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Nickel and manganese release in serpentine soil from the Ussangoda Ultramafic Complex, Sri Lanka

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ABSTRACT

Ultramafic rocks and their related soils and sediments are non-anthropogenic sources of metal contaminants. In the southeastern region of Sri Lanka, release of Ni and Mn into the surrounding areas and groundwater is an ecological, agricultural and human health concern. Here, we investigate the release and fate of Ni and Mn from serpentine sediment in the Ussangoda ultramafic complex by coupling interpretations garnered from chemical extractions. Sequential extraction experiments, utilized to identify 'elemental pools,' indicate Mn is mainly associated with oxides/(oxy)hydroxides, whereas, Ni is bound in silicates and spinels. Both Ni and Mn demonstrate rapid release rates in water $(2.4 \times 10^{-12} \text{ and } 2.0 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively) and release rates increase with increasing ionic strengths. Sediments evaluated from 0.05 to 10 mM with organic (citric, acetic and oxalic) and inorganic (H₂SO₄, HNO₃ and HCl) acids show that the maximum rate of Ni and Mn release occurs with oxalic acid (10 mM) at 7.11 \times 10^{-11} and $3.56 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively. Summarizing chemical extractions, Ni and Mn release rates increase in the order of HNO₃ \approx HCl \approx acetic<H₂SO₄<citric<ord>citric<ord>citric</rd>

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1. Introduction

Ultramafic rocks (e.g., peridotites, harzburgites, serpentinites) and their respective sediments and soils contain elevated concentrations of heavy metals including Ni and Mn (Bonifacio et al., 1997; Brooks, 1987; Cheng et al., 2011; Gough et al., 1989; Kaupenjohann and Wilcke, 1995; Oze et al., 2008; Rajakaruna and Bohm, 2002; Su and Suarez, 2004). The distribution and bioavailability of Ni and Mn in serpentine soils and sediments are highly variable where total Ni and Mn commonly range as several thousand mg kg $^{-1}$ (Alves et al., 2011; Caillaud et al., 2009; Massoura et al., 2006; Oze et al., 2005). More concernedly, the release of Ni and Mn into surrounding areas is a human health concern related to the contamination of groundwater (Chardot et al., 2007; Wesolowski, 2003) and proximal nonserpentine soils (Rauret, 1998; USEPA, 2004) as well as a source of metal-enriched dusts (Cempel and Nickel, 2006; Oller et al., 2008). In Sri Lanka, a discontinuous belt of several serpentinite bodies and their related serpentine soils marks the geological boundary between

the Highland and Vijayan Complexes (Fig. 1). The largest serpentinite body is found at Ussangoda, Southern Sri Lanka. These serpentinite bodies and soils all contain elevated concentrations of Ni (24,000 mg kg⁻¹) and Mn (6300 mg kg⁻¹) and may provide a source of Ni and Mn contamination to local communities (Dissanayaka, 1982; Ranasinghe, 1987).

The release of heavy metals from rocks, minerals, sediments and soils is regulated by a multitude of variables including solution pH, ionic strength, and the type and concentration of acid available (Meima and Comans, 1999; Tack et al., 1999; van der Sloot et al., 1996). How solution chemistry (i.e., soil solutions) may aid and/or accelerate Ni and Mn release from the Ussangoda ultramafic material needs further evaluation to constrain the fate and pathways of Ni and Mn release into the surrounding environments. Commonly, dissolution and metal release studies focus on pure mineral phases, such as chrysotile, talc, muscovite, biotite, etc. (Acker and Bricker, 1992; Amrhein and Suarez, 1988; Bales and Morgan, 1985; Bloom and Erich, 1987; Brady and Walther, 1989; Gautelier et al., 2007; Hamer et al., 2003; Oelkers et al., 2008). Additionally, several studies have evaluated Ni and Mn release in serpentine soils via chemical extractions (Alves et al., 2011; Cheng et al., 2011) without expanding upon the kinetics of soil mineral(s) dissolution. Chemical extractions



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Fig. 1. Serpentine localities in Sri Lanka along the lithological boundary between Highland and Vijayan Complexes.

are utilized in this study to assess the geochemical partitioning of metals as well as to evaluate metal mobility and bioavailability in soils and sediments. Changes in soil pH, ionic strength and other environmental factors may affect how these metals are mobilized in soil environments with respect to time and land use. By coupling single and sequential extractions with chemical kinetic interpretations, it is possible to gain a greater insight with respect to where and how Ni and Mn are bound. More importantly, the fate and behavior of Ni and Mn as it is mobilized and/or affected by critical zone processes can be interpreted for a wide variety of potential chemical changes related to the addition of fertilizers to changes in rainwater chemistry. Few attempts have been made to investigate the dissolution and release mechanisms in a multiphase media such as serpentine soil and/or sediment at conditions encountered in soil environments (Amir and Pineau, 2003; Quantin et al., 2002; Su and Suarez, 2004). Here, we investigate Ni and Mn sources, release rates and bioavailabilities via multiple chemical extractions from a serpentine soil collected from Ussangoda, Southern Sri Lanka. By coupling chemical extraction interpretations, Ni and Mn release mechanisms as well as the identification of potential routes of environmental input may be identified.

2. Materials and methods

2.1. Serpentine sediment collection, preparation and characterization

Serpentine soil was obtained from Ussangoda, Ambalantota (latitude 6° 05′ 54″ N and longitude 80° 59′ 11″ E), located in Southern Sri Lanka (Fig. 1). This lateritic (Inceptisol) soil is a direct weathering product of the serpentinite rock beneath. The area of the serpentinite and serpentine soil outcrop is ~3 km² where vegetation is sparse with the exception of endemic shrubs and grasses. Soil samples were air-dried and mechanically sieved to both the <2 mm and the 63-105 µm fractions. The 63-105 µm fraction comprises ~90 wt.% of the soil where the remainder of the soil is dominantly ~2 mm in diameter. Soil pH, electrical conductivity (EC), organic carbon, and total elemental concentrations were identical for the <2 mm fraction and 63-105 µm and these values are reported in Table 1. Trace elements for both size fractions were analyzed by completely dissolving the samples in a closed vessel device using temperature controlled microwave heating system with a mixture of hot, concentrated HNO₃, HCl and HF (Milestone ETHOS PLUS Labstation with HRP-1000/10S High Pressure Segmented Rotar) and atomic absorption spectrometry (AAS); (AAS-Model GBC 933 AA, Australia). These analyses are included in Table 1 and support that the serpentine sediment is chemically similar to the serpentine soil.

Due to the 63–105 μ m fraction comprising a majority the soil as well as demonstrating similar chemical characteristics to the total soil (i.e., <2 mm fraction), this particular size fraction was utilized for our experiments and will be referred to as serpentine sediment. Additionally, this size fraction was used to ensure a well-blended and homogeneous solid medium for extraction experiments as well as to reduce 'nugget' effects common in geochemical analyses of these types of soils (Oze et al., 2007).

Serpentine sediments $(63-105 \,\mu\text{m})$ were evaluated via X-ray diffraction (XRD) using a Siemens D-5000 diffractometer operating at 40 kV and 40 mA (using CuK α radiation). X-ray diffraction patterns were collected between 2 θ values of 2.0–80.0° and at a scan speed of 1.0° min⁻¹. The software package OMNIC (version 7.3) was used for XRD data analysis and mineral identification. Analyses reveal that antigorite ((Mg,Fe)_3Si_2O_5(OH)_4) is the dominant mineral present with minor amounts of chrysotile (Mg_3(Si_2O_5)(OH)_4), magnetite (Fe_3O_4), spinels and clays. Major and trace elements of the serpentine sediment were analyzed via X-ray fluorescence (XRF) using a PANalytical MagiX PRO spectrometer (Institute for Geography and Geology, University of Copenhagen); (Table 1).

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Elemental compositions and chemistry of serpentine soil and sediment.

Total metal digestion re	sults (mg kg ⁻¹) with soil fraction	ons							
Fraction	Ni		Mn	Cr		(Со	Cu		Zn
63–105 μm <2 mm pH 6.68	6776 6179		1117 1036 EC	11,3 11,3 265	301 352 μs cm ⁻¹	-	157 121 ГОС	30 24 1.92%	,	173 131
XRF results of the serpe	ntine sediment	(63–105 µm frac	tion)							
Sample (%)	SiO ₂	TiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ 0	P ₂ O ₅
	41.0	1.43	12.27	38.32	0.33	0.94	0.14	0.04	0.45	0.17
Sample (mg kg $^{-1}$)	Ni	Cr	Mn	Pb	V	Zn	Cu	Со	Sr	Rb
	6459	11,020	1120	7	137	156	32	111	29	36

2.2. Zero point of charge (ZPC)

The zero point of charge (ZPC) of the serpentine sediments was determined by conventional potentiometric titration methods (Langmuir, 1997). A 2 g L⁻¹ serpentine sediment (63–105 µm fraction) suspension was equilibrated for 24 h. Three titration experiments were performed utilizing 0.1, 0.01, and 0.001 M NaNO₃. The initial pH of serpentine soil suspension was ~5.5 and it was lowered to ~4 with 0.10 M HNO₃ prior to titrations. At each titration point the pH value and the titrant volume (Model Orion 960 auto chemistry analyzer) was recorded. The surface charge ($\sigma_{\rm H}$) was calculated using the equation (Stumm and Morgan, 1996):

$$\sigma_{\rm H} = \frac{\left(C_{\rm A} - C_{\rm B} + [\rm OH^-] - [\rm H^+]\right)F}{aS} \tag{1}$$

where $\sigma_{\rm H}$ is the surface charge (C m⁻²), $C_{\rm A}$ is the added acid concentration, $C_{\rm B}$ is the added base concentration, [OH⁻] is the hydroxyl ion concentration, [H⁺] is the proton concentration, *a* is equilibrium OH⁻ and H⁺ concentrations for a given quantity of solid used (g L⁻¹), F is the Faraday constant (96,500 C mol⁻¹) and *S* represents the surface area (66.0 m² g⁻¹) determined by N₂ BET isotherm analysis.

2.3. Sequential extractions to determine Mn and Ni mineral phases

Sequential selective extraction techniques are commonly utilized to evaluate solid phase metal fractionation in soils (Antić-Mladenović et al., 2011; Noble and Hughes, 1991). Although several sequential extraction methods are available, extractions performed on the serpentine sediment followed the widely applied procedures of Tessier et al. (1979) and Armienta et al. (1996). Despite the many criticisms of this technique, it remains useful for the general assessment of metal partitioning. More discussion about the use and the caveats of sequential extractions is presented by Gleyzes et al. (2002). Despite Cr being a concern related to this serpentine soil, Cr was not evaluated in this study due to being sequestered in a highly refractory oxide phase (i.e., chromite) where sequential extractions do not adequately identify the source and/or mobility of Cr (Oze et al., 2004).

A mass of 1.00 g sediment (dry weight) was used for the initial extraction. A total of five replicate sequential extraction analyses were completed on the serpentine sediment. Nickel and Mn concentrations were measured in the effluent after each extraction using AAS. Below is a list of the extraction procedures performed on the serpentine sediment.

- (i) *Exchangeable:* Sediment was reacted at room temperature for 1 h with 20 mL of magnesium chloride solution (1 M MgCl₂, pH 7.0) with continuous agitation.
- (ii) Bound to carbonates. Residue from (i) was leached at room temperature for 2 h with 20 mL of 1 M sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid (HOAc) and with continuous agitation.
- (iii) Bound to Fe–Mn oxide: Residue from (ii) was treated with 20 mL of 0.04 M hydroxylamine hydrochloride (NH₂OH-HCl) in 25% (v/v) HOAc heated at 90 °C with slow continuous agitation for 2 h.
- (iv) Bound to organic matter: Residue from (iii) was treated with 3 mL of 0.02 M HNO₃ and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO₃, heated to 85 °C for 2 h with occasional agitation. A 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO₃) was added and the sample was heated again to 85 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added and the sample was diluted to 20 mL and agitated continuously.
- (v) *Residual:* Residue from (*iv*) was treated with a mixture of 10 mL concentrated HF and 2 mL concentrated HClO₄ and heated to

near dryness. It was then treated with 1 mL $HClO_4 + 10$ mL HF and heated again to near dryness; 1 mL $HClO_4$ was added, heated until the appearance of white fumes, and finally dissolved with 12 N HC1 and diluted to 25 mL with deionized water.

Between each successive extraction listed above ((ii) to (v)), the sample was centrifuged at 3500 rpm for 15 min. Additionally, the supernatant was filtered using 0.45 µm filter paper prior to AAS analysis.

2.4. Diethylene triamine pentaacetic acid (DTPA) extraction

Extractable metals in the soil were quantified by the diethylene triamine pentaacetic acid (DTPA) soil test developed by Lindsay and Norvell (1978). Approximately 20 mL of a 0.005 M DTPA, 0.01 M CaCl₂, and 0.1 M triethanolamine buffered solution was added to 10 g of air dried soil for 2 h. The filtrate was analyzed for Cr, Mn, Fe, Ni, Co, Cu and Zn by AAS.

2.5. CaCl₂ extraction

Serpentine sediment (1 g) was extracted with 10 mL of 0.01 M CaCl₂. The solid solution was stirred for 2 h, centrifuged and filtered through membrane filtration (0.45 μ m pore size). The supernatant was analyzed via AAS.

2.6. Metal release with water and at varying ionic strengths

Metal release batch experiments were carried out using distilled water to observe Ni and Mn release with respect to time from the serpentine sediment. A mass of 5 g of solid sample per L of water $(5 \text{ g L}^{-1} \text{ serpentine sediment suspension})$ was initially used where subsamples of 25 mL suspension were taken from the batch experiments over 20 days. Nickel and Mn release with different ionic strengths were also analyzed using 0.1, 0.01 and 0.001 M NaNO₃ solutions by changing the solution pH (4–9). A 5 g L^{-1} serpentine sediment suspension was prepared and adjusted to pH ~4 in desired ionic strengths (0.1, 0.01, and 0.001) by 5 M NaNO₃. The system pH was incremently increased at ~1.0 pH intervals up to ~9. At each point, a 25 mL sample portion was transferred to a capped polypropylene tube. These tubes were equilibrated for 24 h at 75 rpm (EYELA B603 shaker) and the pH of the suspension was measured again and recorded. Membrane filtered supernatant was directed to Ni and Mn analysis using AAS.

2.7. Inorganic and organic acid extractions

Three inorganic (sulfuric, nitric, hydrochloric) and three organic (citric, acetic, oxalic) acids of different concentrations (0.05, 0.1, 0.5, 1.0, 5.0 and 10 mM) were used to evaluate Ni and Mn release from the serpentine sediment. Approximately 1 ml (2 drops) of chloroform was added per L of all organic acid solutions to prevent microbial breakdown of the organic acids. Half a gram of serpentine sediment was placed in polypropylene tubes and 25 mL of each acid was added. The tubes were equilibrated for 24 h at room temperature and agitated at 75 rpm (Model EYELA B603 shaker). The supernatant was transferred by membrane filtration (0.45 μ m) after centrifugation and the solutions were analyzed for Mn and Ni using flame method of the AAS.

Following the methodology of Hamer et al. (2003), Ni and Mn release rates were evaluated with respect to acid concentration and pH to determine the extent of both proton and ligand promoted Ni and Mn release. Fits of the data based on the acid and acid concentration are reflective of the relationship:

$$R_{T_{(NI,Mn)}} = k_{T_{(NI,Mn)}} a_{acid}^{n_{T(NI,Mn)}}$$

$$\tag{2}$$



Fig. 2. Proton titration curves of serpentine sediments as a function of ionic strength. The workable titration window is defined between pH 4.5 and 9.

where k_T is the rate constant for total Ni or Mn released for a particular acid (i.e., hydrochloric, nitric, sulfuric, acetic, citric and oxalic acids) and *n* is the corresponding experimentally determined factor (i.e., the reaction order) and *a* is the activity (assuming activity is equal to concentration) of the acid for that particular experiment. Similar to Hamer et al. (2003), the pH dependency of the total Ni and Mn release rates were evaluated using the equation:

$$\log R_{T_{(NiMn)}} = \log k_{T_{(NiMn)}} - n_{T_{(NiMn)}} pH$$
(3)

using the same variables from Eq. (2).

3. Results and discussion

3.1. Zero point of charge

In Fig. 2, titration curves performed at three ionic strengths provide the ZPC at pH 8.6. At pH values less than 8.6, the serpentine sediment surface bears an overall positive charge and vice versa at pHs greater than 8.6. As observed, it is evident that the surface hydroxyl functional groups in the serpentine sediment behave amphoterically.

Table 2

Serpentine soil chemical extractions.

3.2. Sequential extractions

Sequential extraction results for the serpentine sediment are presented in Table 2. Nickel and Mn concentrations for each chemical extraction step are shown $(mg kg^{-1})$ as well as in terms of the percent (%) extracted from the total value (XRF analyses, Table 1). Manganese is equally bound in the Fe–Mn oxide fraction (420.7 mg kg $^{-1}$, 37%) and in the residual fraction (351 mg kg⁻¹, 31%). The residual fraction is associated with silicates as well as with other primary oxides such as spinels. Nickel is dominantly bound in the residual fraction (4697 mg kg⁻¹, 72%). These results support that antigorite (i.e., the dominant mineral identified in these serpentine sediments via XRD) could be a contributor for both Ni and Mn release, whereas, the Fe-Mn oxide fraction is a potential major source of Mn. The order of the individual geochemical fractions of where Ni and Mn are bound from greatest to least is: 1) Ni: residual>Fe and Mn oxide bound > organic matter bound > exchangeable > carbonate bound and 2) Mn: Fe and Mn oxide bound > residual > organic matter bound>exchangeable>carbonate bound. Even though Ni and Mn are dominantly bound in relatively unavailable forms, changes in the critical zone such as soil acidity, microbial activity, the availability of chelating materials and redox conditions can enhance the mobility of Ni and Mn, thus, providing a continually changing flux of Ni and Mn into the environment. It is important to note that some fractions may have less overall Ni and Mn, such as bioavailable, exchangeable and carbonate bound (Table 2); however, these fractions potentially offer a more labile source in soil environments.

3.3. DTPA and CaCl₂ extractions

The DTPA and CaCl₂ extraction methods provide a proxy for evaluating plant bioavailability of Ni and Mn in soils and soil solutions (Kashem et al., 2007; Peijnenburg et al., 2007). The DTPA treatment extracted 323 mg kg⁻¹ (5.0%) of Ni and 76.3 mg kg⁻¹ (6.8%) of Mn. Since DTPA forms soluble complexes with metals reducing the activity in the soil solutions, Ni and Mn ions may desorbed from the soil and enter in to the solution. Extractions with CaCl₂ are commonly used to assess plant bioavailability and work well in neutral or weakly alkaline soils. Nickel and Mn extractions with CaCl₂ were lower than that of DTPA in the slightly acidic serpentine sediments and recorded as 167.6 (2.6%) for Ni and 45.51 (4.1%) mg kg⁻¹ for Mn (Table 2).

Extractants	Fractions	Amount released (mg kg $^{-1}$)		% of total ^a		Reference ^b	
		Ni	Mn	Ni	Mn		
Sequential extractions							
(i) 1 M MgCl ₂ (pH 7.0)	Exchangeable	257.8 (9.2)	49.4 (4.0)	4.0	4.4	А	
(<i>ii</i>) 1 M NaOAc (pH 5.0)	Carbonates	47.2 (8.8)	10.2 (3.4)	0.7	0.9	Α	
(<i>iii</i>) 0.04 M NH ₂ OH-HCl in 25% (v/v) HOAc (90 °C)	Fe and Mn oxides	464.4 (6.6)	420.7 (1.2)	7.2	37.5	А	
(<i>iv</i>) 0.02 M HNO ₃ , 30% H ₂ O ₂ (85 °C), 3.2 M NH ₄ OAc	Organic matter	268.8 (7.9)	62.24 (6.8)	4.2	5.6	А	
(ν) HF, HClO ₄ , HCl Sum of (i) to (ν)	Residual/silicate	4697 (9.8) 5735	351.5(7.8) 894	72.7	31.4	А	
Individual extractions							
0.01 M CaCle	Bioavailable	1676 (64)	455(30)	2.6	41	B	
0.0005 DTPA	Extractable	323 (2.3)	76.3 (3.1)	5.0	6.8	C	
Water and ionic strength							
Distilled H ₂ O (pH 6.5, 24 h)	_	56.0 (0.8)	4.8 (0.3)	0.9	0.4		
0.1 M NaNO ₃ (pH 7.0)	_	167.0 (5.7)	39.6 (4.1)	2.6	3.5		
0.01 M NaNO3 (pH 7.0)	_	47.0 (0.5)	16.0 (0.1)	0.7	1.4		
0.001 M NaNO3 (pH 7.0)	-	33.8 (0.3)	5.6 (0.2)	0.5	0.5		

Note: Values reported are averages for five determinations and the value in parentheses is the standard deviation (SD) for that element and method.

^a Total Ni and Mn values via XRF are reported in Table 1.

^b A: Tessier et al. (1979); B: Houba et al. (1996); C: Lindsay and Norvell (1978).





Fig. 3. Release of Ni and Mn with distilled water with time.

However, this fraction of metals may be more representative of what is available for plant uptake, including the hyperaccumulating vegetation, in the ecosystem. Although Ni and Mn available for plant uptake are small based on these extractions, vegetation may accumulate these metals over time.

3.4. Release of Ni and Mn with distilled water and varying ionic strength

Rates of metal release from solid phases in water serve as a baseline to evaluate complex solutions (i.e., the effect of inorganic and organic acids). Both Ni and Mn are rapidly released at rates of 1.55×10^{-13} and 7.89×10^{-14} mol m⁻² s⁻¹, respectively, within the first 24 h (Fig. 3). The rate of Ni release decreases after 24 h while Mn reaches a steady value after 4 days. In case of Ni, however, the dissolution process has not reached its maximum value as indicated by the increasing trend even after 12 days. Based on these rates with water, Ni and Mn will achieve values exceeding the World Health Organization's limit (0.02 and 0.40 ppm, respectively) for drinking water within a day (from 1 kg of soil to 1 L of water) if the same conditions are given. The average Ni concentration in groundwater around Ussangoda serpentinite deposit is 0.18 ppm. This suggests that there is a potential of groundwater contamination by Ni in the vicinity which may lead to health problems for the people who use local water sources.

Experiments with varying ionic strengths demonstrate that an increase in ionic strength increases the release rate of Ni and Mn into solution (Fig. 4). Dissolution rates are enhanced by increasing ionic strength due to surface protonation displacing ions from surface

sites (Mogollón et al., 2000). However, no significant effect of ionic strength with respect to Ni and Mn release is apparent at pHs between 8 and 9 (Fig. 4); (i.e., the pH associated with ZPC (pH 8.57) of this sediment). When solution pH approaches the ZPC, the surfaces of the serpentine sediment minerals are neutral (i.e., not charged) and, therefore, the effect of ionic strength is negligible (Mogollón et al., 2000). Due to these serpentine sediments (pH 6.7) as well as serpentine soils worldwide being slightly acidic at pH ~6; (Oze et al., 2005), ionic strength is an important consideration for Ni and Mn release. Those serpentine soils capable of achieving high ionic strengths and acidic pHs will be an environmental concern. The Ussangoda serpentine deposit lies along the coastal belt, hence there is a possibility of having high ionic strength conditions leading to increased metal ion release. The addition of fertilizers and animal waste are additional concerns related to increasing the ionic strength in these soils and soil solutions.

3.5. Release of Ni and Mn with inorganic and organic acids

The total rate of mineral dissolution (R_T) is the sum of the rates hydrogen ion (R_H) and ligand promoted (R_L) dissolution as shown by the equation (Furrer and Stumm, 1986; Stillings et al., 1996; Welch and Ullman, 1996):

$$\mathbf{R}_{\mathrm{T}} = \mathbf{R}_{\mathrm{H}} + \mathbf{R}_{\mathrm{L}}.\tag{4}$$



In this study, we evaluate Ni and Mn release from serpentine sediment where a variety of minerals are present, not the total dissolution

Fig. 4. Release of Ni and Mn in the presence of three different ionic strengths in the soil solution. Errors are smaller than the symbols used.

of one particular mineral. The relationship shown in Eq. (4) is valid whether examining mineral dissolution rates or metal release rates. Hereafter, R is in reference to Ni and Mn release rates from the serpentine sediment where the subscript T refers to total Ni or Mn release and subscripts H and L refer to hydrogen ion and ligand promoted Ni and Mn release.

The rates of dissolution increase with increasing acid concentrations in all cases for Mn and Ni (Fig. 5). At lower acid concentrations, the rate of dissolution change, as indicated by the slope of each fitted curve, is higher as compared to the rate change at higher concentrations. This higher metal release rate change (i.e., steeper slope) at low acid concentrations is observed in all cases but it is more pronounced for Ni than for Mn. Nickel and Mn release rates in HCl and HNO₃ are similar; however, they are less compared to those for organic acids. Overall, oxalic acid (10 mM) demonstrates the highest release rate for both Ni (7.11× 10^{-11} mol m⁻² s⁻¹) and Mn (3.56× 10^{-11} mol m⁻² s⁻¹). Summarizing extractions, Ni and Mn release rates increase in the order of HNO₃ \approx HCl \approx acetic <H₂SO₄<citric<oxalic acids. In the presence of both organic and inorganic acids, Ni is released preferentially relative to Mn.

pH values obtained by calculating H⁺-ion activities for each acid/ solution are plotted with their respective log Ni and Mn release rates as shown in Fig. 6. The pH dependencies result in a linear relationship allowing k_T and n_T values to be determined for Ni and Mn



Fig. 5. Metal releasing rates for Ni and Mn as a function of acids and concentrations. Data, which are the average of triplicate samples (error bars represent the standard deviation of replicates), are fit by means of Eq. (2).



Fig. 6. Metal releasing rates (in log R) of Ni and Mn vs pH in both inorganic and organic acids. Data points are shown in symbols and the pH dependence calculated using Eq. (3) is given in straight line.

in each acid. These rate constants and reaction orders are reported in Table 3. For all six acids, the release rates of Ni and Mn from the serpentine sediment increase with decreasing pH.

Nickel and Mn release related to the three inorganic acids do not demonstrate similar pH dependence. Due to solution pH being directly related to surface protonation, all inorganic acids should demonstrate similar characteristics. Neither chloride nor nitrate ions are expected to have a significant effect on mineral dissolution (Welch and Ullman, 1996). Therefore, the pH dependence of Ni and Mn release from serpentine sediment in the presence of hydrochloric and nitric acids are dominantly controlled by H⁺ activity. Nickel and Mn release in sulfuric acid are higher compared to nitric and hydrochloric acids due to sulfuric acid being a diprotic acid. This finding is in agreement with Hamer et al. (2003) and is also supported where high weathering rates have been reported in soil environments with high SO_4^{2-} (Bloom and Erich, 1987; Hamer et al., 2003).

Ligand and proton promoted mechanisms for metal release are simultaneous. Isolating the effect of ligands (R_L) is possible by calculating the difference between the total metal release rate (R_T) and the proton induced metal releasing rate (R_H) as shown in Eq. (4). R_T in HCl is assumed to be equal to R_H in all acids investigated allowing for the calculation of ligand promoted rate (Table 3); (Hamer et al., 2003). The total Ni and Mn release rates of serpentine sediment at pH 3 where $R_{T(pH3)}$ of HCl is 3.81 × 10⁻¹² mol m⁻² s⁻¹.

Table 3

Rate constants (k_T), reaction orders (n_T), total rate of dissolution (R_T) and ligand promoted dissolution (R_L) of Ni and Mn in the presence of organic and inorganic acids.

Acid	Log k _T	n _T	R _T	R _L	R_T/R_H
			$mol m^{-2} s^{-1} \times 10$	-12	
Release of Mn					
Hydrochloric acid	- 9.90	-0.51	3.82	0.00	1.00
Nitric acid	- 9.92	-0.50	3.84	-0.02	1.01
Sulfuric acid	- 9.75	-0.52	4.75	0.94	1.25
Acetic acid	- 9.83	-0.48	5.45	1.63	1.43
Citric acid	- 8.78	-0.76	9.11	5.29	2.39
Oxalic acid	- 8.72	-0.77	9.33	5.52	2.45
Release of Ni					
Hydrochloric acid	-9.71	-0.35	17.91	0.00	1.00
Nitric acid	-9.49	-0.42	17.36	-0.55	0.97
Sulfuric acid	-9.23	-0.50	19.12	1.21	1.07
Acetic acid	-9.82	-0.30	19.68	1.77	1.10
Citric acid	- 8.97	-0.55	23.77	5.86	1.33
Oxalic acid	-9.07	-0.52	23.93	6.02	1.34

Several studies have used an enhancement factor to compare the dissolution rates of different minerals in different acids (Amrhein and Suarez, 1988; Hamer et al., 2003; Stillings et al., 1996). Based on those studies we considered the enhancement factor, R_T/R_H to compare the proton and ligand promoted rates in different acids (Table 3). In this study, sulfuric acid showed a higher ratio for both Ni and Mn compared to chloride and nitrate respectively (Table 3). Amrhein and Suarez (1988) have reported the effect of oxalic acid on plagioclase dissolution rates at pH 4 and pointed out that the oxalate increased the dissolution rate by a factor of 1-2.2. Similarly, in our case, oxalic acid results in the highest enhancement factor at pH 3 for both Mn and Ni releasing rates (2.4 and 1.3 units, respectively). Several other studies have revealed high enhancement factors for organic acids compared to inorganic acids (Hamer et al., 2003; Stillings et al., 1996; Zhang and Bloom, 1999). According to the calculated enhancement factors of this study, Ni and Mn release rates from serpentine sediment demonstrate both ligand and proton promoted release.

Chelating organic ligands are known to enhance the dissolution of minerals by forming surface complexes facilitating the release of metal ions into the solution (LombnÆS et al., 2008; Welch and Ullman, 1996; Zhang and Bloom, 1999). Our experiments indicate that organic ligands impact Ni and Mn release rates where the ligand-promoted rate is proportional to the activity of the ligand in solution as well as the concentration of adsorbed ligand. Additionally, Ni and Mn release rates are dependent on the nature of the ligand. Thus, the effectiveness of ligands depends on their functional groups, especially the O-containing ligands rather than the total dissolved C content, molecular structure and thermodynamic stability of their surface complexes (Golubev and Pokrovsky, 2006; Inskeep et al., 1991). Ligands with functional groups and phenolic groups which contain two or more oxygen donors and which can form bi- or multidentate mononuclear surface chelates are considered effective mineral dissolvers (Stumm, 1992; Zhang and Bloom, 1999). Thereby, monocarboxylic anions only have a slight effect on the release of Ni and Mn while bi- and tricarboxylic anions in citric and oxalic acids show a significant increase in Ni and Mn release (Table 3). Overall, organic acids, even at low concentrations, are cogent agents with regard to releasing Ni and Mn from serpentine soils.

The geochemical relationships discussed above and shown in Figs. 5 and 6 demonstrate that either: 1) the multiple fractions (Table 2) containing Ni and Mn must release these metals in a similar manner or 2) one specific fraction or mineral is responsible for a majority of the Ni and Mn released. Certain acids as demonstrated by sequential extractions (Table 2) are known to be more effective at releasing Ni and Mn from certain fractions and/or groups of minerals. Thus, we would expect trends present in Figs. 5 and 6 to be more variable, not curvilinear or linear as shown, if multiple fractions were

releasing Ni and Mn. Eqs. (2) and (3), developed to examine dissolution rates for single minerals, works well for our multiphase serpentine sediment suggesting that one major fraction or potentially mineral is responsible for the Ni and Mn released in our experiments. The ratio of Ni and Mn release is approximately 5 to 1 matching well with the geochemistry of the residual fraction (Table 2) dominantly composed of antigorite. Additionally, the residual fraction contains more Ni relative to Mn and the ratio is approximately double compared to metal release ratio. Thus, Ni and Mn release in these sediments appear to be the result of antigorite dissolution demonstrating that silicate phases believed to 'lock in' metals may be a major contributor of metal input into the environment.

4. Conclusions

Understanding Ni and Mn release from serpentine soils is essential for evaluating the current input of these metals into serpentine and adjacent environments as well as for assessing potential implications related to changes in land use (i.e., agriculture, farming, industrial development). This study demonstrates that Ni and Mn in serpentine soils and sediments from Ussangoda, Sri Lanka, are dominantly released from the silicate fraction, specifically from antigorite which is the dominant mineral identified in these soils. Based on a variety of extractions, theses serpentine soils offer a labile source of Ni and Mn that can be released readily over a variety of geochemical conditions. The present study confirms previous findings and contributes additional evidence that Ni and Mn release from serpentine soil is accelerated by complex forming ligands and that both ligands and protons corroborate to accelerate the release of Ni and Mn from serpentine soil into surrounding environs.

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