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Viviana Bolaños-Benítez, Eric van Hullebusch, Jean-Louis Birck, Jérémie Garnier, Piet N.L. Lens, et al.. Chromium mobility in ultramafic areas affected by mining activities in Barro Alto massif, Brazil: An isotopic study. *Chemical Geology*, 2021, 561, pp.120000. 10.1016/j.chemgeo.2020.120000 . insu-03402275

HAL Id: insu-03402275

<https://insu.hal.science/insu-03402275>

Submitted on 2 Jan 2023

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Chromium mobility in ultramafic areas affected by mining activities in Barro Alto massif, Brazil: An isotopic study

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Abstract

This work studies the potential release of Cr from solids to surface water and groundwater, and the related isotopic compositions, in a nickel laterite ore deposit from Barro Alto in Brazil (in the State of Goiás). This ultramafic system is characterized by elevated concentrations of chromium (Cr). Even largely immobile Cr may be naturally leached from weathering profiles such as laterite to the surface and groundwater. This system is exploited for metal production, and both mining and metallurgical activities result in a significant increase in the trivalent (Cr(III)) and hexavalent chromium (Cr(VI)) concentrations released into the environment via runoff. Among all the samples collected, ores contained higher amounts of chemically and isotopically exchangeable Cr(VI) ($E_{Cr(VI)}$) with values as high as $104 (\pm 8) \text{ mg kg}^{-1}$. $\delta^{53}\text{Cr}$ increased from $-0.28 (\pm 0.01)\text{‰}$ to $-0.05 (\pm 0.01)\text{‰}$ and the $E_{Cr(VI)}$ value was up to 30 times higher in deep soils than at the surface (up to $7 (\pm 1) \text{ mg kg}^{-1}$). Chemically extracted Cr(VI) ($E_{Cr(VI)}\text{-KH}_2\text{PO}_4$) displayed positive $\delta^{53}\text{Cr}$ value ($1.69 (\pm 0.03)\text{‰}$) with a similar Cr isotopic composition as the ones measured in freshwater sampled in and around the mine area. It appears that Cr is primarily released as Cr(VI), i.e. the toxic species, and becomes increasingly more available as it moves from the soil profile to the ores and mining residues. Based on the differences in the Cr isotopic composition, this study proves that $\delta^{53}\text{Cr}$ can be used in environmental studies to trace Cr leaching.

Keywords: Chromium mobility, ultramafic area, isotopic fractionation, mining

1. Introduction

Redox reactions control changes in Cr speciation, and these reactions subsequently affect Cr isotopic ($\delta^{53}\text{Cr}$) variations in natural environments (Ellis et al., 2002; Schauble et al., 2004; Qin and Wang, 2017; Rivera et al., 2018). Chromium has two oxidation states, Cr(III) and Cr(VI), and four stable isotopes: ^{50}Cr (abundance 4.31%), ^{52}Cr (83.76%), ^{53}Cr (9.55%) and ^{54}Cr (2.38%). Organic material, sulfides, and ferrous species control the reduction of Cr(VI) to Cr(III) (Fendorf, 1995). During this reduction, the reaction rates of the light ^{52}Cr are faster and thereby the remaining Cr(VI) is isotopically enriched in ^{53}Cr (Schauble et al., 2004; Qin and Wang, 2017). Hydrolyzed Cr(III), can be slowly oxidized to the toxic and mobile Cr(VI), by reducing Mn oxides that are easily reducible (Leita et al., 2009; Vithanage et al., 2019). Cr isotopic fractionation is also caused by this process, and results in a residual Cr(III) that is depleted in ^{53}Cr and a mobile Cr(VI) enriched in heavy isotopes.

The weathering of ultramafic rocks, containing high amounts of Cr, releases Cr(VI) that is usually enriched in heavy Cr isotopes, with values reported up to $\delta^{53}\text{Cr(VI)}_{\text{aq}} = +3.9\text{‰}$ (Farkaš et al., 2013). This Cr(VI) is then retained on positively charged minerals (Crowe et al., 2013) or leached towards the surface and groundwater (Izbicki et al., 2008; Trebien et al., 2011; Novak et al., 2014). Based on studies carried out in ultramafic areas in Brazil (Garnier et al., 2009b, 2008, 2006) and New Caledonia (Becquer et al., 2010, 2006, 2003), it is known that a fraction of Cr is exchangeable under the highly toxic anionic form Cr(VI). However, human activities (e.g. electroplating processes, and the tanning and chemical industry) can also release Cr, and these activities produce significantly higher Cr isotopic fractionation (5.8‰) when compared with Cr released from natural sources (Novak et al., 2017b, 2017a). Raous et al. (2013) found that ores and spoils from nickel mines (Barro Alto, Brazil) have a high concentration of exchangeable Cr(VI) (2% of the total Cr) and that these contents are highly affected by the hydrological conditions (Raous et al., 2010).

Studies of anthropogenic Cr sources usually focus on the release of Cr(VI) (Novak et al., 2017b, 2017a). However, not much is known about Cr(III) release due to human activities such as mining, where the access to the ore deposit implies soil cover removal and transport of large quantities of soil (Losfeld et al., 2014; Vithanage et al., 2019). Furthermore, nothing is known about the environmental relevance of isotopic fractionation, the processes causing it, or the isotopic composition of the materials found in ultramafic mining environments.

The present study was carried out to assess the impact of mining activities on the Cr isotopic composition of the material extracted in the mine, and its effect on Cr mobility in ultramafic areas. The studied site is a Ni-rich laterite deposit (Barro Alto, Goiás state, Brazil). Samples collected from a weathering cover were used to ascertain the degree of natural and human-induced weathering and its correlation with the Cr mobility and isotopic composition. This work also assesses the isotopic signature of Cr found in the material extracted from the mine, to determine whether Cr isotopes can be used as tracers of mining activities.

2. Field settings and sampling

2.1. Study site

The Barro Alto, Niquelândia and Caña Brava ultramafic complexes belong to a 350 km long belt found in the northern part of the State of Goiás (Brazil). Metamorphic volcanic-sedimentary sequences delimit the boundaries of the Barro Alto complex (Ferreira Filho et al., 1992). This complex is a large mafic-ultramafic layered intrusion that underwent granulite facies metamorphism. Researchers have shown that lateritic ores and limonite, in the Niquelândia and Barro Alto complexes, have high Cr contents with up to 6030 mg kg⁻¹ (Ratié et al., 2015) and 46800 mg kg⁻¹ (Raous et al., 2013), respectively. In ultramafic systems, Cr-rich magnetite (Fe²⁺(Fe³⁺, Cr)₂O₄), chromite (FeCr₂O₄), talc (Mg₃Si₄O₁₀(OH)₂), secondary Fe-oxyhydroxides and chlorite ((Mg, Fe)₅ Al[(OH)₈ AlSi₃O₁₀]) are all mineral phases that contain Cr (Fandeur et al., 2009; Garnier et al., 2009a; Oze et al., 2004). Although these materials are not rich enough in Cr to be extracted, they can potentially be harmful to the environment.

The Barro Alto mine (Figure 1) is located in the Barro Alto complex and occurs as an arc that spreads for 35 km in a southwest to northeast direction. The main mineral resource is saprolite that is overlain by laterites and which contains sequences of serpentized dunites and pyroxenes that are surrounded by gabbros. The Barro Alto mine consists of an open-pit mine exploited since 2011 and a ferronickel plant operated by Anglo American (Raous et al., 2010; Ratié et al., 2016). The laterite and saprolite ore can be accessed without blasting and is loaded using excavators and mixed. Trucks are used to transport the ore to the plant's preparation yard where it is stored until a beneficiation process which includes crushing, calcination, smelting and refining (Moore, 2012).

2.2. Sampling and conditioning of samples

In June 2015, nine water samples were collected from streams, ponds and groundwater in and around the Barro Alto mine (Goiás State, Brazil). Stream 1, used as a reference, is found outside the mine in the ultramafic area, whereas mining activities had a direct impact on stream 2. Three sediment ponds are used within the mine to store runoff water and to discourage the leaching of particles. Four piezometers were used to collect groundwater both upstream and downstream the mine (Piezo 1 and 2, respectively) and upstream and downstream the smelter area (Piezo 3 and 4, respectively, Figure 1). There was no rain right before the samples were taken. Each sample collected contained roughly one liter of water, stored in acid-cleaned polyethylene bottles. On-site *in situ* measurements were taken using a WTW 3410 Set 2 multi-parameter probe, including temperature, pH and electrical conductivity. Some part of the bulk samples were filtered through a pre-cleaned 0.7 µm Whatman™ grade GF/F glass microfiber filter and the suspended particulate matter was retained for analysis. The filtrate was split into two parts: H₃PO₄ was added to the first part, which was stored in amber glass bottles, to lower the pH for the dissolved organic carbon (DOC) analysis. The second part was directly stored for the anion analysis. The remaining bulk samples were filtered using a PES (Polyethersulfone) syringe filter with a 0.22 µm pore size. Ultrapure concentrated HNO₃ was added to acidify the samples for the total major and trace element analyses. All of the samples, i.e. filtered acidified and non-acidified, were stored at 4°C.

Ores, sediments and bedrocks samples and two soil profiles were also collected in June 2015. Soil profile 1 (S1) consists of three layers (0-10 cm, 10-40 cm and 80-100 cm) and soil profile 2 (S2) consists of two layers (0-15 cm and 15-40 cm). The samples taken in the mine exploitation area include eight lateritic (OL1 – OL8) and three saprolitic (OS1 – OS3) ores. The bottom sediment samples were collected in stream 2 (Se1), pond 1 (Se2) and pond 2 (Se3) (Figure 1). The three bedrock samples (B1, B2 and B3) respectively correspond to a serpentinite collected in the area (B1) and to two samples taken at the base of two separate cores at respective depths of 27 m and 28 m (B2 and B3). The mining company Anglo American had previously drilled through the cores to the lateritic regolith. The two latter samples are the same as those studied by Ratié et al. (2018): samples R C26-27 and R C27-28. The solid samples were first dried at atmospheric temperature, sieved with a 2 mm sieve (except for the rocks) and stored in polypropylene plastic bags. A marble mortar was used to crush soils, ores and sediments as well as to homogenize the resulting powder. The rocks were crushed in a ceramic jaw crusher and an agate mill was used to reduce them to powder.

2.3. Samples digestion

Approximately 0.05 g of powdered soils, ores, sediments and rocks were dissolved in a solution combining 2 mL concentrated ultrapure distilled HNO_3 and 1 mL HF. This mixture was heated on a hotplate for 48 hours at 100°C . The samples were then dried and, to dissolve the fluorides, they were flushed with aqua regia (3:1 $\text{HCl}:\text{HNO}_3$). Next, the samples were dried and then dissolved in 1 mL of 6N HCl . If black residues could still be observed (common in samples that contain certain minerals such as chromite), the dissolved fraction was extracted, thereby leaving the black residue and to which a volume of 100 μL of HClO_4 was added. This solution was placed on a hot plate at 120°C for 24 h, and once dissolved, the HClO_4 was evaporated in an evapoclean (Analab) closed low temperature evaporation system. The residue itself was dissolved in 6N HCl and mixed with the original dissolved fraction to perform the trace elements and isotope analysis. Samples taken from the river, ponds and groundwater were evaporated and the residue subsequently dissolved in 1 mL 6N HCl . The SPM that had been collected on the filters was removed and dissolved using the same procedure described above for the solid samples.

3. Methods

3.1. Chemical analyses

A Panalytical MiniPal 4 energy-dispersive X-Ray fluorescence (EDXRF) benchtop spectrometer (Rh X-Ray tube-30kV-9W) was used to analyze the total metal content in the solid samples at a resolution of 150 eV (Mn $\text{K}\alpha$). Measurements were taken as per the thin-layer hypothesis. The bauxite standard BX-N was used to determine the quality of the analysis. A PANalytical grazing incidence X-ray diffraction (GIXRD) diffractometer was used to determine the mineralogical composition using $\text{Cu K}\alpha$ radiation (at 45kV – 40 mA) in the 5° - 70° 2θ range with a scan step of 0.013° .

The anion (F^- , Cl^- , NO_3^- , SO_4^{2-}) concentrations in the water samples were measured using ion chromatography (ICS 1100, Thermo Fisher) equipped with a Thermo Scientific IonPac AS14 analytical column and a Thermo Scientific IonPac AG14 pre-column. A flow rate of 1.2 mL min^{-1} was used to inject 20 μL of the mobile phase (a mixture of Na_2CO_3 and NaHCO_3). Shimadzu's total organic carbon TOC- V_{CSH} analyzer was used to analyze the dissolved organic carbon (DOC) concentrations. The major element concentrations (Fe, Mn, Al, Cr, Ni, Na, K, Mg, Ca, Si) were measured in all the samples after a first dilution in 2% ultrapure HNO_3 using ICP-AES

(ICAP 6200, Thermo Fisher). High-Resolution ICP-MS (Element II, Thermo Scientific) with multi-element standard solutions were used to measure concentrations below $10 \mu\text{g L}^{-1}$. The ICP-AES generally has detection limits that range from 10 to $200 \mu\text{g L}^{-1}$. The detection limits for the ICP-MS are typically between 0.006 and $0.074 \mu\text{g L}^{-1}$. The measurements had standard deviations (1σ) lower than 5%.

3.2. Isotopic analyses

Aliquots of acid digested samples were used to purify the Cr purification as per the measured concentrations and the cation exchange resin method (Birck and Allegre, 1988; Trinquier et al., 2008). A Biorad AG 50WX8 cation exchanger was used to run two successive elutions which involved first dissolving the samples in 0.1N HCl and then passing them through the resin. The Cr was immediately collected right after loading. Then, any Cr still presents in the sample was completely eluted by adding 5 mL 1N HCl. The next step was to add 2 mL of 6N HCl to the resin. The resulting fraction was collected, evaporated and once again dissolved in 0.1N HCl. This fraction was then passed again through the resin, as described above. Then, to dissolve the residue, 60 μL of 16 N HNO_3 was added to the mixed and evaporated Cr fractions from the two elutions. Next, 2 mL of Milli-Q water was added and the mixture was heated to 100°C for a period of 24 hours. When the sample was completely cool, it was passed through a column of the same size as above. This load was discarded. The residual Ti, Na and Al were eliminated by adding 5 mL of 0.5N HF and 22 mL of 1N HCl. Lastly, 10 mL of 2N HCl was added to elute the Cr. Between each elution, 15 mL of 6N HCl was used to wash the columns. Ninety-five percent ($\pm 5\%$) of the elution was recovered (i.e. representing the yield). To eliminate the HCl, the samples were evaporated until dry and once again dissolved in 0.6% HNO_3 .

A Multicollector ICP-MS (Neptune, Thermo Scientific), located at the Institut de Physique du Globe de Paris (IPGP), was used to measure the chromium isotopic compositions. The purified Cr samples were dissolved in 0.5% HNO_3 with Cr concentrations of 100 ppb and 50 ppb for the solid and water samples, respectively. A PFA μFlow nebulizer (at a flow rate of $100 \mu\text{L/min}$) coupled with an Elemental Scientific's desolvating nebulization system (APEX-IR), without additional gas or membrane desolvation, was used to introduce the diluted samples into the plasma. Under high-resolution mode, a sensitivity of 2.8-4.9 V on ^{52}Cr was obtained per 100 ppb Cr with the use of jet sample and H skimmer cones. Faraday cup detectors connected to amplifiers with $10^{11} \Omega$ feedback resistors were implemented to measure all of the ion beams. The possible isobaric interferences of ^{50}Ti , ^{50}V and ^{54}Fe were corrected by measuring and

monitoring the ^{49}Ti , ^{51}V and ^{56}Fe isotopes. To monitor the potential drift, the unprocessed NIST SRM 979 standard was analyzed after running each set of three samples. These results show that there was minimal drift within each analytical session ($< 0.1\%$). The on-peak blanks were measured before and after every sample/standard for correction purposes. The assessment of the analytical accuracy and precision involved the repeated processing and measurement of the USGS reference material BHVO-2 standards ($-0.11 \pm 0.02\%$, 2SD, $n = 3$).

In line with previous studies on Cr isotopes, the δ notation (see equation (1)) was used to express the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio. This notation is a per mil deviation from NIST SRM 979 (the standard reference material):

$$\delta^{53}\text{Cr}(\text{‰}) = \left[\left(\frac{^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}}}{^{53}\text{Cr}/^{52}\text{Cr}_{\text{SRM 979}}} \right) - 1 \right] * 1000 \quad (1)$$

3.3. Chromium mobility

3.3.1. Isotopic exchange

The isotopically exchangeable pool of Cr(VI), $E_{\text{Cr(VI)}}$ -Spike, was determined by using a $^{50}\text{Cr(VI)}$ spike purchased in its oxide form from ISOFLEZ USA and certified with a 96.5% abundance in $^{50}\text{Cr(VI)}$ when the natural ^{50}Cr abundance is 4.345%. The chromium oxide was first dissolved in 6N HCl and evaporated before adding the HClO_4 . The solution was heated at a temperature of 190°C over a period of two days. The spike solution was evaporated in the evapoclean and then dissolved once again in 16N HNO_3 before dilution with Milli-Q water. At the end of this procedure, a stock solution of 100 mg L^{-1} of $^{50}\text{Cr(VI)}$ was obtained.

The soil suspensions contained 1 g of the sample ($< 2 \text{ mm}$) mixed with 10 mL of Milli-Q water and $10 \text{ }\mu\text{L}$ of 24.8 mg L^{-1} NaN_3 used as a biocide. This mixture was placed in an end-over-end shaker for 48 h. The second step involved adding $10 \text{ }\mu\text{L}$ of the spike solution to the suspensions and then shaking the samples for one more day, before filtration using a $0.22 \text{ }\mu\text{m}$ PES (Polyethersulfone) filter. Given that the spike solution has a low pH, a maximum of $10 \text{ }\mu\text{L}$ of the spike was added to each sample to not change the chemical equilibrium. The filtrate was diluted with 2% HNO_3 .

In natural systems, no significant isotope exchange between Cr species occurs over a period from several days to several weeks (Zink et al., 2010; Wang et al., 2015), whereas isotopes are exchanged between Cr(VI) species within 24 hours (Garnier et al., 2009b). Therefore, one can

assume that the isotopic equilibrium results from the exchange between the added $^{50}\text{Cr(VI)}$ and the labile natural Cr(VI) species and that the measurement of the isotopic signature in the filtrate provides direct information about the (isotopically) exchangeable pool of Cr(VI).

High-Resolution ICP-MS (Element II, ThermoScientific) was used to determine the isotopic ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr abundances in the filtrates, spike solution and unspiked sample. Analyses run on other isotopes, e.g. ^{47}Ti , ^{51}V and ^{57}Fe were used to correct the isobaric interferences for ^{50}Cr and ^{54}Cr . The isotopic ratio was calculated based on the average of 20 runs for which the analytical reproducibility is higher than 1% (2SD, $n = 520$). To verify and correct, if necessary, the drifts in signal and intensity, the samples were divided into blocks bracketed with unspiked solutions and standard Cr solutions.

The ratio between ^{50}Cr and ^{52}Cr , i.e. the two most abundant isotopes in the suspension, was used to determine the pool of isotopically exchangeable Cr ($E_{\text{Cr(VI)-spike}}$). Equation (2) (Zelano et al., 2016) was used to calculate the $E_{\text{Cr(VI)}} - \text{spike}$ (mg kg^{-1}) value:

$$E_{\text{Cr(VI)-spike}} = Q * \frac{M_{\text{STD}}}{M_{\text{S}}} * \frac{A_{\text{S}}}{A_{\text{STD}}} * \left[\frac{(I.R.)_{\text{spike}} - (I.R.)_{\text{sample}}}{(I.R.)_{\text{sample}} - (I.R.)_{\text{UN}}} \right] \quad (2)$$

where Q is the volume of spike added (μg of spike per kg of the sample), M_{STD} and M_{S} are the atomic masses of Cr (g mol^{-1}) in the standard and spike solutions, respectively, and A_{STD} and A_{S} are the percentage of ^{52}Cr abundances in the standard and spike solutions, respectively. Both the un-spiked solutions ($(I.R.)_{\text{UN}}$) and the sample ($(I.R.)_{\text{sample}}$) were analyzed to determine their respective isotopic abundances. In the sequence of analysis, triplicate samples were bracketed with their correspondent unspiked solution and the spikes and blanks were analyzed to monitor the signal, isotopic abundances and possible cross-contaminations.

3.3.2. Chemical extraction

The chemically exchangeable Cr(VI) and Cr(III) pools, called $E_{\text{Cr(VI)-KH}_2\text{PO}_4}$ and $E_{\text{Cr(III)-KCl}}$, were assessed using 0.1 M KH_2PO_4 and 1 M KCl, respectively. A solution containing 1 g of soil and 25 mL of the reactant was shaken for 1 h (Garnier et al., 2006). The supernatant was placed in a centrifuge for 15 min at 2500 rpm and then filtered through a 0.22 μm PES membrane to separate the supernatant. Concentrations of Cr in the latter were determined by ICP-AES and High-Resolution ICP-MS.

4. Results

4.1. Characterization of soils, ores, sediments and rocks

Table 1 provides the chemical and mineralogical characteristics of the bedrocks, ores, soils and sediments studied in the present work. The mineralogy of bedrock B1 is dominated by serpentine with trace amounts of chromite, while B2 and B3 are also comprised of chlorite and olivine. Si and Mg occur in the highest amounts in B1, B2 and B2. Their respective contents varied between 188 and 194 g kg⁻¹, and between 183 and 156 g kg⁻¹. In bedrocks B2 and B3, Al, Cr and Mn had an average content of 1.2, 1.3 and 1.0 g kg⁻¹, respectively.

Although lateritic ores display high content of Fe, ranging from 85 to 536 g kg⁻¹, saprolitic ores contain more Si than Fe, with values reaching 167 g kg⁻¹. The third most abundant element found in lateritic ores is aluminum with contents between 14 and 70 g kg⁻¹. Contents in the saprolitic ores were found to be 18 g kg⁻¹ for OS1, 16 g kg⁻¹ for OS2 and 14 g kg⁻¹ for OS3, indicating that this element is more variable in lateritic ores. Lateritic (OL1-OL8) and saprolitic (OS1-OS3) ores are characterized by iron mineral phases that contain both hematite and goethite. The saprolitic ores also contain Mg, which could be related to the occurrence of serpentine. Saprolites contain quite high contents of Ni (between 22 g kg⁻¹ and 32 g kg⁻¹). Lower nickel contents are found in laterite, except for ores OL2 (22 g kg⁻¹), OL4 (22 g kg⁻¹) and OL6 (21 g kg⁻¹). Lateritic ores contain higher Cr contents (10-19 g kg⁻¹) compared to saprolitic ores (ores OL3, OL2 and OL1 have respective values of 3, 4 and 4 g kg⁻¹).

The soil1 (S1) and soil2 (S2) profiles show Fe contents between 250 and 281 g kg⁻¹ and between 272 and 330 g kg⁻¹, respectively. The Cr content for S1 ranges from 10 to 12 g kg⁻¹ and 16 to 12 g kg⁻¹ in S2. Both Fe and Cr occur in higher contents in the first layer (0-15 cm) of both soil profiles. The other mineral phases present, if the Fe(III) oxides and Fe(III) (oxy)hydroxides (i.e. hematite) are not considered, are chlorite and quartz. Soil profile S2 also contains chromite and magnetite. Further down in the S1 soil (at a depth of 80-100 cm), contents of Al are higher (79 g kg⁻¹) compared to the superficial soils (74 g kg⁻¹), while in soil profile S2 Al contents are higher at the surface (77 g kg⁻¹). The reverse trend is found for Fe and Cr. The S1 soil profile shows that the contents of both Ni (with an average content of 6 g kg⁻¹) and Mn (4 g kg⁻¹ on average) remain stable along the soil profile. Compared to S1, the contents of Ni (9 g kg⁻¹) and Mn (11 g kg⁻¹) are higher in the surface soil of S2. The contents of the elements found in the sediment ponds, in decreasing order, are as follows: Fe (202-332 g kg⁻¹), followed by Mg (66-86 g kg⁻¹), Al (11-44 g kg⁻¹), Ni (9-17 g kg⁻¹), Cr (3-9 g kg⁻¹) and Mn (3-4 g kg⁻¹). The dominant

minerals in the sediments are iron oxides (goethite and hematite), serpentine, clinocllore and quartz, which correspond to the mineralogy found in the ore and overburden (soil) deposits from the Barro Alto mine.

4.2. Exchangeable chromium pool

Higher amounts of the chemically extracted Cr(VI) ($E_{Cr(VI)-KH_2PO_4}$) are found in ores, sediments and soils, compared with chemically extracted Cr(III) ($E_{Cr(III)-KCl}$) (Table 2). In the ore samples, the $E_{Cr(VI)-KH_2PO_4}$ pool ranges from 1 to 104 mg kg⁻¹ (Figure 2), whereas $E_{Cr(III)-KCl}$ varies between 0.2 and 10 mg kg⁻¹. Ponds 1 and 2 sediments (Se2 and Se3) have $E_{Cr(VI)-KH_2PO_4}$ values of 10 and 2.4 mg kg⁻¹, which are higher than the value of 1.2 mg kg⁻¹ obtained for stream 2 sediments (Se1). For the soil profiles, the $E_{Cr(VI)-KH_2PO_4}$ values are close to 30 times lower for samples taken at depths within the first 10 cm compared to up to 100 cm (0.7 mg kg⁻¹ versus 21 mg kg⁻¹). The same pattern is observed for $E_{Cr(III)-KCl}$, with values starting at 0.39 mg kg⁻¹ in the shallower soil layer (10-40 cm) and increasing to 3.7 mg kg⁻¹ in the 80-100 cm layer (i.e. the deepest one).

Figure 2 compares the chemically ($E_{Cr(VI)-KH_2PO_4}$) and the isotopically exchangeable pool of Cr ($E_{Cr(VI)-spike}$). In the ores, sediments and soils, there is a positive correlation between $E_{Cr(VI)-KH_2PO_4}$ and $E_{Cr(VI)-spike}$ ($R^2 = 0.9$). It has been shown that the reactive metal content in soils can be accurately measured, in a reproducible manner, by diluting the stable isotope (Marzouk et al. 2013). This measurement provides more information than a single extraction procedure. Based on this statement, $E_{Cr(VI)-KH_2PO_4}$ sampled at depths ranging between 10 and 40 cm is underestimated in saprolitic ores and soil 1 (S1). However, for the saprolite ores, the presence of sub-micrometer colloidal particles (SCPs) may explain the difference between the $E_{Cr(VI)-KH_2PO_4}$ pool compared to the one-one line (Bolaños-Benítez et al., 2018; Lombi et al., 2003; Marzouk et al., 2013), as these particles are comprised of non-isotopically exchangeable metals and may result in over-estimated $E_{Cr(VI)-spike}$. The total Cr content can be broken down into a non-mobile reservoir of Cr(III), making up 99% of this total content, and an exchangeable pool of Cr(VI) comprising the remaining 1%. Cr(III) could be oxidized and mobilized in freshwater systems.

4.3. Water chemistry

The physicochemical characterization of the samples collected is presented in Table 3. The highest electrical conductivity values, 167 $\mu S\ cm^{-1}$ and 292 $\mu S\ cm^{-1}$ respectively, are found in samples of groundwater collected from the piezometers located upstream of the mine (Piezo 1) and the smelter (Piezo 3). These values respectively decrease to 155 $\mu S\ cm^{-1}$ and 48 $\mu S\ cm^{-1}$ in

the piezometers located downstream from the mine (Piezo 2) and the smelter (Piezo 4). There is a simultaneous decrease in the concentrations of calcium and magnesium by 90% along with decreases in the alkalinity (from 79 to 11 mg L⁻¹) and decreased pH neutralization capacity (from 6.6 to 5.7) throughout the smelter area. The groundwater samples taken from the piezometers located at the smelter indicate that the concentrations of other elements, such as K and Na, also decreased (by 62 and 63%, respectively).

In stream 1, the dissolved major elements are hereafter listed by their concentrations in decreasing order: Mg²⁺ (12 mg L⁻¹), Ca²⁺ (3 mg L⁻¹) and Na⁺ (0.5 mg L⁻¹). In pond 2, the Mg²⁺ and Ca²⁺ concentration is 13 mg L⁻¹ and 5 mg L⁻¹, respectively. The present work shows that the concentrations of the major elements generally decrease in the order Mg²⁺ > Ca²⁺ > Na⁺ > K⁺ and the anion concentrations decrease in the order NO₃⁻ or SO₄²⁻ > Cl⁻ > F⁻. The highest SPM concentrations (166 to 317 mg L⁻¹) were found in the ponds. These concentrations are up to 30 times higher than those determined in fresh and groundwater (Table 3). Ponds 1, 2 and 3 exhibit dissolved Cr concentrations of 757, 58 and 89 µg L⁻¹, respectively. Due to the release of Cr from waste materials coming from the mine, the concentration of Cr is 130 times higher in stream 2 than in stream 1 (13 µg L⁻¹ versus 0.1). The Cr concentration in the groundwater is higher upstream the mine (2.4 µg L⁻¹) and the smelter (1.1 µg L⁻¹) than downstream (0.2 µg L⁻¹).

The groundwater of the mining area had slightly higher DOC concentrations that observed in the other areas with concentrations of 3.74 mg L⁻¹ for piezometer 1 and 4.65 mg L⁻¹ for piezometer 2. Table 3 shows that higher particulate carbon concentrations are found in groundwater sampled before and after the smelter area (6.51% and 9.63%, respectively) compared to groundwater in the mine (5.84% on average). The particulate organic carbon content determined in the freshwater varied between 0.64 and 3.65wt% (Table 3).

4.4. Cr isotopic composition

Solid and liquid samples collected in the ultramafic area, both inside and outside the mining area, were analyzed to determine the δ⁵³Cr values as these values help to identify the natural and human-derived processes controlling Cr fate. The measured δ⁵³Cr values for all the samples collected are given in Table 1 for solids and in Table 3 for liquids, and displayed in Figure 3. Negative δ⁵³Cr values, related to a depletion of light Cr isotopes (Frei and Polat, 2013; Berger and Frei, 2014; Qin and Wang, 2017), were found for certain solid samples such as lateritic ores (-0.76 ± 0.07‰ to -0.24 (± 0.02)‰), soils (-0.28 (± 0.06)‰ to -0.10 (± 0.04)‰), sediments (-

0.77 (± 0.05)‰ to -0.22 (± 0.04)‰) and part of the SPM (-0.89 (± 0.01)‰ to -0.18 (± 0.07)‰). A negative $\delta^{53}\text{Cr}$ value (-0.17 ± 0.01)‰ was found in bedrock B1, whereas this value is positive for B2 and B3 (+0.18 (± 0.08)‰ and +0.10 (± 0.04)‰, respectively). The $\delta^{53}\text{Cr}$ values in the saprolitic ores are positive and range from +0.93 (± 0.05)‰ to +1.05 (± 0.12)‰. Stream 2 (+0.94 (± 0.09) ‰) and the two piezometers located before (Piezo 1) (+0.65 (± 0.09) ‰) and after (Piezo 2) (+0.93 (± 0.08) ‰) the mine record the highest $\delta^{53}\text{Cr}$ values for the SPM.

High $\delta^{53}\text{Cr}$ values, from +2.10 (± 0.13)‰ to +3.66 (± 0.04)‰, were found in the water samples. The variation of these values is within the same range as that for the isotopic signatures determined in Cr(VI) extracted with KH_2PO_4 from the ores OL1, OL3, OL5 and OL8 as well as sediment samples Se1 and Se2, with values of $\delta^{53}\text{Cr}$ ranging from +1.34 (± 0.07)‰ to +4.37 (± 0.06)‰ (Figure 3).

5. Discussion

5.1. Weathering in tropical ultramafic environments

Assuming that the mining activity in Barro Alto has had a significant effect on the natural stratigraphic column, all the surface samples collected in this study may have originally held a different position in that column. Based on the assumption that this position has a direct relationship with the extent of alteration, the calculation of an index of alteration for bedrocks, ores, soils and sediments can be used to reconstruct a theoretical stratigraphic column. Babechuk et al. (2014) followed by Aiglsperger et al. (2016) have proposed to develop an ultramafic index of alteration (UMIA). The UMIA accounts for the following: magnesia (MgO) and silica (SiO_2) are dominant in ultramafic rocks whereas CaO , Na_2O , K_2O occur in very small amounts. MgO and SiO_2 are depleted near the surface in the majority of Ni laterites while iron and alumina oxides (Fe_2O_3 and Al_2O_3 , respectively) are simultaneously enriched (Aiglsperger et al., 2016). The following equation is used to calculate the UMIA:

$$UMIA = \frac{Al_2O_3 + Fe_2O_3}{Al_2O_3 + Fe_2O_3 + MgO + SiO_2} * 100 \quad (3)$$

The UMIA produces values between 0 and 100 and is used to identify incipient ($UMIA < 20$), intermediate ($UMIA = 20-60$) or intense to extreme ($UMIA > 60$) mineralogical transformations. Table 1 shows that, except for OL2, the lateritic ores have UMIA values higher than 60 (82-98), indicating that an intense mineralogical transformation occurred and that the mobile elements were leached. Accordingly, it is associated with Cr enrichment mainly as Cr(III). Our results are

similar to those found by Raous et al. (2013), who reported an enriched lateritic horizon in goethite, hematite and chromiferous spinel. Conversely, the UMIA values for saprolite ores and bedrock, ranging from 8 to 13, indicate an incipient degree of alteration (Table 1). Similar results were obtained by Rivera et al. (2018) who found UMIA values between 4 and 47 in the saprolitic and limonitic horizons. The less weathered saprolite sample resembles the bedrock content with a small degree of weathering, and the highest values were reached out in the limonitic horizons.

The saprolitic and lateritic ores in the soils have UMIA values between 47 and 62. Even though lateritic ores and soils have similar chemical compositions, soils have different mineralogy that includes hematite, chlorite and quartz. It is not surprising to find hematite, goethite, maghemite, and amorphous Fe (oxy)hydroxides in soils given that they are part of the soil-forming phases in serpentine soils (Coleman and Jove, 1993). However, it is possible to find quartz as a secondary mineral in lateritic regoliths found in soils covering ultramafic rocks (Vojcu and Bardoux, 1997). It seems likely that this quartz may come from eolian sources in the surrounding sites that are not ultramafic. Lastly, the UMIA values of the sediments indicated an intermediate mineralogical alteration. This result most likely has to do with the fact that sediments contain particles from various sources. This implies that these UMIA values represent the averages found in soils and ores.

The UMIA value interpretation was combined with an Al-Fe-Si-Mg molar ternary plot that illustrates the trend for mafic and ultramafic minerals (primarily serpentine) with regards to weathering. There is a clear weathering trend, as shown in Figure 4, from the less weathered to more weathered samples, i.e. from the bedrock to the lateritic ores. Compared to the bedrock, lateritic ores (OL1-OL8) are highly-enriched in Fe and Al. This is due to i) the strong leaching of alkali and Si during hydrolysis, and ii) the precipitation of secondary minerals such as Fe oxides, e.g. goethite and, to a lesser degree, hematite. Saprolitic ores (OS1, OS2 and OS3) contain small amounts of Al and Fe and are enriched in Mg, with serpentine and smectite as the main mineral phases (Table 1). The presence of Mg-bearing alteration minerals such as serpentine and talc, which can be formed in ultramafic rocks, may explain these Mg enrichments regardless of fact that chlorite is the main Mg-mineral phase in saprolite (Vojcu and Bardoux, 1997).

Table 1 shows that there is a low degree of alteration in the bedrocks (B1, B2 and B3). Samples of this type typically display high Mg contents and extremely low Al, Cr, Mn and Ni contents given that incipient weathering has occurred and therefore certain soluble elements, e.g. Mg, are

still present. The mineralogy assemblage contains serpentine and chlorite with trace amounts of chromite, amphibole and olivine. The content of the elements in these soils decreases in the order $\text{Fe} > \text{Al} > \text{Mg}$, indicating that these soils are found close to the lateritic ores. Conversely, for the sediments, the Mg content was higher than the Al content and Fe remained the dominant element (Table 1).

5.2. Chromium behavior during weathering

Figure 5(a) depicts a graph plotting the total Cr content in the samples against the ultramafic index of alteration (UMIA). The samples containing the lowest Cr contents ($0.3\text{--}1.3\text{ g kg}^{-1}$) and least-altered materials are the bedrock samples. This parent material undergoes weathering leading to the formation of lateritic and saprolitic ores and soils. The Cr content found in this type of weathering product depends on the degree of alteration as Cr is not very soluble, particularly when included in chromite. Lateritic ores, which have some of the highest Cr contents (from 10 to 19 g kg^{-1}), are among the most altered materials. The low solubility of Cr, compared with the highly leachable element from the bedrock such as Si and Mg, result in higher Cr contents in altered materials. Soils are also characterized by high levels of Cr ($10\text{--}15\text{ g kg}^{-1}$), whereas the average Cr content in saprolite is only 4 g kg^{-1} . Finally, sediments contain a mixture of both soils and ores (with a Cr content ranging from 3 to 9 g kg^{-1}) and are possibly the material that has been altered to a higher degree. As displayed in Figure 1, the sediments from pond 1, which collects the runoff from the ore extraction area, have a high Cr content (9 g kg^{-1}). Our results are very comparable with those of Paulukat et al. (2015) who published data on the total Cr content found in a weathering profile in an Odisha Mining Corporation-chromite mine (Sukinda Valley, India). These authors report a total Cr content ranging from 24 to 60 g kg^{-1} in the laterite, 33 g kg^{-1} in the saprolite and with significantly lower average contents of 7 g kg^{-1} in the bedrock.

The exchangeable pool of Cr(VI) is plotted against the UMIA in Figure 5(b) and shows that the highest content of exchangeable Cr(VI) is found in the most weathered material. This result is consistent with the oxidative weathering of rocks, during which Cr(III) is oxidized to Cr(VI). This oxidation is more likely to occur if compounds with high redox activities, such as elemental oxygen and manganese oxides and hydroxides, are present (Trebien et al., 2011). It is expected that the metals present in Mn oxides will be subjected to co-precipitation and substitution, particularly when alternating wetting and drying cycles occur in the soil (Essington, 2005 in Trebien et al., 2011). This is an essential step for laterite to form. Our results show that, except for soil 2 (S2) which is the only sample containing magnetite and chromite, there is a significant

positive correlation between Mn and Cr contents ($R^2 = 0.9$), and Mn content and UMIA ($R^2 = 0.8$). An identical correlation can be seen between the extracted Cr(VI) and the total Mn content, indicating that Mn is involved in the oxidation of Cr(III) and the subsequent production of the toxic Cr(VI) (Fendorf and Zasoski, 1992; Garnier et al., 2013; Rai et al., 1989). However, it should be noted that the amount of easily reducible Mn oxides present, and not only the total content of Mn, determines the extent of Cr(III) oxidation (Trebien et al., 2011).

Cr(VI) adsorption may occur through outer-sphere complexes (Fendorf, 1995) onto iron oxides which have a high point of zero net charge (PZNC), and they can effectively adsorb oxyanions such as Cr(VI) when the pH values fall between 2 and 7 (Zachara et al., 1989). Positive correlations are found for Fe and Cr in bedrock, saprolitic ores, lateritic ores, soils and sediments ($R^2 = 0.8$). As seen in Table 2, the highest contents of exchangeable Cr(VI) in the lateritic ore samples (12-104 mg kg⁻¹) are found in OL1, OL3, OL5, OL7 and OL8, which primarily contain Fe oxides. The remaining samples display a smaller $E_{Cr(VI)}$ range of variation concerning the previously described ores (0.7-21 mg kg⁻¹).

Tau (T) factors (Equation 4) are used to calculate mass balances, useful to quantify the mass gains and losses of individual chemical elements with regards to the bedrock (Rivera et al., 2018):

$$\tau_{Ti,Cr} = \frac{Cr_{sample}/Ti_{sample}}{Cr_{Bedrock}/Ti_{bedrock}} - 1 \quad [4]$$

where Cr_{Sample} and $Cr_{Bedrocks}$ represent the total Cr content (in g kg⁻¹) present in both the samples and bedrock, respectively. Titanium, in the sample (Ti_{sample}) and bedrock ($Ti_{bedrock}$), was used as the immobile element to normalize the Cr content (Table 1). The samples have a higher Cr content compared to the bedrock, except the sediment samples from stream 2 (Se1) and pond 2 (Se3). In this latter, the negative tau values suggest that Cr is gradually lost. It has been demonstrated previously that isotopic fractionation may occur as a result of Cr enrichment or loss due to redox processes (Crowe et al., 2013; Frei and Polat, 2013; Wang et al., 2015a). The changes in $\delta^{53}Cr$ versus the UMIA values is shown in Figure 5(c). Two end members are present: one of the members is comprised of lateritic ores that have been enriched in lighter ⁵²Cr isotopes and which have a high index of alteration. The second member contains saprolitic ores with incipient alteration and Cr that has been enriched in heavy ⁵³Cr. When heavy and exchangeable Cr is removed, the remaining Cr is enriched in lighted isotopes thereby explaining

the negative $\delta^{53}\text{Cr}$ values of the lateritic ores. Conversely, when previously mobilized and isotopically heavy Cr is once again deposited in saprolitic ores, this may lead to positive $\delta^{53}\text{Cr}$ values (Crowe et al., 2013; Frei and Polat, 2013; Berger and Frei, 2014).

The only geological reservoir that contains negative $\delta^{53}\text{Cr}$ is found in weathered rocks (Qin and Wang, 2017). This was observed in the present study, except for the light isotope enrichment found in the saprolitic ore samples (Figure 5(c)). A previous study found high $\delta^{53}\text{Cr}$ values in serpentinites (up to +1.22‰) in response to serpentinization processes (Farkaš et al., 2013). These authors interpreted the possible shift of altered peridotites to isotopically high $\delta^{53}\text{Cr}$ as being due to less isotopically heavier Cr(VI) in serpentinizing fluids (Farkaš et al., 2013). It has also been suggested higher $\delta^{53}\text{Cr}$ values occur in peridotite that has been altered and which is characterized by lower Cr content (Wang et al., 2016). These authors offered two possible explanations for this phenomenon: a) kinetic fractionation resulted in heavy Cr isotopes being left behind when the fluids removed light Cr isotopes during the serpentinization process; or b) fluids without isotopic fractionation first removed the light Cr isotopes and then isotopically heavy Cr was accumulated during the reduction of sulfate, which occurred at a later stage. A third explanation may also be the re-deposition of mobilized isotopically heavy Cr, along with the enrichment of Cr (Crowe et al., 2013; Frei and Polat, 2013; Berger and Frei, 2014).

To assess this point, Figure 5(d) plots the isotopic signature of the total Cr against the corresponding chemically extracted Cr(VI). The $\delta^{53}\text{Cr}$ values for the total Cr ($+0.97 \pm 0.08\text{‰}$) and the extracted Cr(VI) ($+1.34 \pm 0.07\text{‰}$) contained in saprolitic ores are positive and are relatively similar, suggesting that only minor losses of heavy Cr(VI) isotope occur in saprolitic ores. This result is in line with the incipient degree of alteration of this material. Conversely, lateritic ores display a considerably higher fractionation between total Cr ($-0.76 \pm 0.07\text{‰}$) and Cr(VI) ($+4.37 \pm 0.06\text{‰}$). This is due to the loss of Cr(VI) that has been enriched in heavy isotopes during weathering. Frei and Polat (2013) and Crowe et al. (2013) have stated that the oxidative weathering of Cr is caused by the presence of oxygen in the atmosphere. As a result, runoff removes the pool of ^{53}Cr -enriched Cr(VI) and the residual solid remains depleted in ^{53}Cr .

5.3. Interactions between water and rocks during natural weathering

The stream 1 is located outside of the mining area (Figure 1) and is used as a reference of the natural processes at work in this ultramafic environment. The total dissolved Cr concentration in stream 1 is much lower ($0.1 \mu\text{g L}^{-1}$) than the concentration determined in the bulk sample (8.7

541 $\mu\text{g L}^{-1}$). This suggests that the majority (over 98%) of the Cr found in the stream waters is
542 contained in the SPM. Serpentine soils are commonly comprised of a mixture of 90% solid
543 Cr(III) oxy(hydr)oxides and 10% adsorbed Cr(VI). At pH values greater than 7, the runoff from
544 these soils is dominated by dissolved Cr(VI) (Mcclain and Maher, 2016; Novak et al., 2017a;
545 Coyte et al., 2020) that can therefore be released to the surface waters. Wu et al. (2017) studied
546 samples collected in the Connecticut River (United States) fed by a watershed with high
547 amounts of basalts and reported positive $\delta^{53}\text{Cr}$ values in the SPM. Most likely, one of the
548 dominant factors controlling the weathering rates in watersheds is the lithology. Therefore, the
549 weatherability of minerals decreases from carbonate > mafic silicates > feldspars > quartz
550 (White and Blum, 1995). In the present study of the Barro Alto area, the $\delta^{53}\text{Cr}$ composition in the
551 SPM ($0.015 \pm 0.09\%$) collected in stream 1 and the inheritance of high amounts of $\delta^{53}\text{Cr}$ from
552 dissolved Cr(VI) may be explained by the lithology ($+2.60 \pm 0.04\%$).

553
554 The positive $\delta^{53}\text{Cr}$ values found in the dissolved fraction may either be the direct result of the Cr
555 isotopic fractionation processes in an ultramafic profile, or they may be related to additional
556 processes occurring during riverine transport such as redox fractionation processes, adsorption
557 and/or mixing from riverine water with different $\delta^{53}\text{Cr}$ values (D'Arcy et al., 2016). It is also
558 possible that the sorption of Cr(VI) onto Cr(III)-bearing oxy(hydr)oxides leads to decreased $\delta^{53}\text{Cr}$
559 values in the solid phase and discharged of the residual aqueous Cr(VI) into streams and rivers
560 (Wang et al., 2015a). These scenarios seem less likely though, as the fractionation of Cr is less
561 than 0.3‰ and there must be long-term contact between Cr(VI) and Cr(III) oxy(hydr)oxides
562 (D'Arcy et al., 2016). The positive $\delta^{53}\text{Cr}$ values in stream 1 can be explained by the oxidation of
563 Cr(III) to Cr(VI). However, it should be borne in mind that the large activation energy needed to
564 carry out this transformation will not show a high fractionation (Zink et al., 2010). Wang et al.
565 (2015a) evoked a “rind effect” to explain the low fractionation of solid Cr(III): Cr(III)
566 oxy(hydr)oxide particles are comprised of several micro-layers, each of which is essentially
567 completely oxidized, thereby resulting in limited isotopic fractionation. Stream 1 is characterized
568 by both a large Cr isotopic fractionation and an elevated Fe concentration, consistent with
569 processes dominated by the reduction of Cr(VI) into Cr(III), leaving ^{53}Cr -enriched Cr(VI) behind.
570 It is also necessary to take into account the release of Cr(III) during weathering, as this may
571 decrease the global amount of $\delta^{53}\text{Cr}$ present in the dissolved fraction (D'Arcy et al., 2016).

572 573 5.4. Mining activities resulting in accelerated weathering

When the ore is exploited in mines, a large amount of material must be removed and taken elsewhere. The scale of this operation is comparable to the effects of extensive physical erosion. Physical erosion has been described by White and Blum (1995) as one of several factors that control weathering rates. The concentrations of the SPM found in the water bodies inside the mine are significantly higher than the ones found in stream 1 (3.3-316 mg L⁻¹ versus 1.1 mg L⁻¹, respectively). This shows unequivocally that the extraction, transport and stockpiling of the residues produced during mining activities results in the release of particles that find their way into sources of water. The analysis of the water bodies inside the mine showed that the SPM contains high concentrations of Cr (from 24 to 1064 µg L⁻¹). This enrichment in Cr could even be observed in the dissolved fraction (Cr concentrations < 757 µg L⁻¹). Wu et al. (2017) reported that there was no significant effect of oxide loads on the $\delta^{53}\text{Cr}$ values for the suspended Cr, particularly since the suspended Cr would have been isotopically heavy due to the inheritance of dissolved Cr(VI) $\delta^{53}\text{Cr}$ via adsorption. This result is in line with what we observed for the particulate Cr in stream 2, enriched in isotopically heavy Cr up to $\delta^{53}\text{Cr}$ value of +0.94 (± 0.09)‰, whereas the particulate Cr present in stream 1 remains unfractionated.

Material issued from the erosion of the overburden, waste rock, and extracted ores are released to the ponds via runoff water and as a result, these sediments are a mixture of various products. As observed in Figure 5(c), the negative $\delta^{53}\text{Cr}$ values determined for the sediments can be related to the enrichment in light isotopes of the lateritic ores (-0.76 (± 0.07)‰ to -0.16 (± 0.05)‰) and soils (-0.05 (± 0.04)‰ to -0.28 (± 0.06)‰). In pond 1, both Cr in the SPM and Cr in the sediments display negative isotopic signature (-0.38 (± 0.08)‰ and -0.50 (± 0.04)‰, respectively). The slightly higher values observed for Cr in sediments may be the result of the oxidation of Cr(III) as well as the release of Cr(VI) enriched in heavy isotopes. The basis of this hypothesis is that the sediments in the ponds are also a source of isotopically heavy Cr(VI) for the pond water column.

The groundwater sampled upstream and downstream from the smelter area shows enrichment in the total dissolved Cr ($\delta^{53}\text{Cr}$ equal to of +2.18 (± 0.08)‰ and +2.19 (± 0.16)‰, respectively; Figure 3). These values are in agreement with the range of $\delta^{53}\text{Cr}$ values (0.7 to 5.1‰) found by Izbicki et al. (2008) in 32 uncontaminated wells and by Coplen et al. (2002) in a study on native groundwater (1.1 to 5.8‰). In these samples, a significant fractionation occurs either on the mineral-grain surfaces or in bulk solutions when the dissolved oxygen concentrations decline and Cr is removed from solution as Cr(III) (Izbicki et al., 2008). Figure 3 shows that the depletion in heavy ^{53}Cr in the particulate fraction is higher before the smelter area than after (-

0.55 (± 0.06)‰ versus -0.34 (± 0.05)‰). Based on this result, it appears that the reductive smelting process used on the ore to produce Fe-nickel (smelting at 1600°C) preferentially liberates Cr(III) (Economou-Eliopoulos et al., 2016). When oxygen is depleted in the groundwater, this can also lead to Cr(VI) being reduced to Cr(III) and, as a result, decreased $\delta^{53}\text{Cr}$ values.

The isotopic signature of the Cr(VI) extracted was analyzed to determine how much of the Cr(VI) found in the water bodies derived from the solid residues and ores. The $\delta^{53}\text{Cr}$ distribution for the solids, extracted Cr(VI) and surface waters is given in Figure 6. The surface waters and extracted Cr(VI) are characterized by variations within the same range, suggesting that surface water and groundwater ^{53}Cr enrichment occurs as a result of the release of Cr(VI) oxidized from Cr(III) in the solid phases. The natural weathering is partly contributing, while producing higher Cr(VI) contents in more altered materials and, subsequently, ^{53}Cr depletion in the remaining solid (Figure 6). Furthermore, a large contribution is directly related to anthropically enhanced erosion caused by mining activities, which accelerates natural weathering processes.

6. Conclusions

This study is an important step towards improving our understanding of Cr isotope behavior in ultramafic environments and more specifically in mining areas. The reconstructed pedological profile combined with the results of the UMIA (ultramafic index of alteration) shows that the lateritic ores and soils were subjected to an intense mineralogical transformation. They are enriched in both Cr (10-18 g kg⁻¹) and Fe (85-536 g kg⁻¹) and the exchangeable pool of Cr(VI) ($E_{\text{Cr(VI)}}$) also becomes larger with increasing degrees of alteration.

The analyses performed on the saprolitic ores suggest that very small amounts of heavy Cr(VI) are lost as attested by the positive $\delta^{53}\text{Cr}$ values total Cr (+0.97 (± 0.08)‰) and extracted Cr(VI) (+1.34 (± 0.07)‰) as well as the close similarity between the values. Conversely, there is a considerably larger difference between the fractionation of the total Cr (-0.76 (± 0.07)‰) and the extracted Cr(VI) (+4.37 (± 0.06)‰) observed in the lateritic ores as a result of the loss/leaching of isotopically heavy and exchangeable Cr(VI) during weathering. Consequently, negatively fractionated Cr is left behind.

Our study shows that ^{53}Cr enrichment in both the surface water and groundwater is related to the release of Cr(VI) due to the Cr(III) oxidation in the solid phases. This is demonstrated by

comparing the range of variation of $\delta^{53}\text{Cr}$ between the surface waters and the extracted Cr(VI). The former (+2.10 ($\pm$ 0.04) to +3.66 ($\pm$ 0.04) ‰) falls within the range of the latter (+1.34 ($\pm$ 0.07) to +4.37 ($\pm$ 0.06) ‰). Some of the enrichment in Cr is due to natural weathering, however, erosion due to mining activities is playing an important role as this accelerates natural weathering. In our study, the pristine area is represented by stream 1 which has lower total Cr concentrations than the other surface waters evaluated. Nevertheless, it should be noted that the $\delta^{53}\text{Cr}$ value still falls within the range of variation for the extracted Cr(VI). It may be possible to use $\delta^{53}\text{Cr}$ values to trace sources of Cr in the dissolved fraction, assuming the combination of this tool with other parameters such as total Cr, Fe and Mn concentration, organic carbon and, most of all, Cr speciation to obtain the full picture and to accurately interpret these data.

Acknowledgements

The authors would like to thank Anglo American for access to their field facilities and for releasing samples. We would also like to thank the Anglo American staff for their help during the sampling campaign. Sincere thanks go to Dr. Sophie Nowak for performing the XRD acquisition in the RX platform in the Paris Diderot Chemistry Department. The authors thank the European Commission (EC) for providing financial support via the Erasmus Mundus Joint Doctorate Program ETeCoS³ (Environmental Technologies for Contaminated Solids, Soils and Sediments, grant agreement FPA no 2010-0009). This work was carried out as part of the Marie Curie International Research Staff Exchange Scheme Fellowship within the seventh European Community Framework Program (NIDYFICS, n°318123). Some of this work was supported by the IPGP multidisciplinary program PARI, and by Paris-IdF region SESAME Grant no. 12015908. This work was also supported by the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) under contract N° 445423/2014-5, 420697/2018-7 and 302722/2018-1.

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Figure 1. Map of the study area in Barro Alto mine and location of the sampling sites. Names in parenthesis are the ones used for the solid samples.

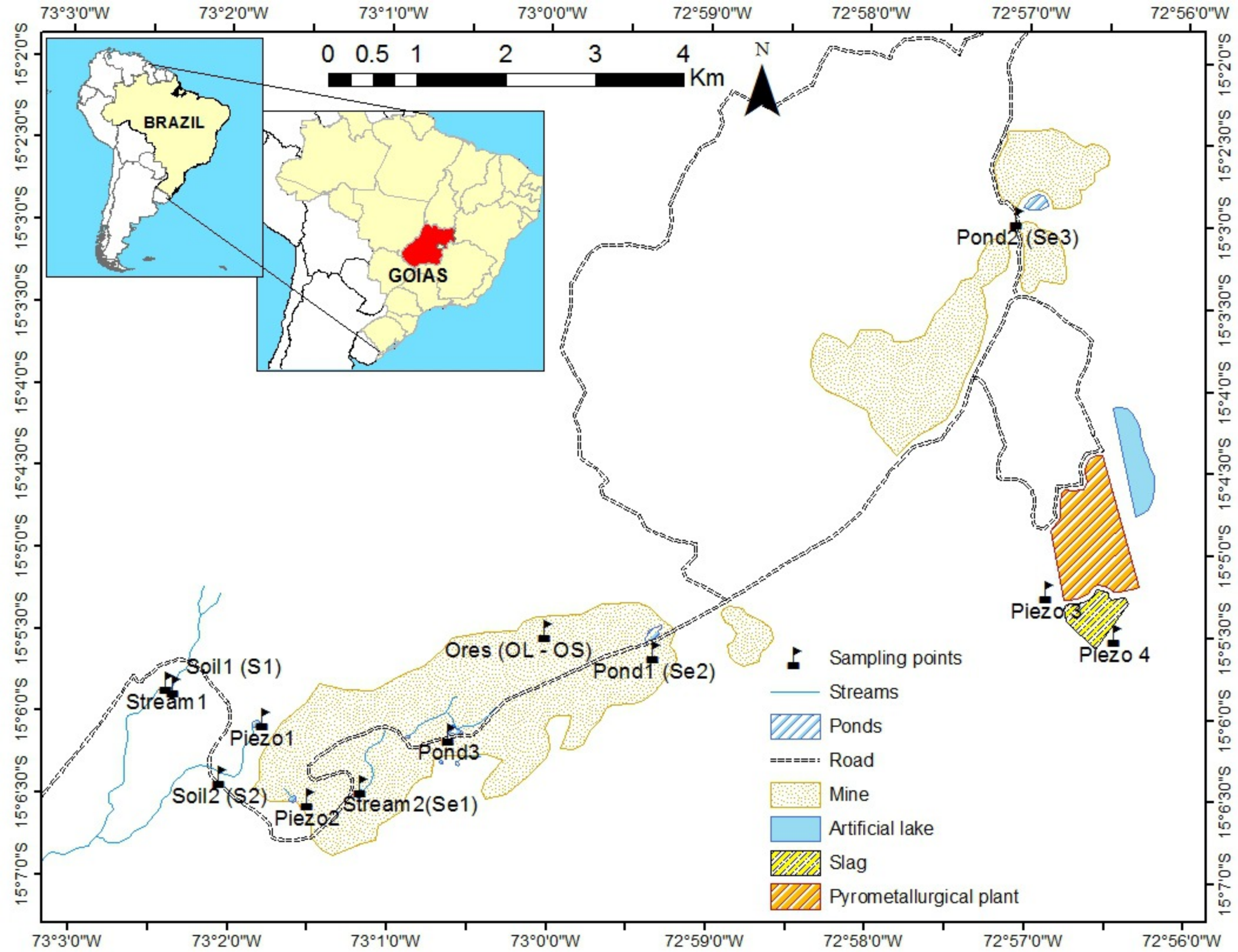
Figure 2. Positive correlation between isotopically and chemically exchangeable pool of Cr(VI) in solid samples of Barro Alto.

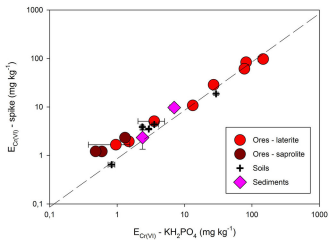
Figure 3. Cr isotopic composition in ‰ of the samples from this study, including solid samples (soils, ores, bedrock and sediments), Cr(VI) extracted with KH_2PO_4 and liquid samples (surface and ground water).

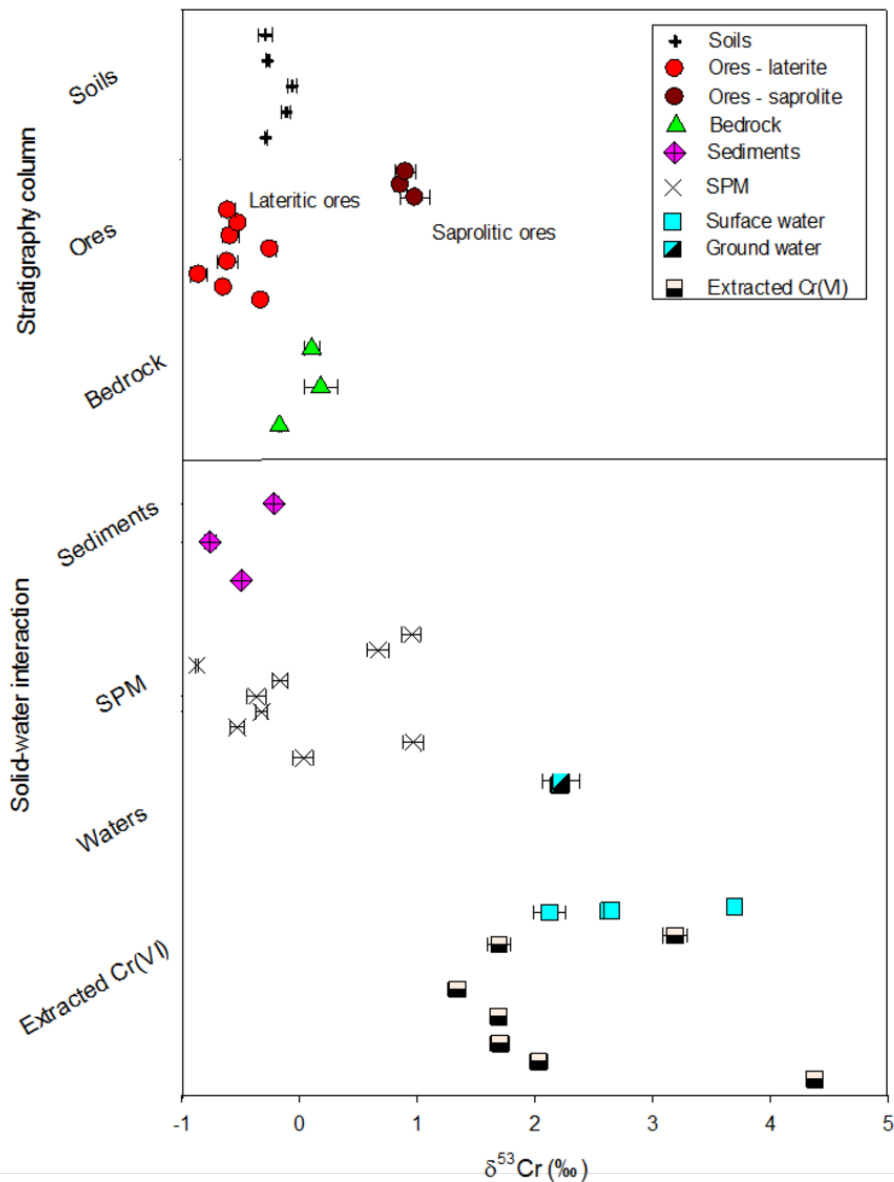
Figure 4. Ternary plot in the Al-Fe-Mg-Si space and its relationship with the ultramafic index of alteration (UMIA).

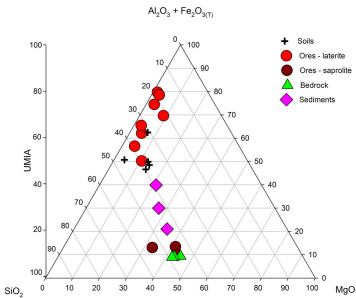
Figure 5. Evolution, according to the ultramafic index of alteration of a) the total Cr content, b) the exchangeable pool of Cr, c) the Cr isotopic composition of the bulk samples and d) the Cr isotopic composition of both bulk samples and corresponding extracted Cr(VI) (KH_2PO_4).

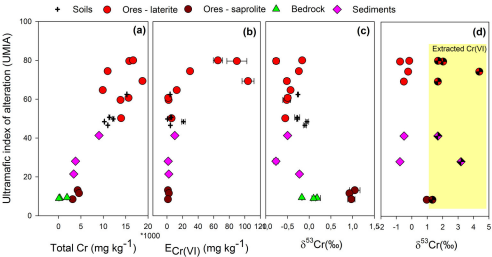
Figure 6. Total chromium contents in solid samples and their correspondent $\delta^{53}\text{Cr}$ values. The blue band represents the $\delta^{53}\text{Cr}$ range of variation in surface water, which is within the range found for Cr(VI) extracted with KH_2PO_4 .











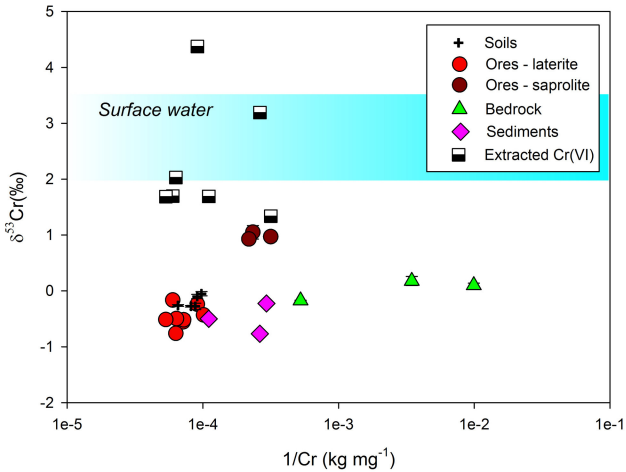


Table 1 Total content of elements, $\delta^{53}\text{Cr}$ value and mineralogical composition of the solids collected in Barro Alto (soils, ores, bedrock and sediments). Sm: smectite; Srp: serpentine; Chl: chlorite; talc, Oli: olivine; Hem: hematite; Goe: goethite; Spi: Spinel and Qz: quartz (n.d. = not determined). τ represent the enrichment or depletion of Cr respect to the bedrock. UMIA is the Ultramafic Index of Alteration (Aiglsperger et al., 2016).

Sample type	Sample code	T Cr/Ti	UMIA	δ ⁵³ Cr (‰)	±2σ	Concentration (g kg ⁻¹)								Mineralogy									
						Si	Al	Cr	Fe	Mg	Mn	Ni	Ti	Sm	Srp	Chl	Talc	Oli	Hem	Goe	Spi	Qz	Others
Soils	S1(0-10 cm)	0.19	50	-0.28	0.01	97.28	76.97	12.23	280.71	34.51	4.04	6.68	1.24			+			+			+	
	S1(10-40 cm)	0.25	47	-0.10	0.04	107.96	74.29	11.01	250.13	38.16	3.75	6.45	1.06			+			+			+	
	S1(80-100 cm)	0.06	48	-0.05	0.04	101.08	79.47	10.24	271.35	35.96	3.02	6.12	1.16			+	+		+				
	S2(0-15 cm)	0.88	62	-0.26	0.01	69.47	76.62	15.26	330.05	15.96	10.69	8.75	0.98			+	+		+	+		+	Magnetite
	S2(15-40 cm)	0.83	51	-0.28	0.06	109.55	62.44	11.37	272.25	11.67	9.98	6.47	0.75						+	+		+	Chromite
Lateritic ores	OL1	1.06	74	-0.24	0.02	27.33	48.43	10.97	331.82	10.92	3.92	8.08	0.64								+	+	+
	OL2	3.60	50	-0.55	0.03	60.59	30.56	13.98	369.02	32.74	5.85	21.73	0.37	+	+						+		
	OL3	1.83	80	-0.76	0.07	20.82	42.13	15.80	536.17	9.14	6.92	3.90	0.67			+			+	+	+	+	
	OL4	1.09	60	-0.52	0.09	51.54	69.72	13.85	424.30	21.54	6.27	22.19	0.80							+			
	OL5	0.97	80	-0.16	0.05	19.59	66.91	16.65	465.59	15.59	7.05	12.23	1.02							+			
	OL6	1.91	61	-0.50	0.07	46.75	57.97	15.64	403.85	24.52	6.22	21.10	0.65		+					+			
	OL7	1.15	65	-0.43	0.02	42.65	42.02	9.88	297.78	13.80	4.66	10.05	0.55	+						+			
	OL8	1.52	69	-0.51	0.06	26.47	63.13	18.75	451.98	24.80	6.49	15.35	0.89							+	+		
Saprolitic ores	OS1	1.38	13	1.05	0.12	167.68	17.89	4.28	109.58	105.95	2.47	31.51	0.22		+								Vermiculite
	OS2	0.93	12	0.93	0.05	158.76	15.78	4.58	133.78	156.44	2.40	22.16	0.29	+	+								
	OS3	1.45	8	0.97	0.08	179.15	13.84	3.16	84.93	146.54	1.03	21.56	0.16	+	+								
Bedrock	B1	-	10	-0.17	0.01	n.d.	0.60	0.27	103.34	202.23	0.20	1.00	n.d.		+								Chromite
	B2	-	11	0.18	0.08	188.00	1.59	1.23	22.40	182.70	1.01	2.67	0.10		+	+		+					Amphibole
	B3	-	11	0.10	0.04	194.00	0.79	1.33	22.40	156.20	1.01	2.75	0.21		+	+		+				+	
Sediments	Se1	-0.65	28	-0.77	0.05	145.65	20.50	3.81	264.19	65.87	3.30	16.84	1.30		+	+				+		+	
	Se2	1.28	41	-0.50	0.04	108.53	43.65	9.05	331.93	48.54	3.79	8.85	0.48			+					+	+	
	Se3	-0.41	21	-0.23	0.04	162.24	11.43	3.40	201.81	86.14	2.82	12.97	0.70		+	+		+					

* n.d.= not determined

Table 2 Exchangeable pool of Cr(VI) ($E_{Cr(VI)}\text{-KH}_2\text{PO}_4$) and Cr(III) ($E_{Cr(III)}\text{-KCl}$) in the solid samples.

Sample type	Sample code	$E_{Cr(VI)}\text{-KH}_2\text{PO}_4$ (mg kg ⁻¹)	SD	$E_{Cr(III)}\text{-KCl}$ (mg kg ⁻¹)	SD
Soils	S1(0-10 cm)	0.74	0.06	<LoD	-
	S1(10-40 cm)	4.43	0.34	0.39	0.02
	S1(80-100 cm)	21.14	2.17	3.69	0.54
	S2(0-15 cm)	4.06	0.30	0.34	0.03
	S2(15-40 cm)	5.39	1.05	0.43	0.01
Lateritic ores	OL1	29.65	2.64	7.49	0.43
	OL2	5.84	0.68	0.57	0.05
	OL3	89.79	1.82	7.30	0.30
	OL4	2.04	0.25	0.25	0.02
	OL5	65.44	5.96	10.46	0.38
	OL6	1.68	0.16	0.20	0.03
	OL7	12.53	0.59	1.15	0.15
	OL8	104.09	7.70	6.56	0.68
Saprolitic ores	OS1	1.31	0.09	0.39	0.02
	OS2	2.46	0.18	0.72	0.08
	OS3	1.27	0.15	0.44	0.13
Sediments	Se1	1.57	0.03	20.89	5.50
	Se2	10.06	1.60	0.62	0.17
	Se3	2.37	1.84	1.49	0.71

*Limit of detection (LoD) Cr = 0.1 mg kg⁻¹

Table 3 Major and trace cations and anions, alkalinity and dissolved organic carbon (DOC) in dissolved fraction of water samples. Suspended particulate matter (SPM) and carbon (C) content in filters. Conductivity, temperature and pH values at time of sampling.

Element		Stream2	Pond1	Pond2	Pond3	Mining area Piezo 1 (before mine)	Piezo 2 (after mine)	Piezo 3 (before smelter)	Piezo 4 (after smelter)	Pristine area Stream1
Major elements (mg L ⁻¹)	K	0.05	0.13	0.32	0.29	0.22	0.16	2.80	1.06	0.02
	Mg	7.99	6.69	13.13	7.25	23.90	20.05	17.21	1.31	11.81
	Ca	0.87	1.28	5.06	1.13	0.67	1.79	31.70	3.36	2.54
	Na	0.25	0.32	0.17	0.43	0.22	0.19	10.11	3.78	0.55
Trace elements (µg L ⁻¹)	Fe	1.09	4.91	3.68	2.16	1.69	0.36	2.20	1.25	242
	Mn	6.17	1.43	<LoD	0.81	0.84	0.09	1.20	79	86
	Al	0.73	0.32	1.42	1.31	7.49	4.37	1.31	0.90	<LoD
	Cr	13	757	58	89	2.39	0.21	1.09	0.16	0.09
	Ni	76	14.21	9.52	7.48	12	0.91	1.96	11.07	37
	Sr	1.91	1.36	2.85	1.26	1.29	2.51	94	8.13	5.23
	Zn	1.60	18	3.87	19	18	0.93	10.57	56	2.78
Anions (µg L ⁻¹)	F ⁻	< LoD	32	61	n.d.	99	60	254	53	< LoD
	Cl ⁻	330	436	1604	n.d.	447	393	820	2990	359
	NO ₃ ⁻	726	3352	353	n.d.	5042	24	419	4007	260
	SO ₄ ²⁻	97	1884	1385	n.d.	729	2441	2986	168	55
δ ⁵³ Cr (‰)		2.10	2.62	3.66	n.d.	n.d.	n.d.	2.18	2.19	2.60
DOC (mg L ⁻¹)		1.66	2.03	2.31	5.48	3.74	4.65	2.94	2.28	1.78
Alkalinity (mg L ⁻¹)		29	15	37	15	50	54	79	11	29.77
SPM (mg L ⁻¹)		3	166	316	176	5	8	8	18	1.08
Particulate Organic Carbon (wt %)		1.6	1.18	0.64	1.13	5.86	5.01	6.51	9.63	3.65
Temperature (°C)		23.3	22.2	26.5	26.1	27.8	25.8	25.3	27.2	24.4
Conductivity (µS cm ⁻¹)		60	58	105.6	62.6	166.7	155	292	48.3	96.2
pH		7.5	7.5	8.3	7.8	7.4	9.2	6.6	5.7	7.4

* Limit of detection (LoD) F⁻ = 20 µg L⁻¹; NO₃ = 20 µg L⁻¹

n.d.= not determined