



The fate of chromium during tropical weathering: A laterite profile from Central Madagascar



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ABSTRACT

We performed a mineral, geochemical and Cr–Sr–Pb isotope study on a laterite profile developed on ca. 540 Ma old tonalitic bedrock in Madagascar with special emphasis on the behavior of chromium during tropical weathering. The observed strong depletions of Ca, Si, and P, and enrichment of Fe and Al, in the soil, relative to bedrock and underlying saprolite, are the characteristic features pertinent to laterites. The enrichment of Fe in topsoil horizon can be correlated with enrichment of P, and the redox sensitive elements Mn and Cr, and indicates redistribution of these elements related to oxidation–reduction processes. The slight scatter of $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{206}\text{Pb}/^{208}\text{Pb}$ values in the profile is one consequence of such redistribution processes. Our results are compatible with a two stage process during alteration: (1) an incipient alteration stage characterized mainly by a pervasive, effective and complete loss of sulfides accompanied by patchy alteration constrained along fissures and cracks, and (2) a main stage of soil formation (actual laterization) with loss of Na, K, Ca, and Si, and accumulation of Fe and Mn relative to the unaltered bedrock. This two stage evolution is also depicted by Cr concentrations and $\delta^{53}\text{Cr}$ values along the studied profile, where the first incipient alteration stage caused a pronounced depletion of Cr particularly hosted by sulfides, and where the second alteration (laterization) led to redistribution and a small increase in Cr concentration in the uppermost portions of the soil profile relative to stage one altered saprolite. This gain in Cr is accompanied by decreasing $\delta^{53}\text{Cr}$ values and can be explained by partial immobilization (possibly by adsorption/coprecipitation on/with Fe-oxy-hydroxides) of mobile Cr(III) during upward transport in the weathering profile. The negatively fractionated $\delta^{53}\text{Cr}$ values measured in the weathering profile relative to the unaltered tonalitic bedrock characterized by a high temperature magmatic inventory Cr isotope signature are consistent with loss of a positively fractionated Cr(VI) pool formed during weathering. The predicted existence of a former, positively fractionated and mobile chromium pool has been experimentally constrained in circumneutral and basic leachates of powdered tonalite bedrock where $\delta^{53}\text{Cr}$ of +0.21 to +0.48‰ was measured. Our results show that mobilization of chromium is effective under highly oxidative conditions, which in well drained sulfide-bearing parent bedrocks potentially lead to both, acid dissolution of sulfide-hosted Cr and redox-promoted mobilization of Cr(VI) from silicates during later stages of weathering under basic pH conditions.

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1. Introduction

Laterization comprises a prolonged process of mechanical and chemical weathering that produces profiles of great variability in thickness, grade, chemistry and mineralogy. Chemical reactions are above all controlled by the mineral composition of the rocks and their physical properties (e.g., porosity), which favor the access of water. The second relevant factor is the property of the water (dissolved constituents, temperature, pH, Eh), which is controlled by the climate, vegetation and the morphology of the landscape. Chemical and mineralogical results have shown that primary minerals are generally not fully dissolved, but

partially transformed into secondary minerals, which are more stable under the intensive weathering conditions. The elements in the primary rock minerals are released and undergo different reactions in aqueous solutions. The elements Na, K, Mg and Ca do not react with other elements and are removed by percolating waters. The initial dissolution is predominantly promoted by a higher acidity (lower pH) of the water. A high percentage of dissolved Si is also removed but much of the released Si reacts with dissolved Al and forms kaolinite. Gibbsite is formed if the concentration of dissolved Si is extremely low due to a very strong drainage. Dissolved Fe is very reactive with hydroxyl ions and upon oxidation forms goethite and hematite which cause the red-brown color of laterites. Thus the dominant process of laterite formation is the residual (or relative) enrichment of Fe and frequently of Al caused by the removal of silica, alkalis and alkaline earth elements. This chemical alteration corresponds mineralogically with the secondary

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formation of goethite, hematite, kaolinite and gibbsite. These minerals together with relicts of partially dissolved quartz usually form the bulk of laterites.

In an attempt to contribute to the discussion regarding the potential use of Cr isotope as a paleo-redox proxy and eventually, as a paleoclimate tracer, we report geochemical data of a weathering profile. Cr mobility and correlated solubility depend mainly on its oxidation state. In this context, the mobility of Cr(VI) in soils and natural waters is much higher than Cr(III) because Cr(VI) forms anionic complexes and more soluble compounds. The oxidation and reduction of Cr in soil and natural water are dependent on the presence of oxidants and reductants (Bartlett and James, 1979). During oxidative weathering of rocks, some Cr(III) is oxidized to Cr(VI) which, at the neutral pH of most meteoric and groundwater, is highly soluble and mobile as the chromate oxyanion (CrO_4^{2-} ; Bartlett and James, 1979, 1988; Oze et al., 2007). The main oxidants of Cr(III) toward Cr(VI) in soils are Mn-oxides (Bartlett and James, 1988). On the other hand, Fe(II) (Buerge and Hug, 1999; Eary and Rai, 1988), organic matter (Wittbrod and Palmer, 1995), and reduced S (Patterson et al., 1997) can reduce Cr(VI). The isotope fractionation of Cr is controlled by its oxidation state (e.g., Ellis et al., 2002; Schauble et al., 2004; Zink et al., 2010). The largest stable isotope fraction is related to such a transition from Cr(III) to Cr(VI). The reduction Cr(III) toward Cr(VI) favor the light Cr isotope, enriching the residual Cr(VI) pool in the heavy isotopes (Døssing et al., 2011; Ellis et al., 2002; Sikora et al., 2008). These are related to the shorter and stronger bonds in CrO_4^{2-} relative to Cr_2O_3 (Schauble et al., 2004). Recent studies have documented temporal trends in the Cr isotope composition of chemical sediments through geological time (Frei et al., 2009). These authors suggested that Cr isotopes are capable of tracking the redox evolution of the Earth's surface.

In order for the Cr isotope proxy to reach its full potential, however, preserved signatures of present and ancient Cr cycling in the Earth's rock record need to be identified and documented, and the mechanisms of Cr release and possible isotope fractionation need to be carefully studied. The presence of heavy Cr isotope signals in banded iron formations requires that Cr(VI) reduction in shallow oceans is quantitative, thus recording the isotopic composition of Cr(VI) produced during oxidative weathering and maintained as Cr(VI) during delivery to the ocean by rivers (Frei et al., 2009).

Understanding of the incipient steps of alteration and weathering is necessary to investigate the changes in chemistry of an outlet over time. These outlet waters will have different element and isotopic compositions dependent on whether they are related to primary alteration- or to subsequent soil formational processes (as already discussed from an experimental point of view for chromium: Wannier et al., 2011; Døssing et al., 2011). In contrast to incipient present day weathering and its effects on the soil/water system, the outlet waters of primary alteration processes are not available and mass budget calculations, in this case with respect to chromium, are not directly possible. Therefore, we investigated an in situ weathering profile including different alteration zones, and used a multi-disciplinary approach to indirectly reconstruct the alteration processes. We envisage that the comparison of (isotope-) geochemical indicators, with the kinetics of mineral weathering should potentially enable the characterization of element transport inherent to different stages of weathering that affected and still affect the alteration of the tonalitic parent rock in the laterite profile studied on Madagascar (Fig. 1).

2. Geological framework

The highlands of Madagascar are built up of basement units, consisting of plutonic and metamorphic rocks of different age (e.g., Berger et al., 2006; Giese et al., 2011; Kröner et al., 2000). Rocks cooled down in Paleozoic times to temperatures corresponding to the apatite partial annealing zone and remained at these temperature levels until recent times (Emmel et al., 2004; Seward et al., 2004). The rocks may

have been exposed at the surface for a longer time and slow erosion may have taken place in this time. The soils as they are present today are typical laterites forming on granitoid rocks. The profile studied here is located in a quarry of tonalite (S20°26'15.7; E47°11'35.1). The parent tonalite is composed mainly of two feldspars, quartz, hornblende, biotite and ilmenite. The magmatic crystallization has been constrained by zircon U/Pb evaporation dating at 554 ± 1 Ma (Kröner et al., 2000).

3. Methods

Whole-rock major element analyses were performed at AcmeLabs using ICP-OES techniques. Trace elements were analyzed by solution ICP-MS (GEUS, Copenhagen; see Kystol and Larsen, 1999). Mineral and aggregate compositions were determined by electron microprobe (EMP) analysis and EMP/LA-ICPMS combinations. Conditions for the EMP measurements were 15 kV and currents between 6 and 60 μA . Natural and synthetic standards are used. Cr has been measured on 2 spectrometers at the same time and counting times of 200 s on peak and background. A LA-ICP-MS system is located at GEUS (Copenhagen) and consists of a New Wave Laser coupled with a Thermo-Elementary2 ICP-MS. The NIST612 has been used as an external standard and NIST614 as a secondary standard.

Pb and Sr isotope ratios were analyzed from separately dissolved powder aliquots (using the same dissolution acids as described above for the trace element determinations) at the Department of Geosciences and Natural Resource Management, University of Copenhagen, using a VG Sector 54 IT mass spectrometer (see Appendix A). The reported errors are within-run (2σ) precisions of the individual runs.

Cr-isotope measurements are done at the Department of Geosciences and Natural Resource Management, University of Copenhagen (see Appendix A). We achieve a 2σ external reproducibility of the $\delta^{53}\text{Cr}$ value with 1.5 μg Cr loads of the NIST SRM 3112a standard on our IsotopX/GV IsoProbeT thermal ionization mass spectrometer (TIMS) $\pm 0.05\%$ with ^{52}Cr signal intensities of 1 V and of $\pm 0.08\%$ for ^{52}Cr beam intensities of 500 mV. Since the double spike correction returns Cr isotope compositions of samples as the permil difference to the isotope composition of the NIST SRM 3112a Cr standard (used for the spike calibration; Schoenberg et al., 2008), to maintain inter-laboratory comparability of Cr isotope data, we recalculated our data of natural samples relative to the certified Cr isotope standard NIST SRM 979 as follows (Eq. (1)):

$$\delta^{53}\text{Cr}_{\text{sample (SRM 979)}} = \left[\left(\frac{^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}}}{^{53}\text{Cr}/^{52}\text{Cr}_{\text{SRM979}}} \right) - 1 \right] \times 1000. \quad (1)$$

For the Cr leaching experiment, aliquots of 2 g of tonalite rock powder each were spiked with an appropriate amount of ^{50}Cr - ^{54}Cr double spike and then 50 ml of 0.2 N HCl, 50 ml of 0.1 N NaOH and 50 ml of MQ water were added to the respective aliquots in a 50 ml centrifugation tube. After 120 h where the suspensions were placed agitated on an automated horizontal shaker, 20 ml of the centrifuged leaching solutions was transferred into respective 27 ml Savillex Teflon beakers and dried on a hotplate. After addition of 1 ml of *aqua regia*, followed by renewed drying and uptake in 1 ml 6 N HCl, the sample solutions were diluted to 0.5 M HCl with MQ water and passed over 8 ml stem volume columns charged with 100–200 mesh AG-50W cation resin. Cr was eluted in 0.5 N HCl in an elution scheme based on the recipe of Trinquier et al. (2008). The procedure yields for Cr in this separation method varied from 70 to 80%, and Cr procedure blanks were in the order of 5–10 ng, which is negligible compared to the amount of chromium separated from the samples studied herein.

The possible loss or gain of elements is investigated using mass balance considerations (Amundson, 2003; Brimhall et al., 1991; Oh

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