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Mobilization and isotope fractionation of chromium during water-rock interaction in presence of siderophores



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ABSTRACT

Chromium mobilization and isotope fractionation during water-rock interaction in presence of the biogenic siderophore desferrioxamine B (DFOB) was studied with batch leaching experiments on chromitite and other igneous oxide and silicate rocks. Siderophores are a group of organic ligands synthesized and excreted by bacteria, fungi and plants to enhance the bioavailability of key nutrients like Fe. However, the DFOB siderophore also has a strong affinity for complexation with other metals such as Cr, U and rare earth elements. Here we show that leaching of rocks in the presence of the hydroxamate siderophore DFOB significantly increased the mobilization of Cr from all investigated rocks and caused an enrichment of the heavier ⁵³Cr isotope in leachates from chromitite ($\delta^{53}Cr_{leach}$ = +0.15 ± 0.087‰ to +2.14 ± 0.042‰) and from altered silicate rock $(\delta^{53}Cr_{leach} = +0.48 \pm 0.07\%)$. In contrast, stable isotope fractionation of Cr was not observed in DFOB leachates of pristine silicate and low-Cr oxide rocks. Leaching in the presence of citric acid significantly enhanced Cr mobility, but did not result in fractionation of Cr isotopes. Chromium isotope fractionation is used in geochemistry as a quantitative proxy for oxidative weathering, because Cr(III) is oxidized to Cr(VI) in presence of MnO₂ and the associated Cr isotope fractionation is commonly linked to the presence of oxygen in the atmosphere. Our findings indicate that the presence of specific biogenic ligands with a high affinity for Cr may also cause Cr isotope fractionation. The presence of biomolecules like siderophores during weathering, hydrothermal alteration or during mineral precipitation, therefore, may put constraints on the applicability of certain trace metals and their isotopes as redox proxies in modern and past environments. The results of our study also suggest that siderophores may have a high potential for (bio)remediation of Cr-contaminated sites and detoxification of contaminated natural waters.

1. Introduction

Chromium occurs as Cr(III) and Cr(VI) redox species in the natural environment. While the former is rather immobile and non-toxic, the latter is mobile and considered toxic (Fendorf, 1995). Under present-day atmospheric conditions, Cr(VI) is the thermodynamically most stable redox species of Cr and, hence, Cr mobility is significantly increased during oxidative weathering. The mobile anionic species are chromate, CrQ_4^{2-} , and bichromate, $HCrO_4^{-}$. The aqueous Cr(VI) species solubilised during weathering enters streams, rivers, and ultimately the ocean (Oze et al., 2007). Chromium is used in a variety of technological applications such as electroplating, dyeing and tanning, and as such, significant quantities are introduced into the environment as a contaminant. The mobile form, Cr(VI), is considered carcinogenic (Kortenkamp et al., 1996) and its input into groundwater and surface

water may have serious effects on flora and fauna. Hence, the remediation of Cr-contaminated soils and natural waters is of utter importance. Remediation relies solely on the *in-situ* reduction of Cr(VI) to immobile Cr(III). Therefore, it is essential to understand the processes and effects that organisms and their extracellular exudates such as metal-specific organic ligands (siderophores/metallophores) and organic acids, have on Cr mobility and Cr oxidation/reduction in the environment. It has also been shown that plants and bacteria may play an important role in cleaning up Cr-contaminated sites by means of biosorption (Owlad et al., 2009; Veglio' and Beolchini, 1997) or microbially-mediated Cr reduction. Chromium can be reduced *in-situ* to Cr (III) by plants (Lytle et al., 1998) as well as by bacteria, algae and fungi (e.g., Basu et al., 2014; Cervantes et al., 2001; Han et al., 2012; Sikora et al., 2008). Bioremediation, therefore, may become an important future technology for remediation of sites contaminated with Cr.

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In aqueous systems, the mobile form, Cr(VI), is isotopically heavier in equilibrium and enriched by about 7% in ⁵³Cr relative to ⁵²Cr (Schauble et al., 2004). Microbial reduction of Cr(VI) to Cr(III) may produce Cr isotope ratios as low as -4.1% in the product of the reduction reaction (Sikora et al., 2008), whilst abiogenic reduction may lead to a Cr isotope fractionation ranging from $-3.91 \pm 0.16\%$ to $-2.11 \pm 0.04\%$ (Basu & Johnson, 2012). In contrast, Cr(III) oxidation may result in Cr isotope ratios in the range of +0.2% to +0.6% in presence of H_2O_2 (Zink et al., 2010) or up to +1% in presence of Mn dioxide (Ellis et al., 2008). The stable Cr isotope system has received considerable interest in the geochemistry community (Qin and Wang, 2017). Stable isotope ratios of chromium can be used as indicators for microbial or abiotic Cr(VI) reduction in groundwater and to trace Cr pollution in ground- and river water (Berna et al., 2010; Economou-Eliopoulos et al., 2014; Izbicki et al., 2012; Wanner et al., 2012). In soil systems, MnO2 usually acts as an important oxidizer for Cr(III) (Kotaś and Stasicka, 2000; Palmer and Wittbrodt, 1991). Deviations of the δ^{53} Cr signal from the bulk Earth ratio in marine chemical and epiclastic sediments and in paleosols are used as proxies for the presence of free oxygen in the Earth's surface system. This may help to evaluate local redox-conditions of ancient environments and the redox-evolution of Early Earth (e.g., Arcy et al., 2016; Babechuk et al., 2017; Canfield et al., 2018; Cole et al., 2016; Crowe et al., 2013; Frei et al., 2016, 2009; Frei and Rosing, 2005; Gilleaudeau et al., 2016; Holmden et al., 2016; Huang et al., 2018; Planavsky et al., 2014; Rodler et al., 2017; Wang et al., 2016). However, the applicability of Cr isotope fractionation as a paleo-redox proxy is largely based on the assumption that oxidative weathering is the sole producer of heavy Cr isotope enrichment in weathering solutions. Recent studies have questioned this assumption. Serpentinization, for example, leads to Cr oxidation even at low oxygen fugacities (Oze et al., 2016) and ligand-promoted dissolution of Cr(III) (hydr)oxides also facilitates significant Cr isotope fractionation (Saad et al., 2017b). Further research, therefore, needs to investigate whether other mechanisms exist, that produce Cr isotope fractionation in anoxic environments where it is commonly attributed to the presence of oxygen.

Here we report on the influence of certain biomolecules, siderophores, on Cr mobilization and Cr isotope fractionation from igneous rocks. Siderophores (also referred to as metallophores; Kraemer et al., 2014) are a group of natural organic ligands produced by a wide range of bacteria, plants and fungi to mobilize and bind trivalent Fe from sparingly soluble mineral structures and thereby increase the bioavailability of the micronutrient Fe. However, several studies have demonstrated that siderophore chelation may also *reduce* metal uptake by bacteria, fungi and plants and hence, siderophores may play a vital role in natural heavy metal detoxification (Braud et al., 2010; Höfte et al., 1993; O'Brien et al., 2014; Teitzel et al., 2006).

Siderophores are ubiquitous in almost all natural environments where organisms produce siderophores as a response to nutrient limitation (Kraemer et al., 2014). Concentrations in seawater are rather low (in the nanomolar range), whereas the highest concentrations are usually found in soils or soil solutions with concentrations up to the millimolar range (Kraemer, 2004; Watteau and Berthelin, 1994). The hydroxamate siderophore used in our study, desferrioxamine B (DFOB), is one of the most abundant and best-studied siderophores. In the modern environment, the biomolecule occurs in many soils (Winkelmann, 1992) and natural waters (Gledhill et al., 2004; McCormack et al., 2003). Besides a high affinity for binding Fe(III), DFOB is also very effective in binding with a range of other highly charged cations. DFOB readily binds and forms strong complexes with, for example, the rare earth elements and yttrium (REY), Mo, V, the platinum group elements and a range of actinides (e.g., Bau et al., 2013; Bouby et al., 1998; Brantley et al., 2001; Christenson and Schijf, 2011; Dahlheimer et al., 2007; Hernlem et al., 1996, 1999; Hussien et al., 2013; Kraemer et al., 2015a, 2015b; 2017; Liermann et al., 2011; Mullen et al., 2007; Ohnuki and Yoshida, 2012). Enhanced mobilization of Cr and Cr isotope fractionation from artificial Cr(III)-Fe(III)-(oxy) hydroxides in the presence of DFOB and oxalic acid was observed and attributed to two different processes: ligand-promoted solubilisation and incongruent dissolution of the starting solid phases during watermineral interaction (Saad et al., 2017a). Stewart et al. (2016) studied the desorptive release of Fe(III) and Cr(III) from goethite by DFOB. Using batch leaching experiments these authors showed that Cr(III) mobilization is significantly increased in the presence of DFOB compared to ligand-free systems, although Cr(III) mobilization was by a factor of 60 lower than Fe(III) mobilization from goethite (Stewart et al., 2016).

Terrestrial cyanobacteria probably have produced organic compounds to accommodate nutrient deficiencies and heavy metal poisoning since at least 2.6 billion years (Liermann et al., 2005; Watanabe et al., 2000). Hence, the impact of organic ligands such as siderophores on trace metal cycling in the critical zone may have been significant since the late Neoarchean.

Organic ligands such as siderophores are capable of altering the trace element signal of igneous rocks during weathering and also of chemical sediments during their deposition (Bau et al., 2013; Kraemer et al., 2017, 2015b; Neaman, 2005). Duckworth et al. (2014) and Stewart et al. (2016) demonstrated that siderophores readily bind Cr and that the stability of Cr(III) complexes with DFOB are comparable to those of Fe(III)-DFOB complexes. Saad et al. (2017a) indicated that Cr (III)-(oxy)hydroxide solids may be resolubilized in subsurface environments due to the presence of microbial exudates such as siderophores. In this article we summarize the results of leaching experiments with DFOB conducted on different Cr-bearing igneous rocks and demonstrate the potential impact of DFOB on Cr mobility and Cr isotope fractionation in the environment.

2. Methods

2.1. Samples and experiments

2.1.1. Rock samples

We chose a range of igneous rocks and minerals for leaching experiments (described in 2.2) in order to assess whether the amount of Cr present and the rock type itself exert controls on siderophore-promoted Cr mobilization and/or may induce Cr isotope fractionation. Detailed information on the studied samples, their bulk rock Cr concentrations and δ^{53} Cr isotope values are provided in Table 1. For convenience, the samples are grouped into two distinct groups, namely *Group I: Silicate Rocks* and *Group II: Oxide Rocks*.

Group I: Silicate Rocks consists of the certified reference material *BHVO-2*, a Hawaiian basalt standard issued by the United States Geological Survey and the ocean island basalt *OIB-Me*. This is a primitive alkali basalt from Mehetia Island, Polynesia, and described as sample Me90-05 in Binard et al. (1993). The core stone sample *CSAF3* is an Archean dolerite collected near Piet Retief, South Africa, and the komatiite samples Kom1 and Kom2 originate from the Pioneer Creek Formation in the Barberton Greenstone Belt, South Africa. The pyroxenite *PYRX* is a Cr-rich, platiniferous ultramafic rock from the Platreef Formation, Bushveld Igneous Complex, South Africa.

Group II: Oxide Rocks consists of Taberg 1 and Taberg 2 which are (titano)magnetites from Taberg volcano, Småland, Sweden, and of a magnetite from the magnetite-apatite deposit at Kiruna, Sweden (sample Kiruna). The magnetite samples Mag 1a and Mag 1b originate from the upper main magnetite layer of the Bushveld Complex in South Africa. The group further comprises chromitites from mafic/ultramafic layered intrusions in Southern Africa. Sample GDCHR1 is a chromitite ore from the Great Dyke Igneous Complex, Zimbabwe, and samples CHR1, BVCHR1 and BVCHR2 are chromitites from the Eastern Bushveld Complex in South Africa.

Except for the spheroidally weathered dolerite, none of the samples are visibly altered. The crushed samples were rinsed with deionized

Table 1

Sample list, chromium concentrations and obtained bulk rock isotope data, analytical errors and number of conducted analyses on sample aliquots (n). Values marked with an asterisk obtained by portable XRF (Bruker S1 Titan, GeoChem Trace Program). Sample OIB-Me was described in detail as sample Me90-05 in Binard et al. (1993).

Group I: Silicate rocksBHVO2Hawaiian Basalt CRM, USGS290-0.120.074OIB-MeOcean Island Basalt, Mehetia Hotspot500-0.170.067CSAF3Spheroidally weathered dolerite, Piet Retief, South Africa2900-0.050.075PYRXBushveld Pyroxenite, Platreef Formation, South Africa55400-0.020.054Kom1Komatiite, Pioneer Creek Formation, Barberton Greenstone Belt, South Africa1220-0.0630.0364Kom2Komatiite, Pioneer Creek Formation, Barberton Greenstone Belt, South Africa1240-0.0870.0562Group II: "Oxider rocksUU-0.0870.0665BVCHR1Chromitite, Bushveld Igneous Complex, South Africa18.87 wt%*0.040.075GDCHR1Chromitite, Great Dyke, Zimbabwe34.1 wt%*-0.030.075GDCHR1Chromitite, Great Dyke, Zimbabwe9.2-0.150.0673Taberg, 1Taberg Titanomagnetite9.2-0.150.0753Vin de Warder Strander Stran	Sample	Description, Locality	[Cr] in mg kg ⁻¹ (* in wt%)	δ^{53} Cr _{bulk} (‰)	+/- 2s	n
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PYRXBushveld Pyroxenite, Platreef Formation, South Africa55400-0.020.054Kom1Komatiite, Pioneer Creek Formation, Barberton Greenstone Belt, South Africa1220-0.0630.0364Kom2Komatiite, Pioneer Creek Formation, Barberton Greenstone Belt, South Africa1240-0.0870.0562Group II: "Oxide" rocksBVCHR1Chromitite, Bushveld Igneous Complex, South Africa20.01 wt%*0.020.065BVCHR2Chromitite, Bushveld Igneous Complex, South Africa18.87 wt%*0.040.075GDCHR1Chromitite, Bushveld Igneous Complex, South Africa32.8 wt%*-0.050.075GDCHR1Chromitite, Great Dyke, Zimbabwe34.1 wt%*-0.030.075Taberg.1Taberg Titanomagnetite9.2-0.150.0673Taberg.2Taberg Titanomagnetite9.2-0.150.0753	CSAF3	Spheroidally weathered dolerite, Piet Retief, South Africa	2900	-0.05	0.07	5
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Taberg_1 Taberg Titanomagnetite 9.2 -0.15 0.067 3 Taberg_2 Taberg Titanomagnetite 9.2 -0.15 0.075 3 Violation Debt Number of Control of	GDCHR1	Chromitite, Great Dyke, Zimbabwe	34.1 wt%*	-0.03	0.07	5
Taberg_2Taberg Titanomagnetite9.2-0.150.0753Mus lawParkenkik ana antika kana fanta fanta7200.0670.0670.067	Taberg_1	Taberg Titanomagnetite	9.2	-0.15	0.067	3
	Taberg_2	Taberg Titanomagnetite	9.2	-0.15	0.075	3
Mag_1a Bushveid, upper main magnetite layer, south Africa 730 -0.098 0.067 3	Mag_1a	Bushveld, upper main magnetite layer, South Africa	730	-0.098	0.067	3
Mag_1bBushveld, upper main magnetite layer, South Africa410-0.1050.0872	Mag_1b	Bushveld, upper main magnetite layer, South Africa	410	-0.105	0.087	2
Kiruna Kiruna Magnetite-Apatite Deposit 0.3 -0.092 0.087 2	Kiruna	Kiruna Magnetite-Apatite Deposit	0.3	-0.092	0.087	2

water, dried and powdered to $< 63 \,\mu\text{m}$ with a Fritsch Pulverisette-6 planetary mill with agate balls and a sealed agate mortar in order to minimize sample contamination. Fine-milling does not represent natural conditions, but in order to demonstrate the principle viability of our hypothesis and to see whether or not siderophores exert any influence on Cr mobility and isotope fractionation, we decided to run the experiments with homogeneously fine-milled material. Bulk decompositions of the powdered rock samples were carried out using a DAS acid digestion system (Picotrace, Germany) following the mixed HF/HClO₄ acid digestion protocol outlined by Dulski (2001).

2.1.2. Leaching experiments

In this study, the DFOB siderophore was used to assess the impact of siderophores on Cr isotope fractionation. It is the best-studied side-rophore to date and easily available in its mesylate form as the drug *Desferal*[®] (Novartis AG) which is commonly used to treat acute and chronic iron overload (Bernhardt, 2007; Nick et al., 2003). The leaching protocol was adapted from Kraemer et al. (2015b).

All batch leaching experiments were conducted in a trace-metal clean environment with acid-cleaned labware. Aliquots of exactly 1 g of the dried and powdered rock samples were weighed out into acidcleaned LDPE (low density polyethylene) bottles. The siderophore solutions were prepared separately with Desferal® and deionized water (DIW). The purity of Desferal® was checked by reagent blank measurements. The trace-element concentrations in pure Desferal® were found to be at least two orders of magnitude lower than the concentrations retrieved in the experiments. Solutions with 1 mM and 10 mM DFOB were prepared and its pH protocolled. The exact amount of siderophore solution matching a 20 g/l solid content was added to the reaction vessels containing the pre-weighed sample powders. These bottles were handshaken for a minute to facilitate dispersion and then placed on a shaker table set at 180 rpm. After 24 h, the samples were removed from the shaker table and the solution was filtered using an acid-cleaned filter tower with a 0.2 µm cellulose acetate membrane filter (both from Sartorius). The reaction vessels were not aired during the leaching experiments and the experiments were run in the dark in order to avoid the unlikely decomposition of organic matter by UV radiation and to avoid Cr photooxidation (e.g., Dai et al., 2010). The leachates were measured for pH and were then acidified with suprapure hydrochloric acid to pH < 2 and stored for later analysis of Cr isotopes (see 2.2) and for REY analysis using a low-resolution quadrupole ICP-MS Perkin-Elmer NexION 300.

Some experiments were carried out as replicates in order to demonstrate the overall reproducibility of the experimental approach and

the analyses. The DFOB experiments on the magnetite Mag1a and on the chromitites GDCHR1, CHR1 and BVCHR2 were carried out twice, those with BVCHR1 three times. The general reproducibility is good with a maximum standard deviation of +0.054 ‰ units from the mean of the replicates. When Cr isotope determination in the siderophore solutions was impossible due to very low concentrations of dissolved Cr, the experiments were repeated at higher DFOB concentration of 10 mM. In order to check whether simple organic acids may produce different effects, we also conducted experiments with 10 mM citric acid (p.a. grade; PanReac AppliChem) instead of DFOB on representative samples from each of the two sample groups. Citric acid is an extracellular exudate and occurs at μM concentrations as a common constituent of many root and soil systems (e.g., Jones, 1998; Rovira, 1969). Control experiments were also conducted with deionized water without any organic ligands or acids. We emphasize, however, that in the absence of organic ligands, Cr is immobile and the Cr concentrations in the leachates are, therefore, much too low for the determination of δ^{53} Cr values for these control experiments. Chromium concentrations in the DI leachates were below the detection limit of the mass spectrometer (ca. 40 ng kg^{-1}).

2.2. Element and isotope analysis

2.2.1. Chromium concentrations and isotopes

Specific volumes of the different leaching solutions were spiked with an adequate amount of a 50 Cr $-{}^{54}$ Cr double spike in 60 ml Savillex vials before evaporation in a Teflon-coated carbon block on a hotplate at 100 °C. The addition of a double spike enables correction of shifts in isotope abundances that might occur during the chemical purification and mass spectrometric analyses of the samples. Our Cr(III) ⁵⁰Cr-⁵⁴Cr double spike is characterized by the following fractional abundances: ${}^{50}Cr = 0.537971$ 52 Cr = 0.035057, 53 Cr = 0.010869, and $^{54}\text{Cr}=0.416103.$ We aimed for a $\text{Cr}_{\text{sample}}/\text{Cr}_{\text{spike}}$ wgt-ratio of approximately 3:1. The dried samples were treated with approximately 1-2 ml of concentrated aqua regia to ensure spike-sample homogenization and dissolution of organic compounds and evaporated again. The samples were then subjected to a three-step Cr purification chromatography to isolate Cr from matrix elements. The dry samples were first redissolved in 1 ml of 6 mol1⁻¹ HCl and poured onto 2 ml bed volume Poly-Prep[®] chromatographic columns packed with 1.5 ml of DOWEX AG-1 \times 8 anion exchange resin (Bio-Rad Laboratories, 100-200 mesh) which retains Fe and allows Cr(III) to pass through. The Cr-containing solution was dried and subsequently re-dissolved in 25 ml of ultrapure water (Milli-Q system) doped with 2-3 drops of concentrated HCl to which 1 ml of a 0.1 mol l⁻¹ (NH₄)₂S₂O₈ solution (Sigma-Aldrich, BioXra, N98%, St. Louis, MO, USA) was added. This step enables oxidation of Cr(III) to Cr(VI). The 60 ml Savillex beakers were sealed and placed into a microwave oven and the solutions were boiled for 1 h using the lowest (i.e. 90 W) energy level to ensure complete oxidation of Cr. After cooling to room temperature, the Cr(VI) containing solutions were passed over the pre-cleaned and re-conditioned 2 ml bed volume Poly-Prep® chromatographic columns packed with 1.5 ml of DOWEX AG-1 \times 8 anion exchange resin (Bio-Rad Laboratories, 100-200 mesh) used for the respective Fe-clean-ups. In these acidic solutions, Cr(VI)-oxyanions stick to the resin, while most other elements (e.g. those with interfering isobaric Cr masses such as V and Ti) form cationic or neutral complexes and are not adsorbed (Bonnand et al., 2011; Frei et al., 2009; Schoenberg et al., 2008). Separation of the matrix elements and the elution of Cr followed the purification procedure described by Schoenberg et al. (2008), with a few modifications. As one of the modifications, matrix elements were eluted from anion resin using 10 ml of 0.1 mol l^{-1} HCl followed by 2 ml of $2 \mod 1^{-1}$ HCl. Cr was then eluted following reduction and collected into 12 ml SavillexTM Teflon beakers with 8 ml of 2 mol l⁻¹ HNO₃, doped with 7 drops of 5% H₂O₂. The samples were subsequently evaporated on a hot plate. The dried samples were re-dissolved in 100 µl of 12 mol l⁻¹ HCl and placed for 5 min on a hot plate to ensure complete dissolution. Subsequently, they were taken up in 2.5 ml of ultrapure water and loaded on polypropylene chromatographic columns (Evergreen Scientific) packed with 2 ml of 200-400 mesh DOWEX AG 50 W x 8 cation exchange resin (Bio-Rad Laboratories), which was preconditioned with $0.5 \text{ mol } l^{-1}$ HCl. This step separates Cr from matrix cations, such as Ca, K, Mg, Na and Mn. The samples were immediately collected in the same 12 ml Savillex™ Teflon beakers. An additional 8 ml of $0.5 \text{ mol } 1^{-1}$ HCl was added to elute the remaining Cr(III) from the resin. Finally, the samples were evaporated to dryness. The cation exchange procedure was adapted from Bonnand et al. (2011) and slightly modified. The procedural Cr yield is approximately 60-70%. These yields compare to those reported by other authors (Bonnand et al., 2011; Trinquier et al., 2008) for comparative procedures. These relatively low yields do not affect the Cr isotope compositions, as we use a double spike for this study. After drying down, the samples were loaded onto Re filaments in a mixture of 1.5 μ l silica gel, 0.5 μ l of 0.5 mol l⁻¹ H₃PO₄, and $0.5 \,\mu$ l of $0.5 \,\text{mol}\,l^{-1}$ H₃BO₃ as described in Frei et al. (2009). The samples were analysed with an IsotopX PHOENIX thermal ionization mass spectrometer (TIMS) at the University of Copenhagen, Denmark. The mass spectrometer is equipped with 8 F collectors, allowing for simultaneous monitoring of ${}^{50}Cr^+$, ${}^{52}Cr^+$, ${}^{53}Cr^+$, ${}^{54}Cr^+$, and of ${}^{49}Ti^+$, $^{51}\mathrm{V^{+}},$ and $^{56}\mathrm{Fe^{+}}$ which allows for isobaric interference corrections of respective Cr masses ⁵⁰Cr⁺ and ⁵⁴Cr⁺ from Ti, V and Fe, respectively.

In the present work, we will use the established δ^{53} Cr notation which expresses the per mil deviation from standard reference material NIST SRM-979, calculated as:

$$\delta 53 \mathrm{Cr} = \left[\frac{\left(\frac{53Cr}{52Cr}\right) \mathrm{sample}}{\left(\frac{53Cr}{52Cr}\right) \mathrm{SRM} - 979} - 1 \right] x \ 1000 \ \% c \tag{1}$$

Repeated analyses (N > 200 analyses) of unprocessed double spiked SRM 979 standard samples yield Cr-isotope values that are slightly offset from the 0‰ value assigned to this standard. We measure $\delta^{53}Cr=0.04\pm0.06\%$ higher on the Phoenix ($^{52}Cr=500\,mV$) relative to the 0‰ certified SRM 979 value. The measured $\delta^{53}Cr$ values of our samples were corrected for this minimal offset.

The δ^{53} Cr notation uses the deviation from a standard material. In order to assess Cr isotope fractionation from bulk rock during leaching, we also employed a Δ^{53} Cr notation, which is defined as:

$$\Delta^{53} \mathrm{Cr} = \delta^{53} C \eta_{each} - \delta^{53} C \eta_{bulk} \tag{2}$$

2.2.2. Rare earth elements and yttrium

The leachates and bulk rock samples were analysed for rare earth elements and yttrium (REY) with a Perkin-Elmer NexION 300 quadrupole ICP-MS at Jacobs University Bremen, Germany. Ruthenium, Re, Rh and Bi served as internal standard elements to account for instrument drift and matrix effects and the certified reference material BHVO-2 (Basalt; United States Geological Survey) was used for quality control of the REY analysis. Background intensities of procedural blanks (acid digestion, DFOB solution, citric acid solution) were at least two orders of magnitude lower than sample intensities for the studied elements. Deviation from published literature values of sample BHVO-2 was < 5% for all reported analytes.

3. Results

3.1. Bulk rock Cr concentrations and $\delta^{53}Cr_{bulk}$

Chromium concentrations in the bulk samples of *Group I: Silicate* rocks are between 290 mg kg⁻¹ and 55400 mg kg⁻¹ and fall between 0.3 mg kg⁻¹ to 34.1 wt.-% for those of *Group II: Oxide Rocks* (Table 1). Most bulk rock samples investigated in this study plot within the very narrow δ^{53} Cr_{bulk} range defined by Schoenberg et al. (2008) for high-temperature Cr (i.e., magmatic Cr, δ^{53} Cr = -0.124% to +0.101%; Fig. 1). Hence, Cr isotopes of the bulk rocks mostly resemble those of primary magmatic rocks.



Fig. 1. Bulk rock δ^{53} Cr, leachate δ^{53} Cr (left plot) and Δ^{53} Cr (right plot) obtained during the conducted leaching experiments. Note that the bulk rocks plot mostly inside the gray-shaded area which marks the extents of the high-temperature Cr isotope inventory (i.e., igneous rocks) (Schoenberg et al., 2008).

Table 2

Chromium concentrations, isotope data and analytical errors of the siderophore and organic acid solutions after leaching of the respective rocks for 24 h on a shaker table at 180 rpm.

Sample	Reagent	Leachate pH after 24 h	[Cr] in mg kg ⁻¹	δ^{53} Cr _{leach} (‰)	+/- 2s	Δ^{53} Cr (‰)		
Group I: Silicate rocks								
BHVO2	1 mM DFOB	7.0	0.0013	n/a	n/a	n/a		
BHVO2	10 mM DFOB	7.0	0.014	n/a	n/a	n/a		
OIB-Me	1 mM DFOB	8.0	0.003	n/a	n/a	n/a		
OIB-Me	10 mM citric acid	4.6	0.08	-0.30	0.10	-0.13		
CSAF3	1 mM DFOB	9	0.02	+0.48	0.07	+0.53		
PYRX	1 mM DFOB	7.9	0.02	-0.05	0.06	-0.03		
Kom1	1 mM DFOB	9.2	0.03	-0.16	0.086	-0.097		
Kom2	1 mM DFOB	9.4	0.09	-0.15	0.081	-0.063		
Kom2	1 mM DFOB Replicate	9.4	0.1	-0.12	0.031	-0.033		
Group II: "Oxide"	rocks							
BVCHR1	1 mM DFOB	8.2	0.07	+0.43	0.09	+0.41		
BVCHR1	1 mM DFOB Replicate 1	7.6	0.05	+0.34	0.082	+0.32		
BVCHR1	1 mM DFOB Replicate 2	not analysed	0.04	+0.30	0.031	+0.28		
BVCHR2	1 mM DFOB	7.9	0.007	+0.16	0.076	+0.12		
BVCHR2	1 mM DFOB Replicate	7.8	0.007	+0.15	0.087	+0.11		
CHR1	1 mM DFOB	8.0	0.10	+2.14	0.042	+2.19		
CHR1	1 mM DFOB Replicate	7.5	0.11	+2.11	0.075	+2.16		
CHR1	10 mM citric acid	2.9	1.4	-0.18	0.058	-0.13		
GDCHR1	1 mM DFOB	7.3	0.03	+0.49	0.056	+0.52		
GDCHR1	1 mM DFOB Replicate	7.8	0.04	+0.50	0.065	+0.53		
GDCHR1	10 mM citric acid	2.9	0.40	-0.11	0.067	-0.08		
Taberg_1	1 mM DFOB	9.8	0.01	-0.071	0.094	+0.079		
Taberg_2	1 mM DFOB	9.5	< d.1.	n/a	n/a	n/a		
Taberg_2	10 mM DFOB	8.2	0.006	n/a	n/a	n/a		
Mag_1a	1 mM DFOB	6.9	0.001	n/a	n/a	n/a		
Mag_1a	1 mM DFOB Replicate	7.2	0.001	n/a	n/a	n/a		
Mag_1b	1 mM DFOB	6.9	0.002	n/a	n/a	n/a		
Kiruna	1 mM DFOB	8.6	0.007	n/a	n/a	n/a		

3.2. Chromium concentrations, $\delta^{53}Cr_{leach}$, $\Delta^{53}Cr$ of leachates

3.2.1. DFOB leachates

The pH of the DFOB leaching solution was 5.5 before the start of the experiments and went as high as 9.8 after 24 h of leaching (Table 2). Leaching of different rock materials lead to different pH values of the solutions after leaching. The pH rose to a circumneutral value of about 7–8 in most experiments. The highest values with pH > 8 were obtained during the komatiite, Taberg and Kiruna DFOB experiments.

Group I: Silicate rocks: Leaching of samples from this group in the presence of DFOB lead to mobilization of Cr from all investigated samples (Table 2). After 24 h incubation time, dissolved Cr concentrations in the leachates (measured solution concentrations; Table 2) were in the range of $1.3 \,\mu g \, kg^{-1}$ (BHVO-2) to $90{-}100 \,\mu g \, kg^{-1}$ (Kom2 and replicate). The leachate of the weathered dolerite CSAF3 was significantly enriched in 53 Cr relative to 52 Cr and shows a positive δ^{53} Cr leach value of $+0.48 \pm 0.07\%$ and a positive Δ^{53} Cr value with +0.53%. The DFOB leachates of the komatilites and pyroxenite show δ^{53} Cr leach values in the range of -0.16 ± 0.086 to $-0.05 \pm 0.06\%$ and negative Δ^{53} Cr values. Cr isotopes could not be quantified in leachates of basalts BHVO-2 and OIB-Me, due to very low Cr leachate concentrations, independent of the DFOB concentration used.

Group II: Oxide rocks: Cr was mobilized to different extents from all of these samples. Leachate concentrations from experiments with Taberg, Bushveld and Kiruna samples range from $1 \,\mu g \, kg^{-1}$ to $10 \,\mu g \, kg^{-1}$ Cr. However, Cr isotopes could only be determined for one leachate of the Taberg_1 titanomagnetite. This leachate shows the lightest δ^{53} Cr_{leach} value of $-0.071 \pm 0.09\%$ of all analysed leachates. Δ^{53} Cr is positive (+0.079‰), but overlaps with bulk rock composition if the error is considered ($\pm 0.09\%$). Here, DFOB leaching apparently produced a solution that is isotopically similar to the bulk source rock. Unfortunately, this is the only non-chromitite sample of *Group II: Oxide Rocks* for which Cr isotope measurement was possible even though the Taberg_2 sample was also treated with 10 mM DFOB.

DFOB leachates of the chromitites are significantly enriched in Cr

relative to the other Group II experiments with concentrations of $7 \,\mu g \, kg^{-1}$ (*BVCHR2*) to $110 \,\mu g \, kg^{-1}$ (*CHR1*). The siderophore leachates of the chromitites are enriched in ⁵³Cr relative to ⁵²Cr and show positive δ^{53} Cr_{leach} values in the range of $+0.15\% \pm 0.087\%$ to $+2.14\% \pm 0.042\%$. Their Δ^{53} Cr values range from +0.11% to +2.19%.

3.2.2. Citric acid leachates

The leachates of the citric acid experiments conducted with OIB-Me, CHR1 and GDCHR1 are enriched in Cr relative to the DFOB leachates, with concentrations ranging from 0.08 mg kg^{-1} to 1.4 mg kg^{-1} . However, the citric acid leachates are similar in their isotopic compositions relative to the respective bulk rocks, with δ^{53} Cr_{leach} values ranging from $-0.11\% \pm 0.07\%$ to $-0.3\% \pm 0.10\%$. Our results suggest that even a comparatively low concentration of citric acid mobilizes significant amounts of Cr from natural rock samples, but leaching in the presence of citric acid does *not* produce a significant Cr isotope fractionation. In comparison, DFOB leaching shows a stronger tendency toward ⁵³Cr mobilization (see Fig. 1).

3.3. Rare earth elements

Kraemer et al. (2015b, 2017) indicated that decoupling of the redox-sensitive lanthanide Ce from its strictly trivalent rare earth element neighbours La, Pr and Nd is observed when pristine igneous rocks are leached in the presence of DFOB. This decoupling is attributed to the oxidation of Ce(III) to Ce(IV) upon leaching in the presence of DFOB (Kraemer et al., 2015b; 2017) and was referred to as the "siderophore redox pump". As heavy Cr isotope fractionation is commonly observed when Cr(III) is oxidized to Cr(VI), we compared our Cr isotope findings to the REY distribution in the leachates. Bulk rock-normalized rare earth element and Y (REY_{BN}) data of the leachates from the present study are shown in Fig. 2 and leachate concentrations are reported in Table 3. REY determination was only possible on DFOB leachates of samples Taberg_1, Taberg_2, OIB-Me, BHVO-2, Kiruna and GDCHR1.



Fig. 2. Bulk rock-normalized REY patterns of the DFOB leachates where REY determination was possible. Note the decoupling of Ce from its LREY neighbours in all leachates, which indicates oxidation of Ce(III) to Ce(IV) during leaching in presence of the DFOB siderophore (Bau et al., 2013; Kraemer et al., 2015b; 2017).

Unfortunately, REY concentrations in the chromitite leachates, except for GDCHR1, were below the detection limit of the utilized mass spectrometer due to very low REY abundances in the chromitite rocks and hence low concentrations in the leachates. Total REY concentrations in the leachates are in the range of 200 ng kg^{-1} to ca. $21.000 \text{ ng kg}^{-1}$ (Table 3). In order to demonstrate REY fractionation caused by the siderophore DFOB, the concentrations were normalized to bulk rock data (Fig. 2). The REY_{BN} patterns exhibit a distinct *positive* CeBN anomaly in all leachates and a depletion of light REYBN relative to middle REY_{BN} and a concave downward pattern between La_{BN} and Sm_{BN}.

4. Discussion

4.1. Chromium mobilization and isotope fractionation in presence of the siderophore DFOB

The Cr concentrations in all DFOB leachates are similar within one to two orders of magnitude despite the fact that chromitites have up to several orders of magnitude higher Cr concentrations than many of the investigated silicate rocks (see Table 1). This suggests that the ligand concentration is the limiting factor for Cr release and not the amount of Cr in the rocks that is available for binding. The highest Cr concentrations in leachates were obtained in the CHR1-DFOB experiments

Table 3

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and in the Kom2-DFOB experiments. However, the fractionation of Cr isotopes is markedly different between both experiments, with positive isotope fractionation and positive Δ^{53} Cr fractionation in the former and no fractionation and only very minor Δ^{53} Cr in the latter. Hence, neither the Cr concentration in the bulk rock nor the amount of Cr solubilised during leaching control Cr isotope fractionation in presence of siderophores.

Siderophore-promoted dissolution of silicate minerals has been demonstrated by, for example, Buss et al. (2007) and Liermann et al. (2005). These studies showed that siderophores are very efficient in dissolving silicate minerals, although dissolution proceeds at a lower rate than that of oxides. This is corroborated by the smaller amount of Cr mobilized from most pristine silicate rocks compared to chromitites observed in this study.

Fractionation of Cr isotopes from bulk rock values during leaching in the presence of DFOB appears to some extent be limited to rocks in which Cr is bound to oxide or hydroxide minerals. No significant isotope fractionation was observed during leaching of pristine silicate rocks. As all experiments were conducted under the same (atmospheric) conditions, oxygen fugacity can be ruled out as a significant control on DFOB-promoted Cr isotope fractionation. Therefore, other mechanisms must exist that induce Cr stable isotope fractionation during leaching from "oxide" rocks, but which do not cause fractionation when pristine silicate rocks are leached. From the group of silicate rocks, the strongly altered dolerite is the only one that produced a ⁵³Cr-enriched solution after it was leached with DFOB. We suggest that the observed heavy isotope fractionation is related to the presence of secondary mineral phases. Upon weathering, parts of the original mineral assemblage in a pristine rock are decomposed due to chemical, physical and biological processes. Olivine and pyroxene are among the first minerals to decompose during oxidative weathering (Goldich, 1938) and secondary minerals form, which are mostly clay minerals as well as (hydr)oxide minerals. High field-strength elements, i.e. trace metals with high ionic potentials liberated during weathering, are bound to these minerals due to sorption. As indicated above, siderophores are highly efficient in the dissolution of (hydr)oxide minerals (Akafia et al., 2014; Kraemer, 2004; Saad et al., 2017a). Present-day weathering occurs under oxidized conditions and secondary minerals could be enriched in $^{53}\mathrm{Cr}$ due to Cr redox reactions associated with oxidative weathering and Cr fixation in secondary minerals. Hence, a preferred dissolution of these secondary (hydr)oxides and a resolubilization of Cr by DFOB may explain the heavy Cr isotope fractionation in the dolerite experiment.

Interaction of siderophores with Cr has been studied by, for example, Duckworth et al. (2014) and Stewart et al. (2016). They indicated that complexes of Cr(III) with DFOB have stabilities close to

Sample	Taberg_1	Taberg_2	BHVO2	GDCHR	Kiruna	OIB-Me (Kraemer et al. 2015b)
Reagent	1 mM DFOB	1 mM DFOB	10 mM DFOB	1 mM DFOB	1 mM DFOB	1 mM DFOB
Analyte $[ng kg^{-1}]$						
La	34	370	150	3.4	1670	460
Ce	4870	6200	4230	80	15800	11400
Pr	96	410	230	5.1	640	610
Nd	750	2160	1630	30	1800	3070
Sm	340	530	692	11	170	890
Eu	160	275	215	3.1	11	230
Gd	410	540	840	10	n.d.	800
Tb	57	78	130	1.2	14	110
Dy	350	430	760	8.2	81	600
Y	1930	2140	3450	40	860	2400
Но	71	89	140	1.5	22	94
Er	200	260	370	4.5	82	220
Tm	28	37	50	0.4	15	24
Yb	170	250	290	3.7	120	150
Lu	26	40	40	0.4	29	18

those of Fe(III) and estimated stability constants of around log $K_f = 30$. Stability constants of metals with the hydroxamate siderophore DFOB (Hernlem et al., 1996) and with the carboxylate siderophore rhizoferrin (Duckworth et al., 2014) increase with increasing ionic potential of the complexed metal. Therefore, the oxidized form of a metal has significantly higher stability constants with those two siderophores than its reduced form. Reasoning from this observation, Kraemer et al. (2015b) suggested an oxidative mobilization in the presence of DFOB for the redox-sensitive heavy metals Ce and U, a mechanism referred to as the "siderophore-redox pump" (Bau et al., 2013; Kraemer et al., 2015b). It is still unclear whether the DFOB siderophore actively or passively facilitates the oxidation of these redox-sensitive trace metals upon complexation.

Desferrixoamine B is able to directly oxidize Fe(II) to Fe(III), also under strictly anaerobic conditions (Farkas et al., 2003, 2001). At least one of its hydroxamate functional groups is herein reduced to an amide (Eq. (3); Farkas et al., 2001, 2003):

$$2Fe^{2+} + 3H_4DFOB^+ = 2[Fe(HDFOB)]^+ + H_3DFOBmonoamide^+ + H_20 + 4H^+$$
(3)

Oxidation of trivalent Ce to Ce(IV) was also suggested during mobilization of REY, during fluid-rock interaction, or during precipitation of chemical sediments in the presence of DFOB (Bau et al., 2013; Kraemer et al., 2017, 2015b). DFOB is a hydroxamate siderophore which contains three hydroxamate functional groups and past studies indicated that hydroxamate acids are also able to oxidize other redoxsensitive elements like Mo and V (Brown et al., 1996), Rh (Das et al., 2002) and U (Smith and Raymond, 1979).

All DFOB leachates produced in the study presented here exhibit positive Ce_{BN} anomalies (Fig. 2), regardless of whether oxide or (pristine) silicate rocks were leached. It is evident from Fig. 2 that all leachates for which REY concentrations could be determined, show decoupling of redox-sensitive Ce from its non-redox-sensitive, strictly trivalent REY neighbours. This supports previous results for igneous and pyroclastic material (Bau et al., 2013; Kraemer et al., 2015b). Such a decoupling of Ce from its REE neighbours can only be explained by the formation of Ce(IV) species in solution during leaching in presence of DFOB. If trivalent, Ce would, without exception, behave similar to its strictly trivalent REE neighbours La and Pr, also in presence of siderophores. If Ce(III)-DFOB complexes dominated the redox-speciation of Ce in solution, the corresponding REY_{BN} leachate pattern would be flat between La_{BN} and Pr_{BN} and no Ce_{BN} anomaly could have developed. This is incompatible with what is observed in our experiments (Fig. 2). A striking question is why Ce is oxidized in all such experiments, while Cr stable isotope fractionation is limited to leaching of some oxide rocks and weathered silicate rocks. It may be assumed that in analogy to Ce, trivalent Cr is oxidized to Cr(VI) upon siderophore-rock interaction, similar to the oxidation observed during Fe- and Ce-DFOB interaction. However, using x-ray absorption spectroscopy (XAS), Cr(III)-DFOB complexes were shown to form upon leaching of Cr(III)(OH)3 in presence of DFOB (Duckworth et al., 2014). This suggests that DFOB does not promote oxidation of Cr(III) upon solubilisation and ligand-binding. Additionally, the dominant aqueous Cr(VI) species is $Cr(VI)O_4^{2-}$, which results in a different siderophore binding mechanism compared to Ce(IV) and Fe(III), where Ce(IV)- and Fe(III)-DFOB complexes may form rather easily (see e.g., Kraemer et al., 2014; Ozaki et al., 2006). Therefore, other, non-redox-related mechanisms may be responsible for the observed stable isotope fractionation.

Redox-independent isotope fractionation in presence of DFOB was described for Fe (Brantley et al., 2004, 2001; Dideriksen et al., 2008; Morgan et al., 2010) and for Cu (Ryan et al., 2014). A study by Saad et al. (2017b) showed that siderophore and organic acid leaching of artificial Cr(III)-(oxy)hydroxide solids leads to isotope fractionation of dissolved Cr in the range of δ^{53} Cr = +1.23 to -0.27‰, which is similar to the fractionation range observed in all our leachates. Redox-

independent isotope fractionation may occur by one or a combination of several of the following mechanisms:

- (a) Non-redox related Cr isotope fractionation may be caused by kinetic fractionation effects (Babechuk et al., 2018). Here, lighter isotopes are preferentially released from mineral surfaces, but the fractionation is a function of the size of the reactive surface sites and occurs only in the initial stages of a dissolution process (Wiederhold et al., 2006). However, light isotope enrichment was not observed in our experiments with DFOB and citric acid.
- (b) Stable isotope fractionation during leaching may also occur due to incongruent dissolution of polymineralic rocks comprised of minerals that show different isotope ratios. This was shown for Fe (Chapman et al., 2009) and Mo (Voegelin et al., 2010) and recently also for Cr isotopes by Novak et al. (2017), who report a certain δ^{53} Cr isotope fractionation due to incongruent weathering of ultramafic rocks.
- (c) Equilibrium stable isotope fractionation may occur due to different bonding environments between the metal-ligand complex in solution and metal-ligand complexes sorbed to the mineral surface (Wiederhold, 2015). Strong binding ligands, i.e. ligands with high stability constants with the complexed metal, may cause enrichment of heavy isotopes in solution (Criss, 1999). According to Saad et al. (2017a), equilibrium stable isotope fractionation in combination with incongruent dissolution of the starting material lead to the observed Cr isotope fractionation during leaching of artificial Cr (III)-bearing oxyhydroxides. The enrichment of heavy Cr isotopes in solution, therefore, is then caused by the stronger Cr(III)-oxygen bonds in the ligand compared to the Cr(III)-oxygen bonds in the solid (Saad et al., 2017b).

In our experiments, equilibrium stable isotope fractionation must have controlled the isotope fractionation to some extent simply due to the very high complex stability constants of the DFOB siderophore with Cr in the range of log $k_f = 30$ (Duckworth et al., 2014). The different trends in isotope fractionation in the DFOB experiments, however, cannot solely be explained by this process. In most natural rock samples, Cr is polymodally distributed as a trace element over several mineral phases. Novak et al. (2017) present δ^{53} Cr of whole rocks as well as mineral separates of serpentinite and (altered) peridotites and show that especially the minerals chlorite, hornblende and albite are enriched in ⁵³Cr relative to ⁵²Cr. Serpentinite mineral separates, on the other hand, yield δ^{53} Cr isotope variations in the range of -0.29 to +0.4 (Novak et al., 2017). Therefore, each mineral phase in a natural rock sample may have a markedly different Cr isotope composition. The chromitites studied here are mainly composed of (Mg-)chromite (> 95%) and to lesser extents olivine, pyroxene and anorthitic feldspar. As δ^{53} Cr of the bulk rock is unfractionated relative to bulk Earth, we assume that the mineral chromite, which is the major constituent of chromitite, is also unfractionated in δ^{53} Cr relative to bulk Earth. However, the DFOB leachates of the chromitite rocks are significantly enriched in ⁵³Cr, indicating that either i) the mobilized Cr originates from a⁵³Cr-enriched mineral phase (which is not chromite) and/or ii) that Cr was liberated from isotopically unfractionated chromite and the observed isotope fractionation is the result of equilibrium isotope fractionation.

The siderophore DFOB, therefore, may enhance Cr transport into solution and may cause, depending on the rock type, Cr isotope fractionation. Citric acid, on the other hand, leads to an elevated mobilization of Cr compared to DFOB, but the pH suggests that proton-promoted dissolution is prevalent and the solutions are not fractionated in their Cr isotope compositions relative to bulk rock δ^{53} Cr values. Our findings confirm the experimental results of Saad et al. (2017b), which indicate lack of significant isotope fractionation during leaching in presence of citric acid as well as in presence of other organic acids.

4.2. Implications for (paleo-)environmental studies

The widespread use of Cr as an alloy and in electroplating, tanning and dyeing introduces large amounts of Cr into the environment and, hence, Cr can become a serious anthropogenic pollutant (Cervantes et al., 2001; Kotaś and Stasicka, 2000). In terms of toxicity, Cr⁶⁺ is generally considered the most toxic redox-species because of the production of free radicals in living cells during reduction of Cr⁶⁺ to lower oxidation states (Cervantes et al., 2001; Kadiiska et al., 1994). However, Cr³⁺ can also be detrimental to living cells, albeit at higher concentrations than Cr⁶⁺ and via a markedly different uptake mechanism (Skeffington et al., 1976). Dissolved Cr levels of river water are on average 0.7 ug kg^{-1} (Gaillardet et al., 2003) and seawater Cr concentrations are 0.156 µg kg⁻¹ in the open ocean (Bruland and Lohan, 2004). However, river water can be highly enriched in Cr if Cr-processing industries are located in the river catchment. For example, up to 1.46 μ g kg⁻¹ Cr were found in waters of the river Mouttas, Algeria, downstream of a large tannery (Leghouchi et al., 2009). This highlights the need for efficient remediation techniques to clean up ground and river waters and contaminated soils. Cervantes et al. (2001) discuss bioremediation of Cr in detail. Bioremediation of Cr has only been investigated at a lab-scale and is to date not done at a larger scale. The high affinity of siderophores for Cr in general suggests that siderophores are, in principle, viable for the remediation of Cr-contaminated soils and surface waters. Remediation of Cr-contaminated sites usually involves a reduction of Cr(VI) to Cr(III), efficiently immobilizing Cr. However, by means of immobilizing DFOB, e.g. via sorption to clay minerals (Maurice et al., 2009), or by using siderophores for metal removal from contaminated soil as indicated for other heavy metals (Frazier et al., 2005; Nair et al., 2007), remediation of Cr-contaminated sites might be feasible. This opens the venue for future, yet more detailed, studies. Some plants are able to hyperaccumulate Cr (Baker and Brooks, 1989) and the presence of organic ligands like oxalic acid and malate enhances the accumulation of Cr in plants (Srivastava et al., 1999). Siderophores may play a similar, yet more element-specific role in enhancing bioavailability due to their affinity towards highly-charged ions with small ionic radii (high ionic potential) and especially due to their affinity for redox-sensitive trace elements. However, this could not be observed in a most recent study of the potential role of siderophores during REE uptake by the bolete mushroom Suillus luteus (Zocher et al., 2018).

Chromium isotopes are also increasingly used as a paleo-redox proxy (Crowe et al., 2013; Frei et al., 2009, 2016; Planavsky et al., 2014; Gilleaudeau et al., 2016). Other redox-sensitive elements such as Ce and U (Bau and Alexander, 2009; Bau and Dulski, 1996; Kamber et al., 2014; Kendall et al., 2013; Nakada et al., 2016; Partin et al., 2013; Schier et al., 2018; Viehmann et al., 2016, 2015) or Mo (Anbar et al., 2007; Asael et al., 2013; Duan et al., 2010; Kurzweil et al., 2015; Voegelin et al., 2010) are also used as geochemical proxies to evaluate the evolution of the redox level of the Earth's surface environments throughout geological history. However, biogenic ligands were probably produced since at least the Mesoproterozoic (Neaman, 2005; Raven, 1995). Past studies on the interaction of DFOB with Mo reported enhanced Mo mobilization rates as well as an enrichment of heavy Mo isotopes in solutions containing DFOB (Liermann et al., 2005, 2011). Hence, hydroxamate siderophores are also capable of facilitating stable isotope fractionation of other redox-sensitive elements like Mo and supposedly also V, also under strictly anaerobic conditions. As biogenic ligands, especially hydroxamate siderophores, may affect the mobilization and isotope fractionation of certain trace elements, the potential availability of siderophores in these past environments needs to be considered before redox-sensitive elements and their isotopes may be used as robust quantitative paleo-redox proxies. Siderophores and their unique capabilities in binding highly-charged metals may also have a huge potential for a better understanding of the geobiological evolution of Early Earth and the appearance of the earliest life on Earth and in our solar system.

5. Conclusion

The presence of the DFOB siderophore during leaching leads to mobilization of Cr(III) from igneous rock samples and stable Cr isotope fractionation. DFOB-enhanced mobilization is not limited to the redoxsensitive trace elements Ce and U (Kraemer et al., 2017, 2015b; Tanaka et al., 2010 and others), but also affects the redox-sensitive heavy transition metal Cr. Chromium isotopes are fractionated upon leaching with DFOB. These findings further improve the understanding of how redox proxies in modern and ancient environments work and how to evaluate the geochemical interpretation of redox-sensitive elements in geochemical archives. In modern oxidized environments, MnO2 is responsible for Cr oxidation and the isotope fractionation associated with the oxidation process (Kotaś and Stasicka, 2000). In anoxic systems, however, H_2O_2 is able to promote Cr oxidation (Oze et al., 2016). Our findings indicate that the presence of specific organic ligands with a high affinity for Cr are also able to fractionate Cr isotopes, supposedly also under anoxic conditions. This supports the findings of Saad et al. (2017b) and expands the database on Cr-DFOB interaction to natural rock samples.

Stable isotope fractionation as well as the reported mobilization/ fractionation of redox-sensitive elements like Ce, Cr and U, but also of other elements like Mo, V, and W could also act as potential "fingerprints" for the presence of biogenic compounds in rocks and soils and may thus serve as proxies for the presence of "life" in the sense of *biosignatures*. However, this definitely requires further research and any such statements made are premature unless the whole system is understood in detail.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.01.007.

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