and separate the minerals by particle size and was designed to minimize the breakdown of particulate organic matter (i.e., sand-size OM) into smaller particles (Amelung and Zech, 1999; Amelung et al., 1998; Doelsch et al., 2006; Gimbert et al., 2005; Kahle et al., 2003; North, 1976; Oorts et al., 2005; Raine and So, 1994; Schmidt et al., 1999; Sohi et al., 2001; Solomon et al., 2002; Yang et al., 2009).

A probe tip sonicator was calibrated (North, 1976) using a 250 mL glass beaker. A slurry of 20 g of soil (< 2 mm fraction) in 80 mL of 18.2 megohm water (1:4 soil:water ratio) was placed in the beaker for sonication. The probe was always placed 20 mm below the surface of

the slurry. A Branson DIGITAL Sonifier® UNITS Model S-450D was used with a flat tip on the horn. Initially, 60 J/mL were applied to the slurry. Then the slurry was wet-sieved with a 250 μm sieve and 70 mL of water from a fine-mist, hand-pump spray bottle to yield a “sub-250 μm fraction”. By using 70 mL the effluent was clear after passing through the 250 μm sieve. Then 440 J/mL were applied to the 150 mL of sub-250 μm fraction (Amelung et al., 1998). After the second sonication, the collected slurry was wet-sieved again using the spray bottle and a 45 μm sieve until the effluent was clear, yielding a “sub-45 μm fraction”.

From the sub-45 μm fraction, first the < 2 μm clay fraction and then the < 5 μm clay/fine silt fraction were sequentially removed via centrifugation using a swinging-bucket centrifuge rotor. Then the 5-25 μm fraction (fine silt) was separated from the remaining sub-45 μm fraction via wet-sieving using a 25 μm sieve and the spray bottle until the effluent was clear, thus yielding a 25-45 μm fraction. The wet-sieved and centrifuged fractions were dried with warm air at 35° C in typically less than 36 hours. During every sonication the slurry was placed in an ice bath to maintain a slurry temperature of less than 37° C. Particle density was assumed to be 2.65 g cm⁻³.

For the rotor, the sedimentation distances were measured to calculate centrifuge time and speed. Centrifuge speed and time were calculated using a Sorvall RC 6 centrifuge with a HS-4 rotor, taking into account the R1 and R2 distances from the axis of rotation for sedimentation time and speed. Fifty mL conical centrifuge tubes were used. Centrifugation times were calculated from formulas in Soil Chemical Analysis Advanced Course (Jackson, 1985) pages 113 and 127 and Methods of Soil Analysis Part 4, Physical Methods (Gee and Or, 2002).

With respect to the rest of this paper, “clay” always refers to the < 2 μm fraction; “silt” is the 25-45 μm silt fraction, and “coarse sand” or “coarse” or “sand” always refer to 0.5 to 1 mm

diameter particles. Sonication disperses conglomerated clays and clays adsorbed to larger particles and minerals in the silt and sand fractions. These clays were washed out of the silt and sand fractions using the wet-sieving steps. Published methodologies using sonication for clay fraction separation generally do not provide laboratory-specific details; hence, the sonication times, centrifuge times, and decantation distances were all calculated using materials and equipment available for this study.

2.3 Synchrotron-based data acquisition and analysis

Additional methods for synchrotron-based data acquisition and analysis, including beamline characteristics, Principal Component Analysis (PCA), Target Transformation (TT), SPOIL values, LCF, F-Test, and shell fitting methods of EXAFS data are described in the Supplementary Material text and Table S1. Linear Combination Fitting results were grouped into four different categories: “Mafic and Serpentine Related”, “Iron Oxide”, “Manganese Oxide”, and “Adsorbed to phyllosilicate” (Table 3). The results were grouped in this fashion so all of the LCF results could be concisely categorized. The group “Mafic and Serpentine Related” includes multiple standards that, although distinct in origin and formation, are related in the local atomic environment of nickel. The standards that fall into this category are serpentine minerals (layered silicates), chain silicates, and layered hydroxides. Each standard is explicitly identified in Table S3. Nickel adsorbed to gibbsite (Yamaguchi et al., 2002) is included this group because it is similar to nickel incorporated into the octahedral layer of a light-element (aluminum) layered hydroxide mineral, which is similar to the hydroxide sheet in serpentine minerals (e.g., lizardite). The groups “Iron Oxide” and “Manganese Oxide” are standards where nickel is either adsorbed

to the surface or incorporated (doped) into the structure of the iron or manganese oxides. Lastly, the category “Adsorbed to Phyllosilicate” is nickel adsorbed to montmorillonite clay at pH 6.

Linear combination fitting is sensitive to specific standards used in each fit. Metal speciation (i.e., the final fit, or the amount and number of each nickel standard deduced to be contributing to the sample data) can vary drastically when substituting or varying even just one standard as a component. Additionally, when the statistically appropriate number of standards are used (e.g., two to three standards in this case), results can yield similar fits with similar R-factor values. A comprehensive set of LCF results for each soil sample is provided in Table S4 to illustrate this issue. To limit results containing artifacts induced by these problems, the results from the best fits (Table S4) were averaged together to obtain an averaged-based linear combination fitting result and thus average nickel speciation (Table 3). This method buffers the final result (i.e., the final fit) from the wide fluctuations that commonly result from LCF of soil samples with multiple standards. Table S4 and Figure S5 illustrate how similar fits can be obtained by using different standards.

3. RESULTS

3.1. Physicochemical and mineralogical analysis

Table 1 has the physicochemical properties for the < 2 mm soil fraction of the Oregon and Maryland soils. Soil s5t2 is the only sample from Maryland, while all other samples are from Oregon. The pH range of the soils is between 5.6 and 6.9. The clay fractions varied between 20% and 39%, while sand fractions ranged between 25% and 57%. The resulting soil textures ranged between sandy clay loam and clay loam. Nickel concentrations ranged from

1510 mg kg⁻¹ to 5970 mg kg⁻¹. Iron concentration is high in several samples but highest in sample s20unt, at 138,600 mg kg⁻¹.

Physicochemical properties of the Jasper Ridge soils have been previously described (Oze et al., 2004). The soils from Jasper Ridge are dominantly Mollisols formed on top of serpentinized peridotite. In both sites (JR3 & COII), nickel concentrations in the soil were less than in the bedrock. Nickel concentrations ranged from 3510 mg kg⁻¹ to 2400 mg kg⁻¹ in the COII site. The pH of the soils is near neutral and slightly increases with depth, ranging from 6.71 to 6.98. The clay fraction of the JR3 site had the highest concentration of nickel, and the silt fraction the lowest, with about 2900 mg kg⁻¹ and 1800 mg kg⁻¹, respectively.

Concentrations of iron, manganese, and nickel for the citrate-dithionite extractions of the clay fractions are listed in Table S2, along with nickel and iron concentrations in serpentine mineral standards from the Katanax fusion digestion. Samples s20unt and s10t2 have the highest percent iron in the clay fraction with 20.2% and 18.4%, respectively. Sample s11unt clay fraction has the lowest amount of iron at 6.4%. For the serpentine mineral standards, Serp96 had the highest iron and nickel concentrations. Nickel can substitute for magnesium in the octahedral layers of silicates, such as serpentine minerals, because its ionic radius is similar to that of magnesium (0.69 Å vs. 0.66 Å, respectively) (Alexander et al., 2007a; Manceau and Calas, 1985).

Table 2 lists the minerals identified by XRD analysis of soil fractions (s5t2, s9t2, s10t2, s11unt, and s20unt; total 17 spectra). The diffractograms from the whole soil, clay, silt and coarse sand fractions, including diffractograms of clay fractions that were citrate-dithionite treated, were analyzed and are shown in Figure S1. Specific particle size ranges for “sand”, “silt”, and “clay” are defined in Section 2.2. Serpentine minerals, such as antigorite and

lizardite, are commonly present in both the coarse sand and clay fractions of the soils. Talc and quartz are also common. Goethite, hematite, and magnetite are iron oxide minerals found in the soils. Enstatite and pargasite, both chain inosilicate minerals, were found in the XRD patterns of multiple samples. The phyllosilicate clinochlore, which is common in ultramafic rocks, was also identified in multiple samples.

The dithionite treatment of the clay fractions removed iron and manganese oxides and sharpened peaks of silicate minerals (Figure S1). Serpentine minerals in s5t2, such as antigorite and lizardite, are common. In the dithionite treated (DT) clay fraction of s5t2, the peaks for antigorite, brucite, talc, and quartz are clearer as the goethite peaks have disappeared. The DT clay fraction of s9t2 peaks are mostly due to clinochlore as the broad, smaller iron oxide peaks disappeared.

When the clay fraction of s10t2 was treated with dithionite, the lizardite/antigorite peaks became much clearer, as well as some peaks for clinochlore and quartz. When the clay fraction of s20unt was treated with dithionite, the peaks for goethite and hematite were removed and the silicate-mineral peaks are clearer. After treatment of s11unt clay with dithionite, the lizardite/antigorite peaks are clearer and several of the small, wider peaks from goethite and hematite are gone. The coarse sand fraction of s10t2 was ground in a mortar and pestle from which the clay fraction was retrieved via the centrifugation. This sample was labeled “s10t2 coarse < 2 mm” and has peaks for lizardite, quartz, goethite, enstatite, and hematite (Figure S1); thus the coarse fraction of s10t2 has sand-sized goethite and hematite iron oxides.

Figure S2 shows diffractograms of minerals, both natural and synthetic, used as standards for LCF of EXAFS data. COIibr and JR3br have very similar mineralogy; however, COIibr contains some magnetite while JR3br displays clear diffraction peaks for lizardite; the JR3br

peaks line up consistently with pure serpentine mineral phases Serp96, 185 and 5811. Thus, JR3br is a good sample to use as a lizardite standard for LCF of EXAFS data. Peaks for the nickel-doped minerals magnesium oxalate, magnetite, hematite, goethite, and Ni-Fe LDH all correspond to their correct phases.

Mineralogical data of the Jasper Ridge soils have been previously described (Oze et al., 2004). The serpentinite at Jasper Ridge is composed of mainly lizardite and antigorite (70%), chlorite (15%), talc (10%), magnetite (4%), and chromite (1%). Other minerals include olivine, augite, and enstatite. Nickel in these samples was found in three phases in the JR3 bedrock, including olivine, serpentine, and a nickel-iron metal alloy, probably awaruite. Only soils from sites JR3 and COII were used in the present study. The clay size fraction of the JR3 site is composed of smectite, vermiculite, lizardite, antigorite, clinochlore, and Cr-clinoclhorite, with smectite being the most abundant mineral. This mineralogy did not vary significantly at different depths (Oze et al., 2004).

3.2. Particle Size Fractionation

Figure 1 shows how the different particle size fractions (sand, silt, and clay) influence nickel speciation in two soil samples, s20unt and s10t2. EXAFS spectra and their Fourier transform (FT) magnitudes are shown in Figure 1a and b, respectively. The four EXAFS spectra for each soil are from the different particle size fractions, clay, silt, coarse sand, and the whole soil (< 2 mm). Figure 1c shows the LCF results of the whole soil fraction using spectra from each particle size as the components of the fit.

The clay fraction is the dominant component in s20unt, as it accounts for 75% of the nickel species from the whole soil. The s20unt whole soil fraction can be reconstructed using

just the clay and silt fractions. However, for s10t2, the distribution of nickel is more homogeneous between particle sizes as both the clay and coarse components contribute about equally to the whole soil spectrum. The clay fraction comprises 54% of nickel while the coarse sand fraction 46%.

3.3. Synchrotron-based data acquisition and analysis

Figure S3 shows the results of PCA analysis of the soils and indicates that at most four spectra are needed to reconstruct the EXAFS data. This can be determined by visual analysis of the oscillations of components 1-5. Component #4 (blue line) is the last component with discernable oscillations; it has more signal than noise. This method was the most basic, initial way of determining the number of components needed to reconstruct the data. Additionally, a scree plot was employed, where a break in the slope of the scree plot indicates the minimum number of components in the system (Webb et al., 2005). The components that lie on the linear portion of the plot are probably due to noise versus components that come before the break in the slope of the line that are probably structural (Calvin, 2013). The scree plot has a slight break in the slope at four components (Figure S3b, inset), which would again indicate that the EXAFS data can be reconstructed with a minimum of four standards. However, the major break in the slope is at two components, which indicates that at minimum two components are necessary to adequately reconstruct the data. Based on these varied results, between two and four components were necessary to reconstruct the data. Further analyses by F-tests provided additional information to determine the number of standards that statistically improved fits.

Table S3 shows a full list of standards considered for LCF of soil EXAFS data, their SPOIL, chi-square, and R-values. Each of the 45 standards in Table S3 is shown in Figure S4.

Of the 45 total standards considered, 27 were selected to use in LCF. Any standard not previously published (references in Table S3) was characterized via shell fitting of the FT EXAFS data to ensure it was accurately prepared. In total, there were 18 spectra previously unpublished and shell fitting results of those 18 spectra are in Table S5.

Table 3 contains the averaged-based results of LCF for soil nickel speciation. Mafic and serpentine related minerals heavily contribute to nickel speciation in many of the soils. On average, mafic and serpentine related minerals contribute 55% of all nickel species for the whole soil fractions, with a range from 16% in s20unt to 83% in s14t2. This indicates that in these topsoils primary serpentine minerals are the important hosts for nickel. Additionally, iron oxides are also consistently important hosts for nickel, with 42% of nickel species related to iron oxides in the whole soil fraction of s10t2. Nickel adsorption to a phyllosilicate (montmorillonite) is also an important component in s15t2 soil, s5t2 soil and s10t2 soil. Manganese oxides are a minor component in several soils; however there are artifacts in the LCF results caused by spectral similarities between birnessite and several of the standards. Discussion is dedicated to manganese oxides in Section 4.3.1, Section 4.4, and in the Supplementary Materials text.

Select LCF graphing results are shown in Figure 2. The fit for each sample (dotted red line) is labeled with its R-factor that corresponds to the component results in Table S4. The soils have similar major oscillations with differences in the locations of shoulders and beat patterns. Multiple spectra have indentations on the first oscillation at $3.8 \text{ \AA}^{-1}$. Samples COII, JR3, s5t2, s9t2, s11unt, s14t2 and s15t2 have this feature. Multiple fitting results for the same sample are presented in Table S4 because even though a lower R-factor statistically indicates a better fit, the fit with the lowest R-factor or appropriate number of standards may miss structurally relevant features of the sample, such as shoulders at $3.8 \text{ \AA}^{-1}$ or $5.2 \text{ \AA}^{-1}$. This is illustrated in Figure S5.

Table S4 also contains the results from F-tests (Hamilton tests) for each sample, labeled as “*I*” values. Normally two to three standards were used for LCF based on the results of the F-tests. A 95% confidence interval with the F-Test was employed, and no improvement in any fits was statistically significant by adding four standards. By using this method, there is less than a 5% chance that the improvement in a fit is caused by random variation or noise in the data.

4. DISCUSSION

4.1. Physicochemical and mineralogical analysis

In the Klamath Mountains, the well-drained soils which formed from peridotite yield more free iron oxides than soils which formed from serpentinite (Alexander, 2004). This explains the high iron values in the most oxidized soil samples in this study (e.g., s20unt and s10t2) (Table 1, Table S2). The low Ca:Mg ratios are typical of serpentine soils (Table 1), which have characteristically low Ca:Mg ratios (Burt et al., 2001). The high chromium in the samples comes from chromite, which commonly is present in serpentine soils. Although, in the bulk XRD data, few diffraction peaks for chromite are seen (Figure S1). Nickel in chromite is tetrahedrally coordinated and has very distinct X-ray absorption pre-edge and edge features not seen in many serpentine soils (Manceau and Calas, 1986).

For the Jasper Ridge soils, site COII was treated with sequential extractions, and the majority of nickel remained in the solid phase. Most of the nickel in the Jasper Ridge site originated from olivine. During serpentinization, the resulting serpentine mineral also contained nickel, and small grains of a nickel-iron alloy (awaruite) were produced. The concentration of nickel increased as other elements weathered and leached out over time (Oze et al., 2004).

Ultramafic Oregon soils have been studied by several researchers (Alexander, 2004; Alexander and DuShey, 2011; Alexander et al., 2007b; Borine, 1983; Burt et al., 2001; Hotz, 1964; Istok and Harward, 1982). Serpentine minerals are considerably more resistant to weathering than olivine and pyroxene (Alexander, 2004), and so their presence in samples in this study is understandable. In some of the more oxidized samples, such as s20unt, the relative abundance of iron oxides versus serpentine minerals is evident especially in the clay fraction (Table 2, Table S2, Figure S1). Other studies have shown that serpentine minerals in this area had weathered away (Hotz, 1964), but their presence is common in these samples. Serpentine minerals were found to be dominant in the clay fraction of several serpentine soils from other studies in the Klamath Mountains (Burt et al., 2001). In a serpentine soil from Maryland, serpentine minerals were found in the coarse clay and silt fractions but not in the fine clay fraction (Rabenhorst et al., 1982). Serpentine minerals were identified in the clay fraction of the Maryland soil (s5t2) presented here (Figure S1).

Trevorite is a nickel-iron oxide spinel that can occur in ultramafic rocks and has been identified in this area of the Klamath Mountains (Bird and Weathers, 1975; Hudson and Travis, 1981). Pargasite is in the amphibole group, and thus is an inosilicate mineral. It can occur in altered ultramafic rocks (Anthony et al., 2003). Inosilicates, or chain silicates, can originate in mafic rocks (Schaetzl and Anderson, 2005). Pargasite was identified in the ultramafic rocks of Bear Mountain in the Klamath Mountains in California (Snoke et al., 1981), and it is identified in samples s9t2 coarse, s11unt coarse, and s20unt in this study. In s20unt, the presence of enstatite is understandable because enstatite is an orthopyroxene mineral that is found in similar serpentine soils derived from harzburgite (Alexander, 2004). Nickel not incorporated into iron oxides at the soil profile surface can migrate downward and become enriched into silicate phases

(or garnierite) at the bottom of the weathering profile. This enrichment process at the bottom of the profile is a supergene process (Carvalho-E-Silva et al., 2003) and can occur in both nickel sulfide and laterite deposits (Gleeson et al., 2004; Suarez et al., 2011).

4.2. Particle Size Fractionation

Figure 1 is the LCF results of two whole soil fractions using particle sizes as components. It illustrates that a significant portion of nickel is located in the clay fraction of s20unt, where 75% of the whole soil EXAFS spectrum can be fit using the clay fraction. Nickel has been shown to accumulate in the clay fraction of serpentine soils (Oze et al., 2004). In s20unt, there is a more pronounced shoulder in both the silt and coarse sand fractions at $\sim 5.3 \text{ \AA}^{-1}$ and $\sim 7.2 \text{ \AA}^{-1}$ (Figure 1a). For s10t2, all four spectra look similar, indicating that nickel species have similar local atomic environments. Fourier transformed spectra of s20unt in Figure 1b show the second neighbor (the second shell) to nickel is larger in both the coarse sand and silt fractions as compared to the clay and whole soil fractions (dotted circle). A smaller second shell here can indicate a more heterogeneous sorption environment for nickel in the clay fraction. The clay fraction contains higher amounts of iron oxide and phyllosilicates clays, where nickel is likely to be both adsorbed and incorporated in a variety of binding sites. This heterogeneous environment would yield a smaller second shell (smaller amplitude) because of low scattering path degeneracy. Because larger particle size fractions, such as the silt and coarse sand fractions, contain larger, more crystalline minerals, there is more probability for higher path degeneracy and multiple scattering. This would lead to the presence of a larger second shell (larger amplitude) as seen in s20unt Figure 1b.

This trend, however, does not hold true for s10t2, where all size fractions have similar EXAFS spectra as well as amplitudes in the first and second shells of the FT (Figure 1a and b). Given the similarities in the EXAFS spectra of all three size fractions in s10t2, it is not unexpected that nickel is more evenly distributed between particle sizes (Figure 1c). This similarity is most likely because both size fractions contain significant quantities of iron oxides, causing similar nickel species to be present in all size fractions. In s10t2, more nickel is associated with the coarse sand fraction than in s20unt. Sample s10t2 also has a more sandy texture (Table 1), indicating that soil texture plays a role in the differences in nickel speciation for these two samples.

In other studies where nickel was associated with amorphous iron oxides, more than two thirds of total soil nickel was in the clay fraction. However, nickel was less associated with well crystalline iron oxides, and crystallization during pedogenesis was a process that separated nickel from goethite particles (Bani et al., 2009; Bani et al., 2007).

4.3. Synchrotron-based data acquisition and analysis

4.3.1. LCF

Table 3 contains the averaged-based results of LCF carried out on the samples. The results are averages of multiple fits found in Table S4. In the Jasper Ridge COII site, nickel speciation does not change significantly throughout depths. Most samples have features related to mafic and serpentine minerals. This indicates that even in the top layers of the soil, where weathering is most intense, the major species of nickel remain in their primary mineral phases. Different standards consistently created fits with similar R-factors (Table S4). For example, in COII 2-5 cm, Ni-Al Silicate appears in the best fit, but immediately following in the next fit is

gibbsite. Those standards were objectively grouped together in the mafic and serpentine group. Iron oxides make up to 18-27% of the total spectra throughout the COII profile. Similar results are found for the JR3 site, with most of the samples exhibiting spectral features related to mafic and serpentine minerals. These results align with the findings in Oze et al, 2004, where the majority of nickel remained in the solid phase. The most recalcitrant nickel is in the silicate minerals. JR3 bedrock (br) is consistently a major component of all samples from the COII and JR sites (Table S4).

JR3br is a critical standard to characterize accurately because of its inclusion as a standard to fit other samples. Diffraction data for JR3br display clear diffraction peaks for lizardite (Section 3.1, Figure S2). The averaged-based LCF results indicate that nickel in JR3br is 78% mafic and serpentine related and 21% iron oxides. Individual fits of JR3br are shown in Figure S5 to illustrate the accuracy of the fits at low k. There is no F-test value (Table S4) for this sample because of the 3-7 Å⁻¹ k-range used to do LCF of this sample. This range was chosen to focus on characterizing the low k-range with the best accuracy possible and because serpentine mineral standards (e.g., #5811) had more noise at higher k values (e.g., > 8 Å⁻¹).

Sample s5t2 contains diffraction peaks for serpentine minerals including antigorite and lizardite. The LCF results indicate that a majority of nickel is associated with those phases. In the whole soil fraction, nickel is additionally found to be adsorbed to phyllosilicate clays (montmorillonite). This component is not present in the clay fraction because of the different k-range used. The spectrum from the whole soil had increased noise compared to the spectra from the clay and coarse fractions, so a shorter k-range was necessary (Table S4).

Nickel is also associated with mafic and serpentine minerals in s9t2 (52-69%). Pargasite was found in the diffractogram of s9t2, which is a chain inosilicate mineral. Nickel EXAFS

from inosilicate minerals can exhibit features similar to RS birnessite, which was found to compose 52% of the s9t2 whole soil EXAFS spectrum. Section 4.3.3 discusses the cause of this similarity and how it can cause artifacts in LCF results. Thus s9t2 likely has very low contribution from any manganese oxides.

Iron concentrations were high in s10t2 (Table 1, Table S2), and iron oxides comprised a larger LCF percentage in s10t2 than in any other sample on average (Table 3). XRD also indicates that hematite is present in the coarse fraction. Similarly to s5t2, higher noise in the whole soil spectrum reduced the k-range for LCF fitting, and Ni-adsorbed to phyllosilicate (montmorillonite) became an important component in the fit. Enstatite, a chained inosilicate mineral, is present in all fractions (Table 2) and is artificially increasing the manganese oxide percentage in the clay and coarse fractions (see Section 4.3.3.).

In s11unt, mafic and serpentine related minerals are the dominant nickel species, which agrees with the diffraction data and the spectral feature at $3.8 \text{ \AA}^{-1}$ (Figure 2). At this energy, splitting in the first oscillation of the EXAFS signal occurs, indicating nickel is located in the octahedral sheet of a layered-type hydroxide surrounded by magnesium (see Section 4.3.3.). Samples s13t2 and s14t2 also have high amounts of nickel incorporated into mafic and serpentine minerals, with iron oxides contributing 30% and 15% to the sample data, respectively (Table 3). According to elemental data, however, s14t2 has more than twice the total iron in the soil (Table 1) and the second highest amount of iron overall. Thus, concentration measurements do not correlate with nickel speciation. Sample s14t2 has a prominent split in its first oscillation as well, indicating nickel is mostly present in a magnesium-silicate mineral and less so in iron oxides (Figure 2). Sample s15t2 also has a slight split of the first EXAFS oscillation, indicating

a large presence of mafic and serpentine minerals. Additionally in s15t2, nickel is adsorbed to phyllosilicates (montmorillonite), which is indicated as 32% of the average-based nickel species.

Even though RS birnessite (a Ni-manganese oxide standard, Table S3, Figure S4) was found to be an important component in s20unt by LCF analysis, it is likely that this is an artifact. The sonication method employed disperses clays into solution. Then the silt and sand fractions were rinsed clean with water, removing the manganese oxides which are primarily located in the clay size fraction. The reason that RS birnessite fits so well with the s20unt data is because it has a shoulder at $5.2 \text{ \AA}^{-1}$ (Figure S4), just like the s20unt sand and silt fractions. Additionally in s20unt sand and silt fractions, there are truncated oscillations between 7.5 and $8.5 \text{ \AA}^{-1}$, precisely where the same feature occurs in RS birnessite. These spectral similarities are what give this standard a false positive LCF result. It is more likely that silicates such as enstatite are hosting a significant amount of nickel.

Enstatite is an inosilicate, pyroxene mineral common to mafic rocks. Nickel is a metal cation that can bond the tetrahedral silica chains together. Enstatite was found in the XRD pattern of s20unt coarse and silt fractions (Figure S1) as was pargasite, another inosilicate mineral. Trevorite is a Ni-Fe spinel in the magnetite series, and magnetite is identified in the XRD pattern of s20unt silt (Figure S1). Trevorite is also indicated in Table S4 as a component in several of the fits for the s20unt sample. Thus in s20unt, magnetite is most likely another source of nickel. Additionally, the trevorite spectrum (Figure S4) also has truncated oscillations between 7.5 and $8.5 \text{ \AA}^{-1}$. This similarity further compounds the problem of different standards having similar spectral features (see Section 4.4. for further discussion).

4.3.2. *F-tests*

F-tests are an aid to determine an appropriate number of standards to use in a linear combination fit (Calvin, 2013). To employ the F-test, the number of independent data points of the sample EXAFS data should be kept the same for each fit. This way multiple fits can be compared where different numbers of standards are used. Artemis software was used to determine the number of independent data points, and then “*I*” values were determined as in Calvin, 2013. An “*I*” value is the result of the F-test (Table S4). A 95% confidence level was employed, meaning that for a fit with three standards to be statistically better than a fit with two standards, “*I*” must be less than 0.05 (i.e., 5%). The same premise is used to determine if a fit with four standards is statistically better than a fit with three standards and so on. Adding more standards to a linear combination fit almost always reduces the R-factor, so this test provides a quantitative way to determine if the fit improvement is statistically significant or not.

For example in Fit #1 in Table S4, F-tests were carried out on the best fits using two and three standards. Using the R-factor values from the best fits with two and with three standards, the “*I*” value was calculated. For Fit #1, $I=0.053$; thus using three standards does not statistically improve the fit because $I > 0.05$. However, for Fit #7, $I = 0.036$, using three standards statistically improved the fit. The same test was done for fits using three and four standards. In no case were four standards found to have “*I*” values less than 0.05 versus fits using three or two standards. The F-test results prove that visual inspection of the components and the scree plot (Figure S3) may not suffice to determine the significant number of standards to include in the fit. Although PCA and the scree plot indicated four standards were necessary to reconstruct the data, the fits do not statistically improve when four standards were added.

Exceptions to this method can be made when structurally important features are not captured. For example, in Figure S5, fits of s5t2 soil are shown. The F-test ($I=0.161$, Fit #13,

Table S4) determined that s5t2 soil should only need two standards. However, the best fit using two standards (Fit #13, Round #7, R-factor 0.0620) did not capture structurally relevant features. The fit line, although close to the real data, is smoother than the real data and does not follow the structurally relevant shoulders at $3.8 \text{ \AA}^{-1}$ and $5.2 \text{ \AA}^{-1}$. Those shoulders are present because of long range order in the octahedral layers of the minerals antigorite and lizardite, which are found in the diffractograms of s5t2 (Table 2, Figure S1). Nickel is located in the octahedral sites of these minerals (see Section 4.3.3.). Thus, to improve the fit, three standards were used (Fit # 13, Rounds # 1 through 6). Even with the use of three standards, the “best” fit (R-factor 0.0531) is misfit at $3.8 \text{ \AA}^{-1}$ because it does not follow the slight splitting of the first oscillation. This specific portion of the spectra is critical because the splitting creates a shoulder at $3.8 \text{ \AA}^{-1}$ and is caused by multiple scattering of light elements in the octahedral layer. Round #1 of Fit #13 has the lowest R-factor but does not conform to important features of the sample spectra, especially at low k-ranges. Fits with R-factors 0.0531 and 0.062 were not included in the averaged-based result (Table 3).

Analysis of the fit at low k-range was also important for s11unt coarse sand (Figure S5). The fit which most accurately matches the sample at low k actually has a higher R-value (0.0368 vs. 0.0357). These fits were considered to be equivalently good, and both were used to calculate average-based results (Table 3). Sample s13t2 soil in Figure S5 is problematic because statistics from the F-test show that only two standards yield statistically significant results (Table S4, Fit #22, $I = 0.054$). However, with the inclusion of 30% goethite as a third standard, the fit is improved at $3.8 \text{ \AA}^{-1}$, effectively decreasing the shoulder intensity of the fit. Additionally, the shoulder at $5.7 \text{ \AA}^{-1}$ more accurately matches the sample spectra. Thus, here three standards

produce a more appropriate fit than two even though the F-test indicates only two standards should be used.

The fits of s15t2 soil (Figure S5, Fit #24 in Table S4) have R-factors ranging from 0.0520 to 0.0649. All of these fits replicate the major and minor oscillations and shoulders of the sample spectrum except Round #5 (R-factor = 0.0625). It poorly fits the data at $3.8 \text{ \AA}^{-1}$. Between 5 and $5.5 \text{ \AA}^{-1}$, the shoulder is also missed, yet a reasonable R-factor value is still produced. Round #5 is an example of how a poor fit can give a reasonable R-factor. It was not included in the average-based result (Table 3). The s10t2 silt fits (Figure S5, Table S4, Fit # 18) illustrate how different nickel compositions and R-factors can produce similar fits. In Rounds #1-3, different standards are present yet produce similar fits. Round #3 has an R-factor of 0.0476, which is more than 60% larger than the best fit in Round #1.

4.3.3. Mixed metal second shells

In Figure 2, the indentation in the first oscillation of multiple samples at $3.8 \text{ \AA}^{-1}$ indicates the presence of a “light” element, such as magnesium, as a second neighbor to the central absorbing nickel atom in a phyllosilicate or layered hydroxide-type environment. This type of shoulder is commonly present in layered hydroxide octahedra where light elements (e.g., magnesium or aluminum) neighbor “heavier” elements (e.g., zinc or nickel) (Manceau et al., 1987; Manceau et al., 2004). The split of the first oscillation at $3.8 \text{ \AA}^{-1}$ is caused by light elements in the second coordination shell of the absorbing atom (Manceau et al., 2000). The size of the split is affected by the number of heavy atoms surrounding the central absorber. A higher amount of heavy atoms results in a decrease in the splitting. The split can be used as a diagnostic tool for this type of structural environment in unknown materials (Manceau et al., 2004; Schlegel

et al., 2001). The split feature is identifiable in the serpentine minerals standards in this study (Figure S4). Zn-phylosilicates have a similar spectral feature to nickel rich serpentine minerals (Ni-phylosilicates) where light magnesium atoms surround zinc causing the split in the first oscillation (Manceau et al., 2003).

Specific limitations in EXAFS for studying trioctahedral phyllosilicates have been documented (Manceau, 1990). There are *in-and-out* of phase oscillations for magnesium and nickel atoms in the second shell. Nickel can substitute for magnesium because they have similar atomic radii. The presence of magnesium with nickel in the second shell decreases the amplitude of the wave backscattered by the surrounding nickel atoms in such a way that EXAFS cannot separate the contributions of nickel from magnesium (Manceau and Calas, 1986). The addition of silicon at about 3.24 Å may be necessary to fit the second shell data. However, silicon is *in-phase* with nickel oscillations yet magnesium is *out-of-phase*. These *in-and-out* of phase oscillations significantly complicate shell fitting analysis of phyllosilicates. Nickel and iron have similar backscattering phases and amplitudes and cannot be distinguished by EXAFS. Silicon, aluminum, and magnesium as a group and iron and nickel as another group have nearly equal scattering factors and prevent the distinction between atoms in each group based on scattering intensity and phase. Silicon interferes constructively with nickel at low k and increases the total amplitude; however, magnesium interferes destructively and its contribution to the EXAFS spectrum is “subtracted” from that of nickel and silicon atoms (Manceau, 1990).

The EXAFS data of s20unt silt were fit using the crystal structure of enstatite (a chain inosilicate mineral found in this sample), allowing for inclusion of three scatterers in the second shell (Ni, Mg, Si) in a restrained fit (Table S5, Figure S6). From the FEFF input file, there were 6 Ni-O scattering paths for the first shell at an average of 2.081 Å. The number of scattering

paths for the second shell was 9, including 5 total Ni/Mg atoms and 4 Si atoms. The Ni-Mg scattering paths had a range of 2.973 to 3.194 Å. By doping atoms into the FEFF input file, average Ni-Ni and Ni-Mg distances of 3.051 and 3.149 Å, respectively, were determined. The 4 Si scattering paths were between 3.159 and 3.301 Å with an average distance of 3.254 Å. The data show a very close fit to the structure of enstatite (Table S5, Figure S6).

For the fit, the second shell was broken into three parts, Ni, Mg, and Si, where Ni was substituted for Mg in the FEFF input file. The fit showed very close agreement with the FEFF calculated paths, with fitted values of 3.06 and 3.14 Å for the Ni-Ni and Ni-Mg distances, respectively (Table S5). The fitted distance for Ni-Si scattering was 3.294 Å, which agrees closely with the average FEFF calculated scattering distance of 3.254 Å. The fit was restricted to have equal amounts of Ni/Mg in the second shell and 1.6 times more Si than Ni/Mg, as would be the case for the pure phase mineral.

Constructive and destructive scattering (Figure S6b) of the nickel, magnesium, and silicon atoms occurs in the second shell. This type of interference has been well documented in layered hydroxides and phyllosilicates (Manceau, 1990). However, it has not been well documented for chained inosilicate minerals like those found in this study. Figure S6b clearly illustrates the *in-and-out* of phase oscillations which can also cause constructive and destructive interference in inosilicate minerals. In LDHs, this same type of interference is what causes peak truncation between 7 and 9 Å⁻¹ (Scheinost and Sparks, 2000; Siebecker et al., 2014). Ni-Al LDH fits into s20unt silt (Table S4, Fit #27, Round #3), which contains enstatite, because of the peak truncation and double peaks present between 7 and 9 Å⁻¹. EXAFS spectra of inosilicate minerals can have similar features of a Ni-Al layered double hydroxide.

4.4. XRD vs. EXAFS

Figure 3 illustrates a complication that can arise while using LCF to analyze EXAFS spectra of soils. Figure 3a compares the XRD spectrum of the s20unt silt fraction (black line) versus the XRD spectrum of a typical Ni-Al LDH (red line). This being the silt fraction of s20unt, all clays have been removed from the sample via sonication (Section 2.2.). Thus, the spectrum is of particles only in the 25-45 μm range. Vast differences in the XRD spectra are evident, with the Ni-Al LDH notably having much fewer and broader peaks. The crystallinity of the silt fraction is noted by the multitude of sharp diffraction peaks, which are identified explicitly in Figure S1 and Table 2. Although not all of those phases are nickel-rich (e.g., quartz), the silicate and layered hydroxide minerals (such as clinocllore, enstatite, pargasite, talc, lizardite, and forsterite) are potential locations for nickel.

The diffractograms show that the mineralogy of the two samples is very distinct. The comparison of their EXAFS spectra, however, shows clear similarities and hence similar local nickel environments in both samples (Figure 3b). The samples have different mineralogy but similar local atomic environment of nickel. The phase and amplitude of both EXAFS spectra are similar for two samples with such different mineralogy. This similarity, however, should not be surprising because many nickel-rich minerals in serpentine soils, e.g., lizardite, are layered silicate minerals with nickel located in the octahedral layer along with the lighter element magnesium. Magnesium can have a similar effect as aluminum (Section 4.3.3.). The Ni-Al LDH is a layered hydroxide mineral with both nickel and aluminum in the octahedrally-coordinated (hydroxide) layer. Because nickel is located in the octahedral layer and surrounded by light elements, such as magnesium and aluminum, in both serpentine minerals and Ni-Al LDH, it is logical that the spectra are quite similar. The light elements cause dampening of the

upward peak at ca $8.2 \text{ \AA}^{-1}$ in the LDH structure when compared to single metal layered hydroxides (Scheinost and Sparks, 2000).

This type of structural similarity between standards can lead to a false positive result when reporting LCF results. This is why the LCF results reported in this paper (Table 3) are done in an average-based approach of multiple fits: to avoid over-dependence on one specific standard. The Ni-Al LDH standard was grouped into the “Mafic and Serpentine Related” standards (Section 2.3.) because of the structural similarities between LDH and lizardite. Often, lizardite is used as a crystal structure model when shell fitting EXAFS data of LDHs (Scheinost and Sparks, 2000).

LCF results of s20unt silt (Fit #27, Table S4) with similar statistical results indicate the major nickel components are nickel silicates and serpentine minerals. Additionally, with respect to the formation of LDH in serpentine soils, other researchers have identified at $8 \text{ \AA}^{-1}$ a strong double oscillation for nickel adsorbed to phylломanganates (Fan and Gerson, 2011). In Figure S4, the random stacked birnessite (RS Birn) contains a double peak between 7 and $9 \text{ \AA}^{-1}$ that is similar to Ni-Al LDH, which is another reason why the LDH fits well into LCF and why manganese oxides were determined to be a major component of the s20unt silt and coarse fraction (Table 3). Even after sonication, when all clay sized manganese oxides were removed from both coarse and silt particle size fractions, one of the major components determined by LCF were manganese oxides (Table 3). This is a false positive result, and in this particle size the major nickel species are the silicate minerals.

4.5. Conclusions

In this study, when the percent of iron oxides from LCF results are plotted against total iron concentration from digestion data, there is no correlation in the plot. Similarly, when the percent of mafic and serpentine related minerals from LCF results are plotted against total magnesium concentration, there is no correlation in the plot. Because serpentine minerals are high in magnesium, this correlation would be reasonable to find. The lack of correlation indicates that total elemental concentration of a specific metal is not an indicator of the major nickel species in the soil. X-ray diffraction and particle size separation provided information on which minerals can potentially host nickel. Crystallographic data assisted in selecting appropriate standards for LCF of EXAFS data.

Differences in soil texture were related to different nickel speciation for several particle size fractionated samples. Sample s10t2 has more nickel located in the coarse sand fraction than s20unt (Section 4.2, Figure 1). In s20unt, 75% of the nickel could be attributed to the clay fraction. These results correlate to the soil texture of both samples, where s10t2 is a sandy clay loam with 57% sand and 20% clay, and s20unt is a clay loam with 34% sand and 39% clay (Table 1).

Nickel speciation determined by LCF in the Jasper Ridge soils did not vary significantly with depth. Oze et al., 2004 found that mineralogy in these soils did not vary significantly at different depths. Differences in nickel species between soils can be readily identified by the splitting of the first oscillation at $3.8 \text{ \AA}^{-1}$. However, this split is not explicitly linked to metal concentrations in the soil. For example, s14t2 had the second highest iron content (111000 mg kg⁻¹), thus it would be expected that iron oxides would be a major component in this sample. However, even with the high iron content, there is a split in the first oscillation of the EXAFS

(Figure 2), and LCF determined that layered silicate minerals were the major species (Table 3, Table S4).

Regardless of location, several minerals were commonly identified by XRD. Those minerals were lizardite, antigorite, clinochlore, talc, enstatite, and goethite. Other common iron oxides were hematite and magnetite. In addition to enstatite, another inosilicate mineral (pargasite) was identified in several samples.”

Based on LCF of EXAFS data, nickel was often associated with primary serpentine minerals, many of which have a layered octahedral hydroxide and tetrahedral silicon sheets. Primary serpentine minerals are the most important hosts for nickel. Nickel is also likely associated with inosilicate minerals, such as enstatite. In inosilicate minerals, which are common in mafic rocks, a variety of metal cations can balance the negative charge of the silicate tetrahedra chains and bond the chains together. Lastly, nickel was also commonly associated with iron oxides such as goethite, hematite and ferrihydrite. Other researchers have also found that iron oxides, such as goethite, serpentine minerals and talc were the most common nickel bearing minerals in ultramafic soils (Echevarria et al., 2006).

Multiple caveats involved with LCF of EXAFS data using synthetic standards were illustrated. Large variation in calculated percent composition when slightly modifying standards used in the fit is a common problem. A method of averaging the best fits together to obtain a result that is buffered from these large variations was presented. Additionally, different standards can yield statistically similar fits. Chemically different standards can exhibit similar EXAFS features because of structural similarities. Even the best fit can miss important structural features, such as shoulders caused by multiple scattering of light elements. Precautions while

using this method include considering other chemical and mineralogical data to aid in selecting standards and appropriate fitting results.

The F-test is an underutilized tool in the literature for LCF of EXAFS data for metal speciation in soils. Its use here proved that although visual inspection of the principal components and scree plot indicated four standards may be necessary to reconstruct the data, the fits were not statistically improved by using four or even sometimes three standards. Additionally, by developing a sonication method, it was possible to show that nickel species vary depending on particle size, in the sand, silt or clay fraction. An illustration and discussion were presented on how false positive results can occur in LCF. The most appropriate linear combination fit depends on the researcher making informed decisions based on additional mineralogical, chemical, and particle size information for each sample.

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859

Tables and Figures

Table 1. Physicochemical properties of the Oregon and Maryland Soils.

Sample ID	pH	Sand (%)	Silt (%)	Clay (%)	texture	Ni (mg/kg)	Fe (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Ca:Mg
s5t2	6.0	25	49	27	loam	1510	67900	87	580	1340	631	12500	0.05
s9t2	6.4	28	33	39	clay loam	2330	38700	229	2910	2870	4770	15000	0.32
s10t2	6.3	57	23	20	sandy clay loam	4710	46400	243	2300	2970	936	15700	0.06
s11unt	5.6	45	31	25	loam	1660	73800	100	1870	1620	6160	23600	0.26
s13t2	6.4	37	30	33	clay loam	4160	46300	311	1790	3360	8780	21900	0.40
s14t2	6.1	43	31	26	loam	3700	111000	211	2280	2940	1100	18300	0.06
s15t2	6.2	56	24	20	sandy clay loam	2470	38200	119	1020	1400	919	24600	0.04
s20unt	6.9	34	27	39	clay loam	5970	138600	242	1610	3100	477	13900	0.03
average	6.2				average	3310	70100	192	1800	2450	2970	18200	0.15
median	6.3				median	3086	57122	220	1829	2904	1016	16983	0.06

Table 2. XRD results of soils and soil fractions compiled from diffractograms in Figure S1.

	antigorite	lizardite	brucite	talc	clinochlore	chlorite	enstatite	pargasite	goethite	hematite	magnetite	quartz
s5t2 clay DT	x	x	x	x								x
s5t2 clay	x	x		x					x			x
s5t2 coarse	x			x								x
s9t2 clay DT					x							x
s9t2 clay					x				x	x		
s9t2 coarse				x	x		x	x				x
s10t2 clay DT	x	x			x		x					x
s10t2 clay	x	x		x			x		x	x		x
s10t2 coarse (ground <2 um)		x		x			x		x	x		x
s10t2 coarse	x	x		x			x			x	x	x
s11unt clay DT	x	x										x
s11unt clay	x	x							x	x		x
s11unt coarse	x	x			x		x	x			x	x
s20unt clay DT	x	x		x	x	x						x
s20unt clay	x								x	x	x	
s20unt silt	x	x		x	x		x	x			x	x
s20unt coarse	x	x		x	x		x			x	x	x

Table 3. Averaged-based results of LCF for soil nickel speciation. These results are the averaged values of fits in Table S4, which reduces over-dependency on any one particular standard. An in-depth discussion of the values reported here, including the influence of false-positive results and mixed metal second shells, is presented in Sections 4.3 and 4.4.

	Mafic & Serpentine Related	Iron Oxide	Manganese Oxide	Adsorbed to phyllosilicate	Sum
COII 0-2 cm	70%	27%	3%	-	100%
COII 2-5 cm	75%	21%	4%	-	100%
COII 5-8 cm	74%	18%	8%	-	100%
COII 8-11 cm	74%	22%	5%	-	100%
COIIbr	76%	20%	-	-	96%
JR3 0-5 cm	72%	25%	5%	-	102%
JR3 5-15 cm	61%	31%	4%	3%	100%
JR3 15-30 cm	71%	28%	-	-	99%
JR3 30-45 cm	52%	41%	6%	-	98%
JR3br	78%	21%	-	-	99%
s5t2 clay	69%	28%	-	-	97%
s5t2 coarse	59%	38%	-	-	97%
s5t2 soil	52%	13%	9%	24%	98%
s9t2 coarse	69%	31%	-	-	100%
s9t2 soil	52%	-	52%	-	104%
s10t2 clay	51%	29%	22%	-	101%
s10t2 coarse	30%	47%	17%	-	94%
s10t2 silt	42%	47%	-	-	89%
s10t2 soil	23%	42%	-	34%	99%
s11unt clay	83%	15%	-	-	98%
s11unt coarse	96%	-	-	-	96%
s13t2 soil	73%	30%	-	-	103%
s14t2 soil	83%	15%	-	4%	103%
s15t2 soil	46%	16%	7%	32%	101%
s20unt clay	24%	15%	62%	-	101%
s20unt coarse	11%	15%	76%	-	101%
s20unt silt	45%	33%	22%	-	100%
s20unt soil	14%	10%	76%	-	100%

Figure 1. LCF using particle sizes as components. **a.)** EXAFS spectra of s20unt and s10t2 samples and **b.)** Fourier transformed magnitude plots of the EXAFS data. **c.)** LCF of the soil whole-soil fractions using spectra from their respective particle sizes.

Figure 2. Select LCF results for serpentine soils and soil fractions. The solid lines indicate the sample data while the dotted red lines indicate the fits. R-factors for the fits displayed in the legend can be linked to the components shown in Table S4, where other comparable fits are also displayed.

Figure 3 a.) XRD spectra of s20unt silt and Ni-Al LDH*, where * indicates a typical XRD pattern of a Ni-Al LDH [see (Peltier et al., 2006) for comparison]. **b.)** The EXAFS comparison of s20unt silt vs. Ni-Al LDH. Although these two spectra have very distinct diffraction patterns, their EXAFS indicate almost identical local atomic environments for nickel. Mineralogy for s20unt silt is identified in Figure S1. Because the layered minerals present in s20unt silt have similar octahedral structure as Ni-Al LDH the resulting EXAFS are also similar, thus producing a “false positive” result in LCF.