

Dissolution mechanisms of chromitite: Understanding the release and fate of chromium in the environment

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ABSTRACT

An understanding of the formation of toxic hexavalent chromium (Cr^{6+}) in Cr-containing mine tailings and associated soils and sediments, requires an understanding of the underlying dissolution mechanisms of chromitite, a common chromite-bearing rock in both ophiolites suites and ultramafic intrusions. This study will examine dissolution mechanisms of chromitite in various acidic, neutral, and alkaline solutions containing cultivated bacteria, manganese oxides, sulfates, and phosphates. Dissolution of chromitite is non-stoichiometric under acidic, near-neutral, and alkaline pH conditions and involves the release of chromite nanoparticles and complex dissolution/re-precipitation reactions. Chromitite samples are obtained from the Black Thor chromite deposit in Northern Ontario, Canada; part of the “Ring of Fire” intrusive complex. The examined chromitite is composed of chromite, $(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{Al}_{0.6}\text{Cr}_{1.4})\text{O}_4$ and clinochlore; $\text{Mg}_3[\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot [\text{MgAl}_{1.33}(\text{OH})_6]$, the latter phase contains ~3 wt% Cr in the form of chromite nanoparticles. Bulk dissolution data are collected after dissolution experiments with chromitite powders, and the chemical and mineralogical composition of treated chromitite surfaces is characterized with a combination of surface analytical techniques (X-ray photoelectron spectroscopy) and nano- to micro-analytical techniques (scanning electron microscopy, transmission electron microscopy, and focused ion beam technology). In the chromitite systems studied here, the non-stoichiometric dissolution of clinochlore is the dominant reaction, which results in the formation of a hydrous and porous silica precipitate that is depleted in chromite nanoparticles relative to untreated clinochlore. Complete replacement of clinochlore by hydrous silica on the surface of chromitite under acidic conditions promotes the release of chromite nanoparticles and results in higher Cr:Si in solutions and in higher proportions of secondary Cr species on its surface (secondary Cr species are defined as surface terminations that do not occur on an untreated chromite surface, such as $-\text{Cr}^{3+}\text{-OH}_2$ and $-\text{Cr}^{6+}\text{-OH}$). Cultivated bacteria from a sulfide-bearing acid-mine drainage system affect neither the degree of dissolution nor the formation of secondary Cr species, whereas pyrolusite (MnO_2) particles, and adsorbed or precipitated Fe- and Al-bearing hydroxide, -sulfate, and -phosphate species, affect release and re-adsorption of chromite nanoparticles and Cr-bearing species during dissolution of chromitite under acidic, neutral, and alkaline conditions. These results show that weathering of chromitite and the release of Cr into the environment are strongly controlled by factors such as dissolution rates of Cr-bearing silicates and chromite, the release of chromite nanoparticles, re-precipitation of amorphous silica, the presence of particles in solution, and the pH-dependence adsorption (or precipitation) of Fe- and Al-bearing hydroxides and sulfates.

Keywords: Chromite, clinochlore, dissolution, chromate, toxicity, Ring of Fire, X-ray photoelectron spectroscopy, transmission electron microscopy, focused ion beam, bacteria, pyrolusite

INTRODUCTION

Effectively assessing the environmental risks posed by highly toxic hexavalent chromium (Cr^{6+}) in Cr-containing mine tailings, as well as associated soils and sediments, requires an understanding of: (1) its occurrence and speciation in minerals and glasses (i.e., slags); (2) the solubility and dissolution behavior of such phases; (3) the complex redox chemistry of released Cr species; (4) the chemical reactions that influence the mobility of Cr species in soils and sediments; and (5) the occurrence and

behavior of nanoscale chromite particles.

In a recent study at the nanoscale, Schindler et al. (2017) showed that chromite nanoparticles are held within clinochlore and lizardite grains in chromitite ore from the Black Thor chromium deposit in Northern Ontario, Canada, and the Mistake mine, part of the Franciscan Ophiolitic Complex. This is an important observation as the potential release of chromite nanoparticles rather than Cr^{3+} aqueous species during the weathering of chromite-bearing silicate minerals will have an impact on the environmental behavior of Cr^{3+} and its potential oxidation to Cr^{6+} . The study by Schindler et al. (2017) did not address the dissolution of the larger chromite grains or the roles

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of bacteria, manganese oxide particles and mineral surface coatings during dissolution and release of the Cr-rich silicates and chromite nanoparticles, respectively. This study will further investigate the dissolution mechanisms of chromitite from the Black Thor chromium deposit focusing on chemical reactions on surfaces of millimeter-size slabs and the geochemical behavior of released elements and chromite nanoparticles during the dissolution reactions.

Chromitite is an ultramafic rock composed predominantly of the spinel group mineral chromite (FeCr_2O_4) with minor silicates phases (e.g., serpentine, chlorite, amphibole, pyroxene, and olivine groups). It is a common rock in both ophiolite suites and ultramafic intrusions, the latter being exemplified by the Bushveld Igneous Complex in South Africa, the Stillwater Igneous complex in Montana, and the current region of interest. Larger rock fragments, grains, and particulate matter derived from chromitites may occur in soils and tailings piles in close proximity to natural outcrops or mining activities, respectively (Pillay et al. 2003; Oze et al. 2004; Tiwary et al. 2005; Kien et al. 2010). Although the total amount of Cr in chromitite may be controlled by the abundance of refractory chromite, the bioavailability of Cr and formation of hexavalent Cr may ultimately depend on the weathering of serpentine and chlorite group silicates, as they have been shown to be more susceptible to weathering (e.g., Oze et al. 2004, 2007; Fandeur et al. 2009; Hseu and Iizuka 2013; Morrison et al. 2015). For instance, elevated Cr^{6+} concentrations in soil pore water and groundwater have been reported for serpentinite-bearing soils and aquifers (e.g., Izbicki et al. 2008; Wood et al. 2010). On the contrary, spectroscopic studies on the speciation of Cr in serpentine-derived soils from other locations indicated the absence of detectable amounts of Cr^{6+} (Hseu and Iizuka 2013; Fandeur et al. 2009), and hence many aspects of this issue remain unresolved.

Understanding the redox chemistry of Cr is a critical aspect of determining its toxicity. As a trivalent cation, chromium has relatively low toxicity, is a micronutrient, and is relatively insoluble and immobile at neutral to alkaline pH. In contrast, hexavalent chromium is a significant environmental toxicant, a human carcinogen, and is highly mobile at neutral-to-alkaline pH (e.g., Fendorf 1995). The complexity of $\text{Cr}^{3+}/\text{Cr}^{6+}$ redox reactions in natural and anthropogenic systems can make effective risk assessment difficult. For example, Cr^{3+} can be readily oxidized to Cr^{6+} by naturally occurring $\text{Mn}^{3+}/\text{Mn}^{4+}$ -oxides (Bartlett and James 1979; Eary and Rai 1987; Fendorf 1995; Weaver and Hochella 2003; Oze et al. 2007), whereas Cr^{6+} can be reduced to Cr^{3+} by organic carbon, bacteria (aerobic and anaerobic conditions), sulfides, and Fe^{2+} -bearing species and clay minerals (e.g., Kamaludeen et al. 2003; Parthasarathy et al. 2003). Hence, understanding the dissolution mechanisms of chromitite under different pH environments and in the presence of manganese oxides and/or bacterial organisms is critical for assessing aspects of the health risks associated with chromitite-rich rocks, soils, and tailings.

The dissolution mechanisms of chromitite in the presence of different types of acids, bases, and oxidants at varying temperatures have been thoroughly studied to improve the leaching efficiency of Cr from the ore at temperatures commonly above 100 °C (e.g., Zhang et al. 2016). A common process involves the

dissolution of chromitite in oxidizing alkaline solutions, which results in the formation of water-soluble chromate species and allows the physical separation of Cr from the silicate minerals. Less-soluble chromate phases, such as the carcinogenic calcium chromate (CaCrO_4), remain with the silicate residue and require special treatment or waste disposal. An alternative extraction process is the treatment of chromitite with sulfuric acid, which results in the formation of amorphous silica on the surface of the chromitite and in the simultaneous release of Cr, Al, Fe, and Mg into solution (Zhao et al. 2014). This process requires the separation of the latter elements that can be achieved via the precipitation of Fe-hydroxides at higher pH in the presence of an oxidant such as H_2O_2 (Zhang et al. 2016).

DETAILED OBJECTIVES AND APPROACH

The observation that Cr occurs in the form of chromite nanoparticles in silicate minerals within high-grade chromitite ore from the Black Thor chromite deposit requires a unique multi-analytical approach to characterize the dissolution mechanisms of the ore at ambient Earth surface temperatures. As such, this study will combine transmission electron microscopy with surface sensitive methods such as X-ray photoelectron spectroscopy, and bulk dissolution data to examine release, dissolution, re-adsorption, and attachment of chromite nanoparticles and Cr-bearing aqueous species during chromitite dissolution experiments. The occurrence of chromite nanoparticles in solution and their proportion relative to Cr-bearing solutes will be addressed elsewhere.

This study will aim specifically to examine whether:

- (1) The minerals in the ore samples dissolve stoichiometrically or non-stoichiometrically under conditions that may occur in potential mine waste environments;
- (2) The amphoteric elements Al, Fe, and Cr behave similarly during dissolution in acidic, neutral, and alkaline conditions;
- (3) The chemical composition of solutions after the experiments can be directly linked to the composition of altered ore mineral surfaces and vice versa;
- (4) Any secondary Cr species (i.e., those not found on untreated chromitite, such as hydrated Cr^{3+} and Cr^{6+} species) occur on treated chromitite surfaces;
- (5) Bacteria from oxidized portions of sulfide-rich mine tailings affect the dissolution of chromitite under aerobic acidic conditions and contain populations that grow preferentially in Cr-bearing media;
- (6) MnO_2 particles affect the dissolution of chromitite and specifically the proportion of hexavalent Cr species, on both MnO_2 and altered chromitite surfaces;
- (7) Potential liming of tailings material through the addition of e.g., CaCO_3 affects the dissolution mechanisms and the proportion of Cr^{6+} species on altered chromitite surfaces.

In typical studies of mineral dissolution, powders of known total surface area are used, and the chemical reactions are deduced by subsequent bulk compositional analyses of solution and solid phase materials. Here, two types of experiments are conducted: (1) utilizing powdered chromitite materials, and (2)

using single slabs, manually cut from chromitite rock pieces. Powder-based experiments result in the release of sufficient amounts of ions to solution during the dissolution process, thereby facilitating quantification by standard solution chemical analytical techniques. However, the relatively flat surfaces of the slabs are better-suited for studying the chemical reactions occurring on mineral surfaces, as similar locations on their surfaces can be examined with a multi-analytical approach, integrating data from X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), in situ focused ion beam (FIB) sample extraction, and transmission electron microscopy (TEM) techniques. Noteworthy disadvantages of working with chromitite slabs, however, are that their surface composition, area, and roughness cannot be faithfully reproduced between individual experiments, and the very low quantities of ions released into solution are often below the detection limits of even the most sensitive analytical methods. Hence, with material extraction from the same chromite sample, concurrent dissolution experiments are run, one utilizing chromitite slabs and the other utilizing chromitite powders. Comparing the results from both approaches allows greater understanding of the overall, underlying dissolution mechanisms of chromitite ore.

METHODS

A high-grade chromitite ore sample was obtained from the Black Thor chromite deposit, Ontario, Canada, through the Ontario Geological Survey. The Black Thor chromite deposit is part of the Neoproterozoic "Ring of Fire" Intrusive Complex, located in the Oxford-Stull Domain of the Archean Superior Province, and interpreted as an intracratonic rift basin separating the Mesoproterozoic North Caribou and Hudson Bay Terranes (Stott et al. 2010). Cumulate chromite occurs throughout much of the deposit and occurs as a continuous, thickly bedded chromitite horizon at the transition from olivine-dominant to pyroxene-dominant lithologies (Weston and Shinkle 2013; Laarman 2013).

Sample preparation

Both powders and slabs were prepared from the same chromitite sample. Chromitite slabs with dimensions of ca. $5 \times 5 \times 3$ mm³ were prepared with a petrographic micro saw. Powders (100 mg for each experiment) were prepared by crushing and milling the remaining rock sample to an average grain size of $75 \pm$

10 μ m (determined by optical microscopy). All samples were thoroughly washed with double-deionized water prior to initial analyses by optical microscopy, SEM, XPS, TEM, X-ray diffraction (XRD), and X-ray fluorescence spectroscopy (XRF). Experiments and analytics are carried out for chromitite slabs in the sequence (1) dissolution experiment, (2) XPS, (3) SEM, (4) TEM and for powders in the sequence (1) dissolution experiment, (2) ICP-OES (solution), (3) XPS (selected samples).

Dissolution experiments with and without MnO₂ particles and bacteria

Dissolution experiments were carried out on chromitite slabs and powders for four weeks at the pH values and chemical compositions listed in Tables 1–2 and Supplemental¹ Table A1–A3. Both initial and final pH and Eh values were determined using a standard hydrogen electrode calibrated against pH solutions of pH 4, 7, and 10 and a K-iodide standard. The standard deviation of individual measurement pH and Eh measurements is ca. ± 0.2 units, based on repeated measurements of the standard solutions.

Manganese oxide phases containing Mn³⁺ (e.g., birnessite), (Na,Ca)_{0.5}(Mn³⁺, Mn²⁺)₂O₄(H₂O)_{1.5} are commonly more reactive and stronger oxidants of Cr³⁺ than those containing exclusively Mn⁴⁺ (e.g., pyrolusite, MnO₂) (Weaver and Hochella 2003). Mn³⁺-bearing oxides are more common in soils, whereas Mn⁴⁺-bearing oxides such as pyrolusite occur predominantly in coal fly ashes and smelter waste products formed at higher *T* (Eary and Rai 1987). To better assess the alteration of chromitite in mine and smelter wastes, dissolution experiments were thus conducted with pyrolusite powder (U.S. Research Nanomaterials, average grain size 7.98 μ m)

TABLE 2. Elemental ratios in chromitite and clinocllore and elemental ratios in the solutions after the bulk dissolution experiments with 100 mg chromite powder in 25 mL solution for four weeks (with pH value)

Experiment	Cr:Al	Cr:Fe	Cr:Si	pH initial	pH end
Chromitite	4.5:1	2.1:1	18.7:1		
Clinocllore	1:3	2.2:1	1:14		
Bacteria + TK solution ^a	1:2.5	1:1492	1:3.2	2.1	2.18
TK solution ^a	1:2.5	1:1607	1:3.3	2.1	2.36
Solution A	1:2.8	1:1	1:4.5	2.5	2.35
Bacteria + Solution A	1:2.9	1:17.5	1:4.4	2.1	2.2
H ₂ O	2.3:1	2.0:1	1:14.9	7	6.7
TK solution ^a + 0.1 mol/L MnO ₂	1:8.4	1:1461	1:11.5	2.1	2.27
Solution A + 0.1 mol/L MnO ₂	1:3:1	1:1.6	1:145	2.1	4.28
0.1 mol/L MnO ₂	1:4:1	1:1.3	1:135	6.2	6.7
0.1 mol/L MnO ₂ + 0.05 mol/L CaCO ₃	5.6:1	3.7:1	1:18	8.0	7.65
0.05 mol/L CaCO ₃	3.0:1	16.3:1	1:12.6	9.2	7.81

^a Contain Fe²⁺-sulfates.

TABLE 1. Results from dissolution experiments with chromitite slabs [$0.5 \times 0.5(1) \times 0.1$ cm] in 25 mL solution for four weeks: Selected elemental ratios between major elements and proportion of secondary Cr species on the surface of the treated samples determined with XPS after the experiment

Experiment	Cr:Si	Cr:Fe	Al:Si	Fe:(P+S)	Secondary Cr species (%)	N XPS	pH _{initial} pH _{end}	Eh _{initial} Eh _{end}
Untreated	1.8:1	3.0:1	2.1:1	n.a.	0	4		
1 mL bacteria TK + 24 mL TK	1.4:1	2.0:1	1.8:1	2.4	19	2	2.3 _{initial} 2.4 _{end}	0.6 0.5
25 mL TK	1.3:1	1.9:1	1.6:1	S >> P	17	2	2.3 _{initial} 2.4 _{end}	0.6 _i 0.5
25 mL solution A	1.3:1	3.5:1	1.4:1	S >> P	15	2	2.5 _{initial} 2.6 _{end}	0.6 0.5
1 mL bacteria TK + 24 mL solution A	1.2:1	1.7:1	1.5:1	S ~ P	13	2	2.3 _{initial} 2.4 _{end}	0.6 0.5
deionized water	1.1:1	2.25:1	1.5:1	P >> S	6	2	7 6.7 _{end}	0.6 0.5
25 mL Solution A	1.25:1	2.9:1	1.6:1	n.d.	19		2.5 _{initial} 4.5 _{end}	1.1 0.7
0.1 mol/L MnO ₂								
0.1 mol/L MnO ₂	0.73:1	2.0:1	1.2:1	n.a.	21	2	6.2 _{initial} 6.0 _{end}	0.6 0.5
0.1 mol/L MnO ₂ + 0.05 mol/L ⁻¹ CaCO ₃	1.0:1	2.4:1	1.5:1	n.a.	8	2	8.0 _{initial} 6.5 _{end}	0.6 0.5
0.05 mol/L CaCO ₃	1.1:1	3.0:1	1.7:1	n.a.	14	2	9.2 _{initial} 6.3 _{end}	0.6 0.5

Note: N (XPS) = number of spectra taken from the surface; the uncertainty of the pH and Eh (mV) is ± 0.1 .

under acidic, neutral, and alkaline pH conditions (Tables 1–2). Solutions during the dissolution experiments were not protected from solar radiation as Weaver and Hochella (2003) showed that this had no effect on the oxidation of Cr^{3+} aqueous in the presence of pyrolusite.

Bacteria sensitive or resistant to Cr^{6+} can reduce the ion to Cr^{3+} under aerobic and anaerobic conditions, even if they have not been exposed to high concentrations of Cr in the past (e.g., Kamaludeen et al. 2003). At the Black Thor chromite deposit, chromitite is over- and underlain by lithologies containing minor amounts of sulfides (pyrrhotite, pyrite, and chalcopyrite; Laarman 2013). Hence, small proportions of the ore may become exposed to a sulfide-rich environment in mine tailings. As such, dissolution experiments are carried out with bacterial cultures, enriched from oxidized portions of sulfide-rich mine tailings in the Sudbury area (Ontario, Canada). The growth of these cultures was completed in TK media (Tuovinen and Kelly 1974) comprised of stock solutions A and B. Solution A contains 0.51 g/L $(\text{NH}_4)_2(\text{SO}_4)$, $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_7$, and K_2HPO_4 and is adjusted with H_2SO_4 to a pH of 2.5. Solution B contains 33.5 g/L $\text{FeSO}_4(\text{H}_2\text{O})_7$ and is adjusted with H_2SO_4 to a pH of 2.1 and mixed with solution A in a ratio of 4:1 in the final TK media. Dissolution experiments under acidic conditions but without bacteria were also carried out with the solutions A and B (using aseptic techniques) as this allowed a better evaluation of the effect of bacteria on the dissolution of chromitite under acidic conditions. Dissolution experiments simulating potential liming of chromitite-bearing mine tailings were conducted with CaCO_3 powders in the presence and absence of pyrolusite particles.

The ionic strengths and degrees of undersaturation with respect to chromite in these solutions were calculated with the software Visual MINTEQ 2.53 (Gustafsson 2012; Supplemental¹ Table A1). The change in the microbial community during dissolution of a chromitite slab was analyzed with a microbial community profile (Supplementary¹ data B1).

X-ray photoelectron spectroscopy (XPS)

The near-surface composition of treated chromitite slabs and pyrolusite powder was analyzed with a Kratos Axis Ultra X-ray photoelectron spectrometer (XPS) equipped with a magnetic-confinement charge-compensation system. The advantages of this system for insulators have been described in detail by Schindler et al. (2009a, 2009b). A total of 10 high-resolution scans were collected for the Cr 2p photoelectrons using monochromatic $\text{AlK}\alpha$ radiation (1486.6 eV) and the charge-compensation system. Additionally, two survey spectra (0–1100 eV) and three high-resolution scans were collected for the Mg 1s, C 1s, O 1s, Al 2p, Si 2p, Mn 2p, and Si 2p photoelectrons. High-resolution scans were recorded with a step size of 0.1 eV while survey spectra were collected with a step size of 0.5 eV. For all measurements, the analyzer pass energy was 20 eV and the lens and aperture were in hybrid and slot mode, respectively, which allowed the collection of photoelectrons from an area of ca. $700 \times 300 \mu\text{m}$.

The electrostatic sample charging (which was not completely compensated by the charge neutralizer) was corrected by setting the binding energy of the C 1s electrons of adventitious C species on the sample surface equal to 285 eV (Wagner et al. 1979). In some cases, the binding energy of the C 1s photoelectrons can vary with the type of substrate and thus result in false shifts when referenced to other spectra. Hence, corrections applied to the Cr 2p spectrum were also applied to the Mg 1s spectrum, which varies over a smaller range in binding energy for oxide and silicate surfaces (103–104 eV) than the Cr 2p peak (NIST X-ray Photoelectron Spectroscopy Database 2012). This procedure provided more confidence in the shift applied to Cr 2p spectra and is thus crucial in terms of the determination of potential hexavalent Cr species on treated surfaces of chromitite. A detailed summary of characteristic features in the Cr 2p spectrum and their relationship to structural components on the surface of chromite are given in Supplementary¹ data B2.

The inelastic mean-free path (IMFP) of the Cr 2p electrons is calculated to be ca. 1.3 nm, using the NIST X-ray Photoelectron Spectroscopy Database (2012), the binding energy of the Cr 2p electrons (577 eV) and an average specific weight of 4.8 g/cm³ for a chromite surface layer. Information on the chemical composition of a surface can be gained to a depth three times of the IMFP ($3 \times 1.3 = 3.9 \text{ nm}$, so-called information depth) (Hochella 1988).

Both high-resolution and survey scans were processed and quantified using the Vision 2.2.6 software package. Peak fitting of the Cr 2p, Mg 1s, and C 1s was done using multiple bands with constant full-width at half maximum values (FWHM). The FWHM values used in the fitting procedure were 1.2, 1.5, and 1.4 eV for the Cr 2p, Mg 1s, and C 1s spectra, respectively. Bands were only included in the fitting process if inflections points, shoulders, or peaks indicate the occurrence of multiplet splitting, variations in the chemical environment or changes in the valence.

At least two sets of spectra were taken from each mineral surface (Table 1),

whereby a set of spectra includes high-resolution spectra of all major elements, C 1s and a survey scan. Using the optical imaging camera of the XPS system, the two sets of spectra were taken from areas with a higher and lower proportion of clinocllore. Proportions of Mg, Al, Si, Mn, Cr, and Si are based on high-resolution scans and were calculated without considerations of the proportions of C, O, S, and P on the surface (Tables 1 and Supplemental Table A2). As experiments under acidic conditions were carried out in phosphate-bearing sulfuric acid solutions (Tables 1–2 and Supplemental Tables A1–A3), elemental ratios between Fe and (S+P) were also determined using the Fe 2p, S 2p, and P 2p peaks in the survey scans.

Table 1 lists selected elemental ratios of an untreated surface and treated surfaces analyzed with multiple sets of XPS spectra and the number of recorded sets (*N* XPS). The standard deviation of a ratio between the atomic proportions of two elements is ca. ± 0.1 and is based mainly on the uncertainty of the size of the quantification area in a spectrum. Table A2 lists the normalized atomic proportions of Cr, Mg, Si, Al, and Fe for the untreated and treated surfaces of the chromitites.

Inductively coupled plasma optical emission spectrometry

The elemental concentrations of Mg, Al, Si, Cr, and Fe in the solutions after the experiment with the chromitite powders were determined with solution-mode inductively coupled plasma optical emission spectrometry (ICP-OES) at a commercial lab (AGAT Labs, Sudbury, Ontario, Canada). Blanks, sample replicates, duplicates, and internal reference materials, both aqueous and geochemical standards are routinely used in the laboratory as part of the quality assurance. Table 2 lists atomic ratios between selected elements in solution and Supplemental Table A3 their corresponding concentrations.

X-ray fluorescence spectroscopy and determination of loss on ignition

The loss on ignition (LOI) for untreated chromitite powders was assessed prior to analysis by X-ray fluorescence. The LOI gives the proportion of volatile elements or compounds in a sample (H, H₂O, S, N) and was determined by heating the sample to 100 °C under nitrogen atmosphere, and to 1000 °C under oxygen atmosphere, until a constant wt% was reached. The sample was subsequently fused with a borate flux to produce a glass bead for characterization by X-ray fluorescence spectroscopy (XRF). A dilution factor of chromitite to borate flux of 1:24 ensured that no Cr-oxide exsolved from the glass matrix during cooling. The glass bead was subsequently analyzed with a Panalytical Axios Advanced XRF spectrometer. Supplemental Table A4 lists the average concentrations for the major elements in chromitite (on the basis of two measurements).

Scanning electron microscopy, X-ray diffraction (XRD), X-ray fluorescence spectroscopy

Scanning electron microscopy was conducted with a JEOL 6405 at 20 kV, equipped with both backscattered (BSE) and secondary electron (SE) detectors and an energy-dispersive X-ray spectrometer (EDS). Powder X-ray diffraction of an untreated chromitite samples was done with a Philips PW 1729 X-ray diffractometer using $\text{CuK}\alpha$ radiation (1.5418 Å) at a voltage and current of 40 kV and 30 mA, respectively. Spectra from powdered samples were collected over a scan range of 5–75 °2θ with a step size of 0.02 °2θ and a dwell time of 4 s. The XRD patterns are given in Supplementary¹ data A5.

Focused ion beam extraction, high-resolution transmission electron microscopy, and scanning transmission electron microscopy

A FEI Helios 600 NanoLab Focused Ion Beam (FIB) microscope, equipped with an in situ extraction probe, was used to extract two sections of the sample treated with solution A at pH 2.5 for subsequent imaging and analyses by TEM. One section was extracted from inside the chromitite sample, representing an unaltered environment, whereas the other was extracted from along the altered surface (Schindler et al. 2017). Upon extraction, samples were lifted using a platinum gas-glue and thinned to electron transparency by ion gas milling (Ga^+ ions).

Nanoscale mineralogical and chemical compositions of untreated and treated areas were characterized using a JEOL 2100 field thermionic emission analytical TEM at the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth). All measurements were taken with an accelerating voltage of 200 kV and a beam current of approximately 107 μA. EDS point analyses and maps were acquired with the instrument operating in scanning transmission electron microscopy (STEM) mode using a JEOL BF detector, and selected-area electron diffraction (SAED) patterns were acquired using a Gatan Orius SC200D detector.

RESULTS

The examined chromitite consists of the major elements Cr, Fe, Mg, Al, Si, O, and H, minor Ti and traces of Ca, Ba, K, Mn, Na, and V (Supplemental Table A4). Elemental ratios relevant to the following discussion include Cr:Si = 18.7:1, Cr:Al = 4.7:1, and Cr:Fe = 2.1:1. Chromite and clinocllore are the only two minerals with modal abundances exceeding 1% (on the basis of X-ray powder diffraction). The latter silicate is the most common mineral of the chlorite mineral group and commonly forms through the chemical alteration of pyroxenes and amphiboles. The average chemical composition of the clinocllore (on the basis of five analyses with SEM-EDS) is $\text{Mg}_3[\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot [\text{MgAl}_{1.33}(\text{OH})_6]$. Areas composed of clinocllore contain an average of 3 wt% Cr (most likely in the form of chromite nanoparticles) with Cr:Si,

Cr:Al, and Cr:Fe of 1:14, 1:3, and 2.2:1, respectively.

The chromite is Mg- and Al-rich and has the average composition $(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{Al}_{0.6}\text{Cr}_{1.4})\text{O}_4$ ($N = 5$ with SEM-EDS). On the basis of the average compositions of both minerals (SEM-EDS) and the bulk composition of the ore sample (XRF), the modal ratio between chromite and clinocllore is ca. 15:1. Chromite occurs as rounded to angular grains in thin section (Fig. 1a) and is massive in hand samples. Anhedral grains can be up to 5 mm in diameter and display a cumulate texture. Clinocllore appears colorless, anhedral, and displays third-order interference colors in thin section. The mineral occurs between individual chromite grains in areas ranging in size from lower ($\sim 1 \mu\text{m}$) to upper micrometers (400–500 μm) (Fig. 1a).

Schindler et al. (2017) showed that clinocllore in chromitite from the Black Thor chromite deposit contains chromite nanopar-

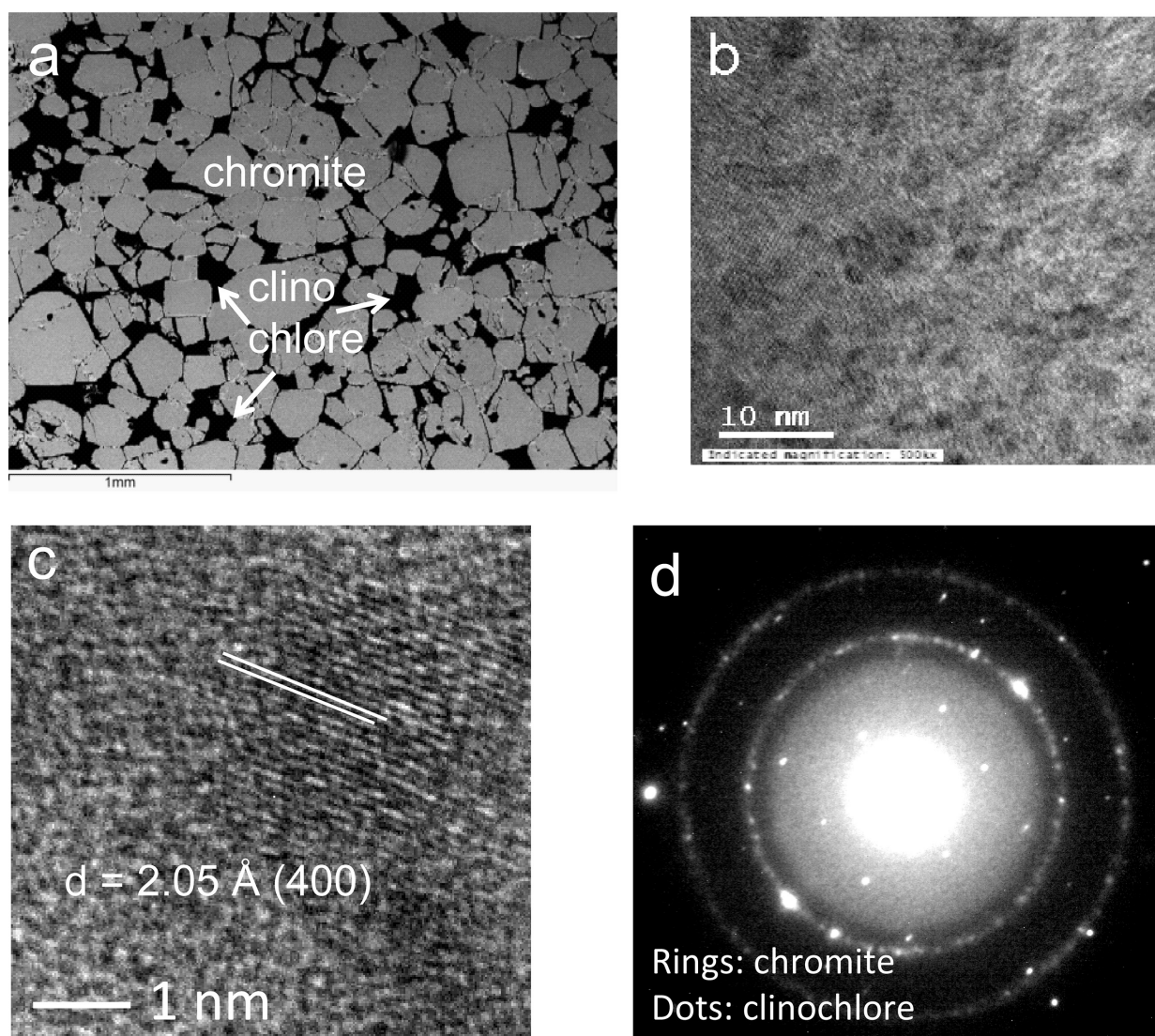


FIGURE 1. (a) SEM image of chromitite from the Black Thor chromite deposit, the occurrence of clinocllore in the interstices of chromite grains is indicated with arrows. (b) TEM image of the clinocllore matrix indicating the presence of chromite nanoparticles. (c) High-resolution TEM images of an individual chromite nanoparticle depicting lattice fringes with $d = 2.05 \text{ \AA}$ (400). (d) SAED pattern of clinocllore indicating the presence of a single crystal of clinocllore (diffraction spots) and chromite nanoparticles (diffraction rings).

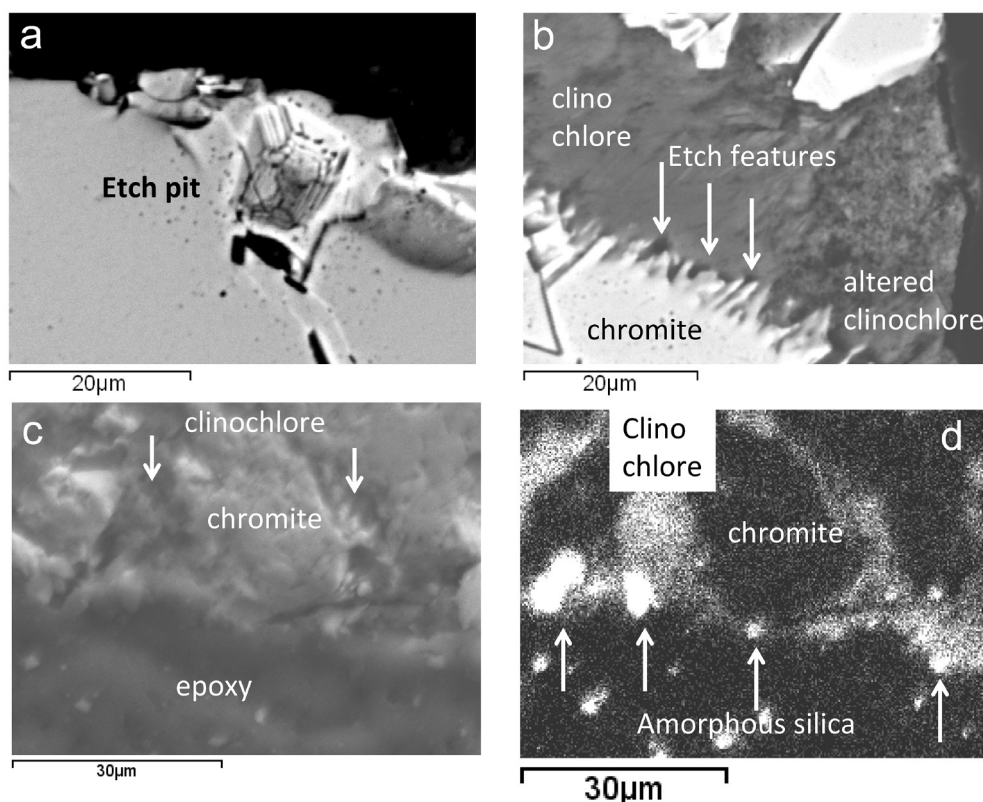


FIGURE 2. (a) SEM image in BSE mode of a nearly symmetrical etch pit on the surface of a chromite grain treated with a bacteria + TK solution of pH 2.0. (b) SEM image in BSE mode of asymmetric etch features along an edge of a chromite grain after treatment with solution A of pH 2.5. (c–d) BSE image in BSE mode and corresponding chemical distribution map for Si of a chromitite grain treated with solution A of pH 2.5; highly altered clinochlore and silica-rich patches on the chromitite surface are indicated with arrows.

ticles (Figs. 1b–1d). Similar average Cr:Fe in clinochlore [2.2:1 (SEM-EDS)] and chromite [2.3:1 (SEM-EDS)] suggest that Cr and Fe occur in clinochlore predominantly as chromite nanoparticles. On the basis of this assumption, the modal ratio between chromite and clinochlore (15:1) and the average concentration of Cr in clinochlore (3 wt%), the calculated mass ratio between the chromite nanoparticles in clinochlore and the micrometer-size grains of chromite is ca. 1:180.

The chemical composition of the untreated chromitite surface

Two XPS spectra were taken from areas with a higher and lower proportion of clinochlore on the surface of an untreated chromitite (Tables 1 and Supplemental Table A1). The Cr:Fe varies in the range of 3.0–3.2 ($N = 2$) to 2.7–3.2 ($N = 2$) in areas containing a lower and higher proportion of clinochlore, respectively. These ratios are higher than those observed by SEM for chlorite (2.2:1) and chromite (2.3:1) and with XRF for the bulk chromitite sample (2.1:1). Similarly the average Mg:Si for chromitite determined with XPS (0.7:1) is much lower than the ratio in the bulk structure (4.7:1). These observations indicate that the sensitivity factors for elements listed in the database of the Vision software package (which were determined using anhydrous minerals) are not appropriate to determine exact elemental ratios for spectra of rocks containing hydrous minerals such as clinochlore. This observation is in agreement with those by Schindler et al.

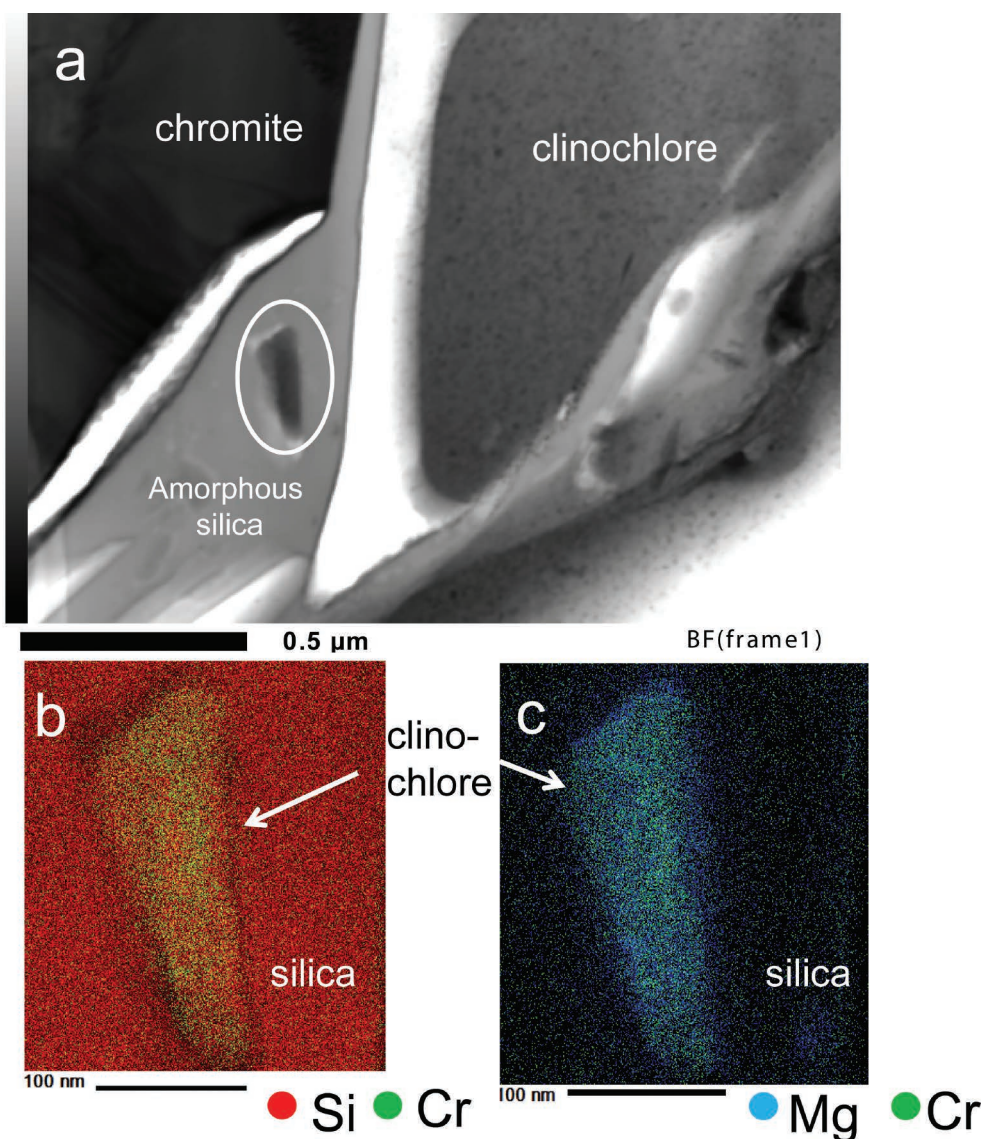
(2009), who showed that the use of the sensitivity factor for Si of 0.325 (Vision 2.2.6) for hydrated mineral samples (amorphous silica, uranyl minerals) results in larger Si: M (M = metal) and Si:O with respect to the bulk composition of the minerals. The authors showed, however, that relative changes in the elemental ratios determined for hydrous minerals with XPS can be used to monitor changes in elemental ratios as a function of surface treatment. Hence, changes in Cr:Si, Cr:Fe, and Al:Si between the various dissolution experiments are still considered in this study (Table 1) as they provide insights into chemical changes on chromitite surfaces under various conditions.

Stoichiometric and non-stoichiometric dissolution features on altered chromitite surfaces at the micrometer and nanometer scales

Non-stoichiometric dissolution commonly yields altered surfaces that differ in their chemical composition from the unaltered mineral, whereas stoichiometric dissolution results in etch features on surfaces with similar elemental ratios as an unaltered surface.

Stoichiometric dissolution features occur on the surface of chromite grains. Although rare, they occasionally occur in the form of symmetrical etch pits (Fig. 2a) and asymmetrical etch features (Fig. 2b). EDS-SEM chemical distribution maps for Si on a chromitite surface treated with solution A indicate the occurrence of non-stoichiometric dissolution features on the sur-

► **FIGURE 3.** (a) STEM image of a selected area in a FIB section extracted from a surface treated with solution A at pH 2.5. Areas composed of chromite, clinochlore, and amorphous silica are labeled accordingly; a fragment of clinochlore within the amorphous silica matrix depicted in **b** and **c** is encircled. (b–c) STEM-EDS chemical distribution maps for (b) Si (red) and Cr (green) and (c) Mg (blue) and Cr (green). (Color online.)



face of clinochlore grains (Fig. 2d). These areas are often highly altered and enriched in Si and depleted in Mg, Al, Fe, and Cr (all <1 wt%) with respect to the chemical compositions of clinochlore and chromite (Fig. 2c).

The absence of diffraction spots and rings in SAED patterns taken from the silica-rich areas indicate the occurrence of an amorphous silica modification (Schindler et al. 2017). STEM images indicate the occurrence of fragments of clinochlore in areas composed mainly of silica (Fig. 3a). Chemical distribution maps for Si, Cr, and Mg indicate a higher abundance of chromite nanoparticles (green) in the clinochlore fragments than in the surrounding silica (Figs. 3b and 3c).

Secondary Cr-species on treated chromitite surfaces

The changes in the chemical environments of Cr on the surfaces of the treated chromitite surfaces can be determined through examination of the binding energies of the various bands in the Cr 2p_{3/2} spectrum (Supplementary¹ data B2). The Cr 2p_{3/2} spectra taken from altered chromitite surfaces are shifted to higher binding energy relative to the spectra recorded from unaltered surfaces (Figs. 4a–4c). Spectra with smaller shifts in binding energy display similar multiplet splitting and peak shape (Fig. 4b), while those with larger shifts in binding energy depict more asymmetric peak shapes (Fig. 4c). Quantification of the proportions of Cr³⁺ and Cr⁶⁺ species in Cr 2p_{3/2} spectra displaying multiplet splitting is complicated by the fact that bands corresponding to anhydrous and hydrated Cr³⁺ and Cr⁶⁺ surface terminations may overlap (Supplementary¹ data B2). However,

the identification of the exact nature of the surface terminations is not a requirement for the quantification of the degree of alteration on a treated chromitite surface. As indicated in Supplementary¹ data B2, the covalency of Cr–O bonds decreases with the degree of protonation of the O atom. As such, a higher number of protonated surface terminations on the chromite surface (i.e., lower electron densities around the Cr³⁺ atoms) results in a shift of the Cr 2p_{3/2} spectrum to higher binding energies (Fig. 4c). Similarly, a higher number of Cr⁶⁺-bearing surface terminations would also result in a shift of the Cr 2p_{3/2} spectrum to higher binding energies. Hence, the degree of chromite surface alteration can be related to the abundance of either protonated surface terminations or Cr⁶⁺-bearing surface terminations (e.g., [6]Cr³⁺–OH₂ or [4]Cr⁶⁺–OH); both such configuration types are defined here as secondary Cr species, which are presumably absent on the untreated surface.

The proportion of secondary Cr species on a treated surface can be calculated from the weighted average binding energy of the Cr 2p_{3/2} spectra (i.e., the total sum of the binding energies of

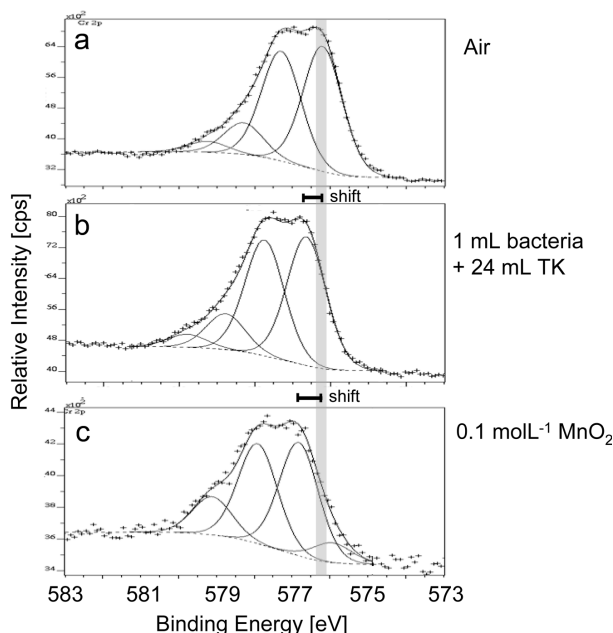


FIGURE 4. Cr 2p_{3/2} spectra for various chromitite surfaces: (a) untreated; (b) treated with a bacteria + TK solution; (c) treated with a 0.1 mol/L MnO₂ solution. A vertical gray-shaded bar indicates the location of the peak at the lowest binding energy of the spectrum for the untreated surface.

the bands multiplied by their respective proportions within the envelope), assuming a linear relationship between the proportions of secondary species on the surface and the weighted average binding energy. Using this approach, we define the weighted average binding energy of an untreated chromite surface (577.0 eV) and the average binding energy for Cr⁶⁺ components (579.4 eV) listed in the NIST X-ray Photoelectron Spectroscopy Database (2012) as the lower (0%) and upper limit (100%) of secondary Cr-components, respectively. The proportion of secondary Cr-components, and thus the degree of surface alteration, is then given by the equation:

$$\text{Secondary Cr-components [\%]} = 41 \times \frac{\text{weighted binding energy Cr 2p spectrum} - 23\,694.7}{579.4 - 577.0} \quad (1)$$

where the numbers 41 and 23 694.7 are the slope and intersection with the y-axis of the linear plot, respectively

Changes in chemical composition on the treated chromitite surfaces: Dissolution features in the absence and presence of bacteria and pyrolusite particles

Quantification of the XPS spectra indicates that treated chromitite surfaces commonly have lower Cr:Si, Al:Si, and Cr:Fe than untreated surfaces (Fig. 5a; Table 1). Surfaces treated with a TK solution, which contains Fe²⁺, P, and S, have lower Cr:Fe and higher proportions of S and P than those treated without TK solutions (Table 1). For example, the surface treated with solution A + bacteria + TK solution (pH 2.3) has the lowest observed Cr:Fe (1.7:1) and the highest proportion of S and P [Fe:(S+P) is 1.1:1 with P >> S] of all surfaces treated with acidic solutions (Table 1).

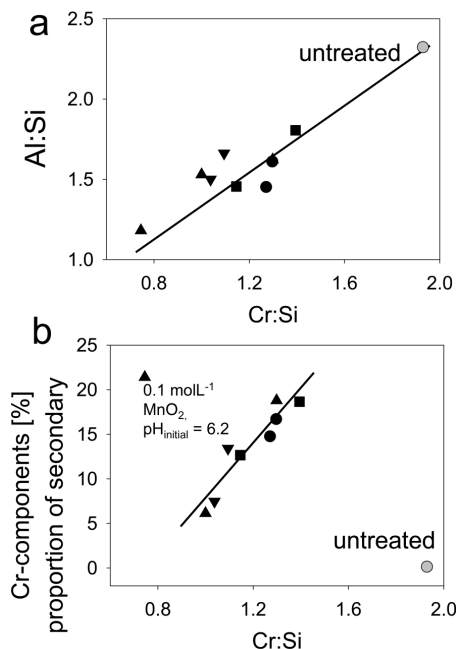


FIGURE 5. (a) plots of the Cr:Si vs. Al:Si determined with XPS for untreated (gray data point) and treated (black data points) chromitite surfaces. (b) Cr:Si vs. proportion of secondary Cr species on the surface of untreated (gray data point) and treated surfaces, data points representing surfaces treated with acidic solutions in the presence and absence of bacteria are indicated with black squares and circles, respectively; data points representing surfaces treated with near neutral and alkaline solutions are depicted with black triangles pointing up and down, respectively.

The latter surface has also the lowest proportion of secondary Cr species (13%). On the contrary, for all surfaces treated with acidic solutions (either Solution A or TK with or without bacteria), the final Cr:Si and Al:Si on chromitite are similar (Table 1) and thus, the addition of cultivated bacteria had a negligible effect on this aspect of the chromitite surface chemistry.

The correlation between Cr:Si and Al:Si indicates that: (1) surfaces treated with near-neutral and alkaline solutions are enriched in Si relative to surfaces either untreated or treated with acidic solutions, and (2) similar changes in the proportions of Cr and Al relative to Si occur between surfaces treated with near-neutral and acidic solutions (Fig. 5a). A plot of Cr:Si vs. the proportion of secondary Cr species (%) indicates that the majority of the data follows a linear trend with higher proportions of secondary Cr species occurring on surfaces with higher Cr:Si (Fig. 5b). Exceptions to this trend are the surface compositions of the untreated surface (gray data point) and the surface treated with a 0.1 mol/L MnO₂ solution of pH 6.2 (Table 1; Fig. 5b).

Proportion of Cr- and Mn-components on the surfaces of MnO₂ particles and chromitites

Optical examinations and XPS spectra recorded after dissolution experiments with MnO₂ powders show that the proportions of attached pyrolusite particles and Mn on the surfaces of the chromitite slabs are significantly higher after treatment with near-neutral (pH_{initial} 6.2) than after treatment with acidic (pH_{initial}

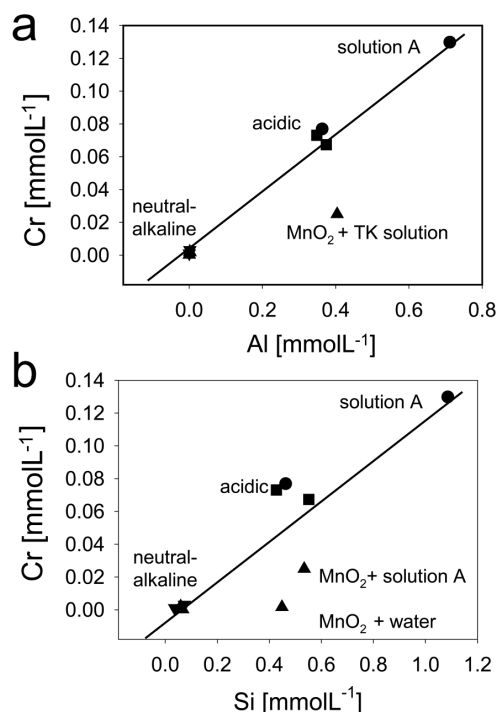


FIGURE 6. (a–d) plots with the concentrations of (a) Al vs. Cr and (b) Si vs. Cr in solutions after experiments with chromitite powders; solid lines indicates calculated linear regression curves. Symbols for data points are the same as for Figure 5.

= 2.5) or alkaline ($\text{pH}_{\text{initial}} = 8$) solutions containing 0.1 mol/L MnO_2 (Table 3). XPS studies of pyrolusite particles separated from the chromite powder indicate the presence of detectable amounts of Cr-Fe-, Si-, and Al-bearing species (or particles) on the surfaces of the pyrolusite grains. For example, concentrations of Cr on the surface of the pyrolusite particles can be up to 8.3 at% Cr, whereby the Cr:Fe on the respective surfaces (2.0:1–2.8:1) are similar to the ratio on the untreated chromitite surface (Tables 1 and 3).

Microbial community composition in dissolution treatments

The initial microbial inoculum was a known mixed community containing at least 60% Fe-oxidizing bacteria including *Acidithiobacillus ferrooxidans*, *Alicyclobacillus* sp., and acidophilic heterotrophs including *Acidiphilium* sp. The 1 mL inoculums that were added with and without TK solution B were sampled at the end of the dissolution experiment. Only the solution from 1 mL bacteria + TK full solution had sufficient biomass to extract DNA with a yield of 2.3 ng/ μL . The community profile

indicated a loss of most of the Fe-oxidizing bacteria (Supplemental Table A6) (0.1% abundance of *Alicyclobacillus* sp. remained) with the vast majority of the community represented by heterotrophic acidophiles, >98% *Acidiphilium* sp. This indicates that no Fe- or S-oxidizing chemolithotrophs were sustained through the duration of the experiment and the population likely declined after the Fe^{2+} from the TK media was consumed.

Chemical composition of the solutions after the experiments

Linear correlations are observed between the elemental concentrations of Al and Cr (Fig. 6a) and Si and Cr (Fig. 6b), with the highest concentration of Cr consistently occurring in solutions treated with the acidic solution A (Table A3). In both correlations, concentrations of Cr in solutions containing pyrolusite particles are below the observed trend. Table 2 lists the Cr:Al, Cr:Fe, and Cr:Si in chromitite and clinocllore as well as in the final solutions; however, the Cr:Fe is only meaningful for experiments in which additional Fe^{2+} was not introduced (i.e., those without TK and bacteria solutions). Closer inspection of Cr:Al, Cr:Fe, and Cr:Si in the solutions shows that dissolution of chromitite was non-stoichiometric in all dissolution experiments, with all solutions being enriched in Si relative to the Si:Cr in the bulk material (Table 2). It is also apparent that Cr:Si and Cr:Fe in solutions after experiments carried out under acidic conditions and deionized water, respectively, are similar to those observed in clinocllore.

DISCUSSION

Laarman (2013) described the abundance, morphology, and chemical composition of chlorite group minerals from the Black Label, Black Thor, and Big Daddy chromite deposits. The author argues that these minerals are the product of retrogressive, hydrothermal alteration of chromite and amphiboles and that the Mg, Al, and Cr contents of clinocllore reflect that of the primary chromite. For example, chlorites with elevated Cr_2O_3 either replace Cr-rich tremolite, occur as interstitial material in massive chromitites, or occur in fractures where Cr becomes relatively mobile with fluid influx. Laarman (2013) also reports that in minerals of the chlorite group, the Cr_2O_3 concentration ranges from 1 to 10 wt%, with minerals occurring in fractures having the highest concentrations of Cr.

The identification of chromite nanoparticles in clinocllore by Schindler et al. (2017) suggests that the high-Cr contents in many chlorites at the Black Label, Black Thor, and Big Daddy chromite deposits are the result of the presence of these nanoparticles and not as commonly assumed a result of the replacement of Al^{3+} by Cr^{3+} in the structure of minerals of the chlorite group (Lapham 1958).

In the next sections, we will address first non-stoichiometric

TABLE 3. Results of the XPS measurement after dissolution experiments with pyrolusite powders

Experiment	pH	Mn (at%) ^a on the surfaces of chromitite slabs	Cr (at%) ^a on the surfaces of MnO_2 particles	Fe (at%) ^a on the surfaces of MnO_2 particles
0.1 mol/L MnO_2	8.0 _{initial}	2.0	6.3	3.1
0.05 mol/L CaCO_3	6.5 _{end}			
0.1 mol/L MnO_2	6.2 _{initial}	22.1	6.4	2.9
	6.0 _{end}			
Solution A	2.5 _{initial}	3.6	8.3	2.9
0.1 mol/L MnO_2	4.5 _{end}			

^a Percentage relative to all other cations (O and H not included in quantification).

dissolution features observed on the surfaces of the treated chromitites, followed by discussions on the occurrence of surficial secondary Cr-species, links between the chemical compositions of surfaces and solutions and the effect of pH, pyrolusite particles, and bacteria on the degree of chromitite dissolution.

Non-stoichiometric dissolution of chromitite

Both major constituents of chromitite, chromite, and clinocllore, appear to undergo non-stoichiometric dissolution under the investigated conditions. According to Zhang et al. (2016), the non-stoichiometric dissolution of chromite, especially under strongly oxidizing conditions, results in the removal of Cr as $\text{Cr}^{6+}_{(\text{aq})}$ and in the re-precipitation of $\text{Fe}^{2+}_{(\text{aq})}$ as Fe^{3+} -hydroxides. Evidence for a similar mechanism on the chromitite surfaces treated with near-neutral and alkaline solutions is seen in lower Cr:Fe and Cr:Al values relative to the untreated surface (Table 1), which are consistent with the presence of Fe- and Al-hydroxide species precipitated or adsorbed to the chromitite surface.

Micrometer-thick silica-enriched surfaces are visible by SEM (Fig. 2d) on surfaces of clinocllore grains after treatment under acidic (but not near-neutral) pH conditions. This observation is in accord with previous observations on the formation of silica-rich surfaces on chlorite-group minerals treated with acidic solutions (Brandt et al. 2003) and on chromitite samples treated with sulfuric acid solutions at higher T (Zhao et al. 2014). As the sole possible source of Si in the studied system is clinocllore, the occurrence of the Si-rich layer indicates complete dissolution of clinocllore followed by re-precipitation of amorphous silica within an interfacial fluid film on the surface of the mineral (Hellmann et al. 2003, 2012; Putnis and Ruiz-Aguda 2013).

The solubilities of clinocllore and chromite are significantly different in aqueous solutions. Chromite is a refractory mineral and sparingly soluble at room temperature, whereas the solubility of chlorite group phases depends on solution pH and the activities of its constituent ions. In a natural environment, the latter may be largely controlled by the presence of secondary minerals such as gibbsite and kaolinite (Kittrick 1982). The absence of these minerals and their higher solubility in an acidic environment (e.g., pH 2–3) suggest that the dissolution of clinocllore has been likely controlled by the solubility of amorphous silica in the experiments under acidic pH conditions (pH = 2–3, Faure 1998). The effect of the higher solubility of clinocllore relative to chromite is consistent with the final Cr:Si ratios observed in the reacted solutions (Table 2). The mean Cr:Si in solution is 1:7.7, which is much closer to the value measured in clinocllore (1:14) than that measured in the bulk chromitite (18.7:1; Table 2).

The occurrence of a visible layer of amorphous silica at low pH indicates the formation of a higher proportion of amorphous silica on the surface of chromitites treated under acidic than near-neutral pH conditions. However, higher concentrations of Si in solution after the experiments under acidic conditions (Table 2) indicate that the re-precipitation of amorphous silica is not a complete reaction (most likely due to the high solubility of amorphous silica; Faure 1998). Hence, with increasing dissolution of clinocllore, the total amount of Cr and Fe on the chromitite surface remains relatively constant (due to the low solubility of chromite), while the total amounts of Al, Si, and Mg on the treated surfaces decrease. As the loss of Al on the surface

is somewhat mitigated by the relatively insoluble chromite, the loss of Si is greater, resulting in the observed increases in Al:Si and Cr:Si (on the surfaces of the chromitites) with decreasing pH value in solution (Fig. 5a; Table 1).

Secondary Cr species on treated chromitite surfaces of treated chromitites

Figure 5b shows an increase in the proportions of secondary Cr species with an increase in the Cr:Si on the surfaces of the treated chromitites. An exception to this trend is the chromitite surface treated with a 0.1 mol/L MnO_2 solution ($\text{pH}_{\text{initial}} = 6.2$; Table 1). This surface has the lowest Cr:Si of all treated surfaces (even lower than that treated with deionized water), but the proportion of secondary Cr species approximates that of surfaces treated with acidic solutions (Table 1; Fig. 5b).

A likely reason for this observation is the presence of a high proportion of pyrolusite particles on the surface of the chromitite after the experiment (Table 3). Particle attachment to mineral surfaces is favored where surfaces and particles have opposing electrostatic charges. The points of zero charge (PZC) for amorphous silica, clinocllore, pyrolusite, and Al-rich chromite are 4.1, 4.7, 5.9, and 7.4, respectively (Kosmulski 2009a, 2009b; Alvarez-Silva 2010; Christiano et al. 2011). Hence in a solution of pH 6.2, the surfaces of amorphous silica, and clinocllore are negatively charged, surfaces of pyrolusite are slightly negatively charged, and those of chromite are slightly positively charged and the attachment of pyrolusite particles to the surface of chromite is thus favored at pH 6.2.

The presence of pyrolusite particles on the surface of chromitite may also be related to particle agglomeration and aggregation. Agglomeration is commonly favored when the surface of the particles has a minimum charge, which is the case when either: (1) the pH is close to the PZC, or (2) when adsorbed species neutralize positive or negative surface charges (e.g., Hotze et al. 2010). The surface charges listed above indicate that attachment, agglomeration, and heteroaggregation of pyrolusite particles on the surface of chromite is favored in the solution of $\text{pH}_{\text{initial}} = 6.2$, as compared to the solutions of $\text{pH}_{\text{initial}} = 2.5$ and 8.0, in accord with the observations in this study (Table 3).

The higher abundance of pyrolusite particles on the surface of chromitite treated with a solution of $\text{pH}_{\text{initial}} = 6.2$ likely provided a higher number of adsorption sites for aqueous species such as $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})^+_2$, which are the predominant Cr^{3+} -bearing aqueous species in weakly acidic conditions (Fendorf 1995). The presence of such species on the surface of the attached pyrolusite particles may explain the observed elevated proportions of secondary Cr species on the chromitite surface treated with a 0.1 mol/L MnO_2 solution of pH 6.2 (Fig. 5b).

Chromate species such as $(\text{HCr}^{6+}\text{O}_4)^-$ and $(\text{Cr}^{6+}\text{O}_4)^{2-}$ form predominantly under alkaline pH conditions in solution but can also form through oxidation of Cr^{3+} by $\text{Mn}^{3+}/\text{Mn}^{4+}$ -bearing Mn-oxides under acidic conditions (Eary and Rai 1987; Fendorf 1995). The occurrence of adsorbed chromate species on the surface of the treated chromitite cannot be completely ruled out because Al-rich chromite and Fe-hydroxide species (or precipitates) that form during dissolution experiments with CaCO_3 -bearing solutions have net-positive surface charges under acidic to near-neutral pH-conditions, which would promote the adsorption of the

negative charged chromate species.

The observation that no Fe- and S-oxidizing bacteria were sustained during the dissolution experiments indicates that the bacteria were either: (1) not resistant to the presence of Cr^{6+} aqueous species, or (2) did not gain enough energy from the potential oxidation of released Fe^{2+} and Cr^{3+} species. This observation may explain the similarities in the proportions of secondary Cr-species after the dissolution experiments under acidic conditions in the presence and absence of bacteria (Table 1; Fig. 5b).

Linking surface composition of chromitite slabs and pyrolusite particles with the chemical composition of solutions

Comparison between the compositions of surfaces (chromitite and pyrolusite) and solution shows that the concentrations of Cr in solution are controlled by: (1) the initial release of chromite nanoparticles during clinocllore dissolution; (2) the adsorption of chromite nanoparticles (and other Cr-bearing aqueous species) to the surfaces of pyrolusite particles; and (3) the potential oxidation of Cr^{3+} to Cr^{6+} .

In addition to the formation of silica-enriched surface layers during dissolution/re-precipitation processes, the dissolution of clinocllore will likely release chromite nanoparticles to solution. This conclusion is in accord with the following four considerations and/or observations:

- (1) In a dissolution-re-precipitation process, all components (including chromite nanoparticles) are initially removed from the surface;
- (2) The highly hydrous and porous character of the hydrous silica layer easily allows the diffusion and transport of aqueous species and nanoparticles (Schindler et al. 2009c; Putnis and Ruiz-Aguda 2013; Schindler and Hochella 2017);
- (3) Chromite nanoparticles occur in lower abundance in the hydrous amorphous silica layer relative to the unaltered clinocllore grain (Figs. 3b and 3c; Schindler et al. 2017);
- (4) Elevated Cr:Si in acidic, as opposed to near-neutral and alkaline solutions likely result from: (a) a higher release rate of chromite nanoparticles, and (b) a higher degree of alteration of the surficial chromite grains (higher proportion of secondary Cr species) (Table 2; Fig. 5b).

In experiments with pyrolusite particles present, solutions are depleted in Cr, relative to Al and Si (Figs. 6a–6b) with Cr:Al and Cr:Si as low as 1:8.4 and 1:145, respectively (Table 2). This depletion in Cr and Cr:Fe of 2:1 to 3:1 on the surfaces of the pyrolusite particles suggest preferential sequestration of chromite nanoparticles over Al- and Si-bearing aqueous species by the pyrolusite particles (Table 3). Conversely, similar Cr:Al in acidic solutions and a similar Cr:Fe in deionized water as in clinocllore indicate that neither Cr, Al, nor Fe have been preferentially removed from the respective solutions though adsorption and precipitation processes.

In solutions after experiments with CaCO_3 in solution, Cr:Al and Cr:Fe are greater than those in the initial clinocllore (Table 2). This indicates an enhanced adsorption or precipitation of Al and Fe-species under alkaline pH conditions (see above). Preferential adsorption or precipitation of Al and Fe relative to

Cr occurs commonly when Cr is in the hexavalent oxidation state, as the geochemical and crystal chemical properties of Cr^{3+} are sufficiently similar to those of Al^{3+} and Fe^{3+} to not result in a significant difference in their environmental fate (Fendorf 1995). Although the XPS studies could not unequivocally identify Cr^{6+} species on the surfaces of the altered chromitites, the latter conclusion is in accord with the observed higher stability of chromate aqueous species under alkaline pH conditions (Fendorf 1995; Zhang et al. 2016).

In conclusion, chemical and mineralogical features on the surfaces of chromitite and pyrolusite particles and the compositions of the respective solutions show that the concentrations of Cr in solution are controlled by the release of chromite nanoparticles, the adsorption of chromite nanoparticles or Cr-bearing aqueous species to the surfaces of pyrolusite particles and the potential oxidation of Cr^{3+} to Cr^{6+} .

Effect of the pH, solution composition, and bacteria on the degree of chromitite dissolution

The occurrence of multiple chemical and physical processes on the surfaces of the treated chromitites makes evaluating the combined effects of solution composition, pH, and bacteria presence on the degree of dissolution of chromitite difficult. The higher concentrations of Cr and more pronounced dissolution features on the chromitite slabs after the dissolution experiments under acidic than under neutral or weak basic conditions indicate that a decrease in pH likely enhances the degree of dissolution and the release of associated chromite nanoparticles. This is supported by the observations that the formation of silica-rich alteration layers on silicate minerals is commonly favored under acidic rather than near neutral and alkaline pH conditions (e.g., Brantley 2003). Higher concentrations of Cr after dissolution experiments in solution A (sulfate-phosphate-bearing solution without Fe^{2+}) than in solution TK (Fig. 6; Supplemental¹ Table A3) suggest that the absence of Fe^{2+} -bearing aqueous species (and thus a higher degree of undersaturation with respect to chromite; Supplemental¹ Table A1) has an effect on the degree of dissolution. However, this is not apparent when considering the respective compositions of the treated slabs (where higher Cr:Si and higher proportions of secondary Cr species occur after the experiments with the TK solution than solution A, Table 1).

The role of bacteria is also unclear during these dissolution experiments as their abundances seem to be controlled primarily by the initial amount of Fe^{2+} in solution rather than by the amount of Fe^{2+} released during the dissolution of the chromite nanoparticles.

IMPLICATIONS

Evaluation of the potential fate of Cr in contaminated soils, tailings, and waste rock piles is a complex issue requiring a thorough characterization of the mechanisms in operation during the non-stoichiometric dissolution of chromitite ore. An understanding of these dissolution mechanisms is fundamental to being able to accurately predict: (1) the compositional evolution of aqueous solutions in contact with chromitite, particularly related to formation of the highly toxic chromate Cr^{6+} species; (2) the compositional, structural, and mineralogical changes occurring on the surface of the affected minerals (i.e., clinocllore

and chromite); and (3) the behavior of nanoparticles upon their release from the dissolving clinocllore phase, thereby affecting the transport, reactivity, and bioavailability of chromium.

Our data shows that the fate of Cr in the environment is affected by dissolution rates of Cr-bearing silicates and chromite, the release of chromite nanoparticles, re-precipitation of amorphous silica, and the pH-dependence adsorption (or precipitation) of Fe- and Al-bearing hydroxides and sulfates. We also show that chemical compositions of aqueous solutions in contact with chemically complex rocks such as chromitite can be only explained when considering physical, chemical, and mineralogical characteristics of each phase present in the rock. Bacterial activities and species appear to have no direct effect on the release of Cr species or on the surface composition of altered chromitites. However, their presence in tailings, mine waste piles, and soils may control pH and Eh due to their ability to either oxidize or reduce redox-sensitive ions such as S^{2-} , $(SO_4)^{2-}$, Fe^{2+} , Fe^{3+} , Mn^{2+} , and Mn^{4+} and thus control indirectly degrees of chromitite alteration and the Cr^{3+} : Cr^{6+} redox-chemistry in solution.

Chromite nanoparticles in silicate minerals are possibly widespread and the ultimate release of these nanoparticles during natural weathering or mine-related rock processing and waste disposal may, therefore, be a significant vector of chromium introduction into the environment. We show that the magnitude of such release can only be assessed by considering the dominant geochemical conditions (e.g., pH, Eh, and counter-ion chemistry) that are driving chromitite dissolution and re-precipitation and adsorption processes. The observations in this study suggest that release of chromite nanoparticles during alteration of chromitite ore fragments are favored at low pH in a sulfide-rich environment, as acidic pH conditions favor dissolution of Cr-silicates. The results of this study also suggest that released chromite nanoparticles will be effectively sequestered by larger colloids or particles in pore solutions within mine tailings settings. Neutralization of acidic pore solutions to near neutral pH conditions through the addition of lime should be then sufficient to limit the amount of chromite nanoparticles released into the environment. Further work would be required to assess the ability of chromite nanoparticles to ultimately control the abundance of $Cr^{6+}_{(aq)}$ in soils and outcrops proximal to mining activities and tailings.

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Endnote:

¹ Deposit item AM-18-26234, Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2018/Feb2018_data/Feb2018_data.html).