

# Pedogenic chromium and nickel fractionation in subtropical serpentine soils

Zeng-Yei Hseu<sup>A</sup>, Shih-Hao Jien<sup>B</sup>, Yoshiyuki Iizuka<sup>C</sup>, and Heng Tsai<sup>D</sup>

<sup>A</sup>Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan, Email [zyhseu@mail.npust.edu.tw](mailto:zyhseu@mail.npust.edu.tw)

<sup>B</sup>Department of Soil and Water conservation, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan, Email [shjien@mail.npust.edu.tw](mailto:shjien@mail.npust.edu.tw)

<sup>C</sup>Institute of Earth Sciences, Academia Sinica, Taipei 11529, Taiwan, Email [yizuka@earth.sinica.edu.tw](mailto:yizuka@earth.sinica.edu.tw)

<sup>D</sup>Department of Geography, National Changhua University of Education, Changhua 50018, Taiwan, Email [geotsaih@cc.ncue.edu.tw](mailto:geotsaih@cc.ncue.edu.tw)

## Abstract

To elucidate the behavior of pedogenic Cr and Ni in serpentine soils at the scales of mineral, profile, and landscape, three pedons on the shoulder (Entisol), backslope (Inceptisol), and footslope (Alfisol) along a toposequence in Taiwan were chosen to explore these metals partition and their parent material origin by a combined approach of bulk soil analyses with selective sequential extraction (SSE) and direct mineralogical methods. Experimental results found deposits from the shoulder by surface erosion and runoff tended to be accumulated in the downhill, and thus total Cr and Ni were the lowest on the shoulder and highest on the footslope. Chromium and Ni were mainly concentrated in chromites and silicates respectively, but the metals were gradually transformed into easily mobile phases during the weathering of parent materials. The concentrations of acid soluble, reducible, and oxidizable fractions of Ni were higher than those of Cr, indicating Ni was more available than Cr. Bulk soil chemical composition supported the increase of extractability of Cr and Ni from the Entisol to Alfisol. The microscopic analyses identified chromites underwent a chemical modification and was a source of Cr in the soils. The chromites can be used as a pedogenic tracer for the soils.

## Key Words

Availability, chromium, nickel, pedogenesis, serpentine, toposequence

## Introduction

Serpentine soils are not derived from ultramafics only those with hydrothermal alteration of ultramafic minerals and a presence of serpentine minerals (Oze *et al.*, 2004). However, serpentine soils are often of ecological or environmental importance due to high levels of potentially toxic metals, such as Co, Cr, Mn, and Ni (Becquer *et al.*, 2006). Pedological studies of the parent material weathering in serpentine soils are numerous in the world. However, such studies on the ultramafic complexes in the island groups of the West Pacific Ocean are relatively rare, particularly in Taiwan (Hseu, 2006; Hseu *et al.*, 2007; Hsiao *et al.*, 2009; Cheng *et al.*, 2009). Due to the wide distribution and occurrence of serpentine soils, pedogenesis of these soils differed from location to location with varying climatic conditions as well as the nature of the parent material and other factors including topography, biota, and time. For serpentinitic parent materials, release of Cr and Ni to the ecosystems and particularly natural water systems during mineral weathering may occur, indicating the metals as a source of non-anthropogenic contamination. The influence of pedological conditions on the partition of metals is very important to the ecological functions of serpentine soils in the environment. Although most Cr and Ni in serpentine soils have been well known to be fixed by primary and secondary minerals corresponding to silicates and Fe oxides (Hseu, 2006), the release of these metals should be given increased attention during pedogenesis at the scales of mineral, profile, and landscape. An attractive question is “Is there any difference in partition between Cr and Ni from serpentine soils at the different scales under humid tropical conditions?” This study partitioned Cr and Ni into different fractions and assessed their mobility at the scales of mineral, profile, and landscape along a serpentine toposequence in eastern Taiwan using a combination of bulk soil analysis approach and mineralogical spectroscopy.

## Methods

### *Area description and sample collection*

The study area, Shih-Tao Mountain corresponding to a succession of landscape between 300 and 350 m of altitude, is located in southern section of the Coastal Range in eastern Taiwan (22°47'32'' N, 121°09'30'' E). The study area is composed of serpentinites and underlain mudstones that belong to the Lichi formation and crop out in the northeastern section. The serpentinitic rocks approximate 10 m thick are exotic blocks of ophiolite from the Philippine Sea Plate developed during the Late Pliocene epoch. Three pedons were selected from Shih-Tao Mountain on different landscapes along the serpentine toposequence within a

distance of 500 m. The reference pedons are pedon ST-1 on the shoulder, pedon ST-2 on the backslope, and pedon ST-3 on the footslope.

#### *Physiochemical and mineralogical analyses*

Soil samples from each pedon were subjected to physiochemical and mineralogical analyses. Total analysis of major element and Cr and Ni in soil samples utilized wavelength-dispersive X-ray fluorescence (XRF) (Spectro Xepos, USA). X-ray powder diffraction (XRD) patterns of rock and soil samples were obtained from  $2^\circ$  to  $70^\circ$   $2\theta$ , at rate of  $0.2^\circ 2\theta \text{min}^{-1}$  (Rigaku D/max-2200/PC diffractometer with Ni-filtered Cu  $K\alpha$  radiation generated at 30 kV and 10 mA). Additionally, three undisturbed blocks from each C horizon were obtained in the field by aluminum boxes. After air drying, polished thin sections with a thickness of 30  $\mu\text{m}$  were prepared. Selected thin sections were analyzed using backscatter electron microscopy (BSE) and energy dispersive x-ray spectroscopy (EDX) on an electron probe microanalyzer (JEOL JSM-6360LV). The microprobe was operated at the beam conditions of 15 kilo Volt (kV), and 18 pico Ampere (pA) for the acceleration voltage and beam current, respectively, in the vacuum condition of 25 Pa (Pascal) without carbon coating.

#### *Sequential extraction of chromium and nickel*

The three-step extraction procedure (SSE) was developed according to the Standards, Measurements and Testing Program (formerly the European Community Bureau of Reference, generally termed the BCR method). A detailed description of the BCR-protocol was given by using dilute acetic acid, a reducing agent and oxidizing agent. However, as an additional step, a mixture of  $\text{HF-HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$  was used to dissolve Cr and Ni from the residue remaining following the three extraction steps. During the SEE procedure the four steps divided Cr and Ni into the following fractions: (1) acid extractable (F1), (2) reducible (F2), (3) oxidizable (F3), and (4) residual (F4).

### **Results and Discussion**

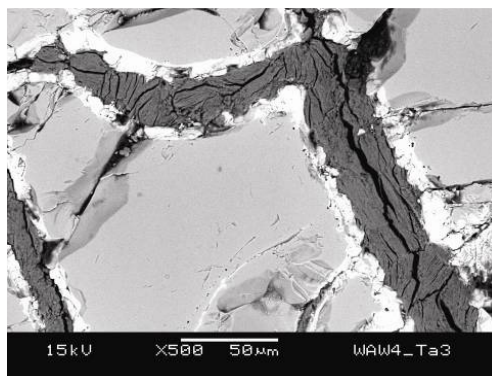
The results from SSE demonstrated that the largest amounts of Cr in the soils were associated with the residual fraction, indicating the original Cr was primarily fixed in the primary and clay minerals of the serpentine soils (Table 1). The Cr-bearing minerals were identified by XRD in this work such as silicates and Cr-spinels (magnetite and chromite) which were only dissolved within the residual fraction, and thus supported the finding of F4 fraction with the SSE. Chromite, a common spinel in mafic and ultramafic rocks, was regarded as highly resistant to chemical weathering (Oze *et al.*, 2004). However, Garnier *et al.* (2008) identified that the soil chromites, accumulated inside serpentine soil profiles, had undergone chemical weathering and led to the Cr enrichment during soil genesis under humid tropical conditions. Fig. 1 shows the chromite matrix is light gray; however, the edges of chromite, with white imperfections, are partly broken and are gradually altered along the cracks on the crystal surfaces in this work. Moreover, proportions of residual fraction decreased towards the surface to support the finding by Garnier *et al.* (2008).

**Table 1. Chemical fractions (mg/kg) of Cr shown as a mean of triplication and its standard derivation in the study soils; recovery was obtained by sum of Cr content in each fraction divided by the Cr total content.**

Pedon	Horizon	Depth cm	F1	F2	F3	F4	Recovery %
ST-1	A	0-10	ND	1.63±0.12	8.96±0.34	959±12.1	91.4
	C1	10-40	ND	1.65±0.14	8.59±0.68	943±28.5	88.2
	C4	100-120	ND	1.49±0.11	4.22±0.34	1482±4.74	89.4
ST-2	A	0-10	0.15±0.05	3.34±0.11	57.9±1.93	2611±54.6	90.9
	Bw	10-30	0.14±0.05	3.05±0.11	72.6±2.25	2906±18.9	101
	C3	90-120	0.13±0.07	2.84±0.30	55.4±2.23	1538±29.4	85.7
ST-3	A	0-15	1.26±0.09	4.20±0.22	86.6±7.66	2951±98.2	95.3
	Bt	50-80	0.87±0.08	12.3±0.32	87.9±3.31	2975±20.5	97.7
	C	130-150	0.69±0.07	9.09±0.55	53.6±0.44	3092±32.6	95.8

Based on the bulk soil analyses by the SSE, the potential mobile Cr phases (e.g., F1, F2, or F3) increased with soil development from pedon ST-1 to pedon ST-3, and thus revealing the increased probability of chromite weathering in the contribution of Cr release in this study. The chromite matrix consisted of Cr

29.5±3.56 wt.%, Fe 25.4±6.55 wt.%, Si 7.61±2.22 wt.%, and Mg 7.53±1.13 wt.% by microprobe analysis (Figure 1). The composition of the imperfect edge toward the serpentine mineral matrix (dark gray veins with black striation) significantly decreased in Cr but increased in Si and Mg. Burkhard (1993) considered the presence of Si in the spinels as a relative index of their alteration degree. By the observation of polarized microscope for the serpentine soils in eastern Taiwan, opaque inclusions of magnetite and chromite stained the parent rocks black and dark brown and small amounts of weakly anisotropic light-yellow clay pseudomorphs were interpreted as hypogene neofomed clay minerals (Hseu *et al.*, 2007). Therefore, the microscopic analyses in this study verified that chromite underwent a chemical modification and led to an enrichment of available Cr in the soils during the rock weathering. The chromites can be used as a pedogenic tracer which was corresponding to the XRD finding.



**Figure 2. BSE image of Cr-spinels in the C horizons of ST-1 pedon.**

Nickel was primarily recovered in the F4 compartment because large parts of Ni were primarily fixed in silicate lattices such as serpentines, smectites, and vermiculites in this study; while it was in minor extend in the reducible (F2) and oxidizable (F3) fractions of the soils (Table 2). The lowest concentrations of Ni existed in the acid extractable forms (F1). However, the concentrations of F1, F2, and F3 fractions of Ni always exceeded those of Cr. In comparison with the proportions of F1, F2, and F3 in total content of metals between Cr and Ni, this study found that Ni was more available than Cr in the toposequence during pedogenesis. Within single pedon, these proportions of Ni increased with decreasing soil depth, indicating that Ni was gradually transformed into easily mobile phases during the weathering of parent materials. Not any Ni-spinel has been found by XRD and BSE analyses in this study, revealing the major mineral origin of Ni in ultramafic soils was from silicates such as olivine, pyroxenes, and serpentine. Nickel released from the weathering of these primary minerals can substitute for magnesium in clay minerals such as smectites and vermiculite during the early stage of serpentine soil development. However, as the chemical weathering increases, these clay minerals became unstable (Hseu *et al.*, 2007). As a result, easily mobile elements like Si, Ca, and Mg were preferentially leached, whereas Cr and Ni remained in the profiles and accumulated along with iron and manganese (Garnier *et al.*, 2009). Nevertheless, nickel is not strongly held on clay and Fe oxide surfaces relative to other transition elements, even though a considerable amount of Ni can be adsorbed on the surfaces of Fe and Mn oxides at a pH ≥5 (Lee *et al.*, 2004). Therefore, the sustainable Ni was found in the F2 (Fe/Mn oxide-binding) fraction for this work.

**Table 2. Chemical fractions (mg/kg) of Ni shown as a mean of triplication and its standard derivation in the study soils; recovery was obtained by sum of Ni content in each fraction divided by the Ni total content.**

Pedon	Horizon	Depth cm	F1	F2	F3	F4	Recovery %
ST-1	A	0-10	4.55±0.11	10.3±0.60	46.1±1.12	1314±96.8	95.4
	C1	10-40	4.75±0.23	33.8±1.13	53.4±1.13	1311±27.3	95.9
	C4	100-120	6.34±0.45	22.0±0.34	33.3±1.96	1173±35.7	93.6
ST-2	A	0-10	14.3±1.78	215±11.1	138±9.65	3289±68.7	101
	Bw	10-30	13.0±1.94	209±16.8	166±11.2	3212±16.4	101
	C3	90-120	9.70±0.43	238±22.3	159±11.0	1367±78.7	90.6
ST-3	A	0-15	32.9±4.77	327±12.9	275±16.4	2786±14.7	106
	Bt	50-80	31.8±2.92	395±14.6	283±11.0	2494±19.2	92.6
	C	130-150	49.9±1.92	220±18.3	314±11.1	3190±91.5	94.1

From a pedological point of perspective, the order of soil development was pedon ST-1 (Entisol) → pedon ST-2 (Inceptisol) → pedon ST-3 (Alfisol). The parent materials of all pedons had similar chemical and mineral compositions. Due to leaching of Mg, the A horizons of pedons ST-1 and ST-2 and all horizons of ST-3 appeared relatively enriched SiO<sub>2</sub>. Iron was leached from surface horizons and accumulated in subsurface horizons with soil development, whereas the DCB-extractable Fe was the highest in the argillic horizons (Bt) of pedon ST-3. At the landscape scale, the deposits from the shoulder by surface erosion and runoff were gradually accumulated in the downhill, so that total Cr and Ni were the lowest on the shoulder and highest on the footslope. At the profile scale, the SSE demonstrated that the largest amounts of Cr and Ni in the soils were associated with the residual fractions, but the metals were gradually transformed into easily mobile phases during the weathering of parent materials under the humid tropical condition. An exchangeable Ca/Mg ratio <0.7 is often used to relate the imbalance of these nutrient elements in serpentine soils (Brooks 1987). The bulk chemical composition of three pedons supported the findings in Ca/Mg ratio with soil development. In addition, it appears from this study that more than one soil mapping unit in the study area should be considered for land management.

## Conclusion

The order of soil development was Entisol on the shoulder → Inceptisol on the backslope → Alfisol on the footslope along the serpentine toposquence. Chromium and Ni were mainly concentrated in chromite and primary silicates, respectively. Despite of differences in parent material composition and in degree of soil development along the toposquence, similar partition of Cr and Ni was found in all soils. The microscopic analyses identified that chromite underwent a chemical modification and led to the enrichment of Cr in the soils during the parent material weathering. Nevertheless, nickel was more mobile than Cr in the soils, released mostly from silicates, and consequently adsorbed on the Fe oxides. The bulk chemical composition of all soils associated with the exchangeable Ca/Mg values supported the increase of extractability of Cr and Ni from the incipient to mature soils.

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