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FATE OF TRANSITION METALS DURING PASSIVE CARBONATION OF ULTRAMAFIC MINE TAILINGS VIA AIR CAPTURE WITH POTENTIAL FOR METAL RESOURCE RECOVERY

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Abstract

Mineral carbonation in ultramafic mine tailings is generally accepted to be a safe and long term means of trapping and storing CO_2 within the structures of minerals, but it poses the risk of releasing potentially hazardous metal contaminants from mineral wastes into the environment. Stockpiles of reactive, finely pulverised ultramafic mine tailings are ideal natural laboratories for the observation and promotion of the carbonation of Mg-silicate and Mg-hydroxide waste minerals via reaction with atmospheric or industrial CO_2. However, ultramafic mine tailings commonly contain first-row transition metals (e.g., Cr, Co, Cu, Ni) in potentially toxic concentrations within the crystal structures of Mg-silicates, sulphides, and oxides. These transition metals are likely to be mobilised by mineral carbonation reactions, which require mineral dissolution to supply cations for reaction with carbon. At Woodsreef Chrysotile Mine, New South Wales, Australia, transition metals (i.e., Fe, Cr, Ni, Mn, Co, Cu) are most concentrated within minor oxides (magnetite and chromite) and trace alloys (awaruite, $Ni_{2-3}Fe$ and wairauite, CoFe) in serpentine tailings, however, mobilisation of transition metals appears to occur predominantly during dissolution of serpentine and brucite, which are more abundant and reactive phases, respectively. Here, we present new synchrotron X-ray fluorescence mapping data that provide insights into the mobility of first-row transition metals (Fe, Cr, Ni, Mn, Co, Cu) during weathering and carbonation of ultramafic mine tailings collected from the Woodsreef Chrysotile Mine. These data indicate that the recently precipitated carbonate minerals, hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] and pyroaurite [$Mg_6Fe_2(CO_3)(OH)_{16} \cdot 4H_2O$] sequester trace metals from the tailings at concentrations of 10s to 100s of ppm, most likely via substitution for Mg or Fe within their crystal structures, or by the physical trapping of small (µm-scale) transition-metal-rich grains (i.e., magnetite, chromite, awaruite), which are stabilised within alkaline carbonate cements.

Trace transition metals are present at relatively high concentrations in the bulk tailings (i.e., ~0.3 wt. % NiO and Cr_2O_3) and they are largely retained within the unaltered mineral assemblage. The weathering products that occur at the surface of the tailings and form a cement between grains of partially dissolved gangue minerals immobilise transition metals on spatial scales of micrometres and at comparable concentrations to those observed in the unaltered tailings. The end result is that trace metals are not present at detectable levels within mine pit waters. Our observations of metal mobility during passive carbonation suggest that mineral products of accelerated carbonation treatments are likely to sequester trace metals. Thus, accelerated carbonation is unlikely to pose an environmental risk in the form of metalliferous drainage so long as the neutralisation potential of the tailings is not exceeded.

Understanding both trace transition metal geochemistry and mineralogy within materials targeted for mineral carbonation could allow optimisation of treatment processes and design for recovery of valuable metals. In *ex situ* reactors employing acid pre-treatments, trace metals mobilised from reactive phases such as serpentine and brucite could potentially be recovered using pH-swing methods, while recalcitrant metal-rich accessory minerals, including magnetite, awaruite and chromite, could be recovered from treated residue material by conventional mineral separation processes. Recovery of valuable metals (i.e., Ni, Cr and Co) as by-products of accelerated mineral carbonation technologies could also provide an important economic incentive to support broader adoption of this technology.

1. Introduction

The increasing concentration of anthropogenic CO_2 in the atmosphere is likely driving long-term changes to Earth's climate (Hallett, 2002; IPCC, 2005, 2013). As such, there is a growing need to develop mitigation technologies, both to reduce anthropogenic CO_2 emissions and to capture atmospheric CO_2 from the air for long-term storage in a stable form.

Mineral carbonation, which was first proposed as a mitigation strategy for CO_2 emissions by Seifritz (1990), captures CO_2 within the structures of environmentally benign carbonate minerals by enhancing natural silicate weathering, promoting the safe, long-term storage of CO_2. Importantly, this is the only proposed CO_2 storage technology that is considered to be permanent over geological timescales, given that many carbonate minerals are known to persist at the Earth's surface for 1000s of years or longer (Lackner et al., 1995; Oelkers et al., 2008; Olajire, 2013; Seifritz, 1990).

Natural carbonation of mine tailings in Australia, Canada, the U.S.A., and Norway (99 – 6200 g $CO_2/m^2/y$; Beinlich and Austrheim, 2012; Gras et al., 2017, Lechat et al., 2016; Levitan et al., 2009; Oskierski et al., 2013; Pronost et al., 2012; Turvey et al., 2017, Wilson et al., 2006, 2009a,b, 2011, 2014) occurs at rates that are typically orders of magnitude greater than average CO_2 uptake associated with silicate weathering (0.7 – 62.1 g $CO_2/m^2/y$, Power et al., 2013, units converted from Ludwig et al., 1998). The enhanced reactivity of mine tailings is largely due to the orders of magnitude increase in mineral surface area that results from crushing during ore processing (Wilson et al., 2009a). The greatest uptake of CO_2 by mine tailings yet reported occurs at the Mt Keith Nickel Mine in Western Australia, where nearly 40,000 t of atmospheric CO_2 are sequestered annually via natural reaction of the tailings with the atmosphere, representing an 11% offset of the mine's annual greenhouse gas emissions (Wilson et al., 2014). This enhanced reactivity of mineral wastes makes historical and operating mine tailings storage facilities provide ideal settings for observing transition metal mobility during passive mineral carbonation reactions on timescales of years to decades.

Ultramafic rocks are commonly mined for Cr, Ni-Cu-platinum group element sulfides, diamonds, talc, and (historically) chrysotile asbestos. They are also the preferred feedstock material for mineral carbonation because they contain high abundances of silicate minerals with high Mg contents {i.e., olivine [$(Mg,Fe)_2SiO_4$] and serpentine [$Mg_3Si_2O_5(OH)_4$]}, and minor amounts of highly reactive phases such as brucite [$Mg(OH)_2$] (Goff and Lackner, 1998; Lackner, 2003; Oelkers et al., 2008; Power et al., 2013). Brucite forms via the hydration of olivine during serpentinisation and is usually present as a common but minor component of ultramafic tailings (1–15 wt. %; Harrison et al., 2012, O'Hanley and Offler, 1992). The lack of strong Si-O bonds within brucite means that it has a reactivity that is orders of magnitude greater than that of Mg-silicates, meaning that the abundance of brucite exerts strong control on mineral carbonation rates under ambient conditions (Harrison et al., 2012; Power et al., 2013). In addition, the serpentine polymorphs, chrysotile and lizardite, consist of a sheet of silica tetrahedra bonded to an octahedral Mg-OH sheet that is commonly referred to as the 'brucite-like' layer (e.g., Wicks and O'Hanley, 1988). This 'brucite-like' layer is more reactive and dissolves faster than the accompanying Si-rich tetrahedral layer (Park and Fan, 2004, Rozalen and Huertas, 2013), increasing the reactivity of serpentine and enhancing release of Mg for CO_2 sequestration. Dissolution of these minerals in meteoric water (containing dissolved atmospheric CO_2 as carbonic acid, pH ~5.5) releases Mg^{2+} cations and increases alkalinity. Mg^{2+} cations in solution subsequently react with dissolved CO_3^{2-} to precipitate as hydrated carbonate minerals such as hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] and nesquehonite ($MgCO_3 \cdot 3H_2O$), with Mg:$CO_2$ ratios and hydration states that are dependent on local environmental conditions (Ballirano et al., 2013; Davies and Bubela, 1973; Hänchen et al., 2008; Morgan et al., 2015; Wilson et al., 2009a). Since carbonic acid in meteoric water is a weak acid, acid leaching, or the addition of acid generating materials, has been widely employed to accelerate CO_2 uptake in ultramafic materials because it increases the rate of silicate mineral dissolution and the availability of Mg^{2+} cations for reaction (e.g., Maroto-Valer et al., 2005; Park and Fan, 2004; Power et al., 2010; Teir et al., 2007b). Following acid leaching, pH-swing methods can then be used to increase pH to alkaline conditions to allow precipitation of carbonate minerals (Park and Fan, 2004). In highly reactive mineral wastes, particularly where brucite is present, mineral dissolution under ambient conditions can provide sufficient alkalinity to induce carbonate precipitation (Harrison et al, 2013; Power et al., 2013). However, ultramafic rocks commonly contain several wt. % Fe as well as low concentrations (< 1 wt. %) of other first row transition metals (e.g., Ni, Mn, Cr, Co, Cu). These are typically found within the crystal structures of Mg-silicate, Mg-hydroxide, sulphide, and oxide minerals as well as within alloy minerals such as awaruite ($Ni_{2-3}Fe$) and wairauite (CoFe) (Challis and Long, 1964; Goff and Lackner, 1998; Kmetoni, 1984; Margiotta et al., 2012; Natali et al., 2013; Schreier, 1987; Sciortino et al., 2015). First row transition metals may be mobilised by dissolution of their mineral hosts during either natural weathering reactions or the artificially accelerated reactions that can be used to enhance mineral carbonation rates (Margiotta et al., 2012; Oelkers et al., 2008; Olajire, 2013; Olsson et al., 2014a,b; Schreier, 1987; Teir et al., 2007a). Because first-row transition metals can be toxic to biota in elevated concentrations, concern has been raised that the release of metalliferous waters from mineral carbonation facilities or geoengineered landscapes could adversely affect natural systems (Olsson et al., 2014b). Consequently, the potential mobility of trace metals during carbonation reactions is an essential consideration for implementation of *ex situ* mineral carbonation technologies, *in situ* enhanced weathering of ultramafic landscapes or mineral wastes, and *in situ* CO_2 injection into rock formations (Hamilton et al., 2016; Kirsch et al., 2014; Marcon and Kaszuba, 2013; Marcon and Kaszuba, 2015; Oelkers et al., 2008; Olajire, 2013; Olsson et al., 2014a; Olsson et al., 2014b; Seal et al., 2010; Thomas et al., 2013; Thomas et al., 2016).

Previous studies have reported elevated concentrations of trace metals (particularly Ni, Cr^{3+} and carcinogenic Cr^{6+}) in soils and waters associated with serpentinites (Margiotta et al., 2012; McClain and Maher, 2016; Morrison et al., 2015; Schreier, 1987; Schreier and Lavkulich, 2015). Uptake of these trace metals by Fe-hydroxide and clay minerals has been documented in serpentinites (Morrison et al., 2015), but the influence of hydrated Mg-carbonate minerals on trace metal mobility within ultramafic environments is relatively unexplored. This is a critical knowledge gap, given that hydrated Mg-carbonate minerals are commonly present in high abundances [up to 14.6 wt. % hydromagnesite; (Oskierski et al., 2013)] in passively carbonated mine tailings, and therefore may provide an important sink for potentially toxic trace metals.

Hamilton *et al.* (2016) demonstrated that Mg-carbonate minerals and Fe-oxyhydroxide phases sequester transition metals during their formation in laboratory experiments designed to emulate the Mg- and transition-metal-rich conditions produced during accelerated mineral carbonation. However, the mobility of potentially toxic trace metals during naturally occurring mineral carbonation in ultramafic landscapes has not yet been extensively explored. Here, we investigate (1) the mineral sources of trace transition metals and the mobility of these metals during weathering, and (2) the sequestration of trace transition metals by carbonate minerals and associated alteration phases at the Woodsreef Chrysotile Mine in New South Wales, Australia. This study provides a framework for understanding the fundamental geochemical processes, and associated environmental risks, that accompany the carbonation of transition-metal-rich ultramafic rocks. This is essential information for both the development of low-temperature technologies for enhancing carbon mineralisation using acidic treatments, and for the geosequestration of industrial CO_2 during injection into mafic to ultramafic formations. In addition, an understanding of transition metal mineralogy and mobility during mineral carbonation reactions is used to identify potential opportunities for recovery of metals from ultramafic mine wastes.

2. Materials and methods

2.1. Site description

The chrysotile deposit at Woodsreef lies within the Great Serpentinite Belt, in the Southern New England Fold Belt of northeastern New South Wales, Australia. The ultramafic rocks at Woodsreef have been variably serpentinised and contain partially serpentinised harzburgite as well as massive and schistose serpentinite (Glen and Butt, 1981). The massive serpentinite has formed from partially serpentinised harzburgite by the transformation of forsterite and pyroxene minerals into serpentine phases and magnetite (Glen and Butt, 1981; O'Hanley and Offler, 1992; Oskierski et al., 2013). Large bodies and small kernels of partially serpentinised harzburgite still remain within the massive and schistose serpentinites, which host the chrysotile [$Mg_3Si_2O_5(OH)_4$] deposit (Glen and Butt, 1981).

The Woodsreef Chrysotile Mine is located approximately 500 km northwest of Sydney in New South Wales, Australia (Fig. 1). The now derelict site occupies approximately 400 ha, and hosts four mine pits, now partially filled with water. The most recent and productive period of chrysotile asbestos mining at Woodsreef was conducted by Chrysotile Corporation between 1971 and 1983. This mining produced 500,000 t of chrysotile, 75 Mt of waste rock, and 24.2 Mt of dry-milled tailings (Assargiotis, 2013; Merrill et al., 1980; Oskierski et al., 2013; Woodsreef Taskforce, 2011). The Woodsreef tailings have since been investigated as a potential resource for nickel (Ni), chromium (Cr), magnetite, magnesium and silica (Kmetoni, 1984; Laughton and Green, 2002; Sylvester and Stagg, 2008). Passive carbonation of tailings at Woodsreef has been occurring over the past three decades (Oskierski et al., 2013; Turvey et al., 2017), resulting in the sequestration of an estimated 1,400 t of CO_2 within the hydromagnesite crusts located in the upper 2 cm of the tailings pile, and up to 70,000 t of CO_2 stored within pyroaurite at depth, although questions remain about source of carbon in this phase (Oskierski et al., 2013).

2.2. Sample Collection

Hand samples of serpentinite ore and waste rock from the mine pits and surrounding stockpiles were targeted to capture both the starting composition of tailings at Woodsreef and the products of mineral carbonation. These samples include serpentinite [n=6, including massive serpentinite (n=2) and partially serpentinised harzburgite (n=4)]. Samples of bulk tailings (n=2), and vertical and horizontal carbonate crusts forming within the tailings storage facility (n=5) were also collected. Sample descriptions and GPS co-ordinates are provided in Table S1. Water samples were also collected from each of the four mine pits, passed through 0.2 µm syringe driven filters and preserved to pH < 2 by addition of a few drops of nitric acid (50%) for later analysis of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES) and anions (Cl^{-} by discrete analyser, HCO_3^{-} by titration, SO_4^{2-} by ICP-AES). The pH of the pit lake water was measured in the field using a calibrated pH meter (Thermo Scientific Orion 5 Star).

2.3. Elemental analysis

The concentrations of a suite of dissolved trace elements (As, Ba, Be, Ca, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, Fe) within the mine pit water samples were determined using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) at the ALS Group Environmental Division laboratories (Brisbane, Queensland). Bulk elemental analysis of solid phase samples was completed using X-ray Fluorescence (XRF), and total C and S concentrations were determined using a LECO instrument at SGS Australia (Newburn, Western Australia).

2.4. X-ray diffraction analysis

Solid phase samples for X-ray diffraction (XRD) were pulverised using a ring mill prior to the addition of a 10 wt. % fluorite (CaF_2) internal standard and micronising under anhydrous ethanol in a McCrone Micronising Mill using agate grinding elements. The samples were then dried, disaggregated and back-loaded into cavity mounts for analysis using a Bruker D8

Advance Eco X-ray diffractometer, fitted with a Cu radiation source and operated at 40 kV and 25 mA, in the Monash X-ray Platform. Data were collected over 2–80° 2θ with a step size of 0.02° 2θ and a count time of 2 s/step. Mineral phases were identified using the ICDD PDF-2 database and the DIFFRACplus EVA Version 2 software package (Bruker AXS, 2004). Rietveld refinements (Bish and Howard, 1988; Hill and Howard, 1987; Rietveld, 1969) were completed using Topas Version 5 (Bruker AXS, 2004). The Rietveld refinement methodology outlined by Wilson et al. (2006) was used for quantification of mineral abundances in these serpentine-rich samples.

2.5. Scanning electron microscopy

Ten samples of waste rock and tailings were set in epoxy resin and cut into 30 µm thick polished thin sections. The least weathered serpentinites and partially serpentinised harzburgites were selected to capture the composition of the original source rocks. Thin sections were also produced from a range of tailings samples to reflect variability in the extent of carbonation at Woodsreef. Thin sections were carbon coated and analysed using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) employing a JEOL 7001F Field Emission Gun Scanning Electron Microscope (FEG-SEM) with backscattered electron (BSE) images collected at 15–20 kV at the Monash Centre for Electron Microscopy, Monash University, Clayton, Australia.

2.6. X-ray fluorescence microscopy

Representative carbonate crust samples (13WR2-4 and 13WR2-8) analysed by SEM were prepared as thin sections on quartz slides for trace element analysis using X-ray fluorescence microscopy (XFM) at the Australian Synchrotron, Clayton, Australia. Synchrotron X-ray Fluorescence Microscopy (XFM) allows rapid quantitative elemental analysis over large areas (such as a geological thin section) at high resolution (using pixel sizes as small as ~2 µm) with ppb-level sensitivity (Paterson et al., 2011; Ryan et al., 2014). In addition, the XFM beamline at the Australian Synchrotron can generate X-ray Absorption Near Edge Spectroscopy (XANES) maps, which are used here to investigate the speciation of Cr within weathered carbonate crusts from Woodsreef Mine.

Fast preliminary scans were conducted with an incident monochromatic X-ray beam of 18.5 keV focused to ~2.0 µm using Kirkpatrick-Baez mirrors, a step size of 2 µm, and a dwell time of 40 msec/pixel. Following this, the energy of the X-ray beam was reduced to 12.9 keV to enable better detection of the trace metals in small areas of interest identified during the preliminary scans of entire thin sections. These areas of interest were mapped using a step size of 1 µm and a dwell time of 1000 msec/pixel to optimise counting statistics. Elemental abundance data were collected using a Maia detector (Ryan et al., 2010; Ryan et al., 2014) and the full spectrum of data were processed using the GeoPIXE software program (Ryan, 2000).

Cr K-edge XANES analysis was undertaken over a region of interest within a carbonate crust sample (13WR2-8) over an energy range of 5.96 to 6.12 keV with a step size of 4 µm and a dwell time of 8 ms. GeoPIXE was used to process the resulting data and to assess spatial variations in oxidation state with spectra compared against published standards (Berry and O'Neill, 2004; Low et al., 2015; Vogel et al., 2014).

3. Results

3.1. Field site observations

Chrysotile was observed as exposed veins and forming slickensides in serpentinite and partially serpentinised harzburgite in the mine pit walls and in cobbles from the waste rock and tailings piles at the Woodsreef Mine (Fig. S1a,b). Partially serpentinised harzburgite is commonly present as kernels within a serpentinite matrix (Fig. S1c) that is dark in colour and has a waxy texture (Fig. S1c). The serpentinite surrounding harzburgite pods appears to have weathered by cracking perpendicular to the surface of the pods and shedding a carbonated alteration halo (Fig. S1c). A number of large boulders appeared to be disintegrating, most likely as a result of expansive forces and reaction-driven cracking generated by carbonate mineral precipitation (Beinlich and Austrheim, 2012). White carbonate minerals, identified by their characteristic effervescence when exposed to HCl, were prevalent on weathering surfaces and in cracks (Fig. S1d). Heavily carbonated crusts within the tailings pile form as both vertical ridges on weathering faces (Fig. S1e) and as horizontal cemented surfaces (Fig. S1f).

3.2.Trace metal analysis

The ICP–MS analysis of the mine pit water indicates that concentrations of Ni, Cr, Mn, Co and Cu are below instrumental detection limits (< 0.001 mg/L) in all samples with the exception of the sample taken from Lake 2 (Fig. 1), which contains 0.002 mg/L Cu (Table S2). The pH of pit water ranges from 8.9 to 9.3 with an average value of 9.2 (Table S2).

Bulk rock XRF results indicate that Ni, Cr, and Mn are present in all rock and tailings samples that were analysed, with Co being detectable in all but a few samples (detection limit was 0.01 wt. % as CoO; Table S3). Average Ni concentrations (as NiO) are 0.29 wt. % in serpentinite waste rock (considered the least weathered samples), 0.26 wt. % in bulk tailings, and 0.25 wt. % in tailings carbonated tailings crusts. Average Cr concentrations (as Cr_2O_3) are highest in serpentinite at 0.36 wt. %, with an intermediate value of 0.34 wt. % in bulk tailings, and lowest in carbonated crusts (0.32 wt. %). Mn concentrations (as MnO) are 0.10 wt. % in serpentinite, 0.12 wt. % in bulk tailings, and 0.10 wt. % in carbonated crusts. Co concentrations (as CoO) are consistently low in all samples and range from <0.01 to 0.02 wt. % with the highest concentrations occurring in serpentinite samples. In general, transition metals are present at similar abundances in all sample types, but average values are slightly more concentrated in the less weathered serpentinite waste rock compared to bulk tailings and carbonate crust samples. However, significant variations are present between samples, reflecting the heterogeneity in lithology and mineralogy observed at the site.

3.3. Mineralogical results

Serpentine minerals dominate the tailings at Woodsreef (67–97 wt. %). Hydromagnesite, pyroaurite [$Mg_6Fe_2(CO_3)(OH)_{16}\cdot 4H_2O$], magnetite ($Fe_3O_4$), chromite [$(Mg,Fe)Cr_2O_4$], brucite [$Mg(OH)_2$], forsterite ($Mg_2SiO_4$), and enstatite ($MgSiO_3$) are present as minor minerals, and both calcite and quartz are present at trace abundances. Although we give the formulae for ideal end-member compositions of these minerals, it should be noted that their elemental compositions are variable and subject to substitution. Relict olivine is heavily fractured, and SEM-EDS analysis indicates that this olivine is Mg-rich, and is confirmed to be forsteritic using XRD. Hydromagnesite and pyroaurite are most abundant in carbonated samples (up to 14 wt. % and 19 wt. % respectively). The relative abundances of (1) the serpentine polymorphs, chrysotile and lizardite (antigorite is rare at Woodsreef; O'Hanley and Offler, 1992), and (2) the spinels, magnetite and chromite, could not be determined using XRD as a result of their structural and compositional similarity (Turvey et al., 2017). However, we were able to confirm the presence of each of these four phases by textural observations (e.g., chrysotile fibres) and elemental analyses using SEM-EDS. Quantitative mineralogical results are provided in Table S4.

SEM-EDS analysis reveals that Cr is present at the greatest concentration in chromite grains, many of which are intergrown with serpentine to resemble a myrmekitic texture (Fig. 2a), or are rimmed with overgrowths of magnetite. Magnetite is abundant as dispersed grains and veins within serpentine (Fig. 2b). Some grains were found to contain small <5 µm inclusions of Co-Fe and Ni-Fe alloys. Follow up SEM-EDS analysis revealed the presence of the Ni-Fe alloy mineral, awaruite, in partially serpentinised harzburgite. This mineral contains approximately 70 wt. % Ni and 3 wt. % Co, and is commonly disseminated as <5 µm inclusions throughout serpentine in very fine-grained, cross-cutting veins (Fig. 2b). The rare Co-Fe alloy is likely wairauite (CoFe), which is found in association with awaruite in serpentinites (Challis and Long, 1964). Hydromagnesite is found extensively in the carbonated tailings and is characterised by a fibrous to platy crystal morphology; it is commonly seen precipitating directly on weathered serpentine grains and in small crevices associated with the disaggregation of grains (Fig. 2c, d). Hydromagnesite also forms extensive cements that trap and aggregate grains of other minerals, such as serpentine, magnetite and awaruite within carbonated crust samples from the tailings surface (Fig. 2e). Pyroaurite is particularly abundant within carbonated chrysotile veins (sample 13WR1-4), where it forms an extensive groundmass (Fig. 2c), and is characterised by a layered morphology (Fig. 2f), and a yellow-red hue when viewed in plane polarised light. Cr, Mn and Ni are detectable in trace amounts (<1 wt. %) in some serpentine grains using EDS; however, they are not observed in hydromagnesite above the detection limit of this technique. Trace Mn is commonly detected in pyroaurite, whereas trace Co is observed in magnetite and awaruite (~3 wt. %).

3.4. Synchrotron XFM analysis

The two regions selected for detailed synchrotron XFM mapping represent two representative styles of carbonate mineralisation at Woodsreef (1) cementation at grain surfaces within pore spaces in the tailings, and (2) a crust at the surface of the tailings. Figure 3a shows an electron micrograph of a reactive weathering front at the grain boundary between serpentine and hydromagnesite in a carbonated crust sample (13WR2-4). XFM element maps (Fig. 3a-f) show the distribution of key metals of interest, and Si within this region. A transect is drawn across this boundary (Fig. 3f), and elemental concentrations from the synchrotron XFM data are averaged along the width of the transect (Fig. 3g). Most notably, elevated Si concentrations are restricted to the serpentine grain (6.4 wt. % in the serpentine region, as opposed to 0.6 wt. % in the carbonate region; Table 1). It is important to note that the Si peak detected in the X-ray fluorescence spectra could only be partially fitted, and as such, data for this element should only be considered to be semi-quantitative. Stoichiometric serpentine (chrysotile and lizardite) is expected to contain up to 20.3 wt. % Si [in pure $Mg_3Si_2O_5(OH)_4$], indicating that our fit gives an underestimate of Si abundance. Regardless, the relative difference in Si concentrations between serpentine and hydromagnesite is significant because it represents an order of magnitude decrease in Si concentrations across the reaction front.

In comparison to Si, Fe and trace transition metals (Mn, Cr, Ni, Co) are present at comparable abundances in both regions (Table 1, Fig. 3). These metals are present within the hydromagnesite that nucleated at the surface of the serpentine grain at average abundances of 1.6 wt. % (Fe), 370 ppm (Mn), 102 ppm (Cr), 917 ppm (Ni), and 155 ppm (Co). The same elements are present at 1.3 wt. % (Fe), 295 ppm (Mn), 115 ppm (Cr), 889 ppm (Ni), and 123 ppm (Co) in the adjacent serpentine grain (Table 1). The high contrast between Si concentrations coincident with less dramatic differences in transition metal concentrations are observed both in Figure 3 and in a carbonate cement that spans a gap at the tailings surface (Fig. 4; Table 2). In the latter example, the carbonate cement appears to have precipitated across a space between grains at the surface of the tailings, as opposed to direct precipitation at a serpentine grain boundary. This is consistent with the process of carbonate formation via evaporation and wicking (Wilson et al., 2011), whereby Mg-rich fluids, in which the Mg is sourced from serpentine and brucite dissolution, are drawn to the surface by evaporation-driven capillary rise. Mineral precipitation occurs when Mg and dissolved CO_3^{2-} are sufficiently concentrated via evaporation to induce hydromagnesite saturation (Wilson et al., 2011).

Fe and trace transition metals (Mn, Ni, Cr, Co) appear to exhibit two styles of distribution within the two forms of hydromagnesite mineralisation described above: (1) homogeneously dispersed within both serpentine and carbonate phases at concentrations of 100s to 1000s of ppm, and (2) concentrated in discrete, µm-scale regions. The highest concentrations of Ni (3.4 wt.%) and Co (1.8 wt.%) occur in discrete regions less than 5 µm in size, and coincide with elevated concentrations of Fe (reported at up to 68.5 wt. % for regions containing the largest, 10 – 20-µm sized, grains of magnetite). Because XFM is a transmission technique that samples the entire volume of a specimen, concentrations of these discrete µm-scale points are averaged over the 30-µm deep thin section, thus actual concentrations of Ni, Co and Fe within those small grains are likely higher. Our SEM-EDS results, which are more appropriate for sampling surface features, confirm that three µm-scale grains exposed at the surface of the sample are high in Fe, or both Fe and Ni, indicating the presence of magnetite and awaruite. As such, the <5 µm-scale grains visible within the whole sample depth in XFM are also interpreted to be trapped magnetite and awaruite grains (Fig. 3c, e, f). Fe concentrations within the serpentine grain shown in Figure 3 (1.6 wt. % Fe, in Table 1), and the silicate mineral region highlighted in Figure 4 (1.0 wt.% Fe, in Table 2), are slightly lower although not dissimilar to measurements of Fe abundance in lizardite [1.6 – 2.3 wt. % Fe; using electron microprobe, O'Hanley and Dyar (1993)] and chrysotile [1.9 – 2.3 wt. % Fe^{2+} and 1.1 – 1.4 wt. % Fe^{3+}; using atomic absorption spectroscopy, Glen and Butt (1981)] in samples from Woodsreef.

The presence of Cr within hydromagnesite cements, at evenly distributed low-level concentrations, and in discrete µm-scale concentrations, indicates that mobilisation of Cr into solution and liberation of small chromite particles is occurring within the weathered tailings. Cr K-edge XANES analysis reveals Cr is present as Cr^{3+} in chromite, serpentine, and pyroaurite, whereas Cr^{6+} is not detected in the scanned area (Fig. S2).

Pyroaurite also contains trace metals at 100s to 1000s ppm level concentrations (107 ppm Cr, 440 ppm Ni, 784 ppm Co, 0.3 wt. % Mn and 8.2 wt. % Fe). However, uncertainty exists about the formation mechanism of pyroaurite at Woodsreef as it can form via reaction of brucite atmospheric CO_2, but it was also detected in fresh tailings at Woodsreef (Slansky, 1983), suggesting it could be a hydrothermal alteration product. Pyroaurite is prone to the exchange of interlayer anions, such as CO_3^{2-}, (Bish, 1980; Miyata, 1983), and stable carbon and oxygen isotopic data for pyroaurite-rich samples reported by Oskierski et al. (2013) give an ambiguous signature that could result from (1) mixing of an atmospheric source of carbon with a metamorphic source of carbon, (2) formation of pyroaurite from a modern organic carbon source (although no such source is present in the tailings at Woodsreef), or (3) kinetic depletion of ^{13}C during either exchange of atmospheric CO_2 for metamorphic CO_2 in pyroaurite or formation of sedimentary pyroaurite from atmospheric CO_2. As such, although pyroaurite is identified as a host for trace metals in the Woodsreef tailings, it is unclear whether these trace metals were inherited in pyroaurite that was originally found in the ore or were sequestered during carbonation in the tailings post-mining. Therefore, this study focuses on hydromagnesite as a model phase for examining trace metal uptake in the products of passive mineral carbonation by air capture.

4. Results

4.1. Mineralogical hosts of trace metals

Weathering has formed a Mg-carbonate-rich crust at the surface of the Woodsreef tailings, but the bulk of the tailings at depth appear to be less altered, thus the tailings are considered an attractive target material for promoting mineral carbonation reactions (McCutcheon et al., 2015, 2016, 2017; Oskierski et al., 2013; Turvey et al., 2017). We find that the bulk of trace transition metals within the tailings remain within the original mineral assemblage, of silicates, oxides and alloys, with some metals having been mobilised and then sequestered within alteration minerals (hydromagnesite and possibly pyroaurite) in surface crusts, and none detected in mine pit waters. XRF analyses of bulk samples show that Cr_2O_3 and NiO are both present at concentrations of ~0.3 wt. % in the Woodsreef Mine tailings (Table S3). Amongst the metals investigated, Cr is of particular environmental concern because it can form the toxic carcinogen Cr^{6+} in its most oxidised state (Kotaś and Stasicka, 2000). Our SEM-EDS analyses show that Cr is predominantly hosted in chromite, whereas synchrotron XFM mapping reveals that Cr is also distributed homogeneously at low concentrations (approximately 100 ppm) within grains of serpentine, possibly by substitution for Mg within the crystal structures of lizardite and chrysotile. This is unsurprising given that a variety of divalent and trivalent cations, including Fe^{2+}, Fe^{3+}, Cr^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, and Co^{2+}, can readily substitute for structural Mg^{2+} in serpentine minerals (Anbalagan et al., 2008; Anbalagan et al., 2010; Cralley et al., 1968; Morgan et al., 1973; O'Hanley and Dyar, 1993, 1998; Ristić et al., 2011; Schreier, 1987).

Our XFM results confirm that Ni is also distributed throughout serpentine minerals at low levels; however, we also commonly observe µm-scale inclusions of the Ni-Fe alloy mineral, awaruite, within partially serpentinised harzburgite, consistent with observations made by O'Hanley and Dyar (1993). Awaruite forms from Ni mobilised by serpentinisation of olivine at low temperature and low water-to-rock ratios (Sciortino et al., 2015).

4.2. Trace metal mobility during passive mineral carbonation

Hydromagnesite and other hydrated Mg-carbonate minerals are common weathering products of serpentine minerals, forsterite and brucite (Harrison et al., 2015; Wilson et al., 2011; Wilson et al., 2009a), all of which are present within the Woodsreef tailings (Oskierski et al., 2013; Slansky, 1983; Turvey et al., 2017). An early investigation of tailings mineralogy did not detect hydromagnesite in the tailings at Woodsreef (Slansky, 1983). Today, evidence of serpentinite weathering to produce carbonate crusts is observed at a large scale in the field, as rocks and boulders disintegrate due to the expansive forces of carbonate mineral formation, and in textural observations and mineral associations viewed in thin sections (Fig. 2). Small grains of minor oxide minerals such as magnetite and chromite, and alloy minerals such as awaruite (Fig. 2e), in contrast, do not appear to be significantly altered, but they are liberated by weathering of serpentine and incorporated as inclusions in the extensive hydromagnesite cements that have developed within the surficial tailings material. These hydromagnesite cements formed recently (since 1983) once tailings were deposited in the storage facility and they are known to have been produced from a modern atmospheric CO_2 source (Oskierski et al., 2013; Turvey et al., 2017). Serpentine minerals, forsterite and brucite are still present in the tailings; therefore, it is likely that weathering reactions will continue to sequester atmospheric CO_2 within hydromagnesite into the future. However, Wilson et al. (2014) found that the nucleation of hydromagnesite on the surfaces of mineral grains, and formation of thick (mm-scale) efflorescent cements at tailings surfaces slows carbonation reactions by passivating reactive surfaces and limiting CO_2 ingress into deeper tailings.

The most likely source of the Mg in the hydromagnesite forming in the Woodsreef tailings is from the dissolution of serpentine minerals, brucite and trace amounts of forsterite (Oskierski et al., 2013). Brucite is the most soluble of these phases under acidic to neutral conditions (i.e., rainwater; Palandri and Kharaka, 2004); thus, it is likely that mineral carbonation at the site is attributable to carbonation of this minor phase as has been observed previously at the Mount Keith nickel mine (Wilson et al., 2014). As such, brucite dissolution could be a significant source of mobilised trace metals, given it forms a solid solution with a wide range of divalent metal cations, including Fe, Ca, Ni, Co, Mn, Zn, Cd (Brindley and Kao, 1984). Serpentinite hosted brucite commonly contains high concentrations of substituted Fe (Mumpton, 1966) and Ni (Grguric, 2003); with the distribution coefficient for Ni partitioning between brucite and serpentine being reported as 63 to 1 under conditions typical of serpentinisation (Perruchot, 1973).

In contrast to brucite, lizardite and chrysotile typically have a much higher surface area (Bea et al., 2012) and are the most abundant phases (>67 wt. %) at Woodsreef; therefore, they are also likely to contribute cations for mineral carbonation. The transition metals of interest in this study (Fe, Cr, Ni, Mn, Co) substitute for Mg^{2+} in the more reactive ‘brucite layer’ within the structures of serpentine minerals (Anbalagan et al., 2008; Anbalagan et al., 2010; Ristić et al., 2011) meaning they are likely to be leached along with Mg during passive weathering or engineering solutions for accelerated leaching of tailings. Si forms strong bonds with oxygen within the serpentine structure, and is expected to be relatively immobile under the circumneutral conditions that occur during weathering of serpentinite (e.g., McCutcheon et al., 2015, 2017). Our XFM data indicate that Si is restricted to serpentine grains whereas Fe and trace transition metals (Cr, Ni, Mn, Co) are incorporated into hydromagnesite cements at comparable concentrations, although slightly lower than those found in unweathered serpentine (Tables 1, 2; Figs. 3, 4). The Fe and trace metals released during dissolution of brucite or serpentine are unlikely to remain soluble under the circumneutral to alkaline conditions expected in Woodsreef mine waters (Stumm and Morgan, 1996). As such, they likely have not travelled far from the source. This may explain why trace metal concentrations are generally higher in both the pyroaurite (which likely formed via carbonation of brucite, although this is not certain), and the hydromagnesite cement precipitated at a serpentine grain boundary (Fig. 3, Table 1), compared to the lower metal concentrations found in hydromagnesite surface cements, which we suggest formed via evapoconcentration and wicking of Mg-rich pore fluids. A small amount of trace metals may also be lost in runoff waters, although we generally do not observe detectable concentrations within the mine pit lakes (Table S2).

Weathering of other minor mineral phases such as forsterite, enstatite, magnetite and chromite likely occurs much more slowly given their slower reaction rates and lower abundances (Palandri and Kharaka, 2004). For this reason, these gangue phases probably do not contribute appreciable Mg and transition metal cations to alteration phases compared to brucite and serpentine. Although dissolution rate constants are not known for awaruite and wairauite, kinetic tests conducted by Kandji et al. (2017) show that awaruite is stable in weathering cells for 6 months and does not release Ni under the tested conditions. It is therefore unlikely that Ni is being appreciably mobilised from awaruite at Woodsreef during passive weathering.

Trace metal concentrations may be particularly elevated in surface and ground waters around ultramafic environments and chrysotile deposits, and in some cases concentrations exceed local water quality thresholds (Fantoni et al., 2002; Margiotta et al., 2012; McClain and Maher, 2016; Natali et al., 2013; Schreier, 1987). For instance, up to 73 µg/L Cr^{6+} has been reported in ground water associated with an ophiolite in Italy, where the local permissible value is 5 µg/L Cr^{6+} (Fantoni et al., 2002). The trace metals of interest in this study are not detected in the pit lakes at Woodsreef (Table S2), indicating that either trace metals are not being mobilised from the surrounding waste rock storage piles, or they do not remain dissolved for long enough or at sufficient concentration to be detectable in nearby water bodies. The general lack of trace metals in the pit lakes suggests that sequestration by secondary mineral precipitates, such as hydromagnesite and possibly pyroaurite, plays an important role in limiting trace metal mobility in runoff waters at Woodsreef.

4.3. Mg-carbonate minerals sequester trace metals in ultramafic mine tailings

Iron and trace metals (Cr, Ni, Mn, Co) are sequestered within the coatings of hydromagnesite that form within pore spaces at the surfaces of serpentine grains (Fig. 3) and as evaporative crusts at the surface of the tailings storage facility at Woodsreef (Fig. 4). The distribution of Fe within hydromagnesite-rich cements appears to be a useful indicator of the extent of trace metal mobilisation during weathering and carbonation reactions, as Fe and trace metals are spatially associated, with different concentrations corresponding to mineralogy (Fig. 3, 4). Elevated concentrations (up to wt.% level) of Cr, Ni and Co are measured in distinct, <5 µm-scale regions that are also associated with higher Fe concentrations, most likely representing the incorporation of oxide and alloy mineral grains, such as chromite, magnetite, awaruite or wairauite, as inclusions within carbonate cements. This could also represent precipitation of secondary Fe-hydroxide or oxide minerals which are widespread in the environment and are also common products of mineral carbonation and weathering reactions (Hamilton et al., 2016; Mumpton and Thompson, 1966; Park and Fan, 2004; Schwertmann and Taylor, 1989). Fe-hydroxide and oxide phases can incorporate trace metals (Cr, Ni, Mn, Co, Cu) by substitution, surface sorption, co-precipitation, or recrystallisation (Manceau et al., 2000; Schwertmann and Taylor, 1989; Trolard et al., 1995). These phases are known to play a role in sequestering trace transition metals from solution during simulated mineral carbonation experiments (Hamilton et al., 2016), therefore is it possible that this also occurs naturally in the Woodsreef tailings.

In addition, trace metals appear to be distributed at low concentrations (10s to 100s of ppm) within hydromagnesite (and pyroaurite), suggesting they have been incorporated into the crystal structure of the mineral, most likely via substitution for Mg (or Mg and Fe in the case of pyroaurite). Common carbonate minerals such as calcite, dolomite and magnesite are known to incorporate a variety of trace metals by substitution for Ca or Mg, or by any of the incorporation mechanisms described above (Calugaru et al., 2016; Wunsch et al., 2013; Zachara et al., 1991). Trace metal concentrations within carbonate cements are comparable with those detected in silicate mineral grains, which are considered, along with brucite, to be the dominant sources of mobilised transition metals. This indicates that (1) sequestration of metals occurs effectively over a spatial scale of ~10 µm and (2) any loss of transitions metals to runoff water is likely to be small under the environmental conditions observed at Woodsreef.

Despite these samples having been collected from a surficial environment in contact with the atmosphere, the oxidised Cr^{6+} species was not detected by Cr K-edge XANES analysis. This is an important finding, since elevated levels of highly toxic, carcinogenic, and mobile Cr^{6+} are often reported in serpentinite-dominated environments (McClain and Maher, 2016; Morrison et al., 2015; Oze et al., 2007). The crushed Woodsreef tailings have a highly reactive surface area and are exposed to oxic conditions, providing an ideal environment to promote weathering reactions. Here, it is likely that any Cr released by the weathering of brucite, serpentine, and possibly chromite has been and continues to be immobilised by incorporation into hydromagnesite cements (e.g., Table 1, 2; Fig. 3b). Extended X-ray absorption fine structure (EXAFS) analysis could possibly be used to shed light on the relative importance of specific mechanisms of trace metal uptake in these samples, such as ad/absorption or co-precipitation. Nonetheless, our observations demonstrate that hydromagnesite cements forming at the Woodsreef Mine trap trace metals, limiting their mobilisation into the surrounding environment.

These findings are consistent with those of Hamilton et al. (2016), who demonstrated that transition metals (up to 100 mg/L of aqueous Cr, Ni, Mn, Co or Cu) are immobilised during the precipitation of nesquehonite in simulated mineral carbonation experiments. Under alkaline conditions, Mg-carbonate minerals should remain stable hosts for these trace metals, as they are known to persist at Earth's surface conditions for thousands of years (Grant et al., 1987). Retention of trace metals within nesquehonite has been demonstrated after recrystallisation of nesquehonite from colloidal particles to mm-scale crystals (Hamilton et al., 2016), although further work should investigate metal retention on longer time scales and during decomposition of Mg-carbonate minerals to less hydrated, more stable phases.

4.4. Outlook for metal mobility during passive and artificially accelerated carbon mineralisation

The capacity for Mg-carbonate minerals to sequester trace metals is particularly relevant to accelerated mineral carbonation projects, where metal leaching is expected to be enhanced by acid treatments or reaction with low pH CO_2 streams (Marcon and Kaszuba, 2013; Oelkers et al., 2008; Olsson et al., 2014a; Olsson et al., 2014b). Field and pilot scale accelerated mineral carbonation projects are beginning trials worldwide. For example, *ex situ* mineral carbonation reactors include the pilot scale Mineral Carbonation International project, which uses serpentine from the Great Serpentinite Belt (where Woodsreef is located) as feedstock material (Brent et al., 2015), and a project based at an undisclosed cement plant in Québec, Canada, which also uses serpentinite tailings material (Kemache et al., 2017). In Iceland, *in situ* CO_2 injection has been trialled in mafic to ultramafic formations (Matter et al., 2011; Matter et al., 2016; Okamoto et al., 2006). Proposed *in situ* treatments include sulfuric acid leaching of mine tailings to induce mineral carbonation (Power et al., 2010; McCutcheon et al., 2015, 2016, 2017), or geoengineering scenarios including the application of ultramafic minerals in major river catchments and along coastlines (Hartmann et al., 2013; Schuiling and de Boer, 2013). Here, we find that Mg-carbonate minerals (hydromagnesite and possibly pyroaurite) are likely to be effective sinks for potentially toxic trace metals released by accelerated mineral carbonation in these scenarios.

Romão et al., (2013) propose that trace metal recovery could be incorporated into mineral carbonation technologies, serving a dual purpose of adding value to the mineral carbonation process, and making low grade and otherwise unfeasible ores potentially economic. The

Woodsreef Mine tailings have been considered in the past as a potential Ni and Cr resource, and while chromite recovery was considered feasible, no high-grade Ni minerals were identified, thus the processing of serpentine to extract Ni was considered unfeasible by Kmetoni, (1984). Here, we find that Ni is most concentrated in inclusions of awaruite and Cr is most concentrated within chromite. Only low (100s ppm) concentrations of Ni and Cr are diffusely distributed by substitution for Mg within serpentine. Given that much of the Ni at Woodsreef appears to be hosted in alloy minerals (56 – 83 % of estimated total Ni), despite the high abundance of serpentine, the potential for Ni recovery may be more optimistic than previously assumed.

The 24.2 million tonnes of tailings at Woodsreef have a bulk Ni content of 0.2 wt. %, yielding an estimated 48,400 t of contained Ni metal. Mineralogical analyses conducted in this study indicate that these tailings contain 67 – 97 wt. % serpentine. In addition, the Ni content of serpentine grains in tailings analysed by XFM range between 510 – 917 ppm Ni. From these ranges of mineral abundance and Ni content, we can estimate that serpentine accounts for 8,300 – 21,500 t of Ni. Comparing this to our estimate of total Ni in the tailings, 26,900 – 40,100 t of Ni remains unaccounted for by substitution into serpentine alone, and is therefore likely hosted in awaruite and as trace components in other minor phases such as brucite, pyroaurite and magnetite. If we assume that all of this Ni is present in awaruite (which stochiometrically contains 58 – 87 wt. % Ni), we would expect this mineral phase to be present at an abundance of 0.1 – 0.3 wt. % in the tailings. As such, it is not a surprise that awaruite is not detected in XRD patterns, where detection limits are on the order of 0.5 to 1 wt. % for most mineral phases under the conditions of data collection used in this study.

Processing of Woodsreef tailings or other ultramafic material for mineral carbonation could release Ni by acid leaching serpentine and liberating alloy minerals and spinels. Trace metals leached by the dissolution of serpentine and brucite could potentially be recovered using a step-wise pH swing method (Azdarpour et al., 2015; Park and Fan, 2004; Teir et al., 2007a), whereby trace metals are initially precipitated with Fe-oxides at circumneutral pH before the pH is raised to induce Mg-carbonate mineral precipitation. In addition, crushing, or mechanical activation, is often used to increase reactive surface area to accelerate mineral carbonation reactions (Li and Hitch, 2016; Park and Fan, 2004). This pre-treatment would likely assist in liberating inclusions of oxides such as magnetite and chromite, and possibly alloys of Ni and Co, although the small size and disseminated distribution of these alloys would likely limit their liberation by mechanical pre-treatment. Magnetic separation has also been recommended as a pre-treatment to enhance the effectiveness of serpentine carbonation because removal of magnetite mitigates the passivating effect of Fe-oxide precipitation on grain surfaces (Huijgen and Comans, 2003; Veetil et al., 2015). Awaruite is a Ni resource of growing interest to the minerals industry (Britten, 2017; Mudd and Jowitt, 2014; Sciortino et al., 2015), and lends itself to gravimetric and/or magnetic separation (Britten, 2017). Thus, if the Woodsreef mine tailings were used as a feedstock in a mineral carbonation reactor, acid leaching of serpentine could be coupled with the above-mentioned separation methods to recover metals of economic value from the Ni-, Cr-, and Co-rich accessory minerals, magnetite, chromite, awaruite, and wairauite, which are more resistant to acid leaching than silicate minerals and brucite. Therefore, extraction of metal resources that are otherwise not economically viable could provide an additional incentive to implement CO_2 sequestration using serpentine-rich materials (Park and Fan, 2004; Romão et al., 2013).

5. Conclusions

Naturally forming Mg-carbonate cements are an important and effective sink for trace transition metals mobilised during weathering of ultramafic mine tailings. Trace metals are immobilised within these cements both by incorporation into the Mg-carbonate mineral, hydromagnesite, likely by substitution for Mg, and by physical trapping of metal-rich grains that are liberated during mineral processing and weathering. This indicates that if mineral carbonation of ultramafic materials were to be accelerated, metalliferous drainage is unlikely to pose an environmental risk. Furthermore, *ex situ* mineral carbonation processes could be optimised for trace metal recovery, which may provide additional value to future reactor projects.

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Table 1. Elemental abundances generated in GeoPIXE for regions selected within serpentine and hydromagnesite in Figure 3.

Element	**Si***	**Fe**	**Mn**	**Cr**	**Ni**	**Co**	**Cu**
Units	*wt. %*	*wt. %*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Serpentine	6.4	1.6	370	102	917	155	<0.07
Hydromagnesite	0.6	1.3	295	115	889	123	<0.07

*Si peak could only be partially fitted; therefore, these data should be treated as semi-quantitative.

Table 2. Elemental abundances generated in GeoPIXE for regions highlighted in green in Figure 4e, f.

Element	**Si***	**Fe**	**Mn**	**Cr**	**Ni**	**Co**	**Cu**
Units	*wt. %*	*wt. %*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Serpentine	3.1	1.0	329	281	510	74	<0.07
Hydromagnesite	<0.013	0.5	114	76	294	11	<0.07

*Si peak could only be partially fitted; therefore, these data should be treated as semi-quantitative.

Figure Captions:

Figure 1. Map of Woodsreef Mine site showing sampling locations. Labels beginning with an "L" indicate water sample locations from the four pit lakes. Solid phase tailings were collected at all other sample locations. Sample descriptions are listed in Tables S1 and S2.

Figure 2. BSE-SE micrographs showing: A) Chromite (Chr) in serpentine (Srp) in sample 13WR5-3. B) Disseminated awaruite (Awr) in a serpentine groundmass (13WR1-5). C) EDS analysis of awaruite grain indicated in panel B. D) Hydromagnesite (Hmg) nucleation on chrysotile (Ctl), with pyroaurite (13WR1-4). E) Hydromagnesite cementation of serpentine and awaruite grains in carbonated crust sample 13WR2-4. F) Pyroaurite (Pau) and hydromagnesite carbonate cement between disaggregated serpentine grains (13WR1-4).

Figure 3. A) BSE-SEM micrograph of weathered serpentine grain and hydromagnesite precipitate, in sample 13WR2-4. B – F) XFM element concentration maps of a serpentine grain undergoing carbonation to form hydromagnesite. Si is mapped in green, and the distribution of each trace metal of interest, Cr, Ni, Mn, Co and Fe is mapped in purple in B, C, D, E, and F, respectively. Note the low level diffuse concentrations throughout the carbonated region, and also µm-scale higher concentrations (especially Ni, Co and Fe) representing trapped grains of minerals such as magnetite and awaruite. G) Plot of elemental abundances, averaged across the width of the transect, from A to B through serpentine into hydromagnesite (as indicated in F).

Figure 4. Carbonate surface cement in sample 13WR2-4. A) Photomicrograph of carbonate cement spanning space between grains at the tailings surface. B) BSE-SEM micrograph of

this area does not show cemented region of interest as it is below the surface of the thin section. C) Association between Si and Fe from XFM data. The region representing serpentine is highlighted in the top ellipse, and the region representing hydromagnesite is highlighted in the ellipse below. D) XFM image showing the distribution of Fe in red, Si in green and Ni in blue. D) Region selected in C (serpentine) is highlighted in green on Fe XFM map. E) Region selected in C (hydromagnesite) is highlighted in green on Si XFM map. Si concentrations should be treated as semi-quantitative.