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Cr(VI) Formation Related to Cr(III)-Muscovite and Birnessite Interactions in Ultramafic Environments

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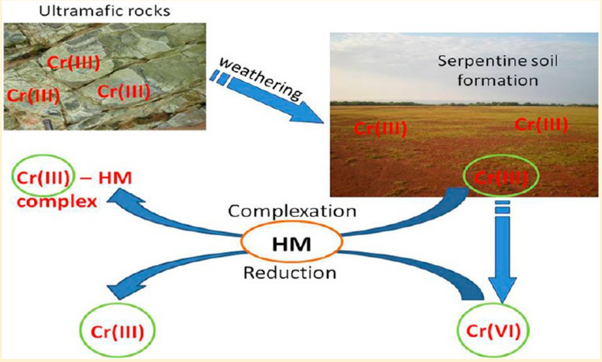
Supporting Information



ABSTRACT: Chromium is abundantly and primarily present as Cr(III) in ultramafic rocks and serpentine soils. Chromium(III) oxidation involving chromite ($FeCr_2O_4$) via interactions with birnessite has been shown to be a major pathway of Cr(VI) production in serpentine soils. Alternatively, Cr(III)-bearing silicates with less Cr(III) may provide higher Cr(VI) production rates compared to relatively insoluble chromite. Of the potential Cr(III)-bearing silicates, Cr(III)-muscovite (i.e., fuchsite) commonly occurs in metamorphosed ultramafic rocks and dissolution rates may be comparable to other common Cr(III)-bearing phyllosilicates and clays. Here, we examine the formation of Cr(VI) related to Cr(III)-muscovite and birnessite (i.e., acid birnessite) interactions with and without humic matter (HM) via batch experiments. Experimentally, the fastest rate of Cr(VI) production involving Cr(III)-muscovite was 3.8×10^{-1} μM h^{-1} (pH 3 without HM). Kinetically, Cr(III)-muscovite provides a major pathway for Cr(VI) formation and Cr(VI) production rates may exceed those involving chromite depending on pH, available mineral surface areas in solution, and the abundance of Cr(III) present. However, when HM is introduced to the system, Cr(VI) production rates decrease by as much as 80%. This highlights that HM strongly decreases but may not completely suppress the formation and mobilization of Cr(VI). A Sri Lankan serpentine soil was utilized to provide context with regards to the experimental results. Despite Cr(VI) in the soil solids and Cr(VI) formation being favorable from Cr(III)-bearing minerals, no detectable Cr(VI) was released into soil solutions potentially due to the abundance of HM. Overall, the dynamic interactions of Cr(III)-bearing silicates and birnessite provide a kinetically favorable route of Cr(VI) formation which is tempered by humic matter.

INTRODUCTION

Weathering of ultramafic rocks can produce soils and sediments with elevated levels of chromium (ranging from 1000 to 60 000 mg kg^{-1}) in which chromium is primarily present as Cr(III).[1] As shown in previous studies, these rocks, soils, and sediments are capable of producing Cr(VI) and are major sources of Cr(VI) in related waters.[1−4] For example, recorded Cr(VI) values in groundwater proximal to ultramafic rocks, sediments, and soils exceeding WHO limits for drinking water (50 μg/L) include La Spezia Province of Italy (5−73 μg/L), the Mojave desert (60 μg/L) in the USA, and the Assopos basin of Greece (2−180 μg/L).[5−8] In some cases, anthropogenic influences may amplify Cr(VI) production as reported in New Calidonia in the southwest Pacific Ocean (700 μg/L) due to the application of phosphate fertilizer. Natural oxidants such as lead dioxide, MnO_2, and H_2O_2 have been shown to oxidize soluble Cr(III) to Cr(VI).[9−13] Of these oxidants, Cr(III) oxidation from Cr(III)-bearing minerals with high oxidation state Mn oxides such as birnessite has been reported as a major geochemical pathway of Cr(VI) generation in these ultramafic-related environments.[1,14−16] In contrast, soil organic matter (OM) has been shown to readily reduce Cr(VI) to Cr(III) in these same environments.[17−19] How the rates of these two processes compete kinetically in ultramafic environments, specifically in soils commonly referred to as serpentine soils, to produce a Cr(VI) surplus is a matter for further investigation.

Chromite is commonly the primary source of Cr (as Cr(III)) in ultramafic rocks and serpentine soils, and it is considered insoluble under near-surface conditions.[1] Oze et al.[1] conducted a series of experiments on the genesis of Cr(VI) using chromite (i.e., a Cr(III)-bearing oxide/spinel) and serpentine soils in the presence of birnessite (i.e., acid birnessite). This study demonstrates that Cr(III) from chromite has the potential to be oxidized and dissolved through natural processes leading to

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hazardous levels of aqueous Cr(VI) in surface waters and groundwater. However, Cr(III)-bearing silicates in serpentine soils with less total Cr(III) may result in faster rates of Cr(VI) production due to being much more soluble compared to chromite. Of the potential Cr(III)-bearing silicates, Cr(III)-bearing muscovite (i.e., fuchsite) was chosen for this study due to its common occurrence with ultramafic rocks,[1,20] availability for experimental investigation, and "comparability" with other common Cr-bearing phyllosilicates and clays, as well as being much more soluble compared to chromite.[1,21] Here, we assess Cr(VI) release and oxidation of Cr(III) related to geochemical interactions between Cr(III)-muscovite and birnessite (i.e., synthetic acid birnessite) in subsurface aqueous environments with and without humic matter (HM). We accomplished these objectives via a series of laboratory batch experiments and compared our results with Cr(VI) generation in a Sri Lankan serpentine soil.

MATERIALS AND METHODS

Fuchsite and Birnessite. Chromium(III)-muscovite (i.e., fuchsite in quartzite) was crushed into a powder and rinsed several times in distilled, deionized water and 0.01 M HCl. The <105 μm fraction was selected for the batch experiments. From this point forward, Cr(III)-muscovite will be referred to as fuchsite. Birnessite was synthesized using the procedure described by Buser et al.[22] and implemented by Fendorf and Zasoski.[11] The specific surface area of fuchsite and birnessite was determined utilizing N_2(g) and the Brunauer−Emmett−Teller (BET) isotherm method. The mineralogy of both fuchsite and synthetic birnessite were confirmed by using an X-ray diffraction (XRD, Shimadzu XD-D1) diffractometer using Cu Kα radiation (λ = 1.54 A°). X-ray fluorescence (XRF) spectrometry (Shimadzu, XRF 1700) was used to determine the Cr concentration in this sample of fuchsite. Additionally, each mineral was examined with scanning electron microscopy (SEM, HITACHI S-4800 FE-SEM). Voltage, magnification, and area % for each sample are displayed in the data bar of each image.

Batch Experiments Involving Fuchsite and Birnessite. A series of batch experiments at 25 °C were conducted in triplicate using a range of fuchsite and birnessite suspension densities (i.e., mineral surface area per volume of solution) to study the formation of Cr(VI) from fuchsite in the presence of birnessite. Each vial (500 mL polypropylene bottles) contained different loadings of birnessite and fuchsite to produce four suspension densities (Table 2). When applicable, pH was adjusted manually with dilute NaOH or HCl. The target pHs were 3, 5, 6, and 8. In order to evaluate rates related to fuchsite−birnessite interactions, Cr(VI) formation was measured under three different conditions.

(1) Variable birnessite suspension densities and constant fuchsite suspension densities were evaluated at pH 5 (Figure 2a).
(2) Variable fuchsite suspension densities and constant birnessite suspension densities were evaluated at pH 5 (Figure 2b).
(3) Variable pH values (3, 5, 6, 8) and constant fuchsite and birnessite suspension densities (Figure 2c) were evaluated.

The effect of humic matter (HM) on the formation of Cr(VI) in this system was also examined by measuring the time dependent concentration of Cr(VI) in batch reaction vessels after introducing the different HM loadings (5, 50, 100 mg L^{-1}). Humic acid sodium salt from Sigma Aldrich, USA, was used for this experiment. The pH values of the samples were constant (±0.2) with respect to time. At the end of each time period, a 10 mL sample was removed using a syringe and filtered using a 0.2 μm filter into a clean vial from a 500 mL bottle. Eight samples were obtained in shorter sampling intervals in the beginning (10, 20, 30, 60, and 75 min) and then at longer sampling intervals thereafter (75, 180, and 380 min). The production of Cr(VI) was measured spectrophotometrically at 540 nm using the diphenylcarbazide method modified from James and Bartlett[23] (UV−visible spectrophotometer, Model, UV-160 A, Shimadzu).

Chemical Analysis of Sri Lankan Serpentine Soils. Serpentine soil was obtained from Ussangoda, Ambalantota (latitude 6°05′54″ N and longitude 80°59′11″ E), located in Southern Sri Lanka. The same soil which has been used in the study of Rajapaksha et al [4] was used in this study. Hence, the physiochemical properties for serpentine soil in Rajapaksha et al.[4] is applicable to this study. Soil is from the surface from 0 to 15 cm below the surface. Altogether, 10 samples were obtained from the study area. All samples were obtained from similar topographic places to have a representative sample. Additionally, a composite sample was prepared by mixing the 10 samples and 5 replicates were carried out for each analysis. According to the XRD data, antigorite ($(Mg,Fe)_3Si_2O_5(OH)_4$) is the dominant mineral present with minor amounts of chrysotile ($Mg_3(Si_2O_5)(OH)_4$), magnetite (Fe_3O_4), spinels, and clays.[4] Sequential extraction procedures were carried out according to the methods used by Tessier et al.[24] and Armienta et al.[25] These methods have been widely used for metal fractionation studies. Six different fractions were considered: exchangeable (1 M $MgCl_2$ at pH 7), bound to carbonates (1 M CH_3COONa at pH 5 with CH_3COOH), bound to amorphous oxyhydroxides (0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) CH_3COOH, 90 °C), bound to organic matter (0.02 M HNO_3, 30% H_2O_2 at pH 2, 3.2 M NH_4OAc in 20% (v/v) HNO_3), and bound to the mineral matrix (also called the "residual fraction", digestion with a mixture of HF, HNO_3, and $HClO_4$). Between each successive extraction, separation was effected by centrifuging 2500 rpm for 15 min. The supernatant liquid was filtered through a 0.45 μm Millipore cellulose acetate membrane filter and analyzed for Cr using atomic absorption spectrometry (AAS; Model GBC 933 AA, Australia).

The soil oxidation capacity was investigated using acidified hydroxylamine hydrochloride solution. If the only mechanism for Cr(III) oxidation in soils is via manganese oxide interactions, then using extraction methods specifically designed for this purpose may provide an operational definition for evaluating the oxidation capacity of the soils. This test specially targets the phase that promotes the oxidation of Cr(III).[26] A 0.50 g of soil was added to a 25 mL $NH_2OH \cdot HCl$ solution, shaken for 30 min, and filtered using a 0.2 μm filter. Then, samples were analyzed for Mn via AAS. The moles of Cr(III) that can be oxidized were calculated by dividing the number of moles of Mn^{2+} per gram of soil obtained in the extraction by 1.5.[27]

A modified alkaline digestion method was used to extract Cr(VI) from each soil sample (USEPA Method 3060A).[23,28] The extractant was prepared by using 0.28 M Na_2CO_3 and 0.5 M NaOH (pH ∼12), and 50 mL of that extraction was added to the soil samples. To suppress any method induced oxidation of Cr(III) to Cr(VI), ∼400 mg of $MgCl_2$ and 0.5 mL of 1.0 M

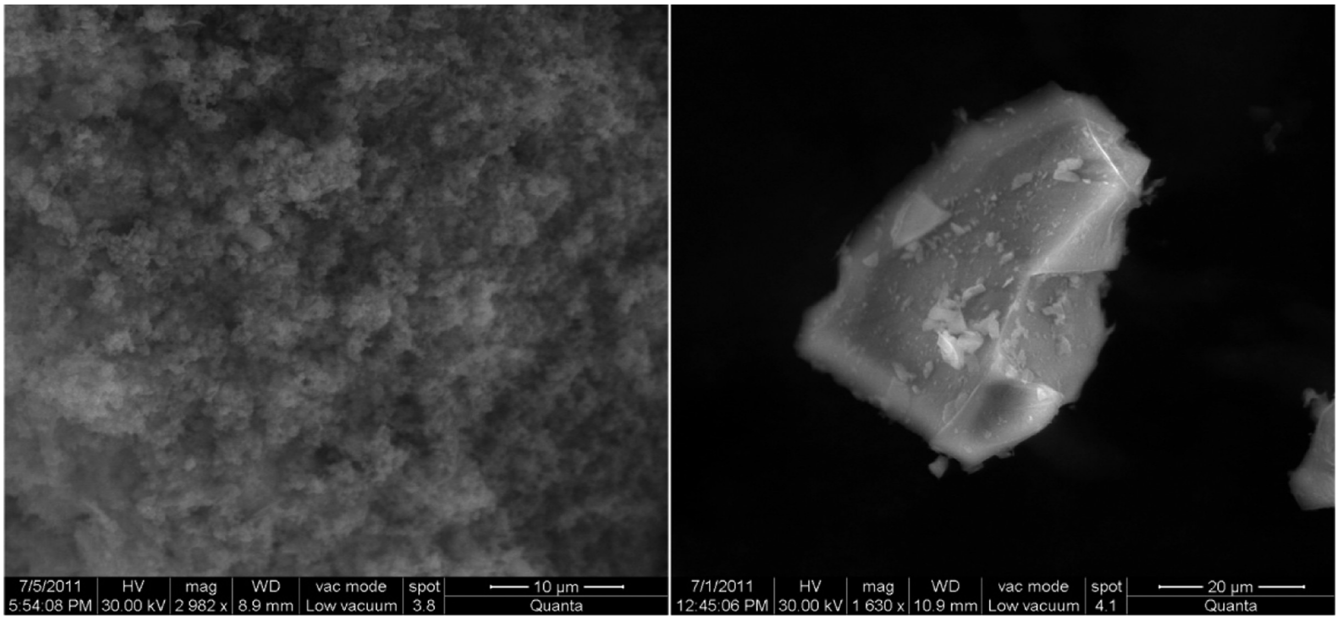

Figure 1. Scanning electron microscopy (SEM) images of birnessite and fuchsite prior to the batch experiments.

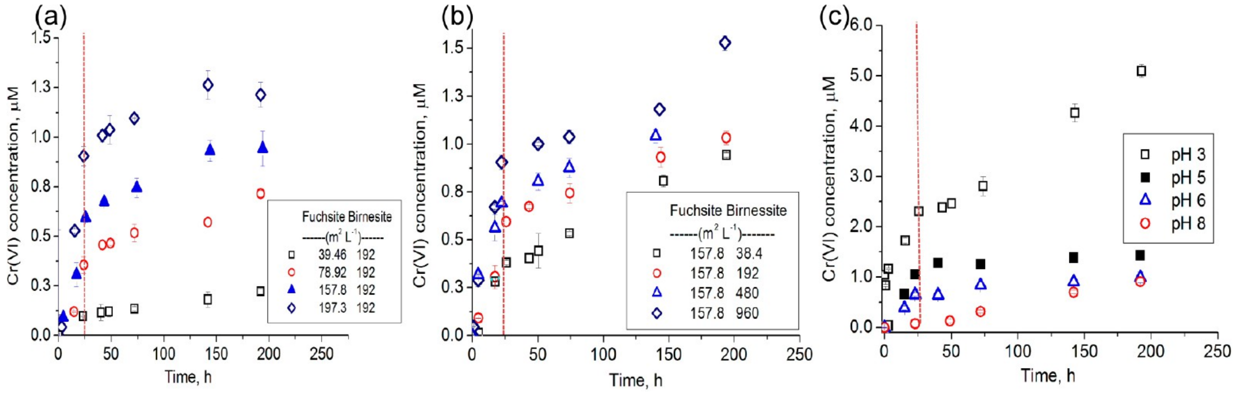

Figure 2. Batch experiments evaluating (a) variable fuchsite suspension densities at pH 5, (b) variable fuchsite birnessite suspension densities at pH 5, and (c) variable pH with constant fuchsite and birnessite suspension densities. Fuchsite and birnessite suspension densities are listed in the key. The red dashed line indicates the 25th hour of the reaction period. Error bars represent the standard deviation of three replicates.

Table 1. Summary of Cr(VI) Formation Rates Obtained from Fuchsite and Birnessite Batch Experimental Details[a]

label	fuchsite (g L^{-1})	birnessite (g L^{-1})	pH	fuchsite suspension density (m^2 L^{-1})	birnessite suspension density (m^2 L^{-1})	rate 1 (μM h^{-1}) (d[Cr(VI)/dt])	rate 2 (μM h^{-1}) (d[Cr(VI)/dt])	equation
(a)	8	0.8	5	157.8	38.4	9.28×10^{-3}	1.58×10^{-3}	3
(b)	8	4	5	157.8	192	2.30×10^{-2}	2.61×10^{-3}	
(c)	8	10	5	157.8	480	3.20×10^{-2}	2.98×10^{-3}	
(d)	8	20	5	157.8	960	4.04×10^{-2}	3.65×10^{-3}	
(e)	2	4	5	39.46	192	2.89×10^{-3}	6.94×10^{-4}	4
(f)	4	4	5	78.92	192	9.41×10^{-3}	1.76×10^{-3}	
(g)	8	4	5	157.8	192	2.30×10^{-2}	2.61×10^{-3}	
(h)	10	4	5	197.3	192	3.75×10^{-2}	2.84×10^{-3}	
(i)	8	4	3	157.8	192	3.77×10^{-1}	2.07×10^{-2}	5
(j)	8	4	5	157.8	192	2.30×10^{-2}	2.23×10^{-3}	
(k)	8	4	6	157.8	192	1.61×10^{-2}	2.27×10^{-3}	
(l)	8	4	8	157.8	192	4.72×10^{-3}	1.42×10^{-3}	

[a] Surface area of fuchsite and birnessite is 19.73 and 48.1 m^2 g^{-1}.

phosphate buffer (0.5 M K_2HPO_4 and 0.5 M KH_2PO_4) were added and the mixture was then stirred unheated for 5 min before heating to 90–95 °C for 1 h, with stirring every 15 min.[29] After cooling, the solution was filtered through a 0.2 μM

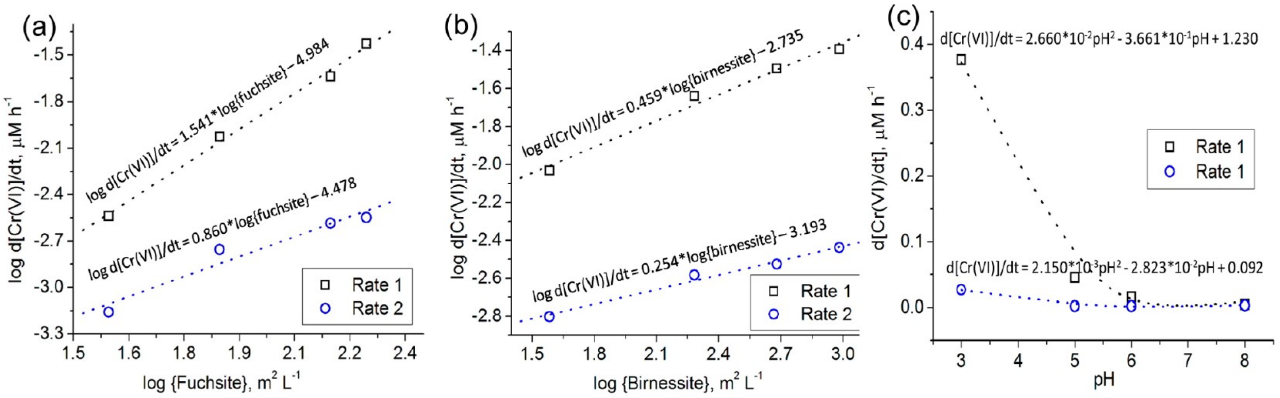

Figure 3. Rates of Cr(VI) as a function of (a) fuchsite, (b) birnessite, and (c) pH. The line in each diagram represents the best fit for data points according to eqs 3−5.

filter Millipore cellulose acetate membrane filter. Then, the solutions were diluted to 100 mL using deionized water, and the amount of Cr(VI) was measured using the diphenylcarbazide (DPC) colorimetric procedure.[29,30]

RESULTS AND DISCUSSION

Fuchsite−Birnessite Batch Experiments. The mineralogy and properties of the fuchsite and synthetic acid birnessite are based on a wide variety of analyses. The XRD diffraction pattern for fuchsite is identical to muscovite (Figure S1, Supporting Information). In the XRD pattern for birnessite, four major broad peaks are present; the most intense peak was at 0.73 nm with weaker signals at 0.36, 0.24, and 0.14 nm (Figure S2, Supporting Information). These values are in good agreement with *d*-spacing for synthetic birnessite reported in the literature.[11,31] On the basis of XRF analysis, fuchsite utilized for the experiments contains 0.25 wt % Cr_2O_3. Surface areas of the fuchsite and birnessite determined via the BET method are 19.7 and 48.1 m^2 g^{-1}, respectively. Scanning electron microscopy images of birnessite and fuchsite are shown in Figure 1. At the microscopic scale, birnessite has a clustered, framboidal morphology similar to birnessite used by Oze et al.[1] and fuchsite demonstrated clear smooth surfaces and a platy appearance typical of muscovite (Figure 1).

The interaction of fuchsite and birnessite leading to the release and oxidation of Cr(III) is a relatively slow process requiring study on the order of hours and days. Rates of Cr(VI) formation increased with increasing fuchsite suspension density (Figure 2a, Table 1), ranging from 2.89×10^{-3} to 3.74×10^{-2} $\mu M\ h^{-1}$ at pH 5 within the first 25 h, and then, the rates decreased to a range of 6.94×10^{-4} to 2.84×10^{-3} $\mu M\ h^{-1}$. Experiments conducted at fixed pH values and with different birnessite loadings show that the higher suspension densities increased the rates of Cr(VI) production (Figure 2b). In Figure 2c, the influence of pH was evaluated by conducting experiments at pH values fixed at 3, 5, 6, and 8. For these experiments, fuchsite and birnessite suspension densities were held constant at 157.8 and 192 $m^2\ L^{-1}$, respectively (Table 1).

Two contrasting rates are observed for Cr(VI) formation, and the rates were inversely proportional to each pH value of the experiment. Within the first 25 h, Cr(VI) rates increase with decreasing pH while at pH 3 the Cr(VI) production rate is 4.72 $\times 10^{-1}$ $\mu M\ h^{-1}$ at pH 3 and at pH 8 the rate is 3.77×10^{-1} μM h^{-1}. However, the rate of Cr(VI) formation decreases after 25 h (1.42×10^{-3} $\mu M\ h^{-1}$ at pH 8 to 2.07×10^{-2} $\mu M\ h^{-1}$ at pH 3) (Table 1). We interpret the two rates to represent when Cr(VI) is allowed to optimally occur (i.e., fastest rate) and when secondary reactions and surface precipitates/complexes interfere with fuchsite−birnessite interactions (i.e., the slowest rate). However, the reactions will be slower in the field due to much less mixing of Cr and Mn reactants, and the very low solubility of Cr(III) in the minerals may result in solubility-controlled processes. Once the Cr(III) is released and diffuses as a hexaquo or hydrolyzed cation, then the reaction with Mn oxide surfaces may be fast. In addition, surface-induced precipitation reactions of Cr(III) as Cr(OH) will compete with those of oxidation, thereby controlling the observed rates of Cr(VI) formation. Besides these reactions, HM in the natural environment may also act as a controller, either by precipitating Cr(III) or reducing Cr(VI) into Cr(III). Groundwater flow rates and mixing in preferential paths may also effect the solubility, so that these rates may be much lower in the natural system.

Developing an overall rate expression for Cr(VI) production in solution requires integrating the factors assessed in Figure 3. The reaction rates are regressed against reactant concentrations to determine the rate dependence on fuchsite and birnessite suspension density and on pH (Figure 3). As fuchsite and birnessite suspension densities increase, the rate of Cr(VI) formation in the solution increases. A pseudo first-order rate dependence is observed on the basis of both fuchsite and birnessite suspension density; the equations regressed for these relationships are shown in Figure 3. The influence of pH on the rate of Cr(VI) production is well-described by a polynomial function (Figure 3). All the Cr measured in solution is in the form of Cr(VI); therefore, the rate law for Cr(VI) in solution can be written as:

$$d[\mathrm{Cr(VI)}]/dt = k\{\mathrm{fuchsite}\}^a\{\mathrm{birnessite}\}^b(a_{\mathrm{H}^+})^c \qquad (1)$$

where k is the overall rate constant (units are dependent on pH integration) for Cr release and oxidation, {fuchsite} is the fuchsite suspension density in $m^2\ L^{-1}$ (Table 1), {birnessite} is the birnessite suspension density in $m^2\ L^{-1}$ (Table 1), and a_{H+} is the activity of H^+. Constants a, b, and c are the order of dependency for each reactant. A general logarithmic rate equation may be derived from eq 1 as

$$\log d[\mathrm{Cr(VI)}]/dt = \log k + a^*\log\{\mathrm{fuchsite}\} + b^*\log\{\mathrm{birnessite}\} + c^*\log(a_{H^+}) \qquad (2)$$

On the basis of this rate equation, rate expressions for (1) variable fuchsite and constant birnessite suspension densities, pH 5 (eq 3; Figure 3a; Table 1), (2) variable birnessite and constant fuchsite suspension densities, pH 5 (eq 4; Figure 3b; Table 1), and (3) variable pH, constant fuchsite and birnessite suspension densities (eq 5, Figure 3c; Table 1) may be expressed as

$$\log \mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = \log k' + a{*}\log\{\mathrm{fuchsite}\} \tag{3}$$

$$\log \mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = \log k'' + b{*}\log\{\mathrm{birnessite}\} \tag{4}$$

$$\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = k'''{*}(a_{\mathrm{H}^+})^c \tag{5}$$

where k', k'', and k''' are dependent on their respective suspension densities and pH. In order to develop rate equations, with reference to other reported literature, we selected a constant pH value (pH 5). Reaction rates were analyzed according to eqs 3, 4, and 5, and constants a, b, and c were obtained; these rates are shown in Figure 3. The overall rate equation (<25 h) can be expressed as,

$$\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = k\{\mathrm{fuchsite}\}^{1.54}{*}\{\mathrm{birnessite}\}^{0.46} \tag{6}$$

where k is $9.757 \times 10^{-5}\ \mathrm{pH}^2 - 1.343 \times 10^{-5}\ \mathrm{pH} + 4.519 \times 10^{-5}\ \mu\mathrm{M\ L\ m^{-2}\ h^{-1}}$. This expression is valid for the first 25 h of reaction time (Rate 1 or the fastest Cr(VI) production rates). Similarly, for the rest of the reaction (>25 h, Rate 2 representative of the slowest Cr(VI) production rates), the rate equation can be expressed as,

$$\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = k\{\mathrm{fuchsite}\}^{0.86}{*}\{\mathrm{birnessite}\}^{0.25} \tag{7}$$

where k is $7.316 \times 10^{-5}\ \mathrm{pH}^2 - 9.607 \times 10^{-5}\ \mathrm{pH} + 3.126 \times 10^{-4}\ \mu\mathrm{M\ L\ m^{-2}\ h^{-1}}$.

These experiments reveal that the rates of Cr(VI) formation are dependent on the suspension densities of fuchsite and birnessite and on pH. This is in contrast to experiments by Oze et al.[1] where Cr(VI) production rates were independent of birnessite suspension density. Additionally, Cr(VI) formation rates at pH 5 (0.5 to 4.1 nM $\mathrm{h^{-1}}$) reported by Oze et al.[1] via chromite–birnessite interactions are comparable with our rates ranging from 0.6 to 40 nM $\mathrm{h^{-1}}$. It should be noted that fuchsite utilized in our experiments has much less Cr compared to chromite; however, fuchsite suspension densities (39–197 $\mathrm{m^2\ L^{-1}}$) are much greater than chromite suspension densities (0.01–0.2 $\mathrm{m^2\ L^{-1}}$) used by Oze et al.[1] Overall, these experiments confirm that Cr(III)-silicates are capable of fast Cr(VI) production rates that may lead to hazardous levels of aqueous Cr(VI) in surface and groundwater. It should be noted that these rates represent an upper limit due to the vigorous mixing and continual solution interactions inherent of batch equilibrium experiments. In the environment, reaction rates will be lower as they are controlled by mineral solubility and fluid availability.

The effect of HM on the formation of Cr(VI) in this system is assessed by measuring the time dependent concentration of Cr(VI) after introducing the different HM loadings (Figure 4). Chromium(VI) formation is observed to decrease with increasing humic matter concentration (Figure 4). This may be due to two reasons: (1) complexation of dissolved Cr(III) ions in the solution and/or (2) reduction of Cr(VI) into Cr(III) by HM. More importantly, HM was able to remove up to ~80% of the Cr(VI) produced, thus providing evidence that HM in the environment is a key factor modulating the production of Cr(VI). This provides a plausible explanation why Cr(VI) in ultramafic environments is not as high as would be inferred from these and other experiments.[1]

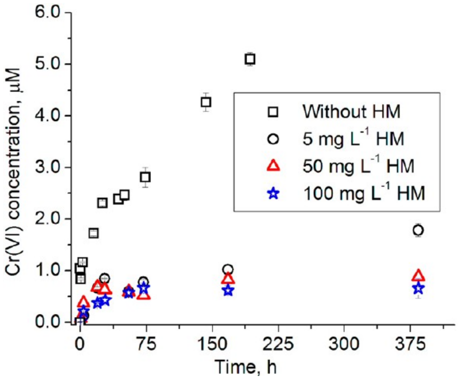

Figure 4. Effects of humic matter (HM) loadings, fuchsite, and birnessite densities were constant (157.8 and 192 $\mathrm{m^2\ L^{-1}}$, respectively), and pH was maintained at ~3.5. Error bars represent the standard deviation of three replicates.

Chromium Geochemistry of a Serpentine Soil from Sri Lanka. Chromium is abundantly present in Ussangoda serpentine soils in Sri Lanka (~10 000 mg $\mathrm{kg^{-1}}$), and this soil was chosen to provide context with regards to our experimental observations.[4] Elemental mapping via EPMA of the serpentine soil shows the distribution of Cr, Ni, and Mn (Figure 5). The oxidation capacity of the serpentine soil was calculated as 4.865×10^{-6} mol $\mathrm{g^{-1}}$, and it indirectly indicates that a similar amount of Cr(III) moles can be oxidized by the soil.[26] However, this capacity is probably based on the ideal conditions for the reaction of Mn and Cr. Table 3 lists the total Cr and Cr(VI) concentrations in the serpentine soil. Different extraction methods have been used to measure Cr(VI) amount in the soil due to some limitations of the ordinary methods such as humic matter interference. Chromium(VI) species are not strongly sorbed to many soils under alkaline to slightly acidic conditions, and therefore, they can be mobile in the environment compared to Cr(III).[32] In contrast, under alkaline to slightly acidic conditions, Cr(III) readily precipitates as an amorphous $\mathrm{Cr(OH)_3}$ or as the solid solution $\mathrm{Fe}_x\mathrm{Cr}_{1\text{-}x}\mathrm{(OH)_3}$.[33,34]

During alkaline digestion[23,30,35] which is used to extract Cr(VI) from soil, the dissolution of humic matter (HM) may occur and it can interfere in the determination of Cr(VI) by the diphenylcarbazide (DPC) method. Humic matter is responsible for both positive and negative interference in the analysis of Cr(VI) during the extraction by the DPC method.[36] Humic substances absorb light at 540 nm as the Cr-DPC product and are able to rapidly reduce Cr(VI) under the pH conditions of the standard DPC method. Therefore, different methods which avoid HM interference were used to measure the Cr(VI) amount in the soil, and these results are presented in Table 3. Wittbrodt and Palmer[32] have investigated the rates of the reaction of Cr(VI) with humic acids and found that they were strongly dependent on pH.

Some researchers have introduced new methods to avoid this interference including removal of HM by sorbents and initial ashing of HM before the analysis (Table 2). Broadway et al.[29] have modified Cr(VI) extraction method involving initial dry-ashing of sample aliquots to remove organic matter because of the solubilization which had been found to rapidly reduce extracted Cr(VI) to Cr(III) under the acidic conditions of the subsequent colorimetric determination method.[36]

According to the XRF results, the Ussangoda serpentine soil showed Cr and Mn as 11 031 and 1137 mg $\mathrm{kg^{-1}}$, respectively.

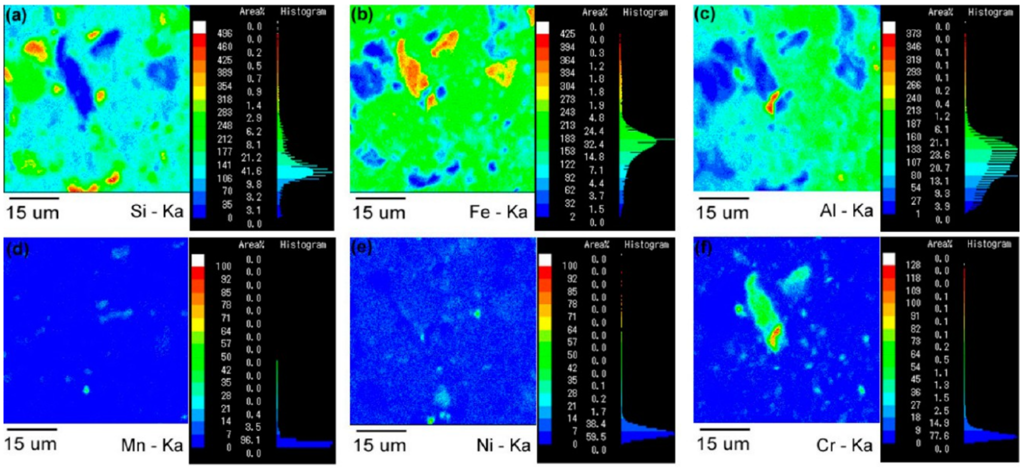

Figure 5. EPMA analysis of serpentine soil in Sri Lanka. Signal amplitudes are given in the scale.

Table 2. Concentration of Total Cr and Cr(VI) Determined in Ussangoda Soil by Various Chemical Methods

method	soil Cr (mg kg^{-1})	reference	remarks
	Total Chromium Content		
acid digestion (total Cr)	11031.00	42	
	Cr(VI) Amount of the Soil Sample		
alkaline digestion (0.28 M Na_2CO_3+ 0.5 M NaOH)	28.60	23,30,35	dissolution of Fe(III) and humic matter
alkaline digestion + XAD 7 resin treatment	202.12	36	XAD 7 was used to remove the humic matter interference
dry ashing (450 °C + alkaline digestion)	374.27	29	dry-ashing was used to remove organic matter

Table 3. Sequential Extractions Results[a]

extractants: sequential extractions	fractions	Cr concentration, mg kg^{-1} (dry weight)	Cr distribution, %
(i) 1 M $MgCl_2$ (pH 7.0)	exchangeable	0.7(0.2)	<0.1
(ii) 1 M NaOAc (pH 5.0)	carbonates	0.4 (0.3)	<0.1
(iii) 0.04 M NH_2OH−HCl in 25% (v/v) HOAc (90 °C)	amorphous oxyhydroxides	90.6 (1.8)	0.4
(iv) 0.02 M HNO_3, 30% H_2O_2 (85 °C), 3.2 M NH_4OAc	organic matter	508.5 (1.9)	4.6
(v) HF, $HClO_4$, HCl	residual/silicate	8568 (14.5)	83.1

[a] Note: Values reported are averages for 3 determinations, and the value in parentheses is the standard deviation (SD).

Manganese is released from serpentine soil into distilled water (~6 mg kg^{-1});[4] however, Cr(III) or Cr(VI) was not observable (<0.1 mg kg^{-1}) in considerable amounts for a duration of 20 days. Chromium(III) in soil appears to not be converted to Cr(VI) even though the soil pH and the presence of MnO_2 favor the Cr oxidation. This could be due to unavailability of dissolved Cr(III).[37] Immobilization of Cr(III) in soil may also occur due to complexation with organic molecules that are adsorbed to surfaces.[38]

Chromium concentrations of each chemical extraction step are shown in Table 3. A sequential extraction technique is useful for the general assessment of metal partitioning, despite the many criticisms of this technique. More discussion about the use and the caveats of sequential extractions is presented by Gleyzes et al.[39] Results are also expressed in terms of the percent (%) extracted from the total value. Chromium predominates in the residual fraction (8567 mg kg^{-1}, 83%) and is also bound in organic matter (508 mg kg^{-1}, 4.6% respectively). These results support that the Cr-spinels (chromite), and Cr(III)-bearing silicates are the major sources of chromium. A substantial proportion of Cr is linked with organic matter, and this high proportion is in good agreement with the high affinity of Cr for organic matter.[4,40] The order of the individual geochemical fractions where Cr is bound from greatest to least is: residual > organic matter bound > Fe and Mn bound > exchangeable > carbonate bound. These chemical extractions indicate that most Cr is bound in the structure of primary minerals. Although the soil contains high chromium concentration, Cr(VI) formation was low, even in the presence of manganese oxides and favorable pH conditions, supporting that soils rich in organic matter have a high reductive capacity for the reduction of soluble Cr(VI).

Environmental Implications. Chromium(III)-bearing minerals whether fuchsite or chromite provide a major pathway related to the production of naturally occurring Cr(VI) in surface and groundwater. As there are a variety of Cr(III)-bearing silicates (i.e., chlorite, epidote, garnet, and clays) more soluble than chromite, these minerals are all potential sources of Cr(VI) coupled to their available surface area and the presence/abundance of birnessite. For example, clays in serpentine soils are enriched with Cr (~1010 Cr mg kg^{-1})[41] and would be expected to be more reactive due to possessing higher surface areas. Another consideration is that these clays can be physically mobilized by the wind and distally deposited from its ultramafic source. This means that the “effect” of the ultramafic body and the potential production of Cr(VI) can theoretically extend beyond the ultramafic source/deposit. Despite the favorable formation of Cr(VI), HM has been shown to moderate the fast kinetics of Cr(VI) formation potentially due to Cr(III)-HM complexation. Fundamentally, the presence of HM significantly decreases Cr(VI) production, supported by observations made on serpentine soils in Sri Lanka. Overall, ultramafic environments and serpentine soils are potential sources of Cr(VI) to soils and groundwater capable of being moderated by the abundance and availability of HM.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing X-ray diffraction (XRD) pattern of fuchsite (Figure S1) and X-ray diffraction (XRD) pattern of synthesized birnessite (Figure S2). This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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