Mobility of High-Technology Metals in Earth’s Surface Environment:
A Study on Siderophore-Promoted Mobilization and Implications for the Extractive Hydrometallurgy of some Critical Metals

by

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Statutory Declaration

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Summary

This study addresses the influence of siderophores on the geochemical behavior of critical metals in rocks, ores and aqueous solutions. Rare earth elements and Y, the platinum group elements as well as other high field strength elements such as Zr, Hf, Th and U are presently referred to as high technology metals with many of them classified as critical metals. These critical metals are facing a distinct supply risk due to high production concentration and/or processing issues but are, however, essential for the development of state-of-the-art industries. Today’s industries rely on a steady supply of these metals for their economic development and the industry’s demand as well as the linked anthropogenic input of these metals will likely increase significantly in the near future.

Siderophores are produced by a variety of microbes and plants in Fe-deficient environments to solubilize sparingly soluble Fe. However, siderophores also complex a range of other polyvalent metal ions. This study elucidates the mechanisms and the geochemical implications behind leaching with the hydroxamate siderophore desferrioxamine B (DFOB) and focuses on the siderophore-promoted mobility of ‘immobile’ high field strength elements. The second goal of this thesis was to elaborate to what extent siderophores can be used for processing and extraction of high technology metals from mineralogically complex ores like oxidized Platinum Group Element (PGE) ores or deep-sea ferromanganese nodules and crusts.

Leaching of rocks and particle-rich aqueous solutions with siderophores leads to a significant mobilization of the ‘immobile’ high field strength elements like rare earth elements, Zr, Hf, Th and U and to distinct features in REY patterns. Bulk-rock normalized REY patterns of leaching solutions with DFOB showed a very distinct positive Ce anomaly and a depletion of La and other light REY relative to the middle REY, with a concave downward pattern between La and Sm. The “siderophore redox pump” that is first described in this thesis leads to a preferential enrichment of redox-sensitive Ce and U relative to redox-insensitive dissolved LREY and Th during siderophore leaching due to changes in the redox equilibrium and preferential complexation of oxidized species by DFOB. The observed fractionation patterns and decoupling of Ce and U by siderophore-induced oxidation might be helpful in constraining the presence of siderophores or chemically similar metal-specific organic chelating agents present during weathering and might be used as a bio-proxy for paleoenvironmental research.
Furthermore, a leaching process was developed and is presented in this thesis that uses siderophores for the extraction of Pt and Pd from oxidized (weathered) Platinum-Group Element (PGE) ores of the Great Dyke, Zimbabwe. Current mining operations focus on the recovery of PGE from pristine and unweathered ore material from the Main Sulfide Zone (MSZ). The oxidized PGE ores are currently not mined, because recoveries using conventional processing techniques render this uneconomic. The data presented in this study indicates chemical extraction of Pt and Pd at alkaline conditions as (Pt,Pd)HDFOB and/or (Pt,Pd)H₂DFOB⁺ complexes. Up to 80% Pt were mobilized using the developed leaching process. Siderophores also represent viable reagents for the hydrometallurgical extraction of high technology metals from ferromanganese nodules and crusts. Deep-sea ferromanganese deposits contain a wide range of high technology metals and are considered an important future resource, but extraction techniques, especially with respect to high technology metals, are still not established. The data on leaching of ferromanganese nodules and crusts presented in this thesis showed that the high technology metals Li, Mo, Zr, Hf, Nb and Ta are significantly extracted using siderophores, whilst base metals are not mobilized to large extents.

This study highlights the importance of siderophores for the mobility and fractionation of certain high technology metals in the environment. The data presented in this study shows that siderophores like desferrioxamine B not only enhance the solubility and mobility of Fe(III), but also strongly enhance the mobility of 'immobile' high field strength and highly siderophile elements such as the rare earth elements, Zr, Hf, Th, U and Pt and Pd. Additionally, siderophores or similar specific metal-binding organic ligands have a promising potential in future processing technologies of oxide deposits like those investigated in this study.
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1. Introduction

1.1. Objectives

The research presented in this thesis focuses on the impact of siderophores, a group of biogenic complexing agents, on the mobility and fractionation of certain high technology metals from rocks, ores and aqueous solutions. Amongst others, the here studied rare earth elements and Y (REY), the platinum group elements (PGE) as well as other high field strength elements (HFSE) like Zr, Hf and U are nowadays referred to as high technology metals and many of them are classified as critical metals. These critical metals are facing a distinct supply risk due to high production concentration or processing issues but are, however, essential for the development of state-of-the-art industries focusing on the production of electronic devices such as smartphones, wind turbines, catalytic converters and nuclear reactors. Today’s industries rely on a steady supply of these metals for their economic development and the industry’s demand as well as the linked anthropogenic input of these metals will likely increase significantly in the near future (e.g., Angerer et al., 2009).

Siderophores are produced by a variety of microbes and plants in oxic environments to cope with iron deficiency (Neilands, 1957). Iron is an essential micronutrient and under atmospheric conditions predominates as Fe$^{3+}$. Thus, Fe is immediately bound to insoluble oxyhydroxide structures and thus not available for metabolism by organisms and plants. Siderophores help organisms and plants to obtain bioessential nutrients like Fe by facilitating the dissolution of oxide and oxyhydroxide minerals and solubilizing Fe as a Fe-siderophore complex. It has been shown in several studies that siderophores do not only have high complex stability constants and thus preferentially complex with Fe$^{3+}$, but also bind with a range of other di-, tri- and tetravalent metal ions: Siderophores have high formation constants with the rare earth elements (Yoshida et al., 2004; Christenson and Schijf, 2011; Tircsó et al., 2013), the platinum group elements (Normand and Wood, 2005; Dahlheimer et al., 2007) and high field strength elements like Zr, Hf (Yoshida et al., 2007) and certain actinides (Bouby et al., 1998; Mullen et al., 2007). Despite all the work that constrains the efficient siderophore-complexation of these metals, the majority of studies to date have focused on the interaction of siderophores with specific single minerals, i.e. various oxides and hydroxides (Cheah et al., 2003; Kraemer, 2004; Duckworth and Sposito, 2007; Reichard et al., 2007), silicates (Liermann and Kalinowski, 2000; Brantley et al., 2001) and sulfides (Cornejo-Garrido et al., 2008). Only a few studies have investigated the influence of siderophores on trace metal
leaching from actual rocks, i.e. solid aggregates of several minerals occurring in the natural environment (e.g., Liermann and Kalinowski, 2000).

In order to draw conclusions on the fate of trace metals in the environment, it is essential to understand the mechanisms and processes that drive the mobilization and fractionation of these metals during organic ligand complexation from actual rocks as well as aqueous solutions like river water, seawater and ground- and porewaters. Organic acids and organic ligands produced by various microbes, fungi and plants have long been recognized as having tremendous impacts on rock and water trace metal geochemistry (see e.g., Neaman et al., 2005). The presence of organic ligands, and especially of siderophores as these are highly effective in binding many of the high technology metals, can efficiently alter the trace metal signature of rocks, of percolating solutions and of surface waters. Siderophores may thus have an influence on, for example, certain geochemical proxies like Ce anomalies as indicators for the redox state of a geochemical system, the fractionation of geochemical twins or isotopic systems like Hf-Nd for tracing changes in the continental weathering regime (Bau and Koschinsky, 2006; van de Flierdt et al., 2004, 2007; Viehmann et al., 2013). This study elucidates the mechanisms and the geochemical implications behind leaching of rocks and rock particles with siderophores and focuses on the mobility of ‘immobile’ HFSE, i.e. the REY and the HFSE Zr, Hf, Th and U, from igneous and sedimentary rocks and particle-rich aqueous solutions. One of the goals of this thesis is to shed some light onto this rarely researched field of geo-siderophore interaction. The question addressed is how and to what extent siderophores are affecting the mobilization behavior and the fractionation of these metals in the environment. Are specific trace metal signatures (i.e. REY patterns, geochemical twin fractionation) typical for geo-siderophore interaction? Can these signatures be used as proxies for the presence of siderophores? What is the implication of the potential siderophore-promoted mobility of ‘immobile’ HFSE on geochemical tracers and proxies?

The second goal of this thesis is to elaborate the extent to which siderophores, sole or in combination with other (in)organic acids, can be used for the processing and the extraction of high technology metals from mineralogically complex ores. The supply risk of some high technology metals is intensified by inadequate processing technologies due to a complex host mineralogy and/or peculiar chemical behavior during (hydro-)metallurgical processing. Given that siderophores have a high tendency to bind and mobilize many high technology metals, it seems reasonable to assume that siderophores might have sound applications in the fields of ore processing and/or (hydro-)metallurgy. Therefore, the second part of this thesis focusses on
the development of two hydrometallurgical techniques for efficiently extracting high technology metals by using siderophores.

1.2. **Structure of thesis and outline**

The thesis is structured into five main chapters as outlined in the Table of Contents. These chapters are (1) an introduction, the published papers and manuscripts in a chronological succession with a focus on (2) geochemistry and (3) hydrometallurgical appliances and (4) concluding remarks as well as an outlook for prospective research. The thesis ends with (5) a chapter on thesis-related scientific work that is not already addressed within the manuscripts and/or publications. The peer-reviewed publications and the manuscripts each consist of an abstract, an introduction covering scientific background information and literature, a detailed methods description, the results, a discussion, a conclusion and the references. For convenience, the references for the whole thesis are also given in chapter 6.

The introductory chapter gives a general overview of the research goals and the field of study. It outlines the importance of the subject matter and the general structure of the thesis. The important terms used throughout the thesis are defined and scientific background and a state of research are presented on the fields of high technology metals research, siderophores, their intrinsic chemical properties and the implications for the geochemistry of trace metals.

The second chapter features three manuscripts with a focus on the siderophore-promoted mobility and fractionation of high technology metals in the environment. This chapter specifically addresses the interaction of the abundant and naturally occurring siderophore desferrioxamine B (DFOB) within river water, experimental aqueous solutions and geologic material like igneous rocks. The first manuscript was published in 2013 in the journal “Earth and Planetary Science Letters” and covers experimental results on the siderophore-promoted mobilization of rare earth elements (REE) from volcanic ash-rich glacial meltwaters from Iceland. We showed that the presence of siderophores significantly leaches rock particles present in the suspended load of natural melt waters and thus enhances the dissolved concentrations of REE in melt waters. Furthermore, leaching in presence of siderophores creates distinct REE patterns which are unique for leaching with siderophores and which cannot be produced with deionized water or other chemical reagents. The second study in this chapter covers the results of siderophore leaching experiments conducted on a
variety of igneous rocks. Here, it was found that siderophores not only enhance the solubility of REY in experimental batch leaching experiments with rocks, but they also promote oxidative dissolution of Ce and U and cause significant mobilization and to some extents fractionation of the Y-Ho and Zr-Hf element pairs. The third study covers experimental results for experiments where REY were scavenged by precipitating Mn (hydr)oxide in the presence of the siderophore DFOB. In siderophore-free scavenging experiments, the lanthanoid Ce is oxidized by Mn (hydr)oxides from Ce(III) to Ce(IV) during scavenging, thus an anomalously high enrichment of Ce (‘positive Ce anomalies’) on Mn (hydr)oxide is observed in such experiments due to a decoupling from its strictly trivalent REY ‘neighbors’. However, our study shows that if the siderophore DFOB is present in the experimental solution during scavenging, negative Ce anomalies, i.e. a depletion of Ce relative to its REY neighbors, are observed on the Mn(hydr)oxides and Ce is detained from scavenging onto the particles. The heavy REY (HREY) are also detained from scavenging and remain in the siderophore-bearing solution, contrary to what is observed in siderophore-free experiments. This has implications for the development of specific REY patterns in (hydr-)oxide minerals and might explain the fractionation of light REY (LREY) from HREY in organic- and Mn-rich natural waters, where these features have been observed.

The third chapter focusses on the application of siderophores in the fields of ore processing and hydrometallurgy. The previous chapter and other studies showed that siderophores significantly enhance the solubility and form aqueous complexes with a number of HFSE that are largely considered as immobile. Many HFSE are nowadays used for high technology appliances and are classified as critical for a vital economic development. It is thus reasonable to assume that siderophores may have a certain use and function for the metallurgical extraction of these and similar elements from complicated (hydroxide-) ore matrices which in fact are from a metallurgical point of view difficult to process. The first publication in this chapter was published in early 2014 in the journal *Applied Geochemistry* and covers experimental results on the phase associations and the potential extraction of high technology metals from deep-sea ferromanganese nodules and crusts. We could show that bulk leaching of deep-sea ferromanganese precipitates with siderophores leads to selective solubilization of many high technology metals such as Li, Zr, Hf, Mo and W, whilst major constituting phases remain intact and are not leached significantly. The second manuscript in this chapter is about siderophore-promoted extraction of Pt and Pd from oxidized PGE ores of the Great Dyke in Zimbabwe and was published in early 2015 in the journal *Hydrometallurgy*. In collaboration with colleagues from the Bundesanstalt für Geowissenschaften und Rohstoffe
(BGR) in Hannover, we developed a hydrometallurgical leaching technique using siderophores for the efficient extraction of Pt and Pd from these ores. Although there are large resources of oxidized PGE ore material available at the Great Dyke, dissatisfactory recoveries of Pt and Pd from these deposits with today’s processing techniques render this “multi-million dollar worth” ore deposit uneconomic. We developed a technique that includes a leaching step with the siderophore DFOB with which the recovery of Pt can be increased to up to 80%, bringing this type of high technology metal deposit one step closer to economically sound exploitation. This manuscript is the result of two research projects conducted for the “Bundesanstalt für Geowissenschaften und Rohstoffe” (BGR) in Hannover and the “Deutsche Rohstoffagentur” (DERA) in Berlin.

The fourth chapter is a conclusion on the results of this study and gives an outlook for prospective research in the field of geo-siderophore interaction and potential hydrometallurgical applications of siderophores.

1.3. Siderophores and high technology metals: a current state of research

1.3.1. Siderophore chemistry, metal coordination, complexation and implications for trace metal geochemistry

In this study, the mobilization behavior of high technology metals from rocks, ores and aqueous solutions in leaching solutions containing chelating agents, known as siderophores, was investigated.

Siderophores, derived from the greek words *sideros* and *pherein* for iron carrier, are ferric iron specific low molecular weight organic chelating agents produced by bacteria and plants in a wide range of natural environments. Siderophores are produced under Fe-deficient conditions to solubilize Fe and make it available for biological metabolism. Under atmospheric conditions, Fe is rapidly oxidized from ferrous Fe(II) to ferric Fe(III) and immediately forms rarely soluble Fe (hydr)oxide minerals. The amount of bioavailable Fe in the oxic environment is very limited and concentrations are in the range of $10^{-18}$ M (Wang et al., 2014). However, almost all living organisms and plants need Fe as a micronutrient since it plays an important role in many cellular functions such as DNA synthesis, respiration and detoxification (Aguado-Santacruz et al., 2012).
In environments with limited amounts of bioavailable Fe, many plants and microbes excrete siderophores to solubilize Fe (Neilands, 1957; Haas, 2003). Siderophores are not only produced by terrestrial microorganisms and plants (Schwyn and Neilands, 1987), but also by marine organisms like phytoplankton (Trick et al., 1983). Velasquez (2011) states that siderophores are potential driving factors controlling primary productivity in the oceans. Several studies have shown that siderophores and similar Fe-specific organic chelators are important in enhancing the bioavailability of Fe in seawater and play an important role in the biogeochemical cycling of Fe in the oceans (e.g., Reid et al., 1993; Rue and Bruland, 1995; McCormack et al., 2003; Gledhill et al., 2004; Mawji et al., 2008; Amin et al., 2012).

Ahmed and Holström (2014) published a review on the role of siderophores in environmental research and stated that siderophores are promising reagents for many biotechnological applications like bioremediation, degradation of petroleum hydrocarbons, nuclear fuel reprocessing and many more.

Siderophores are produced by bacteria, fungi and plants alike. Siderophores produced by microbes and fungi are known as microbial and fungal siderophores, whilst siderophores excreted by plants are referred to as phytosiderophores (Crowley et al., 1991). These ligands are chemically classified into three families based on the functional groups which take part in the complexation of the metal. These families are hydroxamate, catecholate and α-hydroxy-carboxylate siderophores (Winkelmann, 1991).

Whilst the majority of microbial siderophores are catecholates, pure hydroxamate and α-hydroxy-carboxylate microbial siderophores do exist in nature. Some also contain a mix of structurally diverse functional groups (Cornelis, 2010). The metal can be complexed in a linear, tripodal or cyclic coordination. The microbial uptake and exact transport mechanism varies depending on the type of bacteria. The Fe(III)-siderophore complex is transported to the cytoplasm where the ligand-complexed Fe(III) is released from the complex structure by enzymatic reduction of trivalent Fe to divalent Fe (e.g., Crowley et al., 1991; Ardon et al., 1998). Transport mechanisms in fungi also comprise intracellular transport and enzymatic reduction but extracellular release of Fe at the cell membrane is also common (van der Helm and Winkelmann, 1994). Phytosiderophores are mainly produced by graminaceous plants (Kraemer, 2004). The first described and most abundant phytosiderophore is mugineic acid (Takemoto et al., 1978). Ligand exchange of microbial Fe-siderophore complexes with phytosiderophores has been described by Masalha (2000) and appears to be an important mechanism used by organisms and plants for Fe acquisition in oxidized environments.
Organic acids like oxalate have been reported to act as ion shuttles for siderophores and significantly enhanced dissolution rates have been observed in experiments where both low molecular weight organic acids and siderophores were present (Reichard et al., 2007).

According to Kraemer (2004), important parameters for metal acquisition are the affinity and specificity of siderophores for the complexed metal. An important parameter expressing this affinity is the stability constant $K$ of a complex. $K$ is an equilibrium constant for the formation of a complex in solution and is calculated as

$$K = \frac{[ML]}{[M][L]}$$

where $[M]$ is the concentration of the metal, $[L]$ is the corresponding ligand concentration and $[ML]$ is the concentration of the metal-complex in solution based on the reaction

$$M_{(aq)} + L_{(aq)} \leftrightarrow ML_{(aq)}$$

Stability constants for Fe(III)-siderophore complexes are between $K=10^{23}$ and $10^{52}$ (Albrecht-Gary and Crumbliss, 1998) and are significantly higher compared to the stability constants of Fe with organic ligands like oxalic acid ($10^8$) and citric acid ($10^{12}$) (Perrin, 1979). In this study, the hydroxamate siderophore desferrioxamine B (DFOB; Fig. 1) was used because it is one of the most abundant and best studied microbial siderophores. Desferrioxamine B has a 1:1 stability constant with Fe(III) of $K = 10^{30.6}$ (Martell and Smith, 2001). Its mesylate salt is marketed as the drug Desferal® because its high affinity to Fe makes it an ideal drug for treating acute iron poisoning and chronic iron overload in humans. Desferrioxamine B for medicinal uses is commonly produced by the actinobacteria Streptomyces pilosus but is also produced synthetically (Miller, 1989).
1. Introduction

Fig. 2: Chemical structure of a metal $M^{3+}$ and the hydroxamate siderophore desferrioxamine-B. The complexed metal $M^{3+}$ is shown in red. The blue components are the hydroxamate groups each made up of a hydroxylamine group (-NOH). Each hydroxamate group forms a five-membered ring with $M^{3+}$, thus stabilizing and fixing the trivalent metal in a hexavalent coordination sphere. The terminal amine is shown in green. For trivalent metal species, the terminal amine does not participate in coordinating the central metal. However, at high pH the amine can be deprotonated and then takes part in metal complexation. The chemical structure shown here was modified after Reichard, 2005 and Albrecht-Gary and Crumbliss, 1998.

Fig. 3: Speciation curves for DFOB as calculated by HySS2009 modelling using stability constants of Martell & Smith (2001, Table 1; I=0.1, T=25°C).
Most siderophores are like DFOB hexadentate ligands and thus completely satisfy the preferred inner coordination sphere of the iron atom. Desferrioxamine B contains three hydroxamate functional groups as shown in Fig. 2. The fourth ionizable group, the terminal amine, does not deprotonate except at high pH (Hernlem et al., 1999) and is thus usually not involved in metal complexation. The deprotonation of DFOB is pH dependent as is shown in the speciation model in Fig. 3. At low pH, DFOB is almost exclusively present in the fully protonated form $\text{H}_4\text{DFOB}^+$ (Fig. 1), where all hydroxamate functional groups as well as the amine are protonated. Upon increasing the pH, the hydroxamate functional groups are deprotonating, while the amine group deprotonates lastly and only at very high pH. Note that every hydroxamate functional group that binds to Fe(III) forms a five-membered ring with the central metal atom and, depending on the pH, releases a proton upon binding (Fig. 4).

![Fig. 4: Formation of a five-membered ring for Fe$^{3+}$ with a hydroxamate functional group of the ligand desferrioxamine B (DFOB). After Albrecht-Gary and Crumbliss (1998).](image)

The dissolution of metal (hydr-)oxides by siderophores is mostly a ligand-promoted dissolution mechanism, although reductive mechanisms as a result of electron transfer between surface metal and the adsorbed ligand have been suggested as well (Kraemer, 2004; Akafia et al., 2014). Ligand-promoted dissolution has been described by (Furrer and Stumm, 1986) to occur in three dependent steps. The ligand is rapidly adsorbed on the (hydr)oxide surface by exchange of hydroxyl surface groups and binding of the ligand to the surface site. Iron, bound tightly in the oxide structure, is released by slow weakening of the bonds due to changing the electron density (Ludwig et al., 1995). This polarization facilitates the detachment of the metal from the (hydr)oxide structure (Reichard, 2005). In a last step, the detached metal is complexed with the ligand and transported to solution. The (hydr)oxide site is restored by adsorption of protons (Reichard, 2005). Siderophores are not only enhancing the dissolution rate of iron (hydr)oxides (e.g., Hersman et al., 1995; Reichard et al., 2007), but also facilitate dissolution of other mineral structures like Mn and Co (hydr)oxides (Duckworth and Sposito, 2007; Akafia et al., 2014; Duckworth et al., 2014), clay minerals
like smectite and other silicates (e.g., Liermann and Kalinowski, 2000; Neubauer et al., 2000; Brantley et al., 2001; Rosenberg and Maurice, 2003; Duckworth and Sposito, 2005; Maurice et al., 2009; Duckworth et al., 2014) and even sulfide ore minerals like arsenopyrite and galena (Cornejo-Garrido et al., 2008).

Siderophore complexation and mobilization is not limited to Fe. Kiss and Farkas (1998) state that the affinity of DFOB towards a metal is positively correlated to the tendency of the metal to hydrolyze. Thus, DFOB and other siderophores also form strong and stable complexes with a range of other di-, tri-, tetra- and even hexavalent metals. Complex stabilities for these metals with siderophores are mostly higher than with conventional organic acids. Tetravalent metal DFOB stabilities increase with pH by transitioning from $\text{M(IV)(H}_2\text{DFOB)}^{3+} \rightarrow \text{M(IV)(HDFOB)}^{2+} \rightarrow \text{M(IV)(DFOB)}^+$ as shown by Yoshida et al. (2005), for example, for the tetravalent heavy metal Th. Many of these elements are considered as critical metals, which makes siderophores the ideal study target for assessing the bio-promoted mobilization of these metals in the geologic environment. Dahlheimer et al. (2007) showed that the presence of DFOB significantly enhances the dissolution rates of Pt and Pd oxides and that DFOB forms very stable complexes with Pt and Pd. DFOB also efficiently complexes the REY and a wide range of other environmentally important trace metals (Kiss and Farkas, 1998; Christenson and Schijf, 2011). Yoshida et al. (2007) demonstrated very effective DFOB complexation with tetravalent Hf. Brainard et al. (1992) and Wollf-Boenisch and Traina (2007) showed that DFOB may have a significant influence on the mobility of radioactive actinides like U and Pu, whilst Bouby et al. (1998) showed that siderophores also efficiently complex Th. An overview of complex stability constants of DFOB with selected metals is given in Table 1. While Fe(III) forms the most stable complexes with DFOB, Hf(IV)-HDFOB$^{2+}$ stability constants are estimated to be as high as Fe(III)HDFOB$^+$ stability constants (Yoshida et al., 2007). Among the elements commonly incorporated into common rock-forming minerals, Al forms quite stable complexes with DFOB, but is usually fixed in relatively stable silicate structures. Calcium, Mg and other large ion lithophile elements (LILE) only have very low stability constants and thus siderophore complexation of these metals probably does not play a significant role in the natural environment.
Table 1: Reactions and formation constants for the protonation of the siderophore Desferrioxamine B (DFOB) as obtained from Martell & Smith (2001).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log $\beta_{298}$; I=0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$DFOB^{3-} + H^+ \leftrightarrow HDFOB^{2-}$</td>
<td>10.84</td>
</tr>
<tr>
<td>$HDFOB^{2-} + H^+ \leftrightarrow H_2DFOB^-$</td>
<td>20.39</td>
</tr>
<tr>
<td>$H_2DFOB^- + H^+ \leftrightarrow H_3DFOB$</td>
<td>29.37</td>
</tr>
<tr>
<td>$H_3DFOB + H^+ \leftrightarrow H_4DFOB^+$</td>
<td>37.69</td>
</tr>
</tbody>
</table>

Table 2: Stability constants of various cations with the siderophore desferrioxamine B (DFOB) with $K = [\text{MHL}] / [\text{M}][\text{HL}]$ at an ionic strength of I=0.1. Elements studied here are marked in bold.

<table>
<thead>
<tr>
<th>Cation</th>
<th>log $K_f$</th>
<th>Temp.</th>
<th>I</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>30.17</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Hf(IV)</td>
<td>~Fe(III)</td>
<td></td>
<td></td>
<td>Yoshida et al. (2007)</td>
</tr>
<tr>
<td>VO(II)</td>
<td>29.66</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Ga(III)</td>
<td>28.17</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Al(III)</td>
<td>24.14</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Bi(II)</td>
<td>&gt;23.5</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>21.14</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>In(III)</td>
<td>20.6</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>19.2-23.2</td>
<td>25°C</td>
<td>0.1</td>
<td>Dahlheimer et al. (2007)</td>
</tr>
<tr>
<td>U(VI)</td>
<td>17.12-22.93</td>
<td>25°C</td>
<td>0.1</td>
<td>Mullen et al. (2007)</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>16.2-17.2</td>
<td>25°C</td>
<td>0.1</td>
<td>Dahlheimer et al. (2007)</td>
</tr>
<tr>
<td>Ce(IV)</td>
<td>&gt;&gt;15.9</td>
<td></td>
<td></td>
<td>e.g. Bau et al. (2013)</td>
</tr>
<tr>
<td>REY(III)</td>
<td>10.1-15.9</td>
<td>25°C</td>
<td>0.1</td>
<td>Christenson &amp; Schijf (2011)</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>15.7</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>14.12</td>
<td>20°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Be(II)</td>
<td>11.3</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>10.9</td>
<td>20°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Co(II)</td>
<td>10.31</td>
<td>20°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>10.07</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>10</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>7.88</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>7.2</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>4.3</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>2.64</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>2.2</td>
<td>25°C</td>
<td>0.1</td>
<td>Martell &amp; Smith (2001)</td>
</tr>
</tbody>
</table>
1. Introduction

1.3.2. High technology metals and their importance for key industries

This study assesses the siderophore-promoted mobility of certain high-technology metals in the natural environment and the implications on the hydrometallurgical extraction of some of these elements from complex mineral structures using siderophores. These are the high field strength elements (HFSE) Zr, Hf, Th and U, the rare earth elements and Yttrium (REE+Y; REY) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, as well as the platinum group elements (PGE) Pt and Pd. An introduction to these elements is given in the next chapter, while this chapter emphasizes why these elements are important for the world economic development and why research in the field of high technology metal geochemistry and hydrometallurgy combined is of significant interest.

In the last decade a range of commodities gained strong economic and scientific importance. These commodities are clustered under synonymous terms, such as high-technology metals, strategic metals and critical metals. While the term ‘high-technology metal’ strongly refers to the high-technology applications these metals are used for, the term ‘critical metal’ refers to a certain importance for a vital economic development. The term ‘strategic metal’ on the other hand implies that the corresponding metal is of strategic importance and thus implies an importance not only for a vital economy, but also for the national defence of a country (i.e. metals needed for armament industry etc.). This term for example also includes Fe. Although the terms mentioned above are widely used nowadays as synonyms, the term ‘high-technology metal’ is used in this thesis because almost all elements studied here have a distinct application in the high-technology industry.

According to these terms, the defined elements face a restricted and vulnerable supply on the global market. Geological scarcity is usually not a problem for the supply of these metals; instead, changes in the geopolitical and economic framework are much more relevant for assessing the criticality of these commodities. In 2008, the European Union started the program “Raw Materials Initiative (RMI) – meeting our critical needs for growth and jobs in Europe” with the aim of defining critical raw materials for the EU economy and to foster research in this field. Within the scope of this initiative, an ad-hoc working group of the European Commission published a report on defining critical raw materials (European Commission Enterprise and Industry, 2010), which was enhanced and updated by a new “Report on critical raw materials for the EU” in May 2014 (European Commission Enterprise and Industry, 2014). In 2014, 20 raw materials were identified to be of critical importance to
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the EU economy (Table 3). The term ‘raw material’ is used within these reports because not only the criticalities of metals were investigated. The report also covers criticality studies of industrial minerals (i.e. phosphate rock) and some biotic materials (i.e., natural rubber). As shown in Fig. 5, the criteria by which critical metals are allocated from non-critical metals are on the one hand the economic importance for the EU and the industry, that is, the intrinsic value of a metal for the economy. The second factor, the supply risk, comprises political-economic stability of producing countries (‘country governance’), the level of production concentration, a critical metal’s potential for substitution and the recycling rate of the commodity (European Commission Enterprise and Industry, 2010).

![Diagram of EU criticality methodology](image)

**Fig. 5:** Scheme of EU criticality methodology (European Commission Enterprise and Industry, 2014).

**Table 3:** List of critical raw materials as identified by the ad-hoc working group of the European Commission (modified after European Commission Enterprise and Industry, 2014). Note that commodities of importance for this study are marked bold.

<table>
<thead>
<tr>
<th>Antimony</th>
<th>Beryllium</th>
<th>Borates</th>
<th>Chromium</th>
<th>Cobalt</th>
<th>Coking coal</th>
<th>Fluorspar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td>Germanium</td>
<td>Indium</td>
<td>Magnesite</td>
<td>Magnesium</td>
<td>Natural Graphite</td>
<td>Niobium</td>
</tr>
<tr>
<td><strong>PGEs</strong></td>
<td>Phosphate Rock</td>
<td><strong>REEs</strong> (heavy)</td>
<td><strong>REEs</strong> (light)</td>
<td>Silicon metal</td>
<td>Tungsten</td>
<td></td>
</tr>
</tbody>
</table>
Critical raw metals are commonly characterized as metals or elements which supply chain lacks quality or consistency and thus are subject to high fluctuations in either price and/or market availability. Within the group of critical raw metals are elements with industrial applications in the high-technology sector. With regard to mining operations, only some of these metals are actually primary products and have mostly their own production infrastructures, for example to some extents the PGE and the REY, many others are recovered as by-products or co-products and marketing of these is entirely in the hands of the refining industry and/or the producing countries if these have a quasi-monopoly in production. In recent years, the REY have been a very prominent example of how important a steady and invulnerable supply is for the development of markets and industries. These metals have many applications in a wide range of industries, especially among industries with a focus on green technology such as e-mobility (batteries and electric motors) and renewable energies (wind turbines) (Humphries, 2010). They are extensively used as automotive and industrial catalysts and for the production of energy-efficient lighting and LC- and LED-displays. The REY are used independently of each other, as a mixture or as an additive to alloys and chemicals (Golev et al., 2014). A summary of the global uses of REY is given by Schüler et al. (2011). Angerer et al. (2009) estimates that due to a strong increase in REY use by emerging technologies such as green energy, the demand especially of HREE including Y will increase tremendously. China announced at the end of 2010 to restrict its REY exports by 72% (e.g., Milmo, 2010; Service, 2010). In 2014, the People’s Republic of China was close to being the sole producer of HREE (99%) and with 87% of the LREE total production a significant amount of the worldwide production of light rare earth elements also originated from China (European Commission Enterprise and Industry, 2014). The situation in production concentration was even worse in 2010 with China producing about 97% of the total rare earth element world production (BGS, 2013). Thus, solely as a result of the announcement of export restrictions in 2010, there followed an average market price increase for Ce oxide of nearly 400% from 20.17 US-$/kg in 2010 to 98.44 US-$/kg in 2011 (Babies et al., 2012). It is important though to note that in 2014 the price for Ce oxide was almost down to the 2010 price level because of ongoing efforts of other countries to mine REY and because China increased, or had to increase, the export quota of rare earth’s again (e.g., Yap, 2013). However, the market for REY is still considered as vulnerable because of the high production concentration. This is an illustrative example of how important a low production concentration is and how vulnerable the supply and market prices are for such commodities. The supply risks faced with rare earth elements are expressed by the monopoly of China in all
stages of REY production including mining, hydrometallurgical processing and refining (Golev et al., 2014).

For many critical high technology metals, the lack of appropriate processing techniques renders many deposits uneconomic. The PGE are considered as critical metals by the European Union (European Commission Enterprise and Industry, 2014) as stated above. In South Africa and Zimbabwe, mining is technologically limited to pristine, (‘fresh’) PGE ores. However, oxidised or weathered PGE ore deposits of the Great Dyke in Zimbabwe and of the Bushveld Complex in South Africa contain relatively high PGE grades and have very large resource estimates (see Prendergast, 1988; Hey, 1999; Oberthür et al., 2012). They are high tonnage low grade supergene ore deposits extending to maximum depths of about 15 to 30m, so that low-cost open-cast mining of large volumes and/or heap leaching appears to be feasible. For the oxidized PGE ores of the Great Dyke alone, resource estimates range from 160 to 250 Mt of oxidized material (Oberthür et al., 2013) with average grades of 3 to 5 ppm Pt. This equals to about 480 to 1250 tonnes of Pt metal present in oxidised zones of the Great Dyke. The oxidised resources available in the Bushveld Igneous Complex probably even exceed those of the Great Dyke. The pristine materials mined at the Great Dyke and in the Bushveld region are treated following conventional metallurgical practice and recovery grades for Pt of more than 85% are reached (Rule, 1998). However, all metallurgical tests conducted so far on oxidised ore material both from the Great Dyke as well as from the Bushveld suffer from very low Pt recoveries of considerably less than 30% (Oberthür et al., 2013). The low recoveries and thus the current economic inefficiency leads to the simple fact that these vast and physically easily extractable resources of critical metals (PGE) are currently not exploited.

In the event of shortages, regardless of these being caused by contraction of supply or expansion of demand, there will be a severe limiting effect on the development of key high-tech industries, eventually leading to a forced use of substitute metals with potentially less efficiency (if there are any viable possibilities for substitution at all). This is extremely unfortunate if vast deposits of certain high technology elements are known such as the aforementioned oxidised PGE deposits or deep-sea manganese nodules and crusts which cannot be exploited for high technology metals due to inadequate processing technologies.

It is thus of paramount importance to better understand the geochemical behaviour of these metals in the natural environment and to further assess the mobility of these elements which may be promoted by naturally occurring complexing agents such as siderophores as
these compounds may therefore represent viable reagents for the extractive metallurgy and processing of high technology metals.

1.3.3. Investigated elements

The following paragraphs briefly summarize the specific characteristics, the chemistry and geochemical behavior of the elements investigated in this study. This chapter is subdivided into a paragraph covering the high field strength elements (HFSE) investigated here, i.e. the lanthanide series including Y and the elements Zr, Hf, Th and U and another paragraph covering the platinum group elements (PGE). The most economically important deposit types, the host minerals in the distinct deposits and to some extents ore processing and hydrometallurgy are described in greater detail where appropriate for the scope of this study.

High field strength elements are by definition elements with ions having a charge greater than or equal to 3 and effective ionic radii between 70 pm and 110 pm (Best, 2003). The HFSE are characterized as incompatible elements with respect to most rock-forming minerals, i.e. have a partition coefficient D<<1 and thus cannot readily substitute other (major) elements in crystalline phases because their ionic charge and/or their ionic radius are too large. The HFSE are usually enriched in late-crystallizing phases and are among the first elements mobilized during partial melting. HFSE are further characterized in aqueous solutions by high particle reactivities and hence, concentrations in natural waters are usually low due to

Fig. 6: Diagram of ionic charge vs. ionic radius (in Å) showing the classification of positively charged ions of major and trace elements. Rare earth elements in center of diagram are plotted on an expanded scale in the upper right area. LILE are represented by the left polygon, HFSE are clustered in the right polygon (modified after Best, 2003).
scavenging of HFSE on minerals like Fe and Mn oxyhydroxides. The rare earth elements and Y (REY), the geochemical twins Zr-Hf, Nb-Ta and the actinides Th and U belong to the group of HFSE. Fig. 6 gives an overview of the HFSE and the relationship to other elements like the large-ion lithophile elements (LILE), the geochemical counterpart to HFSE, which are strongly lithophile and can easily substitute other major ions in mineral structures.

**Rare earth elements**

Rare earth elements are a group of chemically coherent elements and consist of the lanthanide elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and yttrium (Y). Promethium is radioactive and its most stable isotope, $^{145}$Pm, has a radioactive half-life of only 17.7 years. Thus, Pm does not occur in nature in significant amounts and is omitted in geochemical diagrams by showing a gap in the patterns. In mineral deposit research and mining, the rare earth elements are commonly subdivided into the light REY (LREY), which include La through Sm and the heavy REY (HREY), which include Eu through Lu and Y (Golev et al., 2014).

![Diagram demonstrating the lanthanide contraction](image)

**Fig. 7:** Diagram demonstrating the lanthanide contraction. Note the significant difference in ionic radii for tetravalent Ce and divalent Eu from their trivalent counterparts. This figure nicely depicts why Y is commonly associated with the HREY and is a geochemical twin to Ho (Bau and Dulski, 1995). After Gupta and Krishnamurthy (2005).

However, there is no common classification for grouping the lanthanide series; in geochemistry, the use of three groups, i.e. light REY (LREY), medium REY (MREY) and heavy REY (HREY), is also common (see e.g., Koeppenkastrop and De Carlo, 1992; Bau,
In this study the ‘geochemical’ classification for grouping of the REY is used and the REY are subdivided into three groups as stated above.

In low temperature environments, REY occur exclusively as trivalent ions with the exception of Ce, which may occur as Ce$^{3+}$ and Ce$^{4+}$. Based on the progressive filling of the 4f-orbital, the ionic radii decrease with increasing atomic mass (Shannon, 1976) from 103 pm for La to 86.1 pm for Lu. This observation is commonly referred to as the lanthanide contraction (see Fig. 7). The isovalent REY$^{3+}$ thus show similar charge and radius-controlled behavior. However, some REY are redox-sensitive and can be oxidized or reduced. The associated change in the ionic radii and charge leads to the fractionation of individual REY from their REY neighbors or from the whole REY series. This is commonly observed for Ce which can be oxidized from Ce$^{3+}$ to Ce$^{4+}$. Many of these geochemical anomalies have been identified in past and recent works and are used, for example, as a proxy for different geochemical systems or, in the case of Ce, as a proxy for redox conditions. Cerium fractionation has been described to occur mainly due to oxidation of Ce$^{3+}$ to Ce$^{4+}$ by Mn and Fe (hydr)oxide minerals during scavenging in aqueous solutions such as seawater (e.g., Bau and Koschinsky, 2009). This oxidative scavenging of Ce onto (hydr)oxide mineral surfaces in oxic environments leads to the formation of negative Ce anomalies or depletion of Ce relative to REY neighbors, in the water column and positive Ce anomalies in the precipitating minerals (enrichment of Ce relative to REY neighbors). A contrary observation with enrichment in seawater relative to the precipitates was made for Y. Yttrium is not redox-sensitive, but can be fractionated from its geochemical twin Ho in seawater due to a less strong binding of Y on particle surfaces relative to other REY including Ho (e.g., Bau and Dulski, 1995; Bau, 1999). The contribution of covalent bonding varies with the electron configuration of an element, which leads to a less stable binding of Y on particle surfaces. Another prominent example for REY fractionation is Eu. Europium is, like Ce, also redox-sensitive and can be reduced from Eu$^{3+}$ to Eu$^{2+}$ at elevated temperatures and under reducing conditions such as in igneous and high temperature hydrothermal systems. Eu can thus be decoupled from its neighbors accordingly. Due to the larger ionic radius of divalent Eu, it can substitute strontium or calcium in alkali feldspar and plagioclase minerals and leave the residual melt in a Eu deficient state, thus creating a geochemical anomaly.

Rare earth elements are abundant in the continental crust with concentrations ranging from 350 ppb (Tm) up to 60 ppm (Ce) (Wedepohl, 1995). Although named rare earth elements, they are not rare at all and are e.g. at least 140 times more abundant in the
continental crust than gold (Wedepohl, 1995). However, the REY are rarely found concentrated in economically exploitable deposits. Among the 250 known REY-bearing minerals (Kanazawa and Kamitani, 2006), only a handful of minerals are currently mined and economically exploited. According to Golev et al. (2014), these are:

- Bastnaesite \((\text{Ce,La})(\text{CO}_3)\text{F}\)
- Monazite \((\text{Ce,La})\text{PO}_4\)
- Xenotime \(\text{YPO}_4\)
- Loparite \((\text{Ce, Na, Ca})(\text{Ti,Nb})\text{O}_3\)
- Apatite \((\text{Ca, REE, Sr, Na, K})_3\text{Ca}_2(\text{PO}_4)_3(\text{F,OH})\)

Bastnaesite, monazite and xenotime are by far the most economically important REY minerals with only xenotime incorporating significant amounts of HREE (Jordens et al., 2013).

Rare earth elements occur in primary as well as in secondary deposits. The most dominant source of REY are carbonatites (Jackson and Christiansen, 1993). Carbonatites form from deep-seated magmas rich in \(\text{CO}_2\). REY-bearing carbonatites are tied to greater depths, because the proximity to the surface would lead to a degassing of the magma and thus would prevent REY enrichment (Jackson and Christiansen, 1993). Carbonatite ores are mainly enriched in LREE in the form of bastnasite, allanite, apatite and minor monazite. Other important REY ore deposit types are pegmatites and hydrothermal deposits. The latter are of increasing importance because they are enriched in HREE with mostly xenotime as REY mineral. Secondary deposits are mainly placer type deposits with monazite and xenotime as main minerals. Ion-adsorption clay deposits are residual deposits of weathered granites and genetically closely related to laterites (Kanazawa and Kamitani, 2006). Here, the REY are not related to specific minerals, but are adsorbed as ions on the surface or interlayers of clay minerals. Currently, the only known economically viable deposit is located in Southern China (Kanazawa and Kamitani, 2006). Ion-adsorption clay deposits contain very low grades, but due to the simple processing, i.e. in-situ leaching and cation exchange, are one of the most economic deposit types as the REY are already liberated and loosely sorbed onto clays as ions (Kanazawa and Kamitani, 2006).

The rare earth elements are mainly used as auto catalysts, as petroleum refining catalysts and in electromagnets. Major end uses as reported by Humphries (2010) are the use in phosphors for displays such as those incorporated in TVs, smartphones, laptops and tablet
PCs. In recent years, the REY faced an increased demand from the field of renewable energies and electric-powered engines. Table 4 shows a comprehensive list of major end uses of the single rare earth elements as obtained from Humphries (2013).

<table>
<thead>
<tr>
<th>Light REY</th>
<th>Major end use</th>
<th>Heavy REY</th>
<th>Major end use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>Hybrid engines, metal alloys</td>
<td>Terbium</td>
<td>Phosphors, permanent magnets</td>
</tr>
<tr>
<td>Cerium</td>
<td>Auto catalyst, petroleum refining, metal alloys</td>
<td>Dysprosium</td>
<td>Permanent magnets, hybrid engines</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>Magnets</td>
<td>Erbium</td>
<td>Phosphors</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Auto catalyst, petroleum refining, hard drives, headphones, hybrid engines</td>
<td>Yttrium</td>
<td>Red color, fluorescent lamps, ceramics, metal alloy agent</td>
</tr>
<tr>
<td>Samarium</td>
<td>Magnets</td>
<td>Holmium</td>
<td>Glass coloring, lasers</td>
</tr>
<tr>
<td>Europium</td>
<td>Red color for displays</td>
<td>Thulium</td>
<td>Medical x-ray units</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Magnets, contrast agent</td>
<td>Lutetium</td>
<td>Catalysts in petroleum refining</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ytterbium</td>
<td>Lasers, steel alloys</td>
</tr>
</tbody>
</table>

### Zirconium and hafnium

The transition metals Zr and Hf and the actinides Th and U are like the REY classified as high field strength elements. Zr and Hf are both isovalent and occur as Zr(IV) and Hf(IV). The continental crust abundances as reported by Wedepohl (1995) are 203 ppm (Zr) and 4.9 ppm (Hf). They have effective ionic radii of 72 pm and 71 pm and due to the similar charge and ionic radii, Zr and Hf are regarded as geochemical twins sharing many physical and chemical properties. They are difficult to separate and are usually not fractionated in geochemical systems where Zr and Hf behavior is charge- and radius-controlled (Goldschmidt, 1937). Due to the high particle reactivity of Hf, Zr-Hf fractionation can be significant with Zr/Hf ratios up to 350 and higher (Firdaus et al., 2011) in aqueous solutions such as seawater. In contrast to the REY(III), where scavenging occurs due to surface complexation, Hf(IV) and other highly charged elements with a high affinity to hydrolyze, such as Zr(IV), Th(IV) and Ce(IV) are scavenged via surface precipitation (Bau and Koschinsky, 2006). Thus, these elements are continuously precipitated as long as the mineral surface is in contact with seawater and the
elements are not subject to continuous sorption and desorption. Zr and Hf always occur together and are most strongly enriched in the weathering resistant silicate mineral zircon (ZrSiO$_4$) which is abundant in almost all sedimentary and felsic rocks. Zirconium is commonly mined from placer deposits. Due to the high melting point and the chemical inertness, Zr is mainly used as an opacifier for ceramic production and as a getter material because of its high reactivity towards oxygen. Hf is almost exclusively used for the production of control rods of nuclear reactors, because it has a high affinity to absorb neutrons.

**Thorium and uranium**

The radioactive actinide elements Th and U are both polyvalent elements and occur, unlike Zr and Hf, in more than one oxidation state. At surface conditions, Th occurs as Th(IV) while U is usually present as hexavalent U(VI) in the form of the uranyl complex UO$_2$$^{2-}$. Under reduced conditions, U is present as U(IV). U(VI) is relatively soluble and mobile in aqueous solutions, whereas Th(IV) and U(IV) are commonly considered as very immobile and insoluble. Their average crustal abundances are 8.5 ppm for Th and 1.7 ppm for U (Wedepohl, 1995). Due to their different charge and slightly different ionic radii (Th(IV): 94 pm; U(IV): 89 pm; U(VI): 73 pm) they are not considered as geochemical twins sensu strictu, but their element ratios are often discussed in geochemical literature and Th-U are considered as element pairs. At neutral pH, carbonate complexation is prevalent, but organic ligands also play an important role in the solubility of these elements (e.g., Mullen et al., 2007; Wolff-Boenisch and Traina, 2007; Crancon and van der Lee, 2009; Trenfield et al., 2011) and can dramatically enhance the solubility and mobility of these elements. Thorium is economically enriched in the REY-bearing mineral monazite and is usually mined from monazite-bearing placer deposits. The zircon mineral also incorporates significant amounts of Th. The enrichment of Th especially in monazite leads to major environmental problems during mining of REY due to the radioactivity of Th (Humphries, 2013). Uranium is mined predominantly in the form of uraninite (UO$_2$) and occurs in economic concentrations in a number of deposit types such as unconformity-related and sedimentary deposits. Thorium and U are almost entirely used as nuclear fuels for nuclear power plants.
The platinum group elements

The platinum group elements (PGE) comprise a group of six transition metals. The PGE are further subdivided into the iridium-group PGE (IPGE) and the palladium group PGE (PPGE). The former consists of the elements osmium (Os), iridium (Ir) and ruthenium (Ru), while the latter consists of rhodium (Rh), platinum (Pt) and palladium (Pd). The PGE are a group of metals with highly unique physical and chemical properties. They usually occur together in mineral deposits, but Pt, Pd and Rh are the major economically important commodities amongst the PGE (Koek et al., 2010). Of the six PGE, only Pt and Pd were investigated in this thesis due to analytical constraints and are described in greater detail in the following paragraphs.

PGE neither belong to the large ion lithophile elements nor to high field strength elements, rather they constitute a distinct geochemical subgroup known as highly siderophile elements (HSE). This is attributed to the PGE’s strong preference for iron metal over silicates when fractionating (Carlson, 2005). Hence, they show partition coefficients above $10^4$ between metal and silicates (e.g., Fortenfant et al., 2003). Consequently, they are very rare and only occur in minute amounts in most rocks. PGE are usually most enriched in mafic/ultramafic layered sequences, where sulfide droplets formed during formation and sank to the bottom of the magma chamber. The sulfide droplets scavenge the PGE from the magma and form sulfide layers highly enriched in PGE.

In aqueous solutions, Pt and Pd occur in various oxidation states, yet under surface conditions at 25°C Pt(II) and Pd(II) are the most stable ones (Dahlheimer et al., 2007) based on the equation

$$Pt (s) + \frac{1}{2}O_2 + 2H^+ \leftrightarrow Pt^{2+}_{(aq)} + H_2O$$

(Reith et al., 2014)

$Pt^{2+}$ is relatively insoluble under surface conditions, but forms stable complexes with a wide range of soft ligands, such as chloride, cyanide, amines, thiosulfate, bisulfide as well as hydroxyl groups, ammonium and carboxylic acids (see review by Reith et al., 2014). Although considered as very immobile, it has been suggested that Pt and Pd can be mobilized extensively in the environment, in a similar manner to gold, by means of organic complexation as e.g. shown by (Wood et al., 1994; Wood, 1996; Normand and Wood, 2005 Dahlheimer et al., 2007) for fulvic acid, humic acid and the siderophore desferrioxamine B. Reith et al. (2014) published an extensive review on the mobility of Pt in Earth’s surface
environment and concludes that Pt is mobile and may become bioavailable in the environment under certain circumstances.

The PGE are extremely rare in the Earth’s continental crust with values ranging from about 0.05-0.06 (Rh, Os, Ir) to 0.1-0.4 ppb (Ru, Pt, Pd) (Wedepohl, 1995). Given that most mining operations currently exploit deposits at total PGE grades ranging from 5 to 10 or more ppm, a significant enrichment of the PGE is needed to form exploitable mineral deposits (Koek et al., 2010). The major use of PGE is their function as catalytic converters for various chemical reactions, including the degradation of nitrous oxides, carbon monoxide and unburnt hydrocarbons in exhaust emissions of cars and trucks (Brenan, 2008; Rao and Reddi, 2000). Therefore, the automotive industry is the most important consumer of PGE. Additionally, PGE are used in resistance thermometers or as catalysts in fuel cells, for crude oil processing and for the oxidation of ammonia (Reith et al., 2014). Electronics and glass manufacturing are sectors that witnessed a tremendous growth in PGE use for example for magnetic storage media coated with Pt/Co and Cr alloys (Rao and Reddi, 2000). Platinum is also widely used for jewellery, dentistry and is used in anticancer drugs (Brenan, 2008).

According to Maier (2005) and Koek et al. (2010), several major types of primary PGE deposits can be distinguished. PGE occur in stratiform magmatic reef-type mineral deposits in mafic to ultramafic layered intrusions, in mafic intrusions, in Ni-Cu bearing sills or sill-like intrusions and in late magmatic or hydrothermal deposits (Koek et al., 2010; Mudd, 2012). The genesis of PGE deposits in mafic (noritic) intrusions is thought to be related to meteoritic impacts. The most important deposit for this type is the Sudbury Complex in Ontario, Canada. The most prominent example for Ni-Cu bearing sills is the Norilsk District in Russia. PGE also occur in alluvial and eluvial placer deposits (e.g., Cabral et al., 2006), but are, like late magmatic and hydrothermal PGE deposits, of subordinate economic importance.

Most prominent examples of the orthomagmatic stratiform reef-type deposits are the Merensky Reef, the UG2 chromitite and the Platreef formation of the Bushveld Igneous Complex in South Africa as well as the Main Sulfide Zone (MSZ) of the Great Dyke, Zimbabwe, and the Stillwater Complex in the USA. The PGE for example in the pristine MSZ of the Great Dyke occur in form of disseminations of mainly intercumulus sulfides (Oberthür and Melcher, 2005). The pyroxenites contain approximately 0.5-10 vol. % sulfides, which are basically comprised of pyrrhotite, pentlandite, chalcopyrite and minor pyrite. The PGE-minerals are enriched mainly in pyrrhotite, chalcopyrite and to minor extents in pentlandite and also occur as sulphide minerals or PGE alloys (Oberthür and Melcher, 2005).
In surficial zones, the reef-type deposits can be intensely weathered, which leads to the formation of supergene, or secondary, oxidized PGE ores. For example, the MSZ of the Great Dyke in Zimbabwe is intensely weathered to depths of about 15-30m (Oberthür et al., 2013). Compared to pristine ores, the oxidized PGE ores of the MSZ show a depletion of Pd during weathering as shown in Fig. 8 and an almost complete removal of sulfur (Locmelis et al., 2010). PGE in the oxidized MSZ occur as relict primary platinum-group minerals (PGM; sperrylite, cooperite, braggite), in solid solution of relict sulfides such as pentlandite, as secondary Pt-Fe alloys, as PGE oxides/hydroxides and as substitutes or adsorbed cations in iron- and manganese (hydr)oxides (Locmelis et al., 2010; Oberthür et al., 2013). Similar types of supergene PGE deposits occur in surficial zones of the Platreef, Bushveld Complex, South Africa (e.g. Becker et al., 2014; Schneiderhöhn and Moritz, 1939) and as thick laterite horizons in some locations above the Yilgarn craton in Western Australia (Hoatson, 1998).

Since part of this study focuses on the chemical extraction of Pt and Pd from oxidized PGE ores of the Great Dyke as described above, the following paragraph briefly summarizes the processing and metallurgical techniques commonly applied by the major producers in South Africa for southern African reef-type PGE ores (‘pristine ores’).

The processing of pristine PGE ores, the production of concentrates and the refining process of PGE is described in detail by Crundwell et al. (2011). The major steps in
processing of PGE ores are flotation concentrate production (1), smelting and matte production (2), platinum concentrate production (3) and high-purity metal production (4). Fig. 9 summarizes the processing of pristine PGE ores from mining to the refined metal.

The mined ore which contains roughly 3 to 10 ppm PGE is crushed and ground to liberate the sulfide mineral grains which host the PGE. The liberated mineral grains are separated by froth flotation with copper sulfate and xanthate or dithiophosphate (Crundwell et al. 2011). The flotation underflow is discarded and the froth is cleaned several times to produce a concentrate slurry with about 70 to 100 ppm PGE which is also highly enriched in Fe, Ni and other base metals like Cu and Co. This concentrate is dried and smelted to remove silica, iron and sulfur. This sulfur-deficient matte contains roughly 0.01-0.02% PGE, about 49% Ni, about 30% Cu and still 15-23% sulfur, which is needed for collection of the PGE by forming sulfide droplets in the melt. The matte is slowly-cooled and then either magnetically separated as is done in the Rustenberg refinery, South Africa, or, more commonly, leached over several (five or more) leaching stages to enhance the PGE concentrate and reduce or remove Ni, Cu and other (base) metal concentrations. At the final leaching stage, the concentrate contains about 50 to 70% PGE+Au. This concentrate is then completely dissolved in hydrochloric acid containing chlorine gas as an oxidant and the individual PGE’s are selectively precipitated or separated from solution by a range of processes such as precipitation with ammonium chloride or solvent extraction in case of Pt and precipitation with ammonium acetate, solvent extraction or ion exchange in the case of Pd.

With conventional techniques recoveries of Pt and Pd between 86 and 90 % are reached from pristine MSZ ores at the Hartley open pit mine in Zimbabwe (Rule, 1998).

Already in 1939, Schneiderhöhn and Moritz noted that oxidized PGE ores cannot be processed by means of flotation, because the PGE minerals are too small and are covered by or coated with silicate minerals and/or weathering products – they suggested chemical leaching as the only remaining option for processing these ores. Prendergast (1988) reported processing trials of oxidized MSZ ores by means of gravity concentration and flotation and the reported recoveries were far below 50%. Oberthür et al. (2013) stated that metallurgical test work on oxidized MSZ ores from the Ngezi mine in Zimbabwe achieved Pt and Pd recoveries of only 15-30%. They further state that only bulk leaching methods are apparently viable for a successful treatment of this ore. Following up on this research, siderophores were tested in this study for the hydrometallurgical extraction of Pt and Pd from oxidized MSZ ores.
with the aim to achieve mobilization rates in the order of magnitude allowing profitable economic exploitation of this deposit type.

Fig. 9: Generalized flowsheet for the production of platinum group metals and gold from pristine South African ore material (modified after Crundwell et al. 2011).
2. **Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment**

2.1. Siderophore-promoted transfer of rare earth elements and iron from volcanic ash into glacial meltwater, river and ocean water

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Siderophore-promoted transfer of rare earth elements and iron from volcanic ash into glacial meltwater, river and ocean water

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ABSTRACT

The rare earth elements (REE) are a group of trace elements that have short marine residence times and that in river, lake and marine surface waters are typically associated with organic and inorganic particles. Explosive volcanic eruptions, such as the 2010 eruptions of Eyjafjallajökull volcano in Iceland, produce volcanic ash particles which can be an important source of iron and other nutrients for aquatic organisms. To become bioavailable, however, this iron needs to be solubilized by complexing agents, such as siderophores. A well-studied example of such a chelator is the biogenic siderophore desferrioxamin-B (DFOB). Based on results from incubation experiments with glacial meltwater-rich river waters from southern Iceland, which are rich in suspended volcanic ash and that had been incubated with and without DFOB, respectively, we here show that siderophores not only enhance the release of iron, but also promote the mobilization of REE from these particles. In the presence of DFOB, partial dissolution of volcanic ash (and presumably other lithic particles) produces a flux of dissolved REE into ambient waters, that is characterized by depletion of the light REE over the middle REE and by selective enrichment of cerium, due to the formation of dissolved Ce(IV)-DFOB complexes. In siderophore-rich environments, this siderophore-bound REE flux has the potential to modify the concentrations and distribution of the dissolved REE and of the isotopic composition of dissolved Nd in glacial meltwaters, river waters and seawater and might be a component of the boundary effects between shelf sediments and seawater, which are assumed to account for the "missing Nd flux" to seawater. Thermodynamic data further suggest that siderophore-promoted element mobilization could also be important for other polyvalent (trace) elements, such as Hf.

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1. Introduction

The total rare earth element (REE) inventory of natural surface waters can be subdivided into three different pools (Eldredfield et al., 1990): (i) the “particulate” REE that are bound to solid particles larger than 0.45 μm or 0.2 μm (the pore sizes of the membrane filters commonly used in hydrochemical studies), (ii) the “colloidal” REE that are bound to colloids and nanoparticles of <0.45 μm or <0.2 μm size, and (iii) the “truly dissolved” REE comprising the “free” aquo ions and aqueous chemical REE complexes. The sum of the latter two pools represents the “dissolved” REE, the concentrations of which are usually determined in river and seawater studies. Although the geogenic and the anthropogenic characteristics of the REE distribution in river water have been the focus of numerous studies (e.g., Eldredfield et al., 1990; Sholkovitz, 1995; Gaillardet et al., 2003; Kulakisz and Bau, 2013; and references therein) and the importance of organic complexation is well recognized (e.g., Tang and Johannesson, 2003; Pourret et al., 2007), rather little is known of the effects of specific organic chelators on REE mobilization from lithic particulates. Similar to other major and trace elements/nutrients and their isotopes (e.g., Jones et al., 2012a, 2012b), mobilization processes from the particulate into the dissolved REE pool significantly impact the concentrations and distribution of dissolved REE, and hence of the isotopic composition of Nd in river water, in the riverine REE input into the oceans, and in seawater itself, where REE distribution and Nd isotopes are frequently used as (paleo)proxies. However, some details of the (bio)geochemical behaviour of the REE are still only poorly constrained, such as the “missing Nd flux” to seawater and the “Nd paradox” (i.e. the decoupling of concentration and isotopic composition of Nd in seawater), for example (e.g., Tachikawa et al., 1999; Lacan and Jeandel, 2005; Arrouze et al., 2009). Moreover, because microbes appear to play an important role in subglacial weathering (Montross et al., 2012), biogenic organic compounds may also have a substantial impact on solute concentrations and distribution in subglacial meltwaters which feed sub- and proglacial lakes and rivers that both are typically rich in rock flour, i.e.
silt-sized lithic particles. Widespread melting of glaciated areas during deglaciation periods in the past or as a possible result of global warming in the future suggest that the impact of biogenic chelators on the REE systematics of glacial meltwaters (and hence on seawater) could also be profound.

Explosive volcanic eruptions may result in the input of micron- to nanometer-sized volcanic ash particles into rivers, lakes, and oceans where they represent an important source of nutrients (e.g., Frogner et al., 2001; Duggen et al., 2010; Olgun et al., 2011; Ayris and Delpierre, 2012; and references therein), such as iron and phosphorus. The explosive 2010 eruption of Eyjafajlajökull volcano in southern Iceland, for example, produced large amounts of glass-rich volcanic ash of predominantly andesitic composition (Gislason et al., 2011; Sigmarrson et al., 2011). After the eruption, rivers in southern Iceland (Fig. 1) close to Eyjafjallajökull, such as the Markarfljót River, carried large amounts of this volcanic ash to the sea, whereas more distal rivers transported ash that had been produced during earlier volcanic events in southern Iceland. These river waters represent natural suspensions of volcanic ash and freshwater that are well-suited for geochemical studies.

Although the deposition of volcanic ash into seawater, for example, can promote marine bioproducivity (Frogner et al., 2001; Duggen et al., 2010; Hamme et al., 2010; Langmann et al., 2010; Olgun et al., 2011), the bioavailability of iron from ash particles that dissolve under aerobic conditions in surface waters is limited due to the rapid formation of Fe(III) oxyhydroxides (e.g., Ayris and Delpierre, 2012). To mitigate iron deficiency, terrestrial and marine organisms and plants may produce siderophores which are biogenic chelators that effectively mobilize ferric iron and increase iron bioavailability even inoxic environments (e.g., Kraemer, 2004; Baker and Crook, 2010; and references therein). However, siderophores do not only form strong chemical complexes with iron, but also with a range of other polyvalent metal ions (e.g., Harrington et al., 2011; and references therein) including the REE, and therefore affect the mobilization and scavenging behaviour of these elements (Yoshida et al., 2004a, 2004b; Brantley et al., 2001; Kraemer et al., 2002; Tanaka et al., 2010; Christenson and Schijj, 2011).

Hence, we performed incubation experiments (20°C, 72 h, pH range: 7.04–7.68) to investigate the impact of the well-characterized biogenic siderophore desferrioxamin-B (DFOB) on the mobilization of REE from volcanic ash particles (particulate REE) into river water (dissolved REE) from southern Iceland. Our results suggest that in the presence of siderophores release of iron and REE from ash particles is significantly enhanced and that the mobilized REE fraction is characterized by specific chondrite-normalized (subscript CN, chondrite from Anders and Grevesse (1989)) distribution patterns with light REE ([REE] depletion, convex shape between La and Sm, and positive Ce anomaly.

2. Materials and methods

2.1. Samples

Water samples used in the experiments had been taken in acid-cleaned PE bottles from five glacial meltwater-dominated rivers in southern Iceland (Fig. 1) in September of 2010, i.e. about five months after the eruption of Eyjafjallajökull volcano had covered parts of southern Iceland with fine grained volcanic ash of mostly intermediate chemical composition (Gislason et al., 2011; Sigmarrson et al., 2011). From east to west we studied samples from the following rivers: Markarfljót, Jökulsá í Solheima, Gígjukvisi, Hornafjarðarrjót, and Jökulsá í Lóni (Fig. 1). The Markarfljót and, less strongly, the Jökulsá í Solheima rivers in the west were most strongly affected by ash from the Eyjafjallajökull eruption, whereas the three more eastern rivers were almost unaffected, but still rich in suspended ash particles derived from earlier events. For comparison, we also performed experiments with water samples that had been taken in September of 2011 (i.e. after the 2011 eruption of Grímsvötn volcano which in comparison to the Eyjafjallajökull 2010 eruption had produced less fine grained mafic ashes).

2.2. Experimental and analytical

A well-shaken 1000 mL unfiltered water sample from each river was split into two 500 mL aliquots that were filled into acid-cleaned Nalgene bottles. From each set of twin samples one was spiked with Desferal® (Novartis) which is the commercially available mesylate salt of the trihydroxamate siderophore DFOB, while the other aliquot was used as a DFOB-free control. Compared to DFOB-DFOB complexes, REE-mesylate complexes are weak (Christenson and Schijj, 2011) and hence did not affect REE behaviour in our experiments. REE concentrations in Desferal® are very low (below determination limit) and did not affect the REE distribution in our samples. The DFOB-spiked solutions had concentrations of 1 mM DFOB. This DFOB concentration is at the high end of those observed in natural aqueous environments (e.g., Kraemer, 2004) and hence is exceptional for natural waters.

![Fig. 1. Simplified map of southern Iceland showing the sampling sites at the rivers Markarfljót (1), Jökulsá í Solheima (2), Gígjukvisi (3), Hornafjarðarrjót (4), and Jökulsá í Lóni (5).](image-url)
While Watteau and Berthelin (1994) consider a DFOB concentration of 0.13 mM as typical of soil solutions, DFOB levels in seawater usually fall in the low nanomolar range (e.g., Kraemer, 2004). Hence, our experimental conditions do not reflect conditions typical of natural environments, such as the surface ocean, but may rather represent specific local conditions on or close to particle surfaces in weathering environments.

De-ionized Water (DIW) was added to the DFOB-free control samples in the same amount as had been added as DFOB-solution to the respective twin sample. The samples were shaken for 3 min before pH was measured. After 72 h on a shaker table at 20 °C, the samples were filtered through 0.2 μm membrane filters to remove any particulates, and the pH of an aliquot of the filtrate was measured again.

Even in the presence of DFOB, we did not observe any strong pH changes during the 72 h incubations (ApH < 0.4; Online Supplementary Table S1). Incubation of water from Markarfjöll River (2010) with DFOB, during which pH was fixed at 7.6 with tris(hydroxymethyl)-aminomethane (TRIS) buffer, produced REE patterns similar to those of un-buffered experiments (Fig. 2; Online Supplementary Table S1). However, REE mobilization was almost one order of magnitude more effective in the presence than in the absence of TRIS (Fig. 2). To avoid any potential effects due to REE complexation with TRIS (as has been observed for Eu and Tb; Stieblevskaia et al., 2008; and references therein) and considering the small scale of pH variation occurring during un-buffered incubations, we did all other incubations without pH buffer.

For a long-term experiment, we sampled aliquots of DFOB-spiked water from Hornafjardarfljót River after incubation times of 0, 3, 6, 12, 24, 72, and 168 h, respectively, and measured dissolved Fe (by ICP-OES) and REE concentrations (by ICP-MS). Iron concentrations increased rapidly from 0.2 mg/kg to 1.7 mg/kg within the first 12 h and increased only moderately to 3 mg/kg after 168 h (Online Supplementary Table S1). These results corroborate previous results (e.g., Frogner et al., 2001; Jones and Gislason, 2008) that had shown fast initial release of iron from volcanic ash. After a strong increase in the first 24 h of incubation, REE concentrations showed only minor change between 72 h and 168 h (Fig. 3). While immediately after the addition of DFOB to the river water the positive Ce anomaly was only small (Ce/Ce = 1.08; Ce/Ce = 0.514Ce + 0.5PrCe), it rapidly increased to Ce/Ce = 1.39 after 3 h and stayed between 1.26 and 1.51 for the rest of the incubation time. Hence, all other experiments have been performed with 72 h incubation time.

Prior to analyses by ICP-MS, the REE were separated from the filtrates (except the solutions from the long-term experiment) and preconcentrated following an established protocol (Bau and Dulski, 1996; Kulaksiz and Bau, 2007) routinely utilized in the determination of ultratrace concentrations of REE in natural waters. Blank intensities were in general at least almost two orders of magnitude below those determined for our experimental solutions. Analytical uncertainties are below 10% for the REE concentrations and even smaller for ratios between two REE. The good overall reproducibility of our results is shown by the results of experiments with water from Markarfjöll River and Jökulsá à Loni River, which were performed in duplicate (Fig. 2).

The dried (12 h at 60 °C) filter residues and membrane filters and the milled samples of volcanic ash (Online Supplementary Table S2) taken for comparison were pressure-digested with a PicoTrace DAS digestion unit with suprapure Hf, HCl, HNO₃.

3. Results

3.1. Particulate REE

Although the filter residues (i.e. the > 0.2 μm-sized particulate REE pool) from the river waters we studied are almost exclusively composed of volcanic ash particles, the general REE distribution of the particulates (Fig. 4) from rivers close to Eyjafjallajökull (Markarfjöll, Jökulsá à Solheimar) is rather similar to that of the more distal rivers (Gígjúkviðl, Hornafjardarfljót, Jökulsá à Loni).
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which where rather unaffected by ash from this volcano (Online Supplementary Table S2). Only the particulates from the Markarfljót River show the high La/Yb ratio typical of ash from the 2010 Eyjafjallajökull eruption (Fig. 4, see also Sigmarsson et al. (2011)). We emphasize that none of the filter residues shows REE<sub>cn</sub> patterns with anomalous enrichment of Ce or depletion of the LREE relative to the middle REE (MREE).

3.2. Dissolved REE

Concentrations and distribution of the dissolved REE in the river water samples that had been incubated with the DFOB siderophore show higher iron and REE concentrations than the respective controls without DFOB (Online Supplementary Table S1).

While Fe concentrations in water incubated without DFOB were below the lower limit of determination (which using our analytical method is 0.5 mg/kg, i.e. rather high), it increased to up to 5.5 mg/kg in the presence of DFOB. Concentrations of individual REE increased in the presence of DFOB from ranges between 7.62–54.2 ng/kg to 117–3433 ng/kg for Ce, from 4.84–32.1 ng/kg to 123–282 ng/kg for Nd, from 1.21–10.38 ng/kg to 40.5–290 ng/kg for Dy, and from 0.56–4.53 ng/kg to 8.22–103 ng/kg for Yb (Online Supplementary Table S1).

The distribution of the REE also differs significantly between these sample sets (Fig. 5a,b). In the absence of DFOB, REE<sub>cn</sub> patterns of the river waters decrease systematically from La to Lu with La<sub>cn</sub>/Sm<sub>cn</sub> ratios well above unity and small negative Eu anomalies; they do not show any positive Ce anomaly. In the presence of DFOB, however, the river waters develop convex LREE<sub>cn</sub> patterns that increase from La to Sm, and, except for the 2010 sample from Jökulsá í Lóni River, they all show a strong positive Ce anomaly in addition to a small negative Eu anomaly (Fig. 5a,b).

4. Discussion

The increase of iron and REE concentrations in river waters upon incubation with DFOB indicates that the siderophore mobilized iron and REE from the ash particles and caused their partitioning from the particulate into the dissolved pool.

Fig. 4. REE<sub>cn</sub> patterns of particulates (0.2 μm filter residues) from the Markarfljót, Jökulsá í Solheimar, Gígjökull, Hornafjördurjökull, and Jökulsá í Lóni rivers in southern Iceland and of volcanic ash from the Eyjafjallajökull 2010 eruption.

Fig. 5. REE<sub>cn</sub> patterns of dissolved REE (0.2 μm filtrates) from Markarfljót, Jökulsá í Solheimar, Gígjökull, Hornafjördurjökull, and Jökulsá í Lóni river water in southern Iceland sampled in 2010 (A) and 2011 (B) incubated in the presence and absence, respectively, of DFOB. Note that incubation in the presence of DFOB enhanced dissolved REE concentrations and produced similar fractionated REE patterns in all samples (except for the lack of a positive Ce anomaly in Jökulsá í Lóni 2010 water). *Average of duplicates.
Normalizing the dissolved REE concentrations of a sample to those of its respective particulate REE pool (Fig. 6a,b) reveals the severe fractionation within the REE group during this siderophore-promoted mobilization. The strong difference between the REE patterns of the filter residues (i.e. the particulate REE pool) and that of the filtered river water (i.e. the dissolved REE pool) after incubation with DFOB shows that these increases do not simply result from the breakdown of >0.2 µm-sized particles into smaller colloids or nanoparticulates, but from the enhanced dissolution of the volcanic ash particles and from the incongruent release of REE in the presence of the DFOB siderophore.

The development of positive Ce anomalies in the river waters incubated with DFOB reveals that redox-sensitive Ce is decoupled from its redox-insensitive REE neighbours during siderophore-promoted dissolution of lithic particles. Such decoupling and preferential Ce mobilization requires oxidation of Ce(III) to Ce(IV) and likely results from the stabilization of soluble Ce(IV)-DFOB complexes, as the latter are known to have higher stabilities than Ce(III)-DFOB complexes (Yoshida et al., 2004b). Considering that, similar to DFOB, the approximately 500 other naturally occurring siderophores currently known also prefer to bind to Fe³⁺ rather than Fe²⁺, preferential Ce⁴⁺ complexation may not be confined to DFOB, but may be typical of many other siderophores.

Our results demonstrate that the presence of siderophores preferential complexation of Ce⁴⁺ occurs in near-neutral environments and is not confined to alkaline systems, such as the formation of Ce(IV)-polycarbonate complexes that cause positive Ce anomalies in alkaline lakes (Møller and Bau, 1993; Johannesson et al., 1994). Similar to the effect of organic Ce(IV) solution-complexation observed in sorption experiments (Yoshida et al., 2004b; Tanaka et al., 2010), the dissolution of rocks, lithic particles and minerals in the presence of siderophores has thus the potential to create positive Ce anomalies even in the near-neutral environment typical of river and ground water, and of seawater. However, considering that the highest siderophore concentrations in natural environments have to date been observed in soils (e.g., Kraemer, 2004), the most significant siderophore-enhanced preferential Ce mobilization may occur during weathering and pedogenesis in the critical zone at and near the Earth's surface. While Ce anomalies are common features of REE patterns of supergene minerals, soils, and weathering profiles, their use as (pale)redox proxies is further complicated by this potential impact of biogenic chelators.

The observed LREE-depletion and the convex patterns between La and Sm are compatible with the relative stabilities of REE(III)-DFOB complexes, which increase significantly from La to the MREE (Christensen and Schijf, 2011). It appears that such a LREE distribution is a characteristic feature of REE mobilization in the presence of the DFOB siderophore and supports the potential use of such a LREE distribution as a proxy for the presence of biogenic organic chelators during water-rock interaction. However, a full evaluation of the potential of such a LREE distribution as a biosignature has to wait until further information is available on REE mobilization in the presence of other types of siderophores.

Our results demonstrate that the presence of siderophores, such as DFOB, in river waters promotes the release of iron and REE from suspended volcanic ash particles. Siderophores not only significantly increase dissolved REE concentrations, but also produce a characteristic type of fractionation within the dissolved REE pool. This constitutes a siderophore-bound REE flux from volcanic ash particles (particulate REE) into river water (dissolved REE), that relative to the ash source is characterized by a positive Ce anomaly, depletion of the lightest REE and slight enrichment of the MREE. Interestingly, such REE patterns are observed in some major tropical rivers (e.g., Sholkovitz, 1995; Sholkovitz et al.,

Fig. 6. Particulates-normalized REE patterns of dissolved REE (0.2 µm filtrates) from Markarfljót, Jökulsá í Solheimá, Gígjakvísl, Hornafjarðarljót, and Jökulsá í Loní river water in southern Iceland sampled in 2010 (A) and 2011 (B) incubated in the presence and absence, respectively, of DFOB. Note that incubation in the presence of DFOB enhanced dissolved REE concentrations and produced similar fractionated REE patterns in all samples (except for the lack of a positive Ce anomaly in Jökulsá í Loní water).

*Average of duplicates.
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1999; Gaillardet et al., 2003), such as the Amazon River, suggesting that siderophore-style organic complexation may be an important process that affects the dissolved REE distribution of such rivers.

Considering that our experiments were performed between pH 7 and 8, i.e., within the pH range common in rivers, estuaries, seawater, and porewaters, there is ample reason to assume that whenever siderophore concentrations in local environments are sufficiently high, a siderophore-bound REE flux might also be important in estuaries, (coastal) seawater and across the sediment–water interface. In the low-salinity part of estuaries, for example, the aggregation and subsequent sedimentation of organic(ally stabilized) colloidal and nanometer-sized particles causes the removal of associated REE from the dissolved REE pool (e.g., Elderfield et al., 1990; Sholkovitz, 1995; Lawrence and Kamber, 2006). As a result, REE concentrations in the low-salinity part are usually below those suggested assuming conservative mixing of river and seawater. In the high-salinity part of estuaries and in seawater, however, REE mobilization from river particulates, volcanic ash, atmospheric dust and sediment particles creates a REE flux into the dissolved REE pool in seawater (e.g., Sholkovitz, 1995; Sholkovitz et al., 1999; Greaves et al., 1999; Kulaisiz and Bau, 2007). In the past, this has been explained by the higher ionic strength of seawater than freshwater (e.g., Sholkovitz, 1995). However, the presence of siderophores may also contribute to this process and may cause seawater to be less Ce-depleted and the imprint of local terrigenous particles on the dissolved Nd isotopic composition of seawater to be stronger, than in the absence of siderophores.

One may also speculate that if siderophore concentrations in marine porewaters of continental shelf sediments are sufficiently high (which is currently not known), a siderophore-bound REE flux across the sediment–water interface may contribute to the “missing Nd flux” (Tachikawa et al., 2003) to seawater, and that siderophores, therefore, may play a role in the boundary effects between continent and ocean, that are assumed to cause the Nd paradox (e.g., Lacan and Jeandel, 2005; Arrouse et al., 2009). Moreover, the presence of microbes in subglacial weathering environments (Montross et al., in press) suggests that siderophores might also affect REE (and Iron) concentrations and distribution in glacial meltwaters and hence their impact on seawater. The above possibilities warrant further investigation, and future studies of siderophores in natural environments should be expanded to include marine porewaters and (sub)glacial meltwaters, for example.

5. Conclusions

The results of our experiments demonstrate that strong biogenic chelators, such as siderophores, not only enhance the (bio)availability of iron, but also have the potential to significantly affect the concentrations and distribution of the REE in natural waters. They promote the oxidation of Ce and the dissolution of lithic particles, and induce incongruent release of REE. This may result in a siderophore-bound dissolved REE flux into glacial meltwater, river water and seawater, that shows a positive Ce anomaly in a 1REE depleted REE pattern. Such a REE flux might affect dissolved REE concentrations and distribution and also the isotopic composition of Nd in glacial meltwaters, rivers and oceans. Considering that siderophore complexes of other polyvalent trace elements such as Hf(IV), for example, are also characterized by high stability constants (Yoshida et al., 2004a), siderophore-promoted particle dissolution should also impact the environmental behaviour of certain other high-field strength elements and might help explain certain geochemical peculiarities, such as the biogeochemical behaviour of Hf (Bau and Koschinsky, 2006; Chen et al., 2011) in natural waters, for example.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.01.002.

References


2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment


2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment
2.2. Oxidative Dissolution of Cerium and Uranium and Enhanced Mobilization of “Immobile” High Field Strength Elements from Igneous Rocks in the Presence of Siderophores

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Oxidative Dissolution of Cerium and Uranium and Enhanced Mobilization of “Immobile” High Field Strength Elements from Igneous Rocks in the Presence of Siderophores

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Abstract

Polyvalent trace elements such as the high-field strength elements (HFSE) are commonly considered rather immobile during low-temperature water-rock interaction. Hence, they have become diagnostic tools that are widely applied in geochemical studies. We present results of batch leaching experiments focused on the mobilization of certain HFSE (Y, Zr, Hf, Th, U and rare earth elements) from mafic, intermediate and felsic igneous rocks in the presence and absence, respectively, of the siderophore desferrioxamine B (DFOB). Our data show that DFOB strongly enhances the mobility of these trace elements during low-temperature water-rock interaction.

The presence of DFOB produces two distinct features in the Rare Earths and Yttrium (REY) patterns of leaching solutions, regardless of the mineralogy and the texture of the rock type studied. Bulk rock-normalized REY patterns of leaching solutions with DFOB show (i) a very distinct positive Ce anomaly and (ii) depletion of La and other light REY relative to the middle REY, with a concave downward pattern between La and Sm. These features are not observed in experiments with hydrochloric acid, acetic acid or deionized water. In DFOB-bearing leaching solutions Ce and U are decoupled from and selectively enriched relative to
light REY and Th, respectively, due to oxidation to Ce(IV) and U(VI). Oxidation of Ce$^{3+}$ and U$^{4+}$ is promoted by the significantly higher stability of the Ce(IV) and U(VI) DFOB complexes as compared to the Ce(III) and U(IV) DFOB complexes. This is similar to the relationship between the Ce(IV)- and Ce(III)-pentacarbonate complexes that cause positive Ce anomalies in alkaline lakes. However, while formation of Ce(IV) carbonate complexes is confined to high-pH environments, Ce(IV) DFOB complexes may produce positive Ce anomalies even in mildly acidic and near-neutral natural waters. Siderophore-promoted dissolution processes also significantly enhance mobility of other ‘immobile’ HFSE and may not only cause or modify Ce anomalies and Th-U fractionation, but also mobilization of and fractionation between Zr, Hf, Th and redox-insensitive REY during weathering, pedogenesis, diagenesis and incongruent dissolution of particles in seawater and freshwater.

Siderophores may significantly affect the use of HFSE as geochemical tools. Concave downward light REY patterns may be used as a biosignature for water-rock interaction in the presence of siderophores. Enhanced and preferential mobilization of U relative to Th in the presence of siderophores may produce Th-U signals comparable to those indicative of weathering under oxidized conditions, which might constrain the use of U concentrations and Th/U ratios as a paleoredox-proxy. The enhanced mobilization of Zr and especially Hf from igneous rocks in the presence of DFOB might have implications for the use of the latter as a tracer for the impact of continental weathering on seawater chemistry. Because siderophore complexes affect the particle-reactivity of Hf and Zr, they may prevent effective removal of terrigeneous Hf and Zr during aggregation/coagulation of riverine particles in estuaries. Siderophore-promoted solubilization and stabilization might hence be an additional way to transport continental Hf and Zr to the oceans. Furthermore, siderophore-enhanced mobilization may also have implications for the remediation techniques employed to immobilize HFSE such as U, Th and REY, at nuclear waste and reprocessing sites and at REY ore processing plants, where soils are commonly contaminated with these (sometimes radioactive) heavy metals.

Keywords:
Siderophore, desferrioxamine B, oxidative dissolution, cerium anomaly, biosignature, rare earth elements, high field strength elements, critical zone, remediation of contaminated sites
1. Introduction

The distribution and behavior of large ion lithophile elements such as Rb, Sr and Cs, and of high field strength elements (HFSE) such as the rare earth elements and Y (REY), Zr, Hf, Th and U, in igneous systems are predominantly controlled by their charge and ionic size (Goldschmidt, 1937). Hence, isovalent elements with similar ionic radii (e.g., geochemical twins like \( Y^{3+}\)-Ho\(^{3+}\)) display coherent behavior and maintain a chondritic ratio during igneous processes. The term \( CHARAC \) (CHarge And RAdius Controlled; Bau, 1996) had been introduced for geochemical processes which do not fractionate geochemical twins such as Y-Ho, Zr-Hf, and Nb-Ta, or element pairs like Th and U. Most igneous processes, except for those operating in highly evolved silicate melts, are considered as \( CHARAC \) processes. In contrast, non-\( CHARAC \) trace element behavior is common in aqueous systems and in igneous systems involving large amounts of volatiles such as \( \text{H}_2\text{O} \) and others (Bau, 1996). The most common reason for non-\( CHARAC \) behavior of trace elements in aqueous systems is chemical complexation with inorganic and/or organic ligands.

Due to their coherent behavior in many geochemical systems and processes, the REY have become a powerful diagnostic tool in both igneous and aqueous geochemistry. However, attempts to employ anomalous HFSE patterns as quantitative indicators for specific geochemical conditions are often foiled by limited knowledge of the various processes that can produce such anomalies. For example, the REY are exclusively trivalent in low-temperature systems with the notable exception of Ce which may be oxidized and form Ce(IV) compounds. Cerium oxidation may lead to the decoupling of Ce from its trivalent neighbors in the REY series, resulting in the formation of positive or negative Ce anomalies in normalized REY patterns. The absence or presence of Ce anomalies has been used as a qualitative redox proxy, but any attempt to establish Ce-REY decoupling as a quantitative proxy suffers from limited knowledge of the various parameters that affect the redox behavior of Ce in natural systems.

Organic matter and organic chelators in general have been shown to be amongst the key factors controlling REY and HFSE speciation and mobilization in the critical zone at or near the Earth’s surface and, particularly, in aquatic environments such as groundwaters, rivers, lakes and soil solutions (Davranche et al., 2008, 2004; e.g., Gruau et al., 2004; Neaman et al., 2005; Pourret et al., 2007a). In this study, we focus on the chelation effects of siderophores to
elucidate the potential role that this important group of organic ligands may play in the formation of HFSE patterns during low-temperature water rock interactions.

Siderophores are a group of chemically diverse low-molecular weight organic ligands with extraordinarily high binding affinities for Fe$^{3+}$. They are produced by bacteria, fungi and plants to cope with the scarcity of bioavailable iron in the environment (Boukhalfa and Crumbliss, 2002), and constitute one of the most important groups of biogenic organic ligands in many terrestrial and marine environments. Most of the various siderophores known today incorporate hydroxamic acid, catechol and/or carboxyl functional groups (Albrecht-Gary and Crumbliss, 1998; Kalinowski et al., 2004; Kraemer, 2004) and are highly efficient complexing agents for polyvalent metal ions besides Fe. Many studies have highlighted this important side-effect of siderophores on metal (de)sorption and complexation processes (e.g., Ozaki et al., 2006; Yoshida et al., 2004, 2007; Bau et al., 2013), with few publications aimed specifically at HFSE, platinum group elements and the actinides. Dahlheimer et al. (2007) published an extensive study on the siderophore-promoted mobility of platinum group elements in surface environments and found that the siderophore desferrioxamine B (DFOB) is likely to increase the mobility of Pt and Pd in soils. Yoshida et al. (2007) demonstrated very effective complexation with desferrioxamine B (DFOB) and subsequent solubilization of Hf, while Brainard et al. (1992) and Bouby et al. (1998) demonstrated this for the actinides. Christenson & Schijf (2011) published a dataset for experimentally obtained stability constants for REY at seawater ionic strength (see Fig. 1) and found that REY-DFOB complexes are many orders of magnitude more stable than REY complexes with carbonate which is the most important inorganic REY-complexing ligand in seawater. Previous work on volcanic particle-rich glacial meltwaters from Iceland (Bau et al. 2013) also found that the presence of siderophores in solution significantly enhanced the transfer of rare earth elements (REE) from the particulate to the dissolved fraction, suggesting that the presence of siderophores in natural systems actively modifies the dissolved concentrations and the distribution of dissolved REE in the surface environment.
These environmental observations highlighted the need for a more systematic investigation of the actual impact of siderophores on the mobilization and fractionation of HFSE and REY during weathering processes. Here, we present results from batch leaching experiments with the siderophore DFOB on a range of mafic, intermediate and felsic crystalline igneous rocks to assess the impact of siderophores specifically on the mobility of HFSE and REY during weathering. Desferrioxamine B is a common siderophore in aerobic soils (Müller et al., 1984; Rosenberg and Maurice, 2003), that forms metal complexes through coordination with hydroxamate functional groups (Dhungana et al., 2001), and that has been used extensively in prior work on siderophore sorption, weathering and mineral dissolution (e.g., Farkas et al., 1997; Kiss and Farkas, 1998; Liermann and Kalinowski, 2000; Kraemer, 2004; Mullen et al., 2007; Duckworth and Sposito, 2007; Christenson and Schijf, 2011; Ohnuki and Yoshida, 2012; Bau et al., 2013; Akafia et al., 2014). We chose a wide range of common igneous rock types with different chemical and mineralogical compositions and with different textures to investigate whether or not the geochemical twins Zr-Hf, Y-Ho and the elements Th and U are decoupled from each other, and whether or not a unique REY signature exists that characterizes REY mobilization in the presence of the DFOB siderophore. We also included basaltic glasses in the study to test whether or not any of the specific features observed in the leaching experiments are due to the specific mineralogical compositions of the rocks studied.
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2. Materials and Methods

2.1 Samples

We conducted standardized incubation experiments on igneous rock samples from a variety of geologic settings. The complete sample set comprises four mid-ocean ridge basalts (MORB), two ocean island basalts (OIB), two andesites and a granite.

Sample OL-20b was originally described by Schnurr (1995) and is a basaltic andesite of the Paleoproterozoic Ongeluk Formation of the Transvaal Supergroup, South Africa. The island-arc andesite sample A-Jp originates from a lava flow underlying the Nishiki-numa spring (Hokkaido, Japan) and is described by Bau et al. (Bau, 1998). The mid-ocean ridge (micro)crystalline basalts were collected during research cruises at the East Pacific Rise at 21°S (sample MORB-EPR), described previously by Giese and Bau (1994), as well as from an aphyritic sheet flow in the area of the Turtle Pits hydrothermal field of the Mid-Atlantic Ridge (MORB-TP). For details on the Turtle Pit sample, see Haase et al. (2007). The samples MORB-EPR-glass and MORB-TP-glass represent the outermost, glassy rim of the aforementioned rocks, while the microcrystalline interior of these basalts is represented by samples MORB-EPR-cryst and MORB-TP-cryst, respectively. OIB-Me is a primitive alkali basalt from Mehetia Island (Society hotspot) and is discussed as sample Me90-05 by Binard et al. (1993). The second OIB sample, OIB-Haw, is a vesiculous tholeiite from Kilauea, Hawaii and is also discussed by Giese & Bau (1994). The granite GSAF3 is from the Lebowa Granite Suite, Bushveld Complex, South Africa.

Bulk decomposition of the rock samples was carried out using a DAS acid digestion system (Pico Trace, Germany) following the mixed acid digestion protocol outlined by Dulski (2001) and Alexander et al., (2008).

2.2 Experimental

We used the siderophore desferrioxamine B (DFOB) for our experiments. DFOB is the best studied siderophore to date and easily available in its mesylate form as the drug Desferal® (Novartis AG) which is used to treat acute and chronic iron overload (Nick et al., 2003; Bernhardt, 2007).
Christenson & Schijf (2011) reported that, compared to DFOB complexes, REY complexes with mesylate are weak and do not influence REY behavior. Due to the relatively similar chemical properties of REY and other HFSE, mesylate interactions with investigated elements are considered negligible in comparison to HFSE- and REY-DFOB interactions.

The batch leaching experiments were conducted in a trace-metal clean environment with acid-cleaned labware. Aliquots of exactly 1g of the dried and powdered igneous rock samples were weighed out into acid-cleaned LDPE bottles. The siderophore solutions were prepared separately with Desferal® and deionized water (DIW). The purity of Desferal® was checked by reagent blank measurements; trace-element concentrations in Desferal® were found to be at least two orders of magnitude lower than the concentrations in our experiments. Immediately after preparation of the solution, the pH of the leaching reagent was determined and the exact amount of siderophore solution matching a 20 g/l solid content and a DFOB concentration matching 1mM was added to the bottles containing the pre-weighed sample powder. The bottles were handshaken for a minute to facilitate dispersion and then placed on a shaker table set at 180 rpm. After 24 hours, the samples were taken off the shaker table and the solution was filtered using an acid-cleaned filter tower with a 0.2µm membrane filter. The leachates were measured for pH and were then acidified with supra-pure hydrochloric acid to pH <2 and stored for later analysis by quadropole ICP-MS.

A time-series experiment on sample OL-20B was conducted using 500ml LDPE bottles, 4g of sample powder and 200ml DFOB leaching solution. The sample was mixed with the leaching solution, handshaken for a minute to facilitate full dispersion and placed on a shaker table. The time intervals for sampling were 1h, 8h, 24h, and 48h. The pH was measured at each time point. Sampling was conducted on the dispersed, well-shaken sample with a syringe filter with a 0.2µm membrane size. Sampling volume was 5 ml. After sampling, the bottle was closed and returned to the shaker table.

For contact times greater than 24 hours, HFSE and REY concentrations in the leachates were fluctuating around the 24h values. The HFSE are particle-reactive elements and hence subject to readsoption. Therefore, except for the time-series experiments, all experiments presented here were conducted with contact times of 24h.

The leaching experiments were performed in unbuffered leaching solutions to more closely resemble natural water-rock interaction. The pH values of the solutions of the batch leaching...
experiments increase from a starting pH of 5.5 up to 9. The batch leaching experiments with OIB-Haw, MORB-TP and MORB-EPR were carried out in duplicate for quality control; the replicates demonstrate a good overall reproducibility of the experimental approach and the analysis (e.g., Fig. 7). To verify that the observed element mobilization patterns are characteristic for siderophore leaching, we also conducted control experiments with 1mM HCl, 1mM acetic acid and DIW using the same experimental setup as for the siderophore leaching experiments.

The experimental siderophore concentrations (1mM) used in this study are representative of very organic rich soil systems (Kraemer, 2004) but exceed concentrations commonly encountered in natural waters and other environmental systems (typically below 10µM). However, it should be noted that rocks in natural systems are subject to constant removal and re-supply of aqueous solutions containing a wide range of siderophores and other organic molecules. Considering the long time scales at work in natural weathering processes, the use of high siderophore concentrations is a reasonable surrogate for short-term lab-scale experiments.

2.3 Analytical

For whole rock analysis, exactly 50 mg of the dried sample aliquots of the rock powders (and also of certified reference materials for quality control) were pressure-digested with a concentrated acid-mixture of hydrofluoric acid, hydrochloric acid and nitric acid with a PicoTrace DAS digestion unit. All acids used for digestion and analysis were of supra-pure grade.

The leachates as well as the digested bulk rock samples were measured with a Perkin-Elmer quadrupole ICP-MS ELAN drc-e. Background intensities of procedural blanks were at least two orders of magnitude lower than sample intensities for the studied elements.

2.4 Reporting

REY patterns in the bulk rocks are shown as REY\textsubscript{CN} patterns (REY normalized to C1 chondrite, Anders & Grevesse, 1989). REY patterns in leachates are shown as REE\textsubscript{BN} patterns.
(REY normalized to the composition of the respective bulk rock). We emphasize that because neither chondrite nor any of the bulk rocks display Ce anomalies, the presence or absence of Ce anomalies in the leaching solutions is not affected by the type of reference material used for normalization.

The Ce/Ce* ratio is a measure of the anomalous behaviour of Ce and quantifies a Ce anomaly; values below unity represent negative and those above unity positive Ce anomalies. The Ce/Ce* ratio is calculated from normalized data as:

\[
\frac{Ce}{Ce^*} = \frac{Ce_{CN}}{La_{CN}^{0.67} \cdot Pr_{CN}^{0.33}}
\]

C1 chondrite values obtained by Anders & Grevesse (1989) and average upper continental crust values obtained by Rudnick & Gao (2003) are plotted in the multi element plots in grey.

3. Results

3.1 Bulk samples

The trace element composition of the bulk rocks is listed in Table 1. Our measurements confirm previously published data within analytical uncertainty (Binard et al., 1993; Giese & Bau, 1994). The REY_{CN} patterns of all MORB samples (Fig. 2a) show depletion of the light REY (LREY) relative to the middle REY (MREY) and are flat between MREY and heavy REY (HREY). Such a REY distribution is typical of N-type MORB. There is no difference between the crystalline MORB and the respective MORB glass. The OIBs (Fig. 2a) show LREY-enriched REY_{CN} patterns without any Eu anomaly. The REE_{CN} patterns of the andesitic rocks and the granite (Fig. 2b) decrease (steeply for the basaltic andesite and the granite) from the LREY to the MREY and are almost flat from the MREY to the HREY. None of the samples except for the granite shows a Eu anomaly, and, particularly, no sample shows any Ce anomaly.

The Zr/Hf ratios (32-45; Table 1) of the bulk rocks (except for the granite) are chondritic to slightly higher and indicate CHARAC trace element behaviour. The granite, however, shows a sub-chondritic Zr/Hf ratio of 23.7. Thorium and U concentrations are positively correlated and plot on a straight line defined by the chondritic and the average upper continental crustal Th/U ratio (Fig. 9).
2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment

Fig. 2: Chondrite-normalized REY patterns of oceanic island basalts (OIB) and mid-ocean ridge basalts (MORB) (a) and the two andesites A-Jp and OL20B and the Bushveld granite (b) used in the leaching experiments. Chondrite after Anders & Grevesse (1989).

Table 1: Bulk rock trace element compositions (in mg/kg) of the rock samples used for the leaching experiments in this study.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>OIB-Me</th>
<th>OIB-Haw</th>
<th>MORB EPR</th>
<th>MORB EPR glass</th>
<th>MORB TP</th>
<th>MORB TP glass</th>
<th>A-Jp</th>
<th>OL20B</th>
<th>GSAF3</th>
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</thead>
<tbody>
<tr>
<td>La</td>
<td>41.15</td>
<td>11.47</td>
<td>3.44</td>
<td>3.44</td>
<td>2.92</td>
<td>2.96</td>
<td>19.10</td>
<td>67.36</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>89.60</td>
<td>28.56</td>
<td>11.60</td>
<td>11.70</td>
<td>8.69</td>
<td>8.87</td>
<td>10.50</td>
<td>37.60</td>
<td>147.35</td>
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<td>Pr</td>
<td>11.45</td>
<td>4.18</td>
<td>2.12</td>
<td>2.15</td>
<td>1.48</td>
<td>1.51</td>
<td>1.48</td>
<td>4.32</td>
<td>17.61</td>
</tr>
<tr>
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<td>48.87</td>
<td>19.85</td>
<td>12.10</td>
<td>12.10</td>
<td>8.1</td>
<td>8.19</td>
<td>6.86</td>
<td>16.80</td>
<td>60.16</td>
</tr>
<tr>
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<td>10.52</td>
<td>5.28</td>
<td>4.35</td>
<td>4.34</td>
<td>2.77</td>
<td>2.83</td>
<td>1.87</td>
<td>3.35</td>
<td>16.44</td>
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<tr>
<td>Eu</td>
<td>3.23</td>
<td>1.86</td>
<td>1.51</td>
<td>1.53</td>
<td>1.08</td>
<td>1.1</td>
<td>0.68</td>
<td>1.01</td>
<td>0.38</td>
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<tr>
<td>Gd</td>
<td>9.46</td>
<td>5.75</td>
<td>6.00</td>
<td>6.08</td>
<td>3.86</td>
<td>3.88</td>
<td>2.26</td>
<td>3.25</td>
<td>18.79</td>
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<td>Tb</td>
<td>1.29</td>
<td>0.88</td>
<td>1.07</td>
<td>1.09</td>
<td>0.671</td>
<td>0.68</td>
<td>0.37</td>
<td>0.51</td>
<td>3.73</td>
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<tr>
<td>Dy</td>
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<td>5.16</td>
<td>7.32</td>
<td>7.27</td>
<td>4.49</td>
<td>4.61</td>
<td>2.46</td>
<td>3.16</td>
<td>26.25</td>
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<tr>
<td>Y</td>
<td>27</td>
<td>24.26</td>
<td>40.7</td>
<td>41.1</td>
<td>25.8</td>
<td>26.1</td>
<td>13.94</td>
<td>18.0</td>
<td>160.7</td>
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<tr>
<td>Ho</td>
<td>1.06</td>
<td>0.97</td>
<td>1.58</td>
<td>1.56</td>
<td>0.963</td>
<td>0.98</td>
<td>0.54</td>
<td>0.67</td>
<td>5.41</td>
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<td>2.54</td>
<td>4.62</td>
<td>4.65</td>
<td>2.81</td>
<td>2.86</td>
<td>1.56</td>
<td>1.93</td>
<td>16.43</td>
</tr>
<tr>
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<td>0.33</td>
<td>0.66</td>
<td>0.66</td>
<td>0.4</td>
<td>0.41</td>
<td>0.22</td>
<td>0.28</td>
<td>2.15</td>
</tr>
<tr>
<td>Yb</td>
<td>1.59</td>
<td>1.97</td>
<td>4.28</td>
<td>4.27</td>
<td>2.58</td>
<td>2.64</td>
<td>1.56</td>
<td>1.88</td>
<td>15.64</td>
</tr>
<tr>
<td>Lu</td>
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<td>0.29</td>
<td>0.66</td>
<td>0.65</td>
<td>0.392</td>
<td>0.391</td>
<td>0.23</td>
<td>0.29</td>
<td>2.22</td>
</tr>
<tr>
<td>Th</td>
<td>6.69</td>
<td>0.88</td>
<td>0.14</td>
<td>0.14</td>
<td>0.147</td>
<td>0.157</td>
<td>0.91</td>
<td>5.45</td>
<td>66.97</td>
</tr>
<tr>
<td>U</td>
<td>1.83</td>
<td>0.30</td>
<td>0.07</td>
<td>0.07</td>
<td>0.051</td>
<td>0.056</td>
<td>0.31</td>
<td>1.67</td>
<td>21.1</td>
</tr>
<tr>
<td>Zr</td>
<td>317</td>
<td>145.2</td>
<td>119.7</td>
<td>119.4</td>
<td>80.1</td>
<td>81.2</td>
<td>40.91</td>
<td>100.10</td>
<td>349</td>
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<td>Hf</td>
<td>7.30</td>
<td>3.90</td>
<td>3.26</td>
<td>3.30</td>
<td>2.0</td>
<td>2.03</td>
<td>1.25</td>
<td>2.56</td>
<td>14.71</td>
</tr>
<tr>
<td>Ce/Ce*</td>
<td>0.95</td>
<td>0.99</td>
<td>1.12</td>
<td>1.13</td>
<td>1.06</td>
<td>1.06</td>
<td>0.95</td>
<td>0.92</td>
<td>0.98</td>
</tr>
<tr>
<td>Th/U</td>
<td>3.7</td>
<td>2.9</td>
<td>2.0</td>
<td>1.9</td>
<td>2.9</td>
<td>2.8</td>
<td>3.0</td>
<td>3.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Zr/Hf</td>
<td>43.4</td>
<td>37.2</td>
<td>36.7</td>
<td>36.2</td>
<td>40.1</td>
<td>40.0</td>
<td>32.7</td>
<td>39.1</td>
<td>23.7</td>
</tr>
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</table>
3.2 Leachates

3.2.1 Rare earth elements and yttrium

Trace element data for the leaching solutions are reported in Table 2 and their REY$_{BN}$ patterns are shown in Fig. 3-6. The REY$_{BN}$ patterns for the basalt leachates with DFOB are flat between the MREY and the HREY and show either a (small) negative Eu anomaly (Fig. 3: MORB-EPR, MORB-TP, OIB-Haw, OIB-Me; Fig. 4: A-JP, OL20B, GSAF3) or no Eu anomaly (Fig.3: MORB-TPglass, MORB-EPRglass). The LREY distribution is more variable, but La and Pr are always depleted relative to the other REY. The REY$_{BN}$ patterns of the leachates with DFOB of the more evolved igneous rocks are more diverse with slightly decreasing, flat and slightly increasing patterns between the MREY and HREY (Fig. 4). While La is the most strongly depleted REY in the leachates, all leaching solutions with DFOB show a positive Ce anomaly (Figs. 3 and 4). In the presence of DFOB, Ce and La show this behavior regardless of the pH during the leaching experiment and irrespective of the rock type, the texture and the mineralogical composition of the leached material.

Fig. 5 illustrates the difference between REY mobilization from andesite (OL20B) during leaching with 1 mM DFOB, with 1 mM HCl and 1 mM acetic acid, respectively. Mobilization of the HREY was more effective in the presence of DFOB, and La-depleted LREY-concave patterns with positive Ce anomalies in the leaching solutions only developed in the presence of DFOB. Fig. 6 shows the REY$_{BN}$ patterns of all DFOB leachates normalized to Yb to simplify comparison of the REY patterns.

We emphasize that only in the presence of the DFOB siderophore leaching produces solutions that are significantly depleted in La and anomalously enriched in Ce relative to the respective bulk rock.
2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment

Fig. 3: Bulk-rock normalized REY patterns of leachates from experiments conducted on mid-ocean ridge basalts (MORB) and the ocean island basalts (OIB).

Fig. 4: Bulk-rock normalized REY patterns of leachates from experiments conducted on granite and (basaltic) andesite samples.

Fig. 5: Yb-normalized bulk rock-normalized REY patterns of leachates experiments conducted on andesite sample OL20B with 1mM DFOB, 1mM acetic acid and 1mM HCl and OIB-Me and OIB-Haw with 1mM HCl. Note that neither HCl nor acetic acid produces the LREY-concave patterns and the positive Ce anomaly that are typical of leaching in presence of DFOB.

Fig. 6: Yb-normalized bulk rock-normalized REY patterns of leachates of various rock types with DFOB-bearing solutions. Note that only in the presence of the DFOB siderophore does leaching produce solutions with positive Ce anomaly and La-depleted concave downward LREY patterns (see Fig. 5) and all leachates show negative Eu anomalies except for those from the MORB glasses which do not show anomalous behavior of Eu.
2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment

Table 2: Trace element compositions of the siderophore-bearing leachates after a leaching time of 24h. Concentrations given are ng/kg.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>OIB-Me</th>
<th>OIB-Haw</th>
<th>MORB-EPR</th>
<th>MORB-EPR repl.</th>
<th>MORB-TP</th>
<th>MORB-TP repl.</th>
<th>A-Jp</th>
<th>OL20B</th>
<th>GSAF3</th>
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</thead>
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<tr>
<td>ng/kg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>458.0</td>
<td>168.8</td>
<td>111.9</td>
<td>3.5</td>
<td>202.4</td>
<td>54.8</td>
<td>138.6</td>
<td>73.8</td>
<td>3046.3</td>
</tr>
<tr>
<td>Ce</td>
<td>11439.1</td>
<td>3336.3</td>
<td>4919.1</td>
<td>366.5</td>
<td>2492.9</td>
<td>381.0</td>
<td>3992.5</td>
<td>1620.0</td>
<td>56562.6</td>
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<td>52.3</td>
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<td>1458.4</td>
<td>576.0</td>
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<td>241.6</td>
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<td>97.3</td>
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<td>115.2</td>
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<td>11.1</td>
<td>52.0</td>
<td>21.9</td>
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Table 3: Experimental details for all batch leaching experiments conducted and presented in this study.

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<th>Rock sample</th>
<th>Reagent</th>
<th>Solid contents</th>
<th>Experiment time [h]</th>
<th>pH start</th>
<th>pH end</th>
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<td>5.5</td>
<td>8</td>
</tr>
<tr>
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<td>20 g / L</td>
<td>24</td>
<td>5.5</td>
<td>7.69</td>
</tr>
<tr>
<td>MORB-EPR</td>
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<td>24</td>
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<td>MORB-EPR repl.</td>
<td>1mM DFOB</td>
<td>20 g / L</td>
<td>24</td>
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<td>8.3</td>
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<td>MORB-EPR glass</td>
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<td>20 g / L</td>
<td>24</td>
<td>5.5</td>
<td>8.2</td>
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<td>MORB-TP</td>
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<td>24</td>
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<td>8.8</td>
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<td>MORB-TP repl.</td>
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<td>20 g / L</td>
<td>24</td>
<td>5.5</td>
<td>8.7</td>
</tr>
<tr>
<td>MORB-TP glass</td>
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<td>20 g / L</td>
<td>24</td>
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<td>8.5</td>
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<tr>
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<td>20 g / L</td>
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<td>8.5</td>
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<td>5.5</td>
<td>8.3</td>
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<td>Andesite OL20B</td>
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<td>Granite CSAF3</td>
<td>1mM DFOB</td>
<td>20 g / L</td>
<td>24</td>
<td>5.5</td>
<td>7.82</td>
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</table>
3.2.2 High Field Strength Elements (Zr, Hf, Th, U) and Zr/Hf and Y/Ho ratios

Considerable amounts of Zr, Hf, Th and U are present in all leachates. Their concentrations range from 943 - 10368 ng/kg for Zr, 17.3 - 367 ng/kg for Hf, 7.7 - 7813 ng/kg for Th and 9.6 - 32597 ng/kg for U. Yttrium and Ho concentrations in the leachates are 1350 - 65160 ng/kg and 27.3 - 2731.2 ng/kg, respectively. For all investigated elements, the granite leachate shows the highest HFSE concentrations whereas the leachates of the basaltic volcanic glasses show the lowest HFSE concentrations (see Table 2).

Figures 7 and 8 show graphs of Zr/Hf ratio vs Y/Ho ratio and Ce anomaly (i.e., Ce/Ce* ratio) vs Th/U ratio, respectively, of the bulk rocks and the corresponding siderophore leachates. Both geochemical twin pairs, Y-Ho and Zr-Hf, hardly fractionate during leaching and their ratios differ only slightly from those in the respective bulk rock (Fig. 7). All MORB, OIB and andesite leachates are enriched in Zr over Hf relative to bulk rock, indicating minor incongruent solubilization and fractionation of Zr from Hf with preferential mobilization of Zr in the presence of siderophores. Except for the leachates of the OIBs (OIB-Me, OIB-Haw) and the granite (GSAF3), all leachates are enriched in Y over Ho, i.e. have slightly higher Y/Ho ratios than the corresponding bulk rock. The leachate of the granite is enriched in Ho over Y (relative to bulk rock), and Y-Ho fractionation is insignificant in the leachates of the OIBs.

In the presence of the DFOB siderophore, all leachates show a Ce/Ce* ratio above unity, i.e. a positive Ce anomaly (Fig. 8). Th/U ratios of all leachates are, except for the MORB-TP glass leachate, below the respective bulk rock ratio, i.e. the leachates are significantly enriched in U over Th relative to the bulk rocks (Fig. 9). The leachates of the andesite and the OIBs have slightly higher Ce/Ce* ratios than the other leachates. Regardless of the rock type, the texture and the mineralogical composition, all leachates show fractionated Th/U ratios due to preferential U enrichment, and elevated Ce/Ce* ratios, i.e. preferential Ce enrichment relative to the other REE, suggesting that both U and Ce might be mobilized by a similar mechanism.

The multielement diagrams in Figs. 10 and 11 show bulk rock-normalized leachate compositions. Mobilization of Y, Ho, Zr, Hf, Th and U in the presence of DFOB is significantly more pronounced from the crystalline MORB than from the respective volcanic glasses (Fig. 10). The MORB show preferred mobilization of Th and U over Zr, Hf, Y and Ho. Zirconium, Hf, Y and Ho are virtually unfractionated. Control experiments without
DFOB (plain DI) had concentrations of these trace elements that were below the determination limit of the analytical technique applied, i.e., at least two orders of magnitude lower than the DFOB-bearing solutions.

Yttrium and Ho are enriched in the OIB and andesite leachates relative to Zr, Hf and Th (Fig. 11). Zirconium, Hf and Th exhibit an upward pattern towards U in the siderophore leachates (Fig. 11) for MORBs, OIBs and andesites. U is significantly enriched relative to other HFSEs in all leaching experiments, except for the MORB TP glass.

We emphasize that similar types of rocks (e.g. the two OIBs or the four MORBs) demonstrate very similar trace element mobilization behavior when leached with siderophores. Hence, the Th-U and Y-Ho fractionation is specific for the interacting rock-siderophore system.

Fig. 7: Diagram showing Zr/Hf ratio vs. Y/Ho ratio for batch leaching experiments with powdered igneous rocks. Open symbols represent leachates, while bulk rock ratios are shown in solid symbols. Note that fractionation of Y-Ho and Zr-Hf is small and that replicate experiments (error bars) for the leachates indicate a good reproducibility of the experimental data. C1 chondrite and average continental crust data from Anders & Grevesse (1989) and Rudnick & Gao (2003), respectively.

Fig. 8: Diagram showing Ce anomaly (expressed as Ce/Ce*) in relation to Th/U ratios of bulk rocks and the respective leachates. Note that all leachates show positive Ce anomalies and that Th/U ratios are strongly fractionated. The exceptional Th/U ratio for the MORB-TP glass leachate was verified in three replicate experiments. C1 chondrite and average continental crust data from Anders & Grevesse (1989) and Rudnick & Gao (2003), respectively.
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Fig. 9 (left): Plot of Th vs. U for batch leacheates and corresponding bulk rocks. While Th and U are positively correlated in the bulk rocks \( R^2 = 0.99 \), all leachates are strongly enriched in U over Th relative and plot above the trend line of \( \text{Th}/\text{U}=3.8 \) defined by chondrite and average upper continental crust. C1 chondrite and average continental crust data from Anders & Grevesse (1989) and Rudnick & Gao (2003), respectively.

Fig 10: Bulk rock-normalized trace element patterns for leachates from microcrystalline basalts (EPR cryst and TP cryst) and the corresponding glassy counterparts (EPR glass and TP glass, respectively). Note that error bars obtained by two replicate experiments are smaller than the symbols for all elements except U.

Fig. 11: Bulk rock-normalized trace element pattern for leachates of the ocean island basalts OIB-Me and OIB-Haw and the island-arc andesite A-Jp. Note that error bars obtained by replicate experiments are smaller than the symbols for all elements.
4. Discussion

4.1 REY(III) mobilization with siderophores

The REY are traditionally assumed to be largely immobile during water-rock interaction (e.g., Bau, 1991). While varying concentrations of complexing ligands, pH and other environmental parameters are likely to influence leaching efficiency, the very strong (more than two orders of magnitude) enrichment of the REY in the DFOB-bearing relative to the DFOB-free leachates suggests that siderophores have a very profound impact on REY mobility. This could affect REY mobilization in a variety of natural environments and processes, such as continental weathering and pedogenesis, diagenetic water-rock interaction in unconsolidated sediments, and particle-dissolution in seawater and in freshwater systems. Mobility of REY in supergene environments may offer opportunities for geochemical exploration, but may also increase their potential for environmental contamination and their bioavailability.

The different mineralogical compositions and textures of the samples studied and the different pH conditions during the individual batch leaching experiments led to markedly different absolute trace element concentrations in the leachates. However, the Yb-normalized REY$_{BN}$ patterns (Fig. 6) reveal the general fractionation trend within the REY group and highlight differences between the type of fractionation imposed by the specific chelators present in the different leaching solutions.

Without any exceptions and independent of pH, leaching of volcanic rocks in the presence of DFOB produced REY$_{BN}$ patterns in the leachate that show depletion of the LREY relative to the middle and heavy REY (Figs. 3 and 4) and concave downward LREY patterns. This depletion is most pronounced for La and becomes smaller with increasing LREY atomic number. This feature is neither produced during leaching with DI water, nor with HCl or acetic acid (Fig. 5).

Negative Eu anomalies in leaching solutions of mafic, intermediate and felsic igneous rocks have been suggested to be the ultimate result of the preferential incorporation of Eu into feldspars (Giese and Bau, 1994; Bach and Irber, 1998; Bau, 1998;; Shibata et al., 2006). The melt in the vicinity of a growing plagioclase crystal becomes selectively depleted in Eu due to preferential partitioning of Eu$^{2+}$ into the crystal lattice of plagioclase, leading to REY patterns with negative Eu anomalies at grain boundaries, in the groundmass and in the interstitial space between crystals (Giese and Bau, 1994). Because feldspars and other rock-forming minerals
do not readily dissolve during short-lived water-rock interaction, it is the easily accessible REY load of this Eu-depleted pool that is preferentially mobilized, producing leachates with negative Eu$_{BN}$ anomaly (Giese and Bau, 1994; Bau, 1998). If this was correct, leaching of rocks without a significant feldspar component, such as basaltic glass, should not produce leaching solutions with a negative Eu$_{BN}$ anomaly. Our experimental results fully support this hypothesis (Figs. 3 and 4): both MORB glasses produce leachates without any negative Eu$_{BN}$ anomaly and the glass-rich sample OIB-Me shows only a very small one (Fig. 3).

The granite leachate shows no Eu anomaly in its bulk rock-normalized leachate patterns (Fig. 4), revealing that Eu is leached to a similar extent as its REY neighbors, although the REY$_{CN}$ pattern of the bulk rock shows a significant negative Eu anomaly.

The strong depletion of La relative to the other LREY in the basalt leachates might on first sight suggest decoupling of La from the other LREY. Such partial decoupling and the subsequent formation of La anomalies are known from seawater and from some chemical sediments, and have been observed during REY scavenging by Fe and Mn (hydr)oxides (Bau and Dulske, 1996a; Bau, 1999; Bau and Koschinsky, 2009). The decoupling has been explained by anomalously low hydrolysis constants of La as compared to its LREY neighbours, which ultimately results in positive La anomalies in the aqueous phase and negative La anomalies in the solid (e.g., Bau, 1999). However, in such cases the La anomaly is usually accompanied by Gd anomalies and strong Y-Ho fractionation (Bau, 1996; 1999), which we did not observe in our experiments. It is therefore very unlikely that the La depletion seen in the leachates represents decoupling of La from the other REY. Rather, leaching with DFOB in general produces solutions whose REY$_{BN}$ patterns are concave between La and Sm and which increase smoothly and systematically from La to the MREY. Because this is observed for leaching of both, crystalline and glassy EPR basalt, it can be ruled out that this REY signature is the result of a mineralogical control during REY mobilization, but rather demonstrates that this signature develops specifically during leaching in the presence of DFOB.

A full set of stability constants for REY-DFOB complexes (Fig. 1) is available for the trivalent REY at seawater ionic strength of 0.7 (Christenson & Schijf, 2011). This high-quality data set indicates that the stability constants of the bi-, tetra- and hexadentate REE(III)-DFOB complexes increase most sharply from La to Sm. This relationship compares favorably with the REY$_{BN}$ patterns observed in our leachates, which show only little
fractionation between the MREY and HREY, but more pronounced fractionation between La and the MREY (Figs. 3 and 4). This indicates that the presence of the DFOB siderophore preferentially promotes the mobilization of MREY$^{3+}$ and HREY$^{3+}$ over that of LREY$^{3+}$, and that La is the REY which is least affected by siderophore-promoted REY mobilization.

4.2 Oxidative mobilization of cerium

Cerium is the only REY that in natural low-temperature environments can occur in two oxidation states (+3 and +4). While Ce$^{3+}$ behaves similar to its strictly trivalent REY neighbors, Ce$^{4+}$ shows significantly different behavior during geochemical processes because of different partition coefficients, solubilities and complex stabilities of Ce (IV) as compared to Ce(III) and its respective compounds. This leads to a decoupling of tetravalent Ce from its trivalent REY neighbors and causes the formation of Ce anomalies in normalized REY patterns. Although the inorganic chemical oxidation of Ce$^{3+}$ is slow, surface catalysis and microbial mediation may promote Ce$^{3+}$ oxidation and subsequent formation of Ce anomalies in low-temperature environments (Bau, 1999; Ohta and Kawabe, 2001; Yoshida et al., 2004; Davranche et al., 2005, 2008; Bau and Koschinsky, 2009; Tanaka et al., 2010;). Negative Ce anomalies are common in oxic waters because of oxidative scavenging of Ce on particle surfaces and/or Ce fixation due to formation of insoluble Ce(IV) compounds (e.g. Bau and Koschinsky, 2009 and references therein). The only known exception is the CO$_3^{2-}$-rich water of alkaline lakes which show positive Ce anomalies (Möller and Bau, 1993; Johannesson and Lyons, 1994; Johannesson et al., 1994) due to the stabilization of Ce(IV) polycarbonate complexes in solution (Möller and Bau, 1993). Preferential stabilization of dissolved Ce(IV) compounds has also been observed in experimental studies of competitive complexation of REY by humic acids and CO$_3^{2-}$ (Pourret et al., 2007a). Similar to the situation in alkaline lakes, however, (Pourret et al., 2007a) argue that Ce$^{3+}$ oxidation is promoted by the formation of Ce(IV) pentacarbonate complexes and that only in a second step Ce(IV) is bound to the humates. Because humates are a substantial part of the colloidal REY fraction in organic matter-rich natural waters, this does not produce a positive Ce anomaly in the truly dissolved REY, but in the nanoparticle and colloid REY fraction.

As shown by our experiments (Figs. 3 and 4), leaching of volcanic rocks in the presence of DFOB typically produces solutions with a positive Ce anomaly. This selective decoupling of
Ce from the other REY demonstrates that Ce\(^{3+}\) is oxidized during its solubilization during water-rock interaction. The preferential mobilization of Ce is confined to leaching in the presence of DFOB, regardless of the prevailing pH, and regardless of the type, mineralogy and texture of the rock that is leached. This suggests the formation of a Ce(IV) DFOB complex that is significantly more stable than its Ce(III) counterpart. This interpretation is supported by previous observations that Ce shows anomalously low adsorption on bacterial cells (relative to the other REY) in the presence of DFOB (Yoshida et al., 2004; Ozaki et al., 2006). Trivalent Ce was oxidized during these adsorption experiments and rapidly bound in a highly stable Ce(IV) DFOB complex in solution (Yoshida et al., 2004; Ohnuki et al., 2005). Our results also corroborate the hypothesis that the preferential release of Ce observed during microbial leaching of artificial hornblende glass (Brantley et al., 2001) resulted from the excretion of siderophores by the bacteria and not from changes in pH or by the presence of other low molecular weight organic acids.

Our results demonstrate that the formation of Ce(IV) polycarbonate complexes is not the only complexation mechanism that can promote fractionation of Ce from its REY neighbors. Siderophores like DFOB significantly enhance the solubility of Ce(IV) and can produce positive Ce anomalies in natural waters. While the formation of Ce(IV) pentacarbonate complexes requires high CO\(_3^{2-}\) activity and hence only operates in alkaline environments, complexation by siderophores can occur under mildly alkaline, near neutral and even mildly acidic conditions. This suggests that siderophore complexation can significantly impact Ce behaviour and may cause Ce-REY decoupling in a much wider range of natural environments, including soil solutions, groundwaters, river and lake waters, seawater and marine porewaters.

### 4.3 Mobilization and fractionation of Zr, Hf, Th and U by siderophores

High field strength elements such as Zr, Hf, Th, U and the REY hydrolyze easily and are particle-reactive, i.e. they readily bind to hydroxyl and carboxyl groups, for example, on particle surfaces. As a result, truly dissolved concentrations of these HFSE in natural waters are usually very low, due to their immediate precipitation or sorption onto Mn or Fe (oxyhydr)oxides, clay minerals or organic particles (e.g., Tepe and Bau, 2014, and references therein). There is general consent that in most geological settings HFSE are rather immobile during water-rock interaction (e.g., Jiang et al., 2005, and references therein). In all our
experiments, the presence of siderophores during leaching significantly enhanced the mobilization of the ‘immobile’ HFSE Zr, Hf, Th, U, and REY into the dissolved pool. The granite leachates yield the highest HFSE concentrations due to the higher abundance of these metals in the original rocks. The batch leaching experiments on crystalline MORB and MORB glasses demonstrate that all studied HFSE (including the REY) are more effectively mobilized from crystalline volcanic rock than from volcanic glass. In igneous rocks, the HFSE and REY are incompatible and usually are not incorporated into the crystal lattice of the major rock-forming minerals. Rather, they are enriched in interstitial spaces and in the ground mass of igneous rocks (Giese and Bau, 1994; Bau, 1998). This ‘loose’ bonding leads to an easy availability during leaching. Similar to previous results (Giese and Bau, 1994; Bau, 1998), our experimental results demonstrate that the HFSE and the REY are more readily leached by siderophores when these elements are located along grain boundaries and in a rock’s matrix.

Considering the stability constants of their various chemical complexes (Martell and Smith, 2001), siderophores do not only mobilize iron, but they should also be able to mobilize a wide range of HFSE. This is in general agreement with the results of our leaching experiments, as in all these experiments we observed enhanced HFSE mobilization in the presence of siderophores, although with only minor fractionation of the geochemical twin pairs Zr-Hf and Y-Ho, but with strong Th-U fractionation due to preferential mobilization of U.

In all experiments, Th and U are more effectively mobilized than Zr, Hf, Y, and Ho. Comparing Th and U, U is preferentially mobilized and the leachates are strongly fractionated towards Th/U ratios that are lower than those of the respective bulk rocks. It is well known that Fe(III)-reducing bacteria have an impact on U mobility (see Wilkins et al., 2006 and references therein) and that DFOB forms stable complexes with U (Desouky et al., in press; Mullen et al., 2007; Wolfl-Boenisch and Traina, 2007). We showed that leaching in the presence of DFOB not only enhances the dissolved concentrations of U in the leaching solutions, but that it also strongly promotes decoupling of U from Th.

Considering that in the presence of siderophores, redox-sensitive U behaves similar to redox-sensitive Ce (both are preferentially mobilized relative to redox-insensitive Th and LREY, respectively; Fig. 8), it is likely that this is due to the formation of a U(VI) DFOB complex in the leachate. The stability constant of DFOB with Th(IV) is reported by Martell & Smith (2001) to be in the range of log $K_f = 15.7$. Due to the same oxidation state and similar radius
of Th(IV) and U(IV), U(IV) stability constants with DFOB can be assumed to be in the same range as those of the Th(IV) DFOB complex. Mullen et al. (2007) determined the stability constants of U(VI) in the form of the uranyl ion (UO$_2^{2+}$) with DFOB and showed that the stability constants of U(VI) DFOB complexes (log $K_f$: 17.12 - 22.93) are significantly higher than that of Th(IV) and, thus, likely also of the U(IV) DFOB complex. Thus, if U(IV) formed complexes with DFOB and was mobilized as a U(IV) DFOB complex, Th-U fractionation should only be minor. If, however, U was present as U(VI), then complexation with DFOB resulted in significant decoupling of U from Th. The siderophore leachates show strong Th-U fractionation in almost all experiments, suggesting that a significant fraction of total U in the leachates occurred as U(VI) species. In natural systems, Th is exclusively present as a tetravalent ion and its mobility is very limited due to the formation of Th(OH)$_4$ which is characterized by low solubility (Choppin, 2006). At neutral to alkaline pH, U is mostly present in the surface environment as one of several water-soluble uranyl (U(VI)O$_2^{2+}$) carbonate species (Grenthe et al., 2004; Choppin, 2006). In our experiments U(VI) carbonate speciation is negligible, because DFOB concentrations are two orders of magnitude higher than total CO$_2$ concentration (assumed to be in equilibrium with atmosphere) and because DFOB complexes with uranyl are several orders of magnitude more stable (Mullen et al., 2007) than the carbonate complexes commonly prevailing in low-temperature aqueous solutions (Grenthe et al., 2004; Choppin, 2006).

Y-Ho and Zr-Hf are both slightly fractionated during mobilization in the presence of DFOB. How strong this fractionation is appears to depend on the specific rock type that interacts with the siderophore. Christenson & Schijf (2011) give the stability constants, log $K_f$, of Y and Ho with DFOB for hexadentate complexes as 13.98 and 14.13 - 14.53, respectively. The stability constants of these two elements with DFOB are thus rather similar, suggesting that fractionation of Y and Ho induced by DFOB complexation should be minor. This is in agreement with the rather small Y-Ho fractionation observed in our leaching experiments (Fig. 7).

Yoshida et al. (2007) suggested that the stability constant for the Hf(IV) DFOB complex is similar to that of the Fe(III) DFOB complex and, hence, should be in the range of log $K_f = 30.7$ for hexadentate complexes (Martell & Smith, 2001). No data are available for the Zr(IV) DFOB complex. Our batch leaching experiments showed only minor Zr-Hf fractionation with Zr/Hf ratios in the leachates only slightly above the bulk rock ratios. The minor fractionation
of the Zr-Hf twin pair towards super-chondritic ratios suggests that the stability of Zr(IV) DFOB complexes is probably slightly higher than that of Hf(IV) DFOB complexes given that the mode of binding in the host minerals is similar. Considering the chemical similarity of Zr and Hf, this is a reasonable assumption. Both, the mobilization of Zr-Hf and Y-Ho in the presence of DFOB can be partially explained by published thermodynamic data as a function of the specific stability constants with the DFOB siderophore. The dissolved concentrations of Zr and Hf in the granite leachates are orders of magnitude higher than in the mafic and intermediate rock leachates (see Table 2). In evolved rocks, almost all of the Zr and Hf are hosted in the zircon structure. The observed high mobility of Zr and Hf during leaching of the granite with siderophores (see Table 2 and Fig. 9) may imply that siderophores potentially solubilize Zr and Hf from zircons, a mineral which is usually regarded as very weathering resistant.

Because of the preferential scavenging of Hf relative to Zr onto particles (e.g., Bau and Alexander, 2009; Schmidt et al., 2014), modern seawater shows super-chondritic Zr/Hf ratios (Godfrey et al., 1996, 2008; Firdaus et al., 2011), i.e. seawater is enriched in Zr over Hf. However, Firdaus et al. (2011) indicated that terrigenous sources are important for the budget of Zr and Hf in seawater. It has been suggested that Hf is removed from the dissolved pool when river water mixes with seawater in estuarine systems because of aggregation and sedimentation of particles (see e.g. Godfrey et al., 2008). Thus, the overall amount of Hf that actually enters seawater via fluvial pathways is considered to be very small (Bau and Koschinsky, 2006). Our experiments corroborate results of incubation experiments (Bau et al., 2013) and demonstrate that Zr and Hf are complexed and mobilized in the presence of the DFOB siderophore (Figs. 10-11; Table 2). Considering that siderophore complexes are chemically stable over a wide range of pH and Eh conditions (Kraemer, 2004), the transport of e.g. Hf(IV) as a Hf(IV) siderophore complex might limit sorption to river particles and suppress removal of Hf (and Zr) in estuarine systems, but effectively facilitate the transport of continental Hf through estuaries into the open ocean.

4.4 Impact of siderophores on geochemical applications using Ce and U

Our experiments demonstrate that redox-sensitive Ce and U are oxidized and eventually decoupled from LREY and Th, respectively, during leaching in presence of siderophores. For
both elements the reduced redox-species (Ce(III) and U(IV), respectively) are released from minerals and rocks, and depending on the physico-chemical environment (e.g., oxygen fugacity, temperature, pH) the specific Ce\(^{4+}\)\(_{aq}\)/Ce\(^{3+}\)\(_{aq}\) and U\(^{6+}\)\(_{aq}\)/U\(^{4+}\)\(_{aq}\) redox equilibria are established. However, oxidized Ce\(^{4+}\)\(_{aq}\) and U\(^{6+}\)\(_{aq}\) are immediately bound and removed as Ce(IV) DFOB and U(VI) DFOB complexes and in the attempt to maintain the redox equilibria, additional Ce\(^{4+}\)\(_{aq}\) and U\(^{6+}\)\(_{aq}\) are produced. The overall effect of this “siderophore redox pump” is the preferential enrichment of dissolved Ce and U relative to dissolved LREY and Th, respectively.

This may have a profound impact of the use of Ce and U as paleo-redox-proxies. In anoxic natural environments, Th and U are both tetravalent and considered ‘immobile’ due to their very low solubilities. Thus, these two elements are not fractionated from each other during their release from minerals/rocks because of their same oxidation state. However, ‘immobile’ U(IV) is oxidized to ‘mobile’ U(VI) in Earth’s (near-)surface systems during oxidative weathering of minerals and rocks (e.g., Collerson and Kamber, 1999). Soluble U(VI) compounds such as uranyl (U(VI)O\(_2\)\(^{2+}\)), therefore, predominate over less soluble U(IV) species (Wilkins et al., 2006) and modern oxic seawater, for example, shows dissolved Th/U ratios below unity (e.g., Asmerom and Jacobsen, 1993). These low Th/U ratios are eventually transferred to marine chemical sediments which act as archives of the Th/U ratio of seawater. Therefore, coupled or decoupled Th-U behavior may be used as a paleo-redox-proxy for tracking the evolution of the redox level of a geochemical system such as the Earth’s atmosphere and oceans (e.g., Rosing and Frei, 2004; Bau and Alexander, 2009). Similarly, presence or lack of Ce anomalies in chemical sediments and precipitates, and in paleosols and paleoweathering profiles is used as a paleo-redox proxy (see e.g. Möller and Bau, 1993; German and Elderfield, 1990; Pattan et al., 2005).

However, our experimental results suggest that the presence of strong organic ligands such as siderophores is sufficient to promote oxidation and mobilization of U and Ce. If there is ample reason to believe that significant amounts of siderophores or other strong ligands were present during the deposition of a studied rock, the use of proxies such as U and Ce might be severely hampered.

Our result may also be important in the field of applied environmental science. Extensive research has been conducted on the long-term U removal from contaminated soils and waters by fixing aqueous U(VI) to insoluble U(IV) minerals via bacterial activity (see Newsome et
al., 2014 and references therein). Ganesh et al. (1997), for example, found that multidentate complexation with organic ligands substantially lowers the rate of U(VI) reduction by sulfate-reducing and ferric iron-reducing bacteria. Such a ‘shielding effect’ might also be observed for the very stable U(VI)-DFOB complexes, and complexation of U(VI) with DFOB, therefore, might suppress microbially induced U reduction in the environment. This may have widespread implications for the (bio-) remediation of U-contaminated sites near e.g. nuclear waste repositories or for microbial bioleaching of low-grade U ore deposits (Choi et al., 2005; Qiu et al., 2011). (Desouky et al., n.d.) presented a method to bioleach Th-U concentrates with siderophores and showed very promising results for Th and U extraction. However, given the stabilities of U and Th DFOB complexes (Mullen et al., 2007) in the environment and given that DFOB complexes are stable over a wide range of pH and Eh (Kraemer, 2004), a potential leakage may cause severe environmental damage and hamper remediation efforts due to very strong binding of Th and U to multidentate organic ligands like DFOB.

Stern et al. (2014) already showed that humic acid complexation plays a vital role for the speciation and mobility of Th, Hf and Zr in the environment. Our data show that siderophores, as another group of organic molecules, apparently play an equally important role in the mobilization and fractionation of these and other HFSE.

5. Conclusions

We studied the mobilization of REY, Zr, Hf, Th and U from volcanic rocks in the presence of the siderophore desferrioxamine B (DFOB), to see how low-temperature water-rock interaction during weathering, pedogenesis, or partial dissolution of particles in seawater and freshwater may affect the behavior of these trace elements.

Our results demonstrate that chemical complexation with the DFOB siderophore significantly enhances the mobility of these HFSE and leads to two distinct features in REY patterns, that develop independently of pH and regardless of the mineralogy and the texture of the rock being leached: (i) all leaching solutions display a positive Ce anomaly, and (ii) all leachates are depleted in the LREY (especially La) relative to the other MREY with a concave downwards LREY pattern. These features do not develop in the absence of DFOB during leaching with DIW, hydrochloric or acetic acid. Other features, such as a negative Eu
anomaly, are related to mineralogy and texture and may also be produced during leaching in the presence of hydrochloric or acetic acid.

The positive Ce anomalies are evidence for siderophore-promoted oxidative dissolution of Ce during low-temperature water-rock interaction and indicate the formation of a very stable, water-soluble Ce(IV) DFOB complex. These Ce(IV) siderophore complexes have the potential to create natural waters with positive Ce anomalies over a much wider pH range than Ce(IV) pentacarbonate complexes that are confined to CO$_3^{2-}$-rich alkaline environments. Weathering by siderophore-bearing solutions may thus produce Ce anomalies in environments that are too reducing to develop Ce anomalies in the absence of siderophores.

The fractionation and shape of the REY pattern between the LREY and MREY is consistent with REY(III) DFOB stability constants (Christenson & Schijf, 2011) and the La-depleted concave downward LREY pattern could potentially be used as an indicator for the presence of biogenic chelators such as DFOB during water-rock interaction. While it is clearly premature to use La-depleted concave downward LREY patterns as a siderophore-imposed biosignature, this possibility warrants further study of water-rock interaction in the presence of siderophores.

We also showed that the presence of siderophores significantly enhances even the concentrations of ‘immobile’ HFSE such as Zr, Hf, Th and U, in aqueous solutions. Analogous to Ce, preferential mobilization of U is attributed to siderophore-induced oxidative dissolution. In the presence of DFOB, U is oxidized from U(IV) to U(VI), which may have widespread implications for the use of Th-U as a paleo-redox proxy. In presence of the DFOB siderophore, U is significantly more effectively mobilized than Th, leading to Th/U signals comparable to those indicative for weathering under oxidized conditions.

Mobilization of the two geochemical twin pairs Y-Ho and Zr-Hf is characterized by ligand-promoted dissolution mechanisms and the mobilization with only minor fractionation observed in the leaching experiments appears to be a function of the specific metal-DFOB stability constant.

Our experiments showed that natural biogenic ligands such as siderophores are capable of solubilizing and complexing elements like the HFSE investigated here and, hence, facilitate the mobilization of ‘immobile’ trace elements during the weathering of rocks. Metal transport as siderophore-complexed compounds might represent an important pathway from rocks and
volcanic ashes to the oceans. Additionally, the transport of dissolved HFSE like Hf as siderophore complexes might efficiently alter their respective particle-reactivity and prevent their sorption onto particles during estuarine mixing processes. The enhanced mobilization of Zr and Hf from igneous rocks and volcanic ash particles might represent an important pathway for Hf from the continents into the oceans. This might have implications on the use of Hf isotopes for tracing water masses and continental weathering regimes.

Although DFOB concentrations in seawater samples are usually in the nanomolar range (e.g., Kraemer, 2004), DFOB concentrations can reach more than 0.13mM in soil solutions (Watteau and Berthelin, 1994; Kraemer, 2004). Considering the wide range of siderophore compounds identified in natural systems (Boukhalfa & Crumbliss, 2002) it is most likely that oxidative mobilization of Ce and U as well as enhanced mobilization of other HFSE such as Zr and Hf, is not unique to desferrioxamine B, but likely promoted by other natural siderophores as well. This suggests a significant impact of siderophores on trace element (re)distribution during weathering of rocks and minerals.
2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment

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2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment


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Scavenging of REY by Mn (hydr)oxides in Presence of Siderophores: Evidence for Negative Ce Anomalies and LREE Fractionation in Manganese Precipitates

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Abstract

We present experimental results on the scavenging behavior of rare earth elements and yttrium (REY) on precipitating manganese (hydr)oxide in the presence of the siderophore desferrioxamine B. In contrast to siderophore-free systems, where surface oxidation of Ce(III) to Ce(IV) during sorption onto manganese hydroxides and dioxides is commonly observed, our findings demonstrate that oxidative scavenging of Ce onto Mn (hydr)oxide is prevented in the presence of the hydroxamate siderophore desferrioxamine B and the minute amount of Ce⁴⁺ present in solution is preferentially bound by the siderophore ligand. The resulting redox disequilibrium between Ce³⁺ₐq and Ce⁴⁺ₐq promotes continuous oxidation of Ce³⁺ₐq, so that with time more and more Ce(IV) is strongly complexed by the siderophore and hence shielded from scavenging by Mn (hydr)oxide. In addition to this, the scavenging of heavy REY with ionic radii larger than the radius of Sm on Mn (hydr)oxides is impeded in the presence of siderophores, which is also in stark contrast to earlier findings dealing with siderophore-free systems. Apart from Ce, which is decoupled from its geochemical neighbors by the siderophore desferrioxamine B, the distribution of the other REY between the manganese (hydr)oxide phases and the remaining ambient solution strictly mimics the stability constants for multi-dentate complexes of REY with desferrioxamine B, i.e. the heavier REY are forming stronger complexes with the ligand and are hence more shielded from scavenging than the lighter REY La, Pr and the like. Negative Ce anomalies in Mn precipitates are commonly attributed to biogenic Mn oxides. Our findings are experimental results for negative Ce anomalies on abiogenic Mn precipitates.
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1. Introduction

The rare earth elements (REE) are a group of chemically coherent elements and consist of the lanthanides La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and the element Y. The rare earth elements and Y (REE+Y; REY) are widely used for geochemical applications, such as the reconstruction of chemical properties of aqueous and magmatic systems based on fractionation and decoupling of some REY or of a group of REY from their geochemical REY neighbors. These processes create distinct rare earth element patterns.

In low-temperature aqueous systems, the REY usually occur in a trivalent oxidation state as REY$^{3+}$ and hence exhibit a similar charge and radius-controlled behavior for the whole series (Goldschmidt, 1937). However, some REY are redox-sensitive, like Ce which can be oxidized to Ce$^{4+}$ under certain circumstances and the corresponding increase in charge and decrease in ionic radius consequentially leads to a decoupling of Ce from its REY neighbors, which in the end results in the formation of geochemical anomalies in minerals, rocks and aqueous solutions.

A range of these features have been identified in past and recent works, like Ce anomalous behavior in aquatic systems, Eu anomalies in magmatic rocks caused by fractional crystallization and tetrade effects in low-temperature aquatic environments (Bau, 1996, 1998; Ohta and Kawabe, 2001; Bau and Koschinsky, 2009; Tanaka et al., 2010). Yttrium anomalies or fractionation of Y and Ho are commonly used as an indicator for aqueous or highly evolved magmatic systems (Bau, 1996).

Most natural oxic aqueous systems on Earth’s surface, and especially seawater, exhibit negative Ce-anomalies in the trace metal profile, meaning a depletion of Ce with respect to other REY in the aqueous solution (Elderfield and Greaves, 1981). This circumstance is widely used as a proxy for redox conditions and in paleoceanography as an indicator for oxidized environments (German and Elderfield, 1990; Sholkovitz et al., 1994). Cerium oxidation in seawater occurs mainly due to oxidative scavenging (Bau and Koschinsky, 2009) of Ce$^{3+}$ to Ce$^{4+}$ by both Mn and Fe oxide and oxyhydroxide compounds. The REY speciation in the water column is mainly dominated by monocarbonate and dicarbonate complexation. The resulting competition with hydroxyl ligands located on the surfaces of the metal oxide structures leads to constant sorption and desorption of REY at and from the oxide particle...
surfaces (Bau and Koschinsky, 2009). In the water column, Mn and Fe oxides and oxyhydroxides are very efficient scavengers of particle-reactive trace metals from sea water. These particles, which effectively represent exchange equilibria with the ambient waters because of surface complexation, exhibit positive Ce anomalies, whereas the remaining solution, i.e. seawater, is consequentially depleted in Ce and hence exhibits negative Ce anomalies.

Experimental evidence for preferential sorption and the development of specific REE signatures is given by Bau (1999) for scavenging onto Fe oxyhydroxides and Ohta and Kawabe (2001) for REY sorption onto Mn oxides, respectively. While both experimental sets demonstrate that M-type lanthanide tetrad effects develop and Ce is oxidatively scavenged onto the particulate phases, Mn oxide exhibits a stronger oxidizing potential for Ce$^{3+}$ than Fe oxyhydroxides (Ohta and Kawabe, 2001). Bau (1999) has shown that for scavenging experiments with coprecipitating Fe oxyhydroxides, a positive Ce anomaly and a negative Y anomaly develops in all experiments conducted at pH smaller 5, but tetrad effects become more pronounced at higher pH and are small for lower pH. In contrast, REE sorption experiments with Mn oxide as conducted by Ohta and Kawabe (2001) revealed that REE sorption onto Mn oxides leads to positive Ce anomalies on the oxides and significant tetrad patterns in the pH range of 4.78 to 6.8.

However, there are some reports about natural waters in oxidized environments which do not exhibit negative Ce anomalies, in contrast to what should be expected by lab experiments by e.g. Bau (1999) and Ohta and Kawabe (2001). Some studies showed that oxidative scavenging of Ce during Fe oxyhydroxide formation and a consequential formation of negative Ce anomalies in the studied aqueous systems were not observed (e.g., Koeppenkastrop and De Carlo, 1992; Carlo and Wen, 1998; Quinn et al., 2006a; Quinn et al., 2006b; Quinn et al., 2007; Schijf and Marshall, 2011).

Fig.1 shows REY partition coefficients between MnO$_2$ and ambient solution as obtained by the studies from Ohta & Kawabe (2001) for REY sorption in organic ligand-free systems and Davranche et al. (2004) for REY sorption as humate complexes. Davranche et al. (2004, 2005) suggested that the occurrence of organic ligands in solutions effectively prevent the oxidation of Ce on particle surfaces of both Fe and Mn oxides and hydroxides. The authors further suggested that REE are predominantly bound as humate complexes, which either prevents sorption to particles or which adsorbs to particles as a ternary complex and
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hence shield Ce from the strong oxidizer Mn dioxide. They conducted REE sorption experiments with Fe oxyhydroxide (Davranche et al., 2004) and Mn dioxide (Davranche et al., 2005) and showed that for both Fe oxyhydroxides and Mn dioxides, the complexation of REE with humate ligands effectively prevents the development of Ce anomalies during REE partitioning between ambient solution and precipitates.

In contrast, Tanaka et al. (2010) conducted an experimental study on the sorption behavior of REE on biogenic Mn oxide in the presence of organic-ligand producing bacteria and showed that Ce is preferentially oxidized and negative Ce anomalies develop in biogenic Mn oxide precipitates (Fig. 1). In summary, manganese and iron oxides and hydroxides

![Graph showing REE partition coefficients between MnO₂ and ambient solution](image-url)
efficiently scavenge REY. In ideal solutions, i.e. without organic ligands sensu lattu, the particles oxidatively scavenge Ce and this scavenging leaves the remaining solution in a Ce-depleted state with respect to other REY.

However, on addition of organic ligands or in presence of organic ligand-producing bacteria, both no Ce anomalies as well as negative Ce anomalies in the particulate phases have been described in literature. Loges et al. (2012) published analytical data on secondary hydrothermal fluorite vein samples, which are accompanied by syngenetic Mn oxide formation. The manganese oxides show a distinct geochemical peculiarity as they exhibit extremely negative Ce anomalies of up to 4 orders of magnitude. In accordance to this, the mine draining and surface water samples have significantly high amounts of dissolved organic carbon, which indicates high concentrations of organic ligands in the solutions percolating the surrounding rock structures. Loges et al. (2012) indicated that these considerably high negative Ce anomalies observed in the Mn precipitates may be caused by siderophore-enriched waters percolating from the soil at the surface to depth via the fracture network of the veins and veinlets present in the system.

Siderophores are a group of low-molecular weight organic molecules synthesized by bacteria and plants in oxic environments to cope with iron deficiency. In oxic systems, Fe is usually occurring as Fe$^{3+}$ and is immediately bound to insoluble hydr(oxide) structures and hence removed from the dissolved pool. Thus, Fe$^{3+}$ in the oxic environment is not easily available as a trace nutrient for organisms because of the very low solubility of its (hydr)oxide minerals (Wang et al., 2014). Siderophores help organisms to obtain bioessential nutrients like Fe by facilitating the dissolution of oxide and oxyhydroxide minerals and complexing these liberated trace metals (Neilands, 1957). However, it was shown that siderophores not only have high complex stability constants for Fe, but also for other trivalent metals such as the REY. Christenson and Schijf (2011) presented a dataset on stability constants at seawater ionic strength for REY with the siderophore desferrioxamine B (DFOB), which is also the siderophore used in our experiments. Fig. 2 shows the stability constants for bidentate (log $\beta_1$), tetradentate (log $\beta_2$) and hexadentate (log $\beta_3$) complexes of DFOB with trivalent REY as determined by the works of Christenson and Schijf (2011). They showed that complex stability constants for the REY are significantly high and increase with increasing atomic numbers of the trivalent REY with the exception of the redox-sensitive Ce$^{3+}$, for which siderophores induce oxidation to Ce$^{4+}$ (Bau et al., 2013; Ohnuki and Yoshida, 2012).
They also demonstrated that stability constants for REY DFOB complexes are many orders of magnitude higher than for REY-carbonate complexes, which is the main complex species for REY in seawater. A study by Bau et al. (2013) demonstrated that REE are significantly leached from the particulate pool of volcanic ash-rich meltwater from Iceland when the samples are incubated with siderophore-bearing solutions and that the presence of siderophores like DFOB increases the dissolved concentrations of REE by several orders of magnitude. Furthermore, positive Ce anomalies were found in the dissolved pool after incubation with DFOB, indicating oxidative solubilization and preferential mobilization of tetravalent Ce over trivalent REE from volcanic ash particles to solution.

We here conducted experiments similar to the ones presented by Bau (1999), Ohta and Kawabe (2001) and Davranche et al. (2005). Instead of scavenging from organic ligand-free solutions (Bau, 1999; Ohta & Kawabe, 2001) or from humic acid bearing solutions (Davranche et al., 2005), REY scavenging experiments were conducted in the presence of the siderophore DFOB. We will show via scavenging experiments with precipitating Mn (hydr)oxide that oxidative scavenging of Ce can be impeded and negative Ce anomalies form.
in the particulate phases by siderophore-mediated oxidation and a retention of Ce\(^{4+}\) together with contemporaneous heavy REE retention in solution.

2. Methods

2.1. Experimental

The scavenging experiments were conducted after a modified approach of the Fe oxyhydroxide-REE-scavenging experiments conducted and published by Bau (1999). Instead of Fe, Mn is precipitated as Mn (hydr)oxide during the experiment by rising the pH of a mixed Mn-REY-siderophore solution and REY are scavenged during precipitate formation.

There is no mineralogical data available for the precipitating Mn (hydr-)oxides and thus the surface properties and mineral characteristics are not known. Thus, we will stick to the general term Mn (hydr)oxides throughout this study. A clear distinction of whether the REY are surface-sorbed or structurally incorporated into the crystal lattice is not possible. Therefore, we decided to use the unspecific term ‘scavenging’ instead of sorption and coprecipitation, but both pathways are possible. All experiments were carried out as time-series experiments with time intervals of 6.5, 15, 30, 60, 120 and 240 minutes.

All reagents used for experimental setups were of suprapure grade and lab work was done with acid-cleaned lab equipment and in a trace-metal clean environment. De-ionized water used in this study for preparation of chemical reagents was purified by reverse osmosis and ion exchange in a MilliQ Millipore purification system to an electric conductivity of 18M\(\Omega\)/cm. Element standards by InorganicVentures Inc. were used to prepare the REY stock solutions needed for the experiments. The exact compositions of the REY solution used for the scavenging experiments are given in table 1.

The model siderophore used for this study is the hydroxamate compound desferrioxamine B, or in short DFOB. Desferrioxamine B is one of the most thoroughly studied siderophores and occurs in nearly all oxidized environments with concentrations from the nanomolar up to the millimolar range (Römheld, 1991; Kraemer, 2004). The mesylate salt of DFOB is sold as a drug to treat chronic iron overload under the trademark Desferal™ and was used for this study. Christenson and Schijf (2011) reported that mesylate-REE stability constants are negligible compared to the high DFOB REE complex stability constants and
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hence there should be no significant interference by REE complexation with mesylate ions. Purities of all reagents were cross-checked by blank measurements with ICP-MS and were found to be at least two orders of magnitude below element concentrations presented in this study.

The REY solutions for the scavenging experiments are composed of $\Sigma$REY=52 ppb (see Table 1) in 0.01M hydrochloric acid. Exactly 50ml of the REY solution was transferred to an acid-cleaned LDPE bottle. The pH of the solution was set with 1M NaOH (suprapure) until a pH of 4 to 5 is reached before DFOB was added to the solution in amounts matching a final DFOB molarity of exactly 100µM in solution. Manganese was pipetted from a 10.000 ppm single element standard by InorganicVentures Inc. to match 10 ppm Mn in the final 50ml REY DFOB solution. After an equilibration phase of ca. 30 seconds, the pH was set to about 9 by addition of 33µl 1M suprapure NaOH to start precipitation of Mn (hydr-)oxides and the LDPE bottle was closed and placed on a horizontal shaker table and shaken at 180 rpm. The time intervals chosen for the scavenging experiments were 6.5, 15 min, 30 min, 60 min, 120 min and 240 min. For each time interval, a separate LDPE bottle was used. All scavenging experiments were run as duplicates for quality control and reproducibility of the experimental results. After time t, the LDPE bottle was taken from the shaker table and the well-mixed solution was immediately filtered with a Sartorius filter tower with a 0.2µm membrane filter to separate the manganese precipitates from the DFOB containing liquid phase. Before filtration, the pH was measured. Due to precipitation of MnOOH and consequential formation of H$^+$-ions, the pH of the solution dropped accordingly to pH lower than 7.5 in the first 10 mins of the scavenging experiments and stabilized around 7.5

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in experimental solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>10 ppm</td>
</tr>
<tr>
<td>La</td>
<td>2.65 ppb</td>
</tr>
<tr>
<td>Ce</td>
<td>10.4 ppb</td>
</tr>
<tr>
<td>Pr</td>
<td>2.62 ppb</td>
</tr>
<tr>
<td>Nd</td>
<td>9.89 ppb</td>
</tr>
<tr>
<td>Sm</td>
<td>2.56 ppb</td>
</tr>
<tr>
<td>Eu</td>
<td>0.54 ppb</td>
</tr>
<tr>
<td>Gd</td>
<td>2.57 ppb</td>
</tr>
<tr>
<td>Tb</td>
<td>0.51 ppb</td>
</tr>
<tr>
<td>Dy</td>
<td>2.73 ppb</td>
</tr>
<tr>
<td>Y</td>
<td>11.7 ppb</td>
</tr>
<tr>
<td>Ho</td>
<td>0.50 ppb</td>
</tr>
<tr>
<td>Er</td>
<td>2.56 ppb</td>
</tr>
<tr>
<td>Tm</td>
<td>0.49 ppb</td>
</tr>
<tr>
<td>Yb</td>
<td>2.59 ppb</td>
</tr>
<tr>
<td>Lu</td>
<td>0.51 ppb</td>
</tr>
<tr>
<td>$\Sigma$REY</td>
<td>52.8 ppb</td>
</tr>
</tbody>
</table>

Table 1: Elemental composition of the experimental solutions used for the scavenging experiments presented in this study.
afterwards. After filtration, the 50ml leachate was acidified with 1ml of suprapure 30% HCl. The Mn (hydr)oxides were digested together with the membrane filters with a mixture of HF/HNO$_3$/HCl in a Picotrace DAS digestion unit at elevated pressure and temperatures. The leachates and the digested filter residues were analyzed with an ICP-MS (see below).

For the analysis, the filtrates and the digested filter residues were normalized to the original dilution factors and sampling-induced volume variations were considered. Recoveries (REY$_{\text{filtrate}}$ + REY$_{\text{filter}}$ / REY$_{\text{stock}}$ *100) for the whole REY series were in the range of 80 to 100% with the lighter REY showing lower recoveries than the heavier REY. The recoveries tend to decrease with increased experiment times, which may be due to adsorption of REY on LDPE bottle walls due to the high pH of the experimental solutions.

### 2.2. Analytical

All filtrates as well as the corresponding dissolved filter residues from the scavenging experiments were measured for REY concentration with a low-resolution quadropole ICP-MS Elan drc-e by Perkin-Elmer. 1 ppb of each Ru, Re and Bi were added as internal standard elements for correction of instrument drift and matrix effects. Blank intensities for the studied elements were at least two orders of magnitude lower than the sample intensities.

### 3. Results

The scavenging experiments were conducted as time-series experiments with sampling intervals of 6.5 min, 15 min, 30 min, 60 min, 120 min and 240 min. Figs. 3a and 3b show the REY distribution pattern of the filtrate, i.e. the siderophore solution (2a), and the filter residues (Mn (hydr)oxide fraction; 2b) normalized to the sums of REY recovered in the solution and the filter residues. All filtrates have a very pronounced positive Ce anomaly. The siderophore solution also exhibits a strong concave downward pattern from the light REY to the heavy REY and a slightly positive Y anomaly for experiment times greater 6.5 minutes. Solution concentrations of all REY decrease progressively with increasing experiment times with La, Pr and Nd being almost below detection limit for the two and four hour experiments. The filter residues exhibit distinct negative Ce anomalies and a depletion of the heavy REY from Gd onward. As suggested by Bau (1999), the behavior of the REY during scavenging is
best described by the apparent bulk distribution coefficient $\text{app}D^{\text{REY}}$, which is the amount of REY scavenged by Mn (hydr)oxide divided by the amount of REY retained in solution:

$$\text{app}D^{\text{REY}} = \frac{[\text{REY}]_{\text{Mn (hydr)oxide}}}{[\text{REY}]_{\text{filtrate}}}$$

Fig. 4 shows the apparent distribution coefficient of REY between the precipitating Mn (hydr)oxide phase and the siderophore solution calculated as stated above. The distribution coefficient has been calculated from the digested and analyzed filter residues (i.e. Mn (hydr)oxides) and the acidified filtrate fraction (siderophore solution).

The REY patterns show distinct features that are present to certain extents in all time-series experiments. The distribution pattern of the apparent distribution coefficient shows a smooth downward curved slope declining less intensively towards the heavier REY, starting with $\text{app}D^{\text{REY}} = 15-70$ for La and ending with $\text{app}D^{\text{REY}} = 0.2-0.8$ for Lu. Ce is decoupled from its neighbors La and Pr and shows a distinct and very pronounced negative Ce anomaly, i.e. Ce is not significantly scavenged by Mn (hydr)oxides in the presence of siderophores. The Y/Ho ratio fractionation towards lower Y/Ho values is apparent in all $\text{app}D^{\text{REY}}$ patterns except for the 6.5 minute experiment.

All experiments presented in this study were conducted twice as duplicates. Error bars are plotted in Figures 3a and 3b as well as in Figure 4. While the lighter REY have slightly higher fluctuations than the heavier REY, most error bars are smaller than symbol sizes and thus the general reproducibility of the experiments is considered adequate. Larger deviations of the partition coefficients with the lighter lanthanides are due to the fact that element abundance in the filtrates was approaching the detection limit of the utilized mass spectrometer due to very effective scavenging by Mn (hydr)oxide.
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Fig. 3a+b: REY in solution normalized to the sum of REY scavenged by Mn (hydr)oxides and REY in solution (a) and REY scavenged by Mn (hydr)oxides normalized to the sum of REY scavenged on Mn (hydr)oxides and REY in solution (b). Note that the larger error bars for La and Pr for 120 and 240 min experiments are caused by element abundance being below or near detection limit of the mass spectrometer (a). The filtered solutions exhibit pronounced positive Ce anomalies and a REY pattern that mimics the REY-DFOB stability constants determined by Christenson & Schijf (2011). The precipitated (hydr)oxides (b) are depleted of the heavy REY and exhibit negative Ce anomalies and a minor negative Y anomaly.
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Fig. 4: Apparent bulk distribution coefficient for the scavenging experiments conducted with $\sum[\text{REY}]=52.8$ ppb, c(Mn)=10 ppm and c(DFOB)=100 $\mu$M. Note the abundant negative Ce anomalies and the typical downward slope of the coefficient towards higher REY. Also note the small negative Y anomaly developing with time, which is in accordance to the results of Christenson & Schijf (2011) on DFOB REY interaction.

Figure 5 shows the time-dependent variation of REY scavenged by Mn (hydr)oxide. Lanthanum and Pr represent light and non-redox sensitive REY, whereas Ce, Dy and Y were chosen to represent a redox-sensitive and two heavy REY. With time, the amount of total REY scavenged by Mn (hydr)oxide increases. The light REY are almost completely removed from solution in the first 6.5 minutes of the experiments. Scavenging of the medium and heavy REY is significantly slowed down after 15 minutes but is still slowly increasing with time due to the increasing abundance of Mn (hydr)oxides. After four hours, about 100 to 90% of La to Sm and from 90% to 40% of Eu to Lu are scavenged. As shown in Fig. 5, redox-sensitive Ce is significantly scavenged in the first minutes of the experiments, but scavenging rates reach climax after about 30 minutes at about 55% total Ce scavenged, from where on the concentrations in the Mn (hydr)oxide fractions go down to 45% after one hour and slightly decrease with time from there on. The heavy REY Dy and Y on the other hand show coherent behavior. About 25-35% of the spiked Dy and Y are quickly scavenged in the first 6.5
minutes, but scavenging significantly slows down afterwards, but does not reach equilibrium even after four hours.

![Graph showing variation of percentage of REY sorbed onto Mn precipitates in scavenging experiments conducted in presence of the siderophore DFO-B.](image)

**Fig. 5:** Variation of percentage of REY sorbed onto Mn precipitates in the scavenging experiments conducted in presence of the siderophore DFO-B. Almost all La and Pr are quickly scavenged by the Mn (hydr)oxides, whilst the redox-sensitive Ce and the heavy lanthanoid Dy and Y remain in solution. Scavenging of Ce and Dy on the Mn precipitate is delayed due to strong siderophore complexation and Ce scavenging reaches equilibrium after 60 min, whereas HREY scavenging still occurs after 240 min, but is significantly slower than LREE scavenging.

**4. Discussion**

In this work we demonstrated that scavenging of REY onto Mn (hydr)oxide is constrained to the light REY when the model siderophore DFOB is present in the experimental solution during precipitation of Mn (hydr)oxides. The heavy REY including Y and the redox-sensitive Ce are retained in solution in the presence of siderophores. As shown in Figs. 3a-b and 4, the redox-sensitive lanthanoid Ce is deterred from scavenging onto the precipitating Mn (hydr)oxide particles, which eventually leads to a pronounced positive Ce anomaly in the filtrates or a pronounced negative anomaly in the precipitating Mn (hydr)oxides. After 30 minutes, a portion of the already scavenged Ce is re-solubilized and
also complexed as Ce(IV)-DFO complex, so that potential re-scavenging by Mn (hydr)oxides is prevented by a shielding mechanism (see Fig. 5).

The scavenging of Ce onto Mn (hydr)oxide is prevented and the minute amount of Ce$^{4+}$ present in solution is immediately bound by the siderophore ligand and surface complexation onto Mn(hydr)oxide is prevented. The resulting redox disequilibrium between Ce$^{3+}$(aq) and Ce$^{4+}$(aq) promotes continuous oxidation of Ce$^{3+}$(aq), so that with time more and more Ce(IV) is complexed by the siderophore and hence shielded from scavenging by coprecipitating Mn (hydr)oxide. The heavy REY are forming stronger complexes with DFOB than the lighter REY and hence are effectively shielded from scavenging onto the solid manganese mineral phase for a longer time. The fluctuating distribution coefficients in the time series experiment of both datasets indicate that there is a subordinate yet constant scavenging and solubilization occurring at the mineral surface sites, which is apparently in direct competition with the immanent REY-DFOB complexation. DFOB and Mn act as efficient counterplayers in the competition for REY scavenging. Thus, it can be assumed that the ratio between the concentrations of DFOB and Mn plays a significant role for the fractionation of the REY between solid (Mn (hydr)oxide) and liquid phases. Lower Mn concentrations will eventually lead to less REY scavenged and the system will reach equilibrium much quicker and vice versa for lower DFOB concentrations.

As described by Christenson and Schijf (2011) and shown by the thermodynamic data from Fig. 2, the stability constants for DFOB with REY are increasing with decreasing atomic radii, that is, DFOB forms stronger and more stable complexes with medium and heavy REY than lighter REY, trivalent Ce included. The stability constant for trivalent Ce with DFOB is in between those of La and Pr. However, stability constants for tetravalent Ce are several orders of magnitude higher than for trivalent Ce (Yoshida et al., 2007). This radius-controlled behavior in complexation with DFOB is mirrored in the apparent bulk distribution coefficient as shown e.g. in Fig. 4. The resulting competition with the ligand DFOB and the REY-scavenging surface sites of the Mn (hydr)oxide leads to constant sorption and desorption from the particle surfaces and the distribution among the REY eventually mimics the stability constants of the specific REY.

Ohta and Kawabe (2001) showed for organic ligand free systems that adsorption of REY by oxide and hydroxide particles leads to positive Ce anomalies and significant M-type tetrad patterns. Bau and Koschinsky (2009) showed that Ce is scavenged onto iron
oxyhydroxides in its oxidized form as a tetravalent ion. This process referred to as oxidative scavenging leads to the pronounced enrichment of Ce relative to other light REY onto hydroxide particles and hence the formation of a positive Ce anomaly. These REY patterns do not form in the presence of organic acids (Davranche et al., 2005; Davranche et al., 2008; see Fig. 1) or are mirrored in the presence of the siderophore DFOB as demonstrated in this study.

The observed negative Y anomalies and the fractionation of Y from its geochemical twin Ho shows that the plain presence of organic ligands such as siderophores is capable of altering the Y-Ho ratio in hydroxide mineral structures and the ambient, ligand-bearing aqueous solution.

Davranche et al. (2005) conducted REY sorption experiments in the presence of humic acid, which is in certain environments one of the most abundant organic acids. Davranche et al. (2005) found out that sorption of humate-REY complexes onto manganese dioxides strongly reduces or suppresses the development of positive Ce anomalies on the particulate phases. Additionally, Davranche et al. (2005) state that the complexation of trivalent REY with humate ligands reduces and suppresses the development of M-type lanthanide tetrad effects during sorption onto manganese dioxide. However, our study showed that scavenging in presence of siderophores such as DFOB can in fact lead to completely absent lanthanide tetrad patterns.

The results of this study might help explain certain geochemical peculiarities observed worldwide for REY partitioning between natural waters and natural chemical precipitates.

Loges et al. (2012) already indicated the influence of siderophores during formation of surficial secondary Mn oxides veins, which exhibit a strong negative Ce anomaly and which ambient and percolating waters are strongly enriched in dissolved organic carbon. Organic ligands, and especially siderophores, are abundant in almost all natural settings, hence the impact of such strong ligands on the trace and ultra-trace metal behavior in the supergene environment is significant. The presence of strong organic ligands like siderophores may also effectively constrain the use of Ce decoupling as a proxy for redox conditions.
5. Conclusion

The experimental data presented in this study strongly suggest that the presence of siderophores, or organic ligands in a broader sense, in aqueous solutions such as seawater, river water, marine and terrestrial pore waters and even low temperate hydrothermal systems not only alters the biological availability of trace metals in these waters, but might also effectively modify the particle-reactivity and modifies or even prevents the removal of certain trace elements from solution by mechanisms such as structural incorporation and sorption onto reactive particle surfaces.

In the absence of siderophores and other organic ligands, trivalent Ce is usually surface-oxidized to tetravalent Ce during sorption onto manganese (hydr)oxides. Such Mn precipitates, therefore, often exhibit positive Ce anomalies, whereas the ambient solutions exhibit negative Ce anomalies (Ohta and Kawabe, 2001).

In marked contrast, however, REY sorption in the presence of DFOB produces negative Ce anomalies in the Mn precipitates and a distinct and characteristic positive Ce anomaly in the residual siderophore-bearing solution. Furthermore, the heavy REY with ionic radii larger than the radius of Sm are also almost completely not scavenged onto the Mn solid phases. Sorption of REY onto Mn (hydr)oxides in the presence of DFOB creates a distinct and pronounced fractionation of Ce and the heavy REY from the light and middle REY. Apart from Ce, which is oxidized in solution by the siderophore, the distribution of the other REY mimics the stability constants for multi-dentate complexes of REY with DFOB, as determined by Christenson & Schijff (2011). Heavier REY are forming stronger complexes (and are hence better “protected” from scavenging) than light REY, excluding Ce. Preferential partitioning of Ce into the liquid phase during the precipitation of Mn (hydr)oxides has only rarely been described for natural Mn (hydr)oxides (e.g., Tanaka et al., 2010; Loges et al., 2012). Our experimental results demonstrate that biogenic organic ligands such as hydroxamate siderophores, may produce solutions with positive Ce anomaly (Bau et al., 2013) and may even counteract the surface oxidation of Ce on Mn (hydr)oxides.
References


2. Siderophore-promoted Mobility and Fractionation of Critical Metals in the Surface Environment


3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

3.1. Phase associations and potential selective extraction methods for selected high-tech metals from ferromanganese nodules and crusts with siderophores.

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3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals
Phase associations and potential selective extraction methods for selected high-tech metals from ferromanganese nodules and crusts with siderophores

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Abstract

Deep-sea ferromanganese deposits contain a wide range of economically important metals. Ferromanganese crusts and nodules represent an important future resource, since they not only contain base metals such as Mn, Ni, Co, Cu and Zn, but are also enriched in critical or rare high-technology elements such as Li, Mo, Nb, W, the rare earth elements and yttrium (REY). These metals could be extracted from nodules and crusts as a by-product to the base metal production. However, there are no proper separation techniques available that selectively extract certain metals out of the carrier phases. By sequential leaching, we demonstrated that, except for Li, which is present in an easily soluble form, all other high-tech metals enriched in ferromanganese nodules and crusts are largely associated with the Fe-oxyhydroxide phases and only to subordinate extents with Mn-oxide phases. Based on this fact, we conducted selective leaching experiments with the Fe-specific organic ligand desferrioxamine-B, a naturally occurring and ubiquitous siderophore. We showed by leaching of ferromanganese nodules and crusts with desferrioxamine-B that a significant and selective extraction of high-tech metals such as Li, Mo, Zr, Hf and Ta is possible, while other elements like Fe and the base metals Mn, Ni, Cu, Co and Zn are not extracted to large extents. The set of selectively extracted elements can be extended to Nb and W if Mn and carbonate phases are stripped from the bulk nodule or crust prior to the siderophore leach by e.g. a sequential leaching technique. This combination of sequential leaches with a siderophore leach enhanced the extraction to 30–50% of each Mo, Nb, W and Ta from a mixed type Clarion-Clipperton Zone (CCZ) nodule and 40–80% from a diagenetic Peru Basin nodule, whilst only 5–10% Fe and even less Mn are extracted from the nodules. Li is extracted to about 60% from the CCZ nodule and a maximum of 80% Li is extracted from the Peru Basin nodule.

Our pilot work on selective extraction of high-tech metals from marine ferromanganese nodules and crusts showed that specific metal-binding organic ligands may have promising potential in future processing technologies of these oxide deposits.

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1. Introduction

The deep sea contains ferromanganese (Fe–Mn) crust and nodule deposits with a high potential for future mining operations. The traditional commodities for these deposits are the base metals Ni, Cu and Mn for nodules and Co, Ni and Mn for crusts (Hein et al., 2013). However, recent economic developments also attracted notice to other metals contained in Fe–Mn marine deposits. Fe–Mn nodules are highly enriched in Co, Li, Mo, the rare earths + Y (REY) and Zr, whilst crusts are enriched in elements like Bi, Mo, Nb, Pt, REY, Te, Th, Ti, W and Zr (Hein et al., 2013). These metals could represent important by-products in the processing chain for deep sea Fe–Mn deposits and could make an important contribution to the economic viability of future mining operations. Most of the aforementioned, 'non-traditional' elements are nowadays considered as high-tech trace elements because they are essential for many high technology applications including renewable energy production such as wind power and photovoltaics and are of strategic importance to a healthy and solid economy.

Fe–Mn crusts and nodules are ubiquitous in the oceanic realm and the tonnages and grades of certain deposits exceed that of land-based deposits (Hein et al., 2013).

Fe–Mn crusts usually occur as hydrogenetically grown encrustations on sediment free submarine elevations. They form by slow precipitation out of relatively cold ambient seawater onto hard rock substrates and grow very slowly with rates of some millimeters per million years (Halbach et al., 1988). Fe–Mn crusts
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consist mainly of manganese oxides and Fe-oxyhydroxides, as well as minor quartz and feldspar (Koschinsky and Hein, 2003). The main mineral observed is Fe-bearing vernadite (δ-MnO₂), which is usually intergrown with an amorphous iron oxyhydroxide phase (Koschinsky et al., 2010a). Metal accumulation occurs out of the surrounding seawater, whereas metals like Mn, Ni, and Zn are sorbed preferentially on the surface of MnO₂ (vernadite) in hydrodynamic crusts. Due to their very large surface area of about 325 m²/g and their very slow growth rates, crusts sorb high quantities of trace metals from surrounding seawater (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003).

The oldest crusts with ages up to about 60 million years occur in the NW Pacific and due to their very slow growth rates these crusts have the highest concentrations and quantities in high-tech metals, hence this area is considered as prime zone for crust exploration (PCZ; Hein et al., 2013).

Fe-Mn nodules are divided into two types based on the mode of metal acquisition and formation: diagenetic and hydrothermal. All Fe-Mn nodules form by the more or less concentric accumulation of Mn and Fe oxides around a nucleus (Hein et al., 2013). Hydrogenetic Fe-Mn nodules are found on tops or slopes of seamounts or other submarine elevations, which are swept sediment-clean by near-bottom currents (Hein et al., 2000). They form under oxic conditions and build smooth surfaces, spherical to elliptical shapes, growing very slowly with rates of some mm per million years (Halbach et al., 1988). Like Fe-Mn crusts, hydrogenetic nodules contain vernadite (δ-MnO₂) as main mineral phase. Their bulk composition is mainly controlled by the surrounding seawater chemistry by precipitation of hydrated Mn- and Fe-oxide colloids. The trace metal accumulation occurs by surface complexation on the surfaces of the Mn- and Fe-oxides.

Diagenetic Fe-Mn nodules are usually found within the top parts of siliceous oozes in deep-sea basins and are characteristic for e.g. the Peru Basin (von Stackelberg, 1997). Pure diagenetic nodules display a typical cauliflower structure and are constituted of the manganese todorokite and binnesite. They form by precipitation around some piece of nucleus, which can be bones or rock substrate lying on the sediment surface. Metals like Cu, Ni, Zn and Co accumulate in the Mn oxides from sediment pore waters, which are the primary dissolved metal source at suboxic conditions in the upper parts of the sediment during the oxidation of organic matter (Koschinsky et al., 2010a). Many nodule deposits show both a diagenetic and a hydrogenetic component due to accumulation of metals both from pore water and from seawater. These nodules are known as mixed-type nodules and are characteristic for the abyssal plains e.g. within the Clarion Clipperton Zone (CCZ) in the Central Pacific. The majority of economically interesting Fe-Mn nodules is concentrated in this zone of the Pacific Ocean at depths of about 5000 m at the interface between bottom waters and sediment, as well as in the upper parts of the sediment column (Koschinsky et al., 2010a). The CCZ contains significant numbers of areas with exploration licenses preparing future nodule mining under the auspices of the International Seabed Authority (ISA; www.iso.org/jm).

During the formation of Fe-Mn oxides, particle-reactive trace metals, which are dissolved or colloidal-bound in seawater, are surface-complexed on MnO₂ and FeOOH⁺ particles (Hein et al., 2013). Generally, positively charged complexes and cations are associated with the negatively charged Mn oxide phase, while neutral and negatively charged complexes are bound to the Fe oxyhydroxide phase, which carries a slightly positive charge. Structural incorporation of transition metals such as Cu, Ni and Zn in the crystallized Mn oxides todorokite and binnesite explains their higher enrichment in diagenetic nodules compared to hydrogenetic ones.

Several methods for processing of Fe-Mn nodule ores for extraction of Mn, Ni, Cu and Zn were proposed in the past by various authors (see reviews by Fuerstenau and Han (1983) and Zhang and Cheng (2007a,b)). Up until now, the majority of researchers focused on chemical leaching techniques, such as glucose-ammonia leaching (Das et al., 1986), reduction-roast-ammonia leaching (Hoover et al., 1975; Jana et al., 1999) and sulfuric acid leaching (Han and Fuerstenau, 1975). Although these processes are relatively effective in terms of output, a high consumption of energy and can create an undesirable impact on the environment.

Following the investigations of Ehrlich (1997) on the mechanisms of bioleaching, a potential microbial recovery of valuable metals from ocean nodules gained importance (Mehta et al., 2010). With regard to bioprocessing of low grade manganese oxide ores, reductive biological treatment procedures were studied by e.g. Abbbruzzese et al. (1990) and Vegliò et al. (1997). They used heterotrophic microorganisms for either direct or indirect leaching. The bacteria are capable of utilizing MnO₂ instead of oxygen as final acceptor of electrons in the respiratory chain of their metabolism (Zhang and Cheng, 2007a). The mechanism of bioleaching in

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe-Mn crust</th>
<th>CCZ nodule</th>
<th>Peru Basin nodule</th>
<th>J-Mn1</th>
<th>NOD-P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode of formation</td>
<td>PCZ, Pacific Ocean</td>
<td>CCZ, Pacific Ocean</td>
<td>Mixed-type</td>
<td>Peruvian Basin, Pacific Ocean</td>
<td>Mixed-type</td>
</tr>
<tr>
<td>Mn (wt%)</td>
<td>24.87</td>
<td>32.51</td>
<td>39.84</td>
<td>25.36 (25.64)</td>
<td>30.8 (29.6)</td>
</tr>
<tr>
<td>Fe (wt%)</td>
<td>0.08</td>
<td>5.48</td>
<td>1.41</td>
<td>10.26 (10.26)</td>
<td>6.09 (5.89)</td>
</tr>
<tr>
<td>Ni (wt%)</td>
<td>0.58</td>
<td>1.40</td>
<td>0.58</td>
<td>1.24 (1.25)</td>
<td>1.39 (1.22–1.38)</td>
</tr>
<tr>
<td>Cu (wt%)</td>
<td>0.05</td>
<td>1.23</td>
<td>0.27</td>
<td>1.0 (1.0–1.2)</td>
<td>1.19 (1.12–1.17)</td>
</tr>
<tr>
<td>Co (wt%)</td>
<td>0.66</td>
<td>0.15</td>
<td>0.00</td>
<td>0.1675 (0.169)</td>
<td>0.23 (0.228)</td>
</tr>
<tr>
<td>Zn (wt%)</td>
<td>0.06</td>
<td>0.17</td>
<td>0.095</td>
<td>0.1025 (0.104–0.109)</td>
<td>0.15 (0.146–0.202)</td>
</tr>
<tr>
<td>ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li (ppm)</td>
<td>1.9</td>
<td>152.0</td>
<td>673.0</td>
<td>63 (69)</td>
<td>140 (140–142)</td>
</tr>
<tr>
<td>Zr (ppm)</td>
<td>342.7</td>
<td>247.6</td>
<td>84.0</td>
<td>341 (350–392)</td>
<td>269.3 (280–298)</td>
</tr>
<tr>
<td>Hf (ppm)</td>
<td>5.5</td>
<td>3.6</td>
<td>1.5</td>
<td>6.34 (6.1–6.4)</td>
<td>4.2 (4.4)</td>
</tr>
<tr>
<td>Mo (ppm)</td>
<td>723.0</td>
<td>678.4</td>
<td>504.0</td>
<td>322 (314–316)</td>
<td>645 (675)</td>
</tr>
<tr>
<td>W (ppm)</td>
<td>129.9</td>
<td>55.2</td>
<td>37.7</td>
<td>40.7 (37.49)</td>
<td>57.2 (57.8)</td>
</tr>
<tr>
<td>Nb (ppm)</td>
<td>43.3</td>
<td>13.7</td>
<td>3.7</td>
<td>30.1 (27.42)</td>
<td>20.7 (21.3)</td>
</tr>
<tr>
<td>Ta (ppm)</td>
<td>0.02</td>
<td>0.20</td>
<td>0.11</td>
<td>0.621 (0.68)</td>
<td>0.35 (0.33)</td>
</tr>
<tr>
<td>Ce (ppm)</td>
<td>1429.6</td>
<td>201.7</td>
<td>33.1</td>
<td>250 (271–286)</td>
<td>318 (305–329)</td>
</tr>
<tr>
<td>Nd (ppm)</td>
<td>94.0</td>
<td>106.3</td>
<td>21.3</td>
<td>115 (123–127.98)</td>
<td>127 (128–130)</td>
</tr>
<tr>
<td>Dy (ppm)</td>
<td>23.7</td>
<td>25.5</td>
<td>5.7</td>
<td>27.9 (25.65–28.6)</td>
<td>27.2 (27.1–27.5)</td>
</tr>
</tbody>
</table>
Abbruzzese's study was found to be predominantly indirect through production of organic acids, with mainly oxalic and citric acid reducing the ore and mobilizing the base metals.

The aforementioned studies on bioleaching did focus on conventional manganese ores. For the biologically-mediated extraction of metals from Fe–Mn nodules and crusts, e.g., Mehta et al. (2010) conducted experiments on the leaching of Cu, Ni and Co from Indian Ocean manganese nodules by using the fungus Aspergillus niger. Their experiments revealed high metal recovery rates of 97% Cu, 98% Ni, 86% Co, 91% Mn and 36% Fe after 30 days at pH of 4.5 and Fe and Co recovery rates of 96% and 66% at a pH of 4. Additionally, a comparison between direct (use of A. niger) and indirect leaching (use of citric and oxalic acids produced by A. niger) showed that the leaching of metals was more effective in the presence of the fungus.

It is noteworthy that most of the studies conducted so far focussed on conventional commodities such as Mn, Fe, Ni and Cu. To the best of our knowledge, there has been no study to date that focussed on the potential extraction of high-tech trace elements present in Fe–Mn nodules and crusts, such as Mo, W, Li, Te and Pt. It is important to note that Fe–Mn deposits will probably never be mined just because of its high-tech metal grades; it is the combination of traditional (base) metals and rare metals that makes these deposits very interesting for the economy. Hence, researching in selective extraction techniques for high tech metals from these deep sea deposits is of utter importance, which is in case of eventual mining followed by conventional processing of base metals in the form of roast reduction or the like.

Hence, we present data on sequential leaching experiments on Fe–Mn precipitates and selective leaching experiments with organic ligands that are known as siderophores. Siderophores are ubiquitous, low-molecular weight organic molecules secreted by bacteria and plants to cope with iron deficiency (Neilands, 1957; Takagi, 1976; Winkelmann, 1992). Inoxic environments, iron is usually present in a trivalent oxidation state and immediately forms insoluble Fe oxohydroxides. The insolubility of Fe leads to intense deficiencies in the supply of iron as a micronutrient. To cope with these deficiencies, bacteria and plants developed mechanisms to facilitate the dissolution of hydroxide structures by producing siderophores, which selectively dissolve the (hydr-)oxide-bearing minerals and readily form soluble complexes with Fe(III) (see Kraemer, 2004 and references therein). Besides siderophores, a range of organic acids like citric acid, oxalic acid and others are also sequenced by plants to facilitate solubilization of nutrient elements and to detoxify certain metals by ligand complexation. Their influence on metal mobilization and hydroxide dissolution in soils has been widely and intensively studied (e.g., Gerke, 1992; Jones and Darrah, 1994; Jones, 1998; Oburger et al., 2009). However, many organic acids are quite aggressive and unspeculative, whereas siderophores are rather element specific. Besides having high stability constants with trivalent Fe, siderophores are also able to complex a wide range of other trace metals. Among these metals are those that are classified today as high tech metals, or metals with an explicit application in the high technology industry and which occur in potentially economic concentrations in Fe–Mn nodules and/or crusts. Several scientific studies in the past showed that especially rare metals such as Mo, the REY, Hf, the platinum group elements and some actinides like U have exceptionally high stability constants with siderophores (see e.g., Bau et al., 2013; Bayssse and Vos, 2000; Bellenger et al., 2008; Bi et al., 2009; Bouby et al., 1998; Christenson and Schijf, 2011; Dahlheimer et al., 2007; Desouky et al., 2011; Hennels, 1996, 1999; Mullen et al., 2007; Yoshida, 2004).

For a detailed overview on siderophore chemistry and complexation mechanisms, see the review by Kraemer (2004).

Dahlheimer et al. (2007) proved that siderophore-promoted dissolution of metal oxides is more efficient than that of metals in a metallic state, so that siderophores might in fact be ideal candidates for the leaching of metals hosted in oxide structures.

2. Material and methods

2.1. Material

We conducted batch leaching and sequential leaching experiments on three Fe–Mn oxide samples from different localities. The mixed-type Fe–Mn nodule sample named CCZ nodule was collected during research cruise SO-205 of the German RV Sonne and originates from the CCZ in the Pacific Ocean. The diagenetic nodule sample from the Peru Basin was collected during cruise SO-106 and the Fe–Mn crust sample is a mixed sample from several non-phosphatized hydrogenetic Fe–Mn crusts of the PCZ.

2.2. Methods

2.2.1. Materials used

All PE-bottles and vials used were acid-cleaned prior to usage to remove trace metal contaminations.

All reagents used within the scope of this study were of suprapure grade except for Deseral™ (Novartis). The drug Deseral™ is the commercially available mesylate salt of the siderophore desferrioxamine-B (DFOB) and is used as a drug for the treatment of hemochromatosis (acute iron intoxication). Its purity is not provided by the vendor, but reagent blank tests with ICP-MS and ICP-DOES showed that trace metal contaminations in the leaching reagents were all below detection limit of the utilized analytical methods.

2.2.2. Sequential leaching

Half a gram of air-dried aliquots of the mixed-type CCZ and the diagenetic Peru Basin nodule were used for the determination of the phase associations of trace elements in the samples. The samples were only air-dried to avoid possible changes in the mineralogical composition and the related trace element associations as was observed by Koschinsky and Halbach (1995). Each aliquot was transferred into acid-cleaned 100 ml PE bottles. The sequential leaching setup was adapted from and described in detail in Koschinsky and Halbach (1995). All sequential leaches were conducted on a horizontal shaker table.

Three reagents were prepared as follows:

1. An acetate buffer solution for the selective extraction of exchangeable cations and Ca carbonates. The powdered sample is shaken on a horizontal shaker at room temperature with 12.5 ml of a 1 M acetic acid/Na acetate buffer set to a pH of 5 for 5 h. The suspension is filtered through a 0.45 μm membrane filter. The residue is washed with deionized water. The leachate contains elements bound in carbonates and easily exchangeable cations.

2. Mn oxide phases ('easily reducible fraction'): The residue is leached with 87.5 ml of a 0.1 M hydroxyamine hydrochloride solution at a pH of 2 at ambient temperatures for 24 h. The suspension is again filtered through a 0.45 μm membrane filter and the residue is washed with deionized water.

3. Fe oxohydroxide phases ('moderately reducible fraction'): The solid residue of leach 2 is now mixed with 87.5 ml of a 0.2 M oxalic acid/ammonia acetate buffer at pH 3.5 at similar conditions. The mixture is shaken on a horizontal shaker for 12 h and then again filtered through a 0.45 μm membrane filter.

4. Residual fraction: The solid residue of leach 3 is pressure-digested at 200 °C with a mixture of suprapure hydrofluoric acid, hydrochloric acid and nitric acid.
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The leachates are evaporated, pressure digested just like the residue fraction and diluted in 0.5 M HCl before analysis for major, minor and trace element composition with an ICP-OES and an ICP-MS.

2.2.3. Selective leaching

Exactly 0.5 g of the air-dried Fe–Mn sample was transferred to acid-cleaned PE bottles. Siderophore solutions were prepared by gravimetric addition of Desferal powder to the amount of deionized water matching the desired siderophore concentration. The reagent was hand-shaken for 1 min and the pH was set by the addition of ultrapure ammonia to the siderophore solution until the final pH is reached. The bottle containing the reagent was hand-shaken and the pH was checked again for verification. For buffered leaching experiments, the organic buffer agent TRIS (THAM, tri(hydroxymethyl)aminomethane) was added to the siderophore solution before the pH setting.

50 ml of the prepared leaching agent were added to the PE bottle containing the Fe–Mn nodules and crusts samples matching a solid content of 10 g/l. The bottle is closed and hand-shaken for 1 min to facilitate full dispersion and then put on a horizontal shaker for the designated amount of time. In a pilot study by Kleint (2011), initial experiments were conducted as time-series experiments with sampling intervals of 24 h, 48 h and 7 days. However, leaching times of 48 h proved sufficient to effectively solubilize high tech metals with only minor deviations in leaching efficiency thereafter, hence leaching experiments in this study were conducted with an experimental time of 48 h.

After 48 h, the suspensions were carefully filtered with a 0.2 μm membrane filter. After filtering, the pH was checked and noted and the leachate was analyzed with ICP-OES and ICP-MS after acidification to pH < 2 with ultrapure hydrochloric acid.

2.2.4. Digestion of bulk samples

For bulk chemical analysis of the Fe–Mn nodules and crust samples, the powdered samples were dried over night at 110°C.

For bulk decomposition, 50 mg aliquots of the powdered samples were digested with an acid pressure digestion block made by PicoTrace using a mixture of concentrated suprapure acids (HF/HNO₃/HCl). For quality control, the certified reference materials NOD-P1 by the United States Geological Survey and J-Mn1 produced by the Geological Survey of Japan were digested along the samples together with a method blank and reagent blanks of the sequential leaching and selective leaching solutions.

2.2.5. Analytical determination

Element concentrations of all the leachates as well as the digested samples were determined with a Spectro Ciros Vision ICP-OES for major, minor and trace element composition and a PerkinElmer Elan DRC-e quadrupole ICP-MS for trace- to ultra-trace element composition. Interference correction was applied for the high field strength elements Hf, Ta, W and Dy. The analytical precision for CRM’s J-Mn1 and NOD-P1 is better than ±5% of published reference values. Details on precision and long-term accuracy of the utilized ICPMS analysis as well as details on the interference correction are provided in the technical report by Alexander (2008).

3. Results

3.1. Phase associations of high-tech metals in ferromanganese nodules and crusts

The results of the sequential leaching experiments are summarized in Figs. 1–3. Percentage associations of the metals are related to the sum of the four leaching steps. The recovery rate of the leaching procedure compared to the bulk data as shown in Table 1 was in the range of 85–95% for all elements except Hf and Ta in the diagenetic nodule for which it was in the range of 75–80%. Considering the numerous working steps and difficult matrix of the analyte solutions, these results can be considered adequate. Note that sequential leaching data for the hydrogenetic Fe–Mn crust is taken from Koschinsky and Hein (2003).

The sequential leaches of the diagenetic Peru Basin nodule show that Li is to two-thirds allocated to carbonates and the fraction of exchangeable cations, whilst the rest is associated with the MnO₂ phase. The traditional commodities Co, Ni and Cu are mainly located in the Mn phases and Zn and Mo are about evenly distributed between Fe-oxides and Mn-oxides. Most of the high-tech metals such as Zr, Hf, Nb, Ta, the rare earths and W are almost exclusively located in the Fe-oxide phase and to subordinate amounts in the Mn-oxide phase (rare earths).

The mixed-type C2Zn nodule shows similar associations for the above mentioned elements with the exception of Mo and Ta associations. 75% of the contained Mo is associated with the Fe oxide phase, whereas the rest is associated with Mn oxides. Only 30% Ta is associated with Fe oxides in the mixed-type nodule and the rest remains unleached in the residual fraction. Besides the herein presented sequential leaching data for the C2Zn nodule, Kleint (2011) conducted sequential leaching experiments on three additional C2Zn nodules, which all showed the same phase associations as the C2Zn nodule presented in this study.

The sequential leaches of the hydrogenetic Fe–Mn crust show that almost all the high tech metals are situated in the Fe oxide phases. In strong contrast to the nodules, Cu as well is almost exclusively bound to Fe oxides. Just like in the nodules, the traditional elements are located in the Mn oxide phase. Unfortunately, Koschinsky and Halbach (1995) and Koschinsky and Hein (2003) did not provide rare earth element data for the sequential leaching experiments reported in their study, hence the phase associations of rare earth elements in the hydrogenetic crust used in our study cannot be provided here. However, Bau and Koschinsky (2009) provide phase associations of REY in Fe–Mn crusts and found that most of the REY are associated with both Mn oxide and Fe oxyhydroxide phases, but the majority is associated to the latter phase.

Given that almost all elements considered to be of high importance for the high-tech industries are – almost exclusively – allocated in the iron-oxhydroxide phases, a ligand specialized in the selective dissolution of iron oxides, such as siderophores, is a promising candidate for selectively leaching of elements such as Zr, Hf, Nb, Ta, the rare earths and W.

3.2. Selective extraction of high-tech metals from ferromanganese nodules and crusts

Based on the results of the sequential leaching experiments, the Fe-specific organic ligand desferrioxamine-B (DFOB) has been chosen for the selective extraction of trace metals associated with the Fe-oxide phase in the Fe–Mn precipitates. Figs. 4 and 5 show the results of standardized batch leaching experiments on the diagenetic Fe–Mn nodule and the hydrogenetic crust with 1 mM DFOB set at pH of 6 and 1, 2, and 3 mM DFOB solutions set at a pH of 8. Leaching times were 48 h at ambient temperatures with solid contents of 10 g/l. The initial time series experiments (1–7 days; Kleint, 2011; data not shown here) showed that Mo extraction tends to decrease in the percent range with experiment times longer than 7 days, whereas Li remains steady and Zr slightly increases by some percent. Fe and Mn as well as the base metals tend to fluctuate to very subordinate amounts with changes less than one percent over time. Due to the very minor fluctuations in base
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Fig. 1. Phase associations in the diagenetic Peru Basin nodule as obtained by sequential leaching experiments.

Fig. 2. Phase associations in the mixed-type CCZ nodule as obtained by sequential leaching experiments.

Fig. 3. Phase associations in the hydrogenetic Fe-Mn crust as obtained by sequential leaching experiments by Koschinsky and Hein (2003).

Metal liberation and the overall leaching efficiency observed over time, the experiments presented here were conducted with leaching times of 48 h. A pH of 8 has been chosen for consecutive experiments since it showed the highest extraction rate in the initial 1 mM experiments.

As can be observed for both experimental data sets, there is a clear trend that concentrations of 2 mM desferrioxamine B work best for the selective extraction of high tech trace elements.

Percentage data for extracted fractions given in the following refer to the total content (100%) in the bulk nodule.

For the diagenetic Peru Basin nodule, Mn and Fe extractions are low with less than 5% extracted Mn and about 5–10% extracted Fe. The base metal Cu is extracted to similar low extents of about 2–5%, whilst nearly all Ni, Co and Zn are omitted during leaching. Li shows relatively high recoveries of up to 62% mobilized in the siderophore leach at 2 mM DFOB, Mo goes up to 40% Zr, Hf and Ta are extracted to a maximum of 15%, 10% and 25% in the 2 mM leach, whilst W, Nb and the rare earth elements Ce, Nd and Dy are not leached significantly with recoveries of about 5%. For the Fe-Mn crust, the results are similar except for a higher base metal
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Fig. 4. Percentage mobilized from the diagenetic Peru Basin nodule with 1 mM, 2 mM and 3 mM DFOB adjusted to pH of 6 and 8. Note the lower recoveries with a DFOB concentration of 3 mM relative to 2 mM for almost all elements investigated.

Fig. 5. Percentage mobilized from hydrogenic crust with 1 mM, 2 mM and 3 mM DFOB adjusted to pH of 6 and 8.

Fig. 6. Percentage mobilized from the hydrogenic crust sample with 2 mM DFOB buffered with TRIS to a pH of 7.5 and 8.5. The light gray bars represent an experiment with non-buffered 2 mM DFOB, where the Mn and carbonate phases and loosely bound cations were stripped from the powdered sample prior to leaching with an acidic reductive leaching technique.

Fig. 7. Percentage mobilized from the diagenetic Peru Basin nodule with 2 mM DFOB buffered with TRIS to a pH of 7.5 and 8.5. The light gray bars represent an experiment with non-buffered 2 mM DFOB, where the Mn and carbonate phases and loosely bound cations were stripped from the powdered sample prior to leaching with an acidic reductive leaching technique.

extraction and a lower Li and Mo extraction. The CCZ mixed-type nodule was only tested with 3 mM DFOB at a pH of 8. About 40% Li and 30% Mo were mobilized, whilst all the rest elements were way below 10% leached including Mn, Fe and the base metals.

Based on the results of the experiments described above, further experiments were conducted with 2 mM DFOB buffered to a pH of 7.5 and 8.5. Additionally, we combined sequential leaching with a DFOB siderophore leach. Here, we sequentially stripped the carbonate and Mn oxide phases by sequential leaching, dried the residue which now should contain only Fe-oxides and residual phases and leached the residues with a non-buffered 2 mM DFOB solution set to a pH of 8 (Figs. 6–8).

The buffered experiments show similar results as the experiments conducted in non-buffered states. The extraction of the base metals increased to values of about 15–20% Cu and 10% Co, whilst Zn and Ni are way below 5% for the experiments conducted at pH 7.5 and 8.5. Li recoveries are between 75% and 80% in the buffered experiments. Except for Mo, the recoveries of all tested elements are about even ±5% when comparing pH 7.5 and pH 8.5 experiments. About 30% Mo is extracted in buffered solutions with a pH of 8.5, whilst only 10% are mobilized a pH of 7.5. A highlight is the diagenetic Peru Basin nodule, which shows Li recoveries in the buffered solutions of about 80%, which is 20% more than observed in non-buffered experiments.
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The mixed-type nodule from the Clarion Clipperton Zone shows results similar to the results of the hydrogenic crust with respect to base metals Ni, Cu, Co, Mn, and Fe. The trace element Li is extracted to about 50–60%, whilst Zr and Hf are about equally extracted to approximately 10%. Similar to the diagenetic Peru Basin nodule, more Mo is extracted at a pH of 8.5 (30%) than at pH 7.5 (12%). W, Nb, Ta, and the rare earth elements are all way below 5%.

The siderophore leach of the stripped FeOOH and residual phases show extremely increased recoveries of elements related to the Fe-oxide phases. In the hydrogenic crust, about 45% Ta is extracted, compared with about 0–25% in the rest experiments. No Li and Mo are leached in these experiments, as these elements are already removed during the previous leaching steps.

An even bigger contrast in recoveries can be observed in the Fe-phase leach experiments of the diagenetic and mixed-type nodules. The Fe-phase leach of the Peru Basin nodule mobilized 50% Mo, 75% W, 40% Nb, and 70% Ta. In the CCZ nodule, about 25–30% Zr and Hf were mobilized, 45% Mo, 35% W, and 50% Nb.

Albeit the high affinity of DFOB for REY (see e.g. complex stability data from Christensen and Schijff (2011)), only insignificant amounts of REY were leached in all the experiments conducted in this study.

4. Discussion

The results of the sequential leaching experiments conducted on the Fe–Mn samples nicely demonstrate that the whole range of commodities that are of importance for mining purposes are distributed over several separate and distinct phases. Li is to two thirds associated with carbonates and the easily exchangeable fraction, whilst the rest of Li is structurally incorporated into the Mn-bearing phases. The metals that are of ‘traditional interest’, i.e. the base metals Mn, Co, Cu, and Zn are almost exclusively associated with Mn-oxides, which is in accordance to the model proposed by Koschinsky and Halbach (1995). The slightly negative charged surface attracts positively charged ions, which are then surface-complexed and lateron incorporated by substitution, surface oxidation and precipitation of discrete phases (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003).

High tech metals like W, Zr, Nb, and the REY Ce, Nd and Dy on the other hand are associated with Fe and residual phases and are only to subordinate extents associated with Mn oxides. This is the result of effective surface complexation or surface precipitation on the FeOOH phase. Redox-sensitive elements like Co and Ce are surface oxidized during sorption on Mn and Fe oxide carrier phases. Since this surface oxidation is a very efficient scavenging mechanism, hydrogeetic precipitates are much enriched in these elements compared to diagenetic nodules. Processes for redox-sensitive metals Mo and W are most likely structural incorporation rather than surface oxidation, since they are already present in the highest oxidation state of the element in seawater and in nodules/crusts. These elements are present in seawater as oxy-anions, which results in a net negative charge of the whole complex. Due to the slightly positive charge of Fe-oxides, these elements are expected to sorb on Fe-oxide colloids or particles (Koschinsky and Halbach, 1995), which is also indicated by the sequential leaching experiments. However, this contrasts with findings from synchrotron studies on MoMo and W, where the comparatively low Fe–Mn oxides, which show an association of these elements with the Mn oxide phase (Kashiwabara et al., 2013, 2009). Hence, our sequential leaching results for Mo and W may possibly be an artifact due to re-adsorption of Mo and W leached with the Mn oxide onto the remaining FeOOH phase, or formation of a discrete Mo- and W phase during leaching.

The siderophore leaching experiments demonstrate that Mo and Li can be selectively extracted to great extents from Fe–Mn precipitates. The extraction efficiencies observed for Zr and Nb are also relatively high, whilst all other metals of interest and especially the base metals highly enriched in crusts and nodules such as Mn, Ni, Cu, Co, and Zn are not significantly mobilized during leaching in the presence of the siderophore desferrioxamine B. The time series experiments (1–7 days) showed that despite minor fluctuations of some percent, the leaching system reaches steady-state comparatively quickly. Mo concentrations tend to decrease very slightly with increasing experiment time, whereas Li and Zr slightly increase. Fe and Mn as well as the base metals tend to fluctuate to very subordinate amounts with changes less than one percent over time. Hence, we assume that reaction kinetics are relevant but of subordinate importance and the dissolution and solubilization of certain metals are mainly thermodynamically driven within the time frame considered in the experiments.

As desferrioxamine B is a Fe-specific organic ligand, Fe extraction from Fe–Mn precipitates is expected to be relatively high with extraction rates of about 5–10% as reported in this study. Fe forms the strongest complexes with desferrioxamine B with a reported log $K_f$ of about 30.7 at an ionic strength of 0.1 (Martell and Smith, 2001) and hence even greater extraction rates would be expected. Cheah et al. (2003) studied the DFOB-promoted steady-state dissolution kinetics of the Fe oxhydroxide mineral goethite and suggest a ligand-promoted dissolution mechanism for Fe oxhydroxide minerals. Hence, the extraction rates for Fe increase with increasing ligand concentration, but the comparatively low concentrations of DFOB in the mM range compared to the high Fe concentration in the nodules and crusts effectively inhibit even greater Fe mobilization. DFOB stability constants for the base metals Cu, Ni, Co and Zn are log $K_f$ = 14.12; 10.9, 10.31 and 10.07 (Martell and Smith, 2001), respectively, and are way below that of Fe. Hence a subordinate extraction of base metals is expected and is reflected in most of the experimental results of this study. Additionally, base metal liberation is restricted during DFOB leaching due to very low Mn extraction rates. Since the base metals are associated with the Mn-oxide carrier phase in the Fe–Mn nodules and crusts, only a limited extraction takes place.

Siderophore-promoted dissolution of Mn oxide phases has been described in the literature by e.g. Duckworth and Sposito (2007, 2011).
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2005), For pH 5–7, reductive dissolution mechanisms have been reported by Duckworth and Sposito (2007), i.e. Mn is reduced to divalent Mn in the presence of the reductant DFOB, which itself is oxidized. However, at pH ranges between 7 and 9, non-reductive dissolution and Mn(III)–DFO complex formation was observed. Since we performed experiments with a pH of 6 and 8, both reductive and non-reductive pathways are possible. Manganese extraction rates in our experiments-only increased with increasing total siderophore concentration, but they did not vary with pH.

No complex stability data have been reported yet for Li. Farkas et al. (1997) reported the occurrence of Mo(VI)–DFO complexes in aqueous solutions with a pH below 7 and Farkas et al. (2003) determined the stability constant for H$_2$DFOB with MoO$_4$ as $\log \beta = 53.54$. Bellenger et al. (2008) also demonstrated that siderophores produced in cultures of Azotobacter vinelandii form very strong complexes with molybdate. Zn–DFO complex stability constants have not been reported yet, however, Guérard et al. (2013) determined the log $K_S$ of Zr(IV) with the alpha-hydroxyacids Me–AHA, an electronically very similar ligand with respect to binding sites, and reported log $K_S$ values of up to 17.32 for one on four complexes. Although the reported Me–AHA complex provides the closed approximation to Zr(IV)–DFO complexes, this might be a less than ideal comparison due to the possibility of chelate effects.

Hafnium complex stability constants are reported by Yoshida et al. (2004) to be in the range of Fe(III)–DFOB stability constants. For the elements Nb and Ta, no data are available on the interactions of these metals with desferrioxamine B and siderophores in general. The very low extraction rates observed for the rare earth elements Ce, Nd and Dy can also be explained by complexation chemical constraints because, although the stability constants are quite high with log $K_S$ ranging from 10 to about 17, the huge amounts of competing cations like Fe with waxy higher complex structures probably inhibits the complexation of REY with DFOB from Fe–Mn precipitates.

The observed mobilization behavior of Fe, the base metals Mn, Ni, Cu, Co and Zn and the high tech trace metals Mo, Li, Zr and Nb is probably influenced by several controlling factors. The high stability constants of DFOB with Fe leads to enhanced solubility and a pronounced dissolution of the Fe–oxyhydroxide phases, which only liberates metals associated with this specific phases, while metals hosted in the Mn-oxide phase are mostly not liberated because of thermodynamically unfavoured and hence subordinate Mn-oxide dissolution. For some elements like Zr and Hf, complex stability indications that probably Zr(IV)–DFO and Hf(IV)–DFO complexes are formed during leaching of Fe–Mn precipitates. However, REY(III)–DFO complex formation should be as high as the aforementioned ones with similar stability constants, but the REY are way less effectively leached than e.g. Zr and Hf.

Ternary sorption of metal–siderophore complexes onto particles has been described in the literature as well (e.g. Neubauer et al., 2000) and might be occurring for a range of metals complexed with DFOB, which would remove the metal-complexes from solution due to re-adsorption of the complex onto particles. Such re-adsorption could be a possible explanation for a lower metal extraction rate than expected from solution complex stability constants.

It is generally difficult to exactly pinpoint factors that drive the actual leaching behavior of elements from geological material. Given the fact that Fe–Mn crusts and nodules comprise several carrier phases and are enriched in a wide range of elements, the determination of actual processes in such a multi-component system is very difficult. Additionally, certain chemical parameters like the redox potential were not monitored during the experiments, but these might have a significant influence on the mobilization of metals from Fe–Mn precipitates as well.

Probably, several factors such as the dissolution of carrier phases, complex stabilities with DFOB, chemical speciation and potential re-sorption of liberated metals and ternary sorption of metal–siderophore complexes on particles and probably even more processes are influencing the distribution of elements between the leach solution and the residual Fe–Mn crusts and nodule powders.

Elucidation of these complex relationships would require a significant number of further experimental investigations but is beyond the scope of this study.

5. Conclusions and outlook

The sequential leaching experiments demonstrated that the majority of elements enriched in the nodules and crusts mineral structures that are considered as high tech metals are actually associated with Fe oxyhydroxide carrier phases, whilst metals such as Co, Ni and Zn are associated with the Mn phases. This is a very important fact, as it gives rise to the question whether there is a unique technique available which can extract trace metals from a single carrier phase of the nodule or the crust, but leaves most of the carrier phase itself and the other elements in place and intact. With the help of the Fe-specific ligand desferrioxamine-B, we demonstrated that a selective extraction of high tech metals such as Li, Mo, Ta, Zr and Hf is possible whilst Mn and the other base metals Ni, Cu, Co and Zn, which are associated with the Mn oxide phase, are not extracted to significant extents. Also the relative amount of Fe is small compared to the efficiently extracted elements listed above. This set of elements can be extended to Nb and W if Mn oxide and carbonate phases are stripped prior to the siderophore leaching by e.g. a reductive leaching step at low pH. By combining this leaching step with siderophore leaching, we extracted 30–50% of Mo, Nb, W and Ta from a mixed type CCZ nodule and 40–80% from a diagenetic Peru Basin nodule, whilst only 5–10% Fe were extracted from the nodules.

The leaching behavior of the investigated elements is probably influenced by a wide range of chemical constraints and processes, such as dissolution of carrier phases, primary and secondary complex formation, re-sorption, ternary sorption and many more. This study also showed that biologically produced ligands such as siderophores are capable to selectively leach certain metals from deep-sea Fe–Mn deposits and that possibly bioleaching, either directly by the use of microorganisms or indirectly by using biologically produced organic ligands as used in this study, might be an important processing option when it comes to the future mining of these deposits. Further necessary developments would include a subsequent recovery and separation of individual metals from the multi-component leachate.

The metals that are now present in a dissolved state in a mixed multi-element solution containing organic constituents also need to be recovered and preferably selectively extracted from solution. Besides a combination of selective precipitation or solvent extraction techniques, novel hydrometallurgical technologies like the use of ionic liquids in solvent extraction as e.g. demonstrated by Vander Hoogerstraete et al. (2013) are promising approaches for facing the issue of trace metal separation from leaching solution.

Additionally, more research is needed for further increasing the selectivity and effectiveness of the siderophore leach by e.g. changing the pH regime, the temperatures and monitoring the redox potential of the leach solution. We also suggest that further organic ligands known to form highly stable complexes with the metals of interest should be tested for their selective extraction efficiency.

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References


3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

3.2. Improving Recoveries of Platinum and Palladium from Oxidized Platinum Group Element Ores from the Great Dyke, Zimbabwe, using the Biogenic Siderophore Desferrioxamine B

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Title of publication

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3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals
Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B

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A B S T R A C T

This study presents results of batch leaching experiments conducted on oxidized (weathered) Platinum-Group Element (PGE) ores from two platinum mines at the Great Dyke, Zimbabwe. The Great Dyke mafic-ultramafic layered intrusion is, after the Bushveld complex in South Africa, the second largest PGE deposit worldwide. Current mining operations focus on the recovery of PGE from pristine and unweathered ore material from the Main Sulfide Zone (MSZ). Besides pristine ores, there are significant resources of oxidized MSZ material at or near the surface. These oxidized PGE ores are currently not mined because insufficient recoveries using conventional processing techniques render this process option uneconomical. The complex, polymodal mineralogical distribution of the PGE in the oxidized MSZ aggravates to the processing issue. The data presented in this study show that a mild hydrochloric acid leach combined with a subsequent leach with the biogenic siderophore Desferrioxamine B (DFIB) in an aqueous solution efficiently extract Pt and Pd from these ores. Although Pt and Pd extraction during hydrochloric acid pretreatment is rather heterogeneous with a maximum Pt recovery of 30%, it nevertheless facilitates mobilization of Pt and Pd in the subsequent siderophore leaching step. Hydrochloric acid pretreatment of the oxidized PGE ores is a prerequisite for liberating the PGE-bearing host phases from weathering products and for the reduction of the amount of easily-available cations such as Fe in hydroxide minerals, which may compete with Pt and Pd for complexation in the subsequent siderophore leaching step. This two-step approach results in a combined extraction of up to 80% of total Pt. Our results further show that Pt and Pd extraction during siderophore leaching is strongly pH-dependent and appears to be most efficient at near-neutral to slightly alkaline conditions, with increasing extraction efficiencies at higher pH. Based on the results of this study, siderophore leaching of oxidized (PGE) ores represents a promising approach for the hydrometallurgical extraction of Pt and Pd from oxidized ores.

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1. Introduction

The metals ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) comprise the Platinum-Group Elements (PGEs). Oxidized PGE ores from the Great Dyke in Zimbabwe have high economic potential for future mining because of the combination of relatively high PGE grades and large resource estimates (Prendergast, 1988; Oberthür et al., 2013). They are surficial ore deposits ranging down to maximum depths of about 15 to 30 m, allowing relatively low-cost open-pit mining of high volumes. For the oxidized PGE ores of the Great Dyke, resource estimates range from 160 to 250 Mt of oxidized material (Oberthür et al., 2013) with average grades of 3–5 ppm Pt, i.e. 480–1250 tons of Pt metal are contained in these deposits.

The pristine (i.e. unweathered or “fresh”) sulfide-bearing PGE ores mined at the Great Dyke are processed following conventional metallurgical practice. This includes froth flotation of milled material, smelting and matte production, and chemical leaching (Crandall et al., 2011). The metallurgical processing route for pristine material reaches Pt recoveries of ~85% (Rule, 1998).

The processing of weathered, oxidized PGE ores, however, is challenging, because PGE extraction with conventional techniques is too inefficient to be economically feasible. Metallurgical tests conducted on oxidized ore material from the Great Dyke suffer from very low Pt recoveries of considerably less than 30% (Oberthür et al., 2013).

The complex polymodal distribution of the PGE is a major challenge for upgrading and processing of this supergene ore and presents commercial mining (Oberthür et al., 2013). Becker et al. (2014) attributed the poor flotation performance of oxidized PGE ores to a combination of poor PGE mineral liberation, a lack of base metal sulfide association and especially the presence of naturally floating gangue (NFG; Becker et al., 2014).
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et al., 2009; Bulatovic, 2003), the oxidized PGE ores from the Great Dyke, Zimbabwe, contain high amounts of NFG (mostly talc and talc-coated orthopyroxene grains; e.g., Becker et al., 2013). The presence of these phases leads to an effective dilution of the concentration grades during flotation. This in combination with the aforementioned factors ultimately results in a considerably decreased flotation performance whenever oxidized portions are present during flotation of PGE ores (Becker et al., 2014).

To address the processing issue, we conducted batch leaching experiments using specific molecular low molecular weight organic molecules known as siderophores, to extract Pt and Pd directly from oxidized PGE ores.

Siderophores are a group of organic molecules synthesized and exuded by plants and bacteria in toxic environments to mobilize and bind trivalent Fe from oxohydroxyde mineral structures. However, besides having high affinities for Fe, most siderophores are also very effective in binding and solubilizing many other elements such as the rare earth elements and yttrium, some PGE and some actinides (Bau et al., 2011; Christenson and Schijff, 2011; Desouky et al., in press; Liermann et al., 2011; Duckworth et al., 2009; Bellenger et al., 2008; Dahlheimer et al., 2007; Mullen et al., 2007; Yoshida et al., 2004, 2007; Brantley et al., 2001; Baysse and Vos, 2000; Bouby et al., 1998; Hernlem et al., 1996, 1999). Kraemer (2004) compiled a detailed review of siderophore chemistry and interactions with metals.

The siderophore used in the present study is the trithydroxamate siderophore Desferroxamine B (DFOB), a common siderophore produced by the bacterium Streptomyces pilosus and others (Müller et al., 1984). The molecule occurs in many soils (Winkelmann, 1992) and natural waters (Gledhill et al., 2004; McCormack et al., 2003) at concentrations in the nano- to millimolar range.

Solution speciation and metal binding modes of DFOB are discussed by Kiss and Farkas (1998), for example. DFOB contains three hydroxamate functional groups and a terminal amine. The terminal amine does not deprotonate except at very pH and thus usually does not take part in the complexation reaction (see deprotonation of DFOB in Table 1; e.g., Christenson and Schijff, 2011; Hernlem et al., 1996). In the case of Fe complexation, each of the three hydroxamate functional groups forms a five-membered ring with the trivalent Fe thus satisfying the preferred octahedral inner coordination sphere of Fe (Kraemer, 2004).

The dissolution of metal oxides by siderophores is mostly a ligand-promoted dissociation mechanism with a one on one stoichiometry (Kiss and Farkas, 1998), although reductive and oxidative mechanisms as a result of electron transfer between surface metal and absorbed ligands have also been suggested (see Bau et al., 2013; Bl, 2009; Yoshida et al., 2004 and others). A study by Molwinkel et al. (2014) demonstrated that DFOB may be a viable reagent in the extraction of high-technology metals like Mo from deep-sea ferromanganese nodules and crusts.

Dahlheimer et al. (2007) conducted experiments on the siderophore-mediated mobility of PGEs in soils and provide metal stability constants for DFOB complexes: Except for tin, Pd and Pt have the highest metal stability constants (Pd: log $K_s = 19.2-23.2$; Pt: log $K_s = 16.2-17.2$) of all divalent metals investigated for hexaentate DFOB complexation. Hence, the extraction of PGE from oxidized PGE ore material with siderophores might be a promising approach, sole or in combination with other acids, for improving the recoveries of PGE from oxidized ores.

The combination of mild hydrochloric acid leach steps with siderophore-mediated extraction of Pt and Pd as presented in this study may be a first step towards the development of a successful process route for material from this special type of currently unexploited ore deposit.

2. Experimental

2.1. Samples

The ore samples used in the experiments originate from the Ngezi Mine and the Hartley Open Pit Mine of the Great Dyke in Zimbabwe and were gratefully provided by Zimplats Inc.

In the Great Dyke, according to Oberthür and Melcher (2005), economic concentrations of PGE, Ni and Cu occur in the form of disseminations of mainly intercumulus sulfides in the Main Sulfide Zone (MSZ). The MSZ is generally between 1.5 and 4 m wide and outcrops to the rims of the Great Dyke on the western and eastern limbs. The MSZ shows the highest PGE grades (3–5 ppm) and thus is the major PGE resource of the Great Dyke.

Close to and at the surface, the MSZ is intensely weathered and oxidized to depths of about 15 to 30 m. Relative to the pristine ore, the oxidized PGE ore shows higher Pt/Pd ratios indicating depletion of Pd during weathering and almost complete removal of sulfur (Locmelis et al., 2010). As reported by Locmelis et al. (2010), PGEs in the oxidized MSZ usually occur as relict primary Platinum Group Minerals (PGM; sperrylite, cooperite, braggite), in solid solution in relict sulfides like pentlandite, as secondary Pt-Fe alloys, as PGE oxides/hydroxides and as substitutes or adsorbed cations in Fe and Mn (hydr)oxides. (Pt, Pd)-bismuthothellurides and sulfides (pyrhotite, pentlandite, chalcopyrite and subordinate pyrite) are almost completely destroyed (Oberthür et al., 2013). According to Oberthür and Melcher (2005), in oxidized MSZ about 50% of the Pt is hosted by discrete PGE oxide and hydroxide minerals, 45% is hosted in either Mn- or Fe-hydroxide structures, and 5% by relict sulfides.

The batch leaching experiments presented here were conducted on two types of sample material. The PtOx composite sample is a mixed sample which contains so-called peak material (i.e. parts of a drill core showing highest Pt grades in the profile) of four different drill cores of the Ngezi Mine. The other two samples, PtOxN001 and PtOxHOP001 from Hartley Open Pit, are made up of Pt peak material of a single drill core.

In both 'peak' samples, PtOxHOP001 and PtOxN001, subhedral to euhedral cumulus orthopyroxene grains (> 80 vol.%) are the most abundant minerals with grain sizes ranging from 1 to 3 mm. Olivine (5 vol.%), interstitial clinopyroxene and interstitial plagioclase are present. Further, some relict sulfide grains are observed in particular in PtOxN001. Relict PGM were observed by electron microprobe (Fig. 1a). In PtOxHOP001, clay minerals, such as smectite and illite-mica, occur as secondary minerals whereas in PtOxN001 only minor amounts of these clay minerals are present. In PtOxHOP001, (Pt, Pd)-oxides were identified using electron microprobe as shown in Fig. 1b. Secondary minerals like oxyhydroxide minerals (viz FeOOH and Mn-Ni-Co-OH), which formed during weathering, are significantly enriched in Pt and Pd with 50–80 ppm Pd and up to 400 ppm Pt (see Fig. 1c, d).

The dried and crushed samples were powdered with a Fritsch Pulverisette-6 planetary mill withagate balls and a sealed agate mortar.

The elemental composition including Pt and Pd grades for all samples are presented in Table 2.

2.2. Leaching

All lab work related to this project was conducted in a trace-metal clean environment. The siderophore mesylate salt of DFOB, Desferal®, is sold as a drug to treat iron hemochromatosis and was used in this

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$log K_{sol}$</th>
<th>$log B_{ac}$</th>
<th>$I = 0.1$</th>
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<tr>
<td>DFOB$^{3+} + 3H^{+} \rightarrow H_2DFOB$</td>
<td>10.84</td>
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<td>37.69</td>
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<tr>
<td>DFOB$^{2+} + 2H^{+} \rightarrow H_2DFOB$</td>
<td>20.39</td>
<td>29.37</td>
<td>37.69</td>
</tr>
</tbody>
</table>
3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

All chemical reagents used for this study (except Desferal®) were of suprapure grade. Purity of all reagents including Desferal® was cross-checked by blank measurements with Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) and was found to be well below the detection limit of the respective elements of interest for both, the siderophores as well as other chemical reagents.

Siderophore solutions were prepared with Desferal®. For these experiments, the pH values of the siderophore solutions were buffered with Tris(hydroxymethyl)-aminomethane (TRIS). The pH adjustment with suprapure HCl was done immediately before the start of the leaching experiments and before the addition of DFOB.

Batch leaching experiments were performed in closed Low Density Polyethylene (LDPE) bottles at room temperature in an overhead shaker. Fig. 2 shows the leaching process as presented in this study, which is comprised of a hydrochloric acid pretreatment of the powdered samples followed by a siderophore leach at a fixed pH. 20 g of ore was mixed with 200 ml of the leaching solutions and filtered using a Sartorius filter tower with 0.45 µm membrane filters after experiment times of 24 to 240 h, respectively. The leachates were analyzed with Inductively Coupled Plasma–Optical Emission Spectrometry and –Mass Spectrometry (ICP–OES and –MS), respectively.

### 3. Results and discussion

Initial siderophore batch leaching experiments on untreated oxidized MSZ ores were conducted with 1 mM siderophore concentrations and solid contents of 100 g/L. These experiments revealed very low Pt and Pd recoveries of < 1% into solution. Between 1% and up to 3% of Co and Ni were leached by the siderophore leach, whereas only about 0.3% Pd and 0.02% Pt were mobilized. Solid content tests revealed that 100 g/L is the most effective ratio with respect to leaching efficiency, with recoveries dropping by more than 50% at solid contents above 100 g/L.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PrOxN001</th>
<th>PrOxHOP001</th>
<th>PrOx-composite</th>
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<td>RSD [%]</td>
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3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

> 100 g/L. The results of the direct leach with siderophores were not satisfactory, although we could demonstrate Pt and Pd mobilization during batch leaching experiments in the presence of siderophores.

We eventually established a pretreatment leach with mild hydrochloric acid, which on the one hand made use of the fact that chloride is a viable complexing agent for PGE and hence extracts some PGE from the oxidized ores, and on the other hand removes many "unwanted" elements like Fe hosted in hydroxide structures. Iron, because of its higher complex stability constants with DFOB, competes with Pt and Pd for ligand-promoted mobilization. Pretreatment settings favorable for subsequent siderophore leaching are 0.5 M hydrochloric acid, solid contents of 100 g/L, and a treatment time of 24 h. More diluted hydrochloric acid concentrations showed a two- to five-fold decrease in Pt recovery during the pretreatment step and a ten-fold decrease in siderophore-promoted Pt recovery (Fig. 3a, b). Higher than 0.5 M hydrochloric acid concentrations produced slightly higher Pt and Pd recoveries (+ 10%) in the pretreatment step (Fig. 3b), but due to the aggressive and unselective nature of the leach, the concentrations of the base metals also increased sharply. After hydrochloric acid pretreatment, siderophore leaching was conducted with pH-buffered solutions using the buffering agent TRIS, because remaining traces of hydrochloric acid in the leaching residues facilitated an immediate pH drop in the leaching solutions to pH ≤ 2 after addition of the pretreated ore powder. Such low pH conditions effectively limit metal chelation with siderophores due to a change in the protonation or even the destruction of the pH-sensitive DFOB molecule.

After drying the residue and subsequent leaching with siderophores in pH-buffered solutions, the recovery of Pt in the siderophore leaches rose from ~ 1% for non-pretreated ores to up to 50% for 0.5 M hydrochloric acid pretreated ones. Fig. 4 shows the results of pH tests with siderophore solutions performed on the pretreated PtOx-composite sample. These experiments show that Pt and Pd extraction is most efficient when buffered to a pH between 8 and 9, while at lower pH the Pt and Pd recoveries are considerably lower (20% Pt and about 15% Pd recovery in siderophore leaching step). For pH values below 7, Pd extraction is strongly suppressed (~5%) whereas Pt extraction is intermediate in the siderophore leaching step with recoveries of about 12%. It should be noted that ΔpH (difference from pH_{leach} to pH_{sol}) was in the range of 0 to -0.2 for all experiments except for the pH 6.5 leach, for which it was about -3. The buffering agent TRIS effectively buffers pH in the range of 7 to 9, which explains the observed pH drop at pH 6.5. Apparently, slightly basic conditions with pH > 8 are preferred by the siderophore DFOB for the extraction of both Pt and Pd.

Interestingly, when the concentration of DFOB in the leaching solutions is gradually increased from 3 mM to 10 mM (Fig. 5), the recoveries of Ni and Co increase, whereas Pt and Pd recoveries drop slightly or remain independent of DFOB concentrations for molarities larger than 3 mM. A similar observation was made for Pt–Pd–DFOB interactions by Normand and Wood (2005) who stated that Pt and Pd dissolution increased up to a certain DFOB concentration, remained independent at higher DFOB concentrations and only increased again at very high DFOB concentrations. Concentrations higher 10 mM were not tested in this study for economic reasons. Figs. 5 and 6 show the leaching kinetics of the DFOB concentration test (Fig. 5) and of a 3 mM DFOB leach at pH 9 for Cu, Co, Ni, Pd and Pt (Fig. 6). Pt is mobilized rather quickly but solution concentrations tend to decrease with experiment times of more than 72 h, whereas Pd is still leached after 72 h in the 3 mM DFOB pH 9 experiments, but shows the same Pt-like behavior in all other experiments. Base metal recoveries (Cu, Co, Ni) are consistently below 5% over the time range investigated.

It appears that given enough time, DFOB will promote dissolution of minerals and forms complexes with those elements that have the highest stability constants. This explains why the concentrations of Fe, which forms the reportedly most stable complexes with DFOB, in the leaches increase significantly with increasing experiment time, but element concentrations of e.g. Pt and Pd, whose stability constants with DFOB are notably lower than that of Fe, fluctuate or decrease with time due to resorption or precipitation (see Table 3 and Figs. 5 and 6).
3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

The combined recoveries for the hydrochloric acid pretreatment and the siderophore leach reached 78% total extracted Pt from bulk rock for sample PtOxN001 from the Ngezi Open Pit Mine Field in Zimbabwe (Fig. 7a), 33% for the Hartley Open Pit Mine sample PtOxH0P001 (Fig. 7b) and 41% for the composite sample (Fig. 7c). Siderophore-mediated extraction of Pt in sample PtOxN001 was highest (0.88 ppm), representing approx. 50% of bulk rock Pt. Extraction efficiency was generally lower for Pd than for Pt and ranged from 5 to 10% for sample PtOxN001 in siderophore solutions at pH 8.2 up to 25% for the PtOx composite experiment at pH 9 (Fig. 7a and c, resp.), whereas Pd extraction in the siderophore leach step was negligible for the Hartley Open Pit mine sample. Cobalt, Cu and Ni recoveries are low in the buffered DFOB experiments and amount to <5% in all conducted experiments. In all experiments, most Co, Cu and Ni are leached during the rather unselective and aggressive hydrochloric acid pretreatment step.

The insignificant extraction of Pt and Pd in a DFOB-free experiment with de-ionized water (DI) after HCl pretreatment confirms that DFOB complexation enhances Pt and Pd extraction. ICP-OES measurements of 3 mM DFOB leachates were conducted to determine the major element concentrations in the leachates and are shown in Table 3 for PtOxN001, PtOxH0P001 and for the time-series experiment of the PtOx-composite sample. As siderophores are ligands originally produced for binding ferric iron and increasing its bioavailability, Fe concentrations in all analyzed leachate solutions are high and range from 29 to 57 ppm, while Al, Ca and Mg concentrations are considerably lower and fall in the range of some tens of ppm. The amount of extracted Cr is below the detection limit (<1 ppm). Potassium, Mn, Pb, Sr, and Zn are also all below detection limit. Interestingly, the element concentrations including Pd (except for the 10 mM DFOB leach) increase in the leachates with increasing experiment times except for Pt. Platinum concentrations fluctuate around the 24 h values.

The oxidized PGE ores of the Great Dyke in Zimbabwe constitute a significant potential for future mining as soon as metallurgical problems have been solved and rates of recovery reached levels at which mining becomes economic. We demonstrated that the combination of a
3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

![Leaching kinetics for a 3 mM siderophore leach buffered to pH 9 over a time range of 24 h to 10 days conducted on 0.5 M HCl pretreated Ptox-composite material.](image)

The mild hydrochloric acid leach facilitates the dissolution of easily soluble mineral phases like FeOOH and reduces the portion of Fe in the residue that is easily bound by siderophores. Without this, easily available Fe in the siderophore leach step would compete with the PGE for complexation with DFOB due to the Fe-specific nature of the siderophore molecule. Furthermore, the hydrochloric acid pretreatment liberates the distinct PGE-bearing host phases by etching the mineral grains, which are coated with weathering products like oxides, hydroxides and phyllosilicate minerals (e.g., Schneiderhöhn and Moritz, 1993). Hence, the removal of easily available competing cations and the liberation of PGE mineral phases from weathering products is an important initial step prior to the actual (siderophore) leach.

Tests at various pH (pH values in the TRIS buffering range from approximately 7 to 9) on the Ptox-composite sample showed that the efficiency of siderophore-promoted extraction is strongly pH dependent, and that metal selectivity can be controlled by buffering the siderophore solutions to specific pH values. Due to limitations of the buffering range of the organic pH buffer, pH values well above pH 9 were not studied.

Given the higher stability constants with DFOB (Dahlheimer et al., 2007), Pt extraction should be higher than Pt extraction provided the host mineral structures are comparable. However, due to significant lower recoveries for Pd, several additional factors apparently play an essential role on the extraction of Pt and Pd from oxidized PGE ores.

In pristine PGE ores, the PGEs are bimodally distributed as Pd is largely hosted by sulfides (mainly pentlandite), whereas Pt forms discrete PGM. Oberthür et al. (2013) estimated that in the ores of the MSZ, 80% of Pd is hosted by sulfides and only 20% occur as discrete PGM, whereas Pt mainly forms discrete PGM and only minor amounts are hosted by sulfides. During weathering of pristine PGE-ore, sulfide minerals are largely destroyed and only relic grains remain in the oxidized ores. Further, only relic PGE (PGE-sulfides and arsenides) are present, whereas PGE-bismuthotelluridurides are largely destroyed (Fig. 1a, b). Weathering of pentlandite forms Ni- and Fe-rich clay minerals, such as smectite and illite/micaceous with Pt and Pd concentrations in the 100 ppm range (Fig. 1c, d). Palladium and Pt are either adsorbed onto these secondary minerals or incorporated into their lattice structures (Locmelis et al., 2010). Pentlandite, as the main host of Pd, and certain discrete PGM, as the main source of Pt, behave differently during weathering which results in a dissimilar distribution of Pt and Pd in different host minerals present in the oxidized ores. In the oxidized ores, PGEs are polymodally distributed and are present in a variety of different PGM and PGE carriers (Oberthür et al., 2013; Locmelis et al., 2010). This may have a major effect on the extraction of Pt and Pd from the oxidized ore using DFOB and the differences in the host mineral structures may also explain the unexpected lower recoveries of Pd over Pt.

Desferrioxamine-B speciation is a function of pH and protonation increases with decreasing pH in the order: DFOB$^{3-}$ → HDFOB$^{3-}$ → H$_2$DFOB$^{-}$ → H$_3$DFOB$^{0}$ → H$_4$DFOB$^{+}$ (see Table 1). In our experiments it is evident that while DFOB in TRIS-buffered solutions below pH 8 mobilizes a lower fraction of Pt and Pd, extraction is significantly enhanced in alkaline solutions with pH > 8. Platinum and Pd recoveries are highest at pH 9. The observed recoveries are in accordance with the results of Dahlheimer et al. (2007) who state that with increasing pH the Pt and

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<th>PtoxH0001 3 mM DFOB leachate 120 h</th>
<th>Ptox-composite 3 mM DFOB leachate</th>
<th>PdoxN001 3 mM DFOB leachate 120 h</th>
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3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals

![Graphs showing metal leaching percentages](image)

Fig. 7. Stacked diagrams showing the total recoveries achieved with the presented leach protocol with 3 mM DFOB on pretreated material of samples PiOsX6001 (a) and PiOsX409001 (b) at pH 8.2 and PtCo-composite (c) at pH 9.

Pd metal solubilities in the presence of DFOB increase as well. At basic pH, only the terminal amine is still protonated and Pt(II) and Pd(II) are able to bind to the deprotonated sites of the hydroxamate functional groups of the DFOB molecule (Dahlheimer et al., 2007).

Based on the results of this study, divalent Pt and Pd apparently bind preferentially with $\text{HFDOB}^2-$ (all hydroxamate groups deprotonated; amine protonated) and with $\text{H}_2\text{DFOB}^+$ (two hydroxamate groups deprotonated). The following reactions can be postulated if divalent metal species in solution are assumed:

$$\text{Pt}^{2+} + \text{HFDOB}^2- \rightarrow \text{Pt}^{(II)}\text{HFDOB}$$
$$\text{Pt}^{2+} + \text{H}_2\text{DFOB}^+ \rightarrow \text{Pt}^{(II)}\text{H}_2\text{DFOB}^+$$
$$\text{Pd}^{2+} + \text{HFDOB}^2- \rightarrow \text{Pd}^{(II)}\text{HFDOB}$$
$$\text{Pd}^{2+} + \text{H}_2\text{DFOB}^+ \rightarrow \text{Pd}^{(II)}\text{H}_2\text{DFOB}^+$$

Already at pH values around 9, a small fraction of DFOB is present in its fully deprotonated state, i.e. all hydroxamate functional groups as well as the terminal amine are deprotonated and are able to participate in binding a metal. In ‘real’ systems, such as the one investigated, the species abundance can be different and is also strongly affected by the amount of potential binding partners present in solution. Thus, the fraction of fully deprotonated DFOB can be higher (or lower) at pH 9 compared to what thermodynamic modeling suggests.

At surface conditions, Pt is stable as Pt(II) and Pt(IV) (Bond, 1991), whereas Pd is only stable at an oxidation state of +2. Thus, it can be assumed that a portion of Pt is oxidized during weathering and fixed as a tetravalent cation in the secondary minerals, whereas Pd still occurs as Pd(II). Unfortunately, there are no (synchrotron-)studies known on the oxidation state of Pt and Pd in secondary reef-type ores which could confirm this hypothesis. However, our results indicate that a significant fraction of Pt in the oxidized ores occurs as Pt(IV) because of the significantly elevated siderophore-promoted mobility of Pt over Pd, which is observed in our experiments. Dahlheimer et al. (2007) reported that Pd(II) DFOB complex stability constants are slightly higher (log $K_r$ 19.2–23.2) than Pt(II) DFOB stability constants (log $K_r$ 16.2–17.2). This would suggest a preferred Pd extraction in the siderophore leach step, provided that both Pt and Pd are divalent. However, complex stabilities of a metal with DFOB are reported to increase with increasing oxidation states of the complexed metal (see e.g. Bau et al., 2013; Herniem et al., 1996) which would favor the complexation of Pt(IV) over Pt(II) and Pd(II). Generally, the stability constants of DFOB with tetravalent cations increase with increasing pH due to an increase in the amount of available binding sites (i.e. functional groups) as noted.
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above. This was demonstrated by e.g. Yoshida et al. (2007) for Th(IV). Thus, in its fully deprotonated state, DFOB can form very stable complexes with Pt(IV) as Pt(IV)DFOB by completely satisfying the coordination sphere of Pt4+ and this may complement the trend observed during leaching. Besides small differences in the host mineralogy, the abundance of Pt(IV) in the ores and the preferred binding by DFOB may explain the elevated extraction of Pt over Pd with siderophores at higher pH.

This pilot study showed that Pt and Pd extraction in the presence of biogenic organic ligands is possible and viable. Hence, research on (in-)direct bioleaching techniques with organisms that produce these or chemically similar compounds at or close to the mining sites, in reaction tanks or in situ as a heap leaching technology may represent promising approaches to study. However, given the corrosive nature of the pretreatment, heap leaching might be a less suitable option for this process and alternatives for the pretreatment need to be developed. Bioleaching with siderophores has been demonstrated earlier by e.g. Desouky et al. (in press), but no information is given about culturing the producing species (i.e. Aspergillus ficuum, Pseudomonas aeruginosa, Streptomyces pilosus) in situ or in tanks. Given the unknown sensitivity of these species with regard to high concentrations of toxic metals and/or the elevated temperatures commonly observed in direct heap and tank (bio-)leach operations, indirect (bio-)leach routes might be the better and more viable option for siderophore leaching of oxidized PGE ores.

Future research will have to focus on the mineralogical selectivity during the leach process, on further improvement and homogenization of the leaching efficiencies and, given the heterogeneity in leaching efficiencies reported in this study, on the identification of the exact processes that drive Pt and Pd extraction in batch leaching experiments with siderophores. Synchrotron studies on weathered and oxidized MSZ material could shed light on the actual occurrence and distribution of Pt(II) and Pt(IV) in the distinct (secondary) mineral phases and could complement the proposed hypothesis of preferential Pt(IV) DFOB complexation. As much of the oxidized material is already stockpiled on site, an upscaling of the process using actual oxidized PGE ore dump material also needs to be investigated. The selective extraction and recovery of Pt and Pd from the siderophore solutions needs to be constrained and tested, which, however, was beyond the scope of the present study. Extraction of Pt and Pd by solvent extraction or ion-exchange resin techniques may also allow the regeneration and recycling of the leaching solutions, which would significantly lower the costs of a hydrometallurgical process.

4. Conclusion

Siderophore leaching of oxidized PGE ores represents a promising approach for the hydrometallurgical extraction of Pt and Pd, but further research is required before upscaling may be considered. The DFOB mesylate salt used in this study is easily available from various chemical distributors as a chemical reagent of industrial grade purity. However, considering the size of the PGE deposit in Zimbabwe, the projected demand for industrial grade DFOB in such an operation would easily exceed the current production. Therefore, in situ or heap bioleaching using siderophore-producing bacteria and fungi might be the better route to follow. The mineralogical composition of the oxidized ore is still a major challenge for processing with siderophores and results in rather heterogeneous Pt and Pd recoveries for the leaching protocol described and utilized in this study.

Hydrochloric acid pretreatment of the oxidized PGE ores is necessary for liberating the PGE-bearing host phases from weathering products and for the reduction of the amount of easily-available cations such as Fe, which may compete with Pt and Pd for complexation with DFOB in the siderophore leach stage.

The results of this study demonstrate that Pt and Pd extraction with biogenic ligands like DFOB is feasible. Average Pt recoveries using the patented two-stage leach protocol (hydrochloric acid pretreatment followed by a siderophore leach) are in a range between 30 and 80%. Based on the data presented, (bio)leaching of oxidized PGE ores with siderophores is a promising option for treating these ores, which are difficult to treat economically with established metallurgical techniques.

Acknowledments

We thank Andrew du Toit and his team from Zimplats Holdings Inc. for providing the oxidized PGE ore samples as well as for hosting the authors during a sampling and mine visit at Hartley Platinum Mines and Nezgi Mines in February 2012. This project was realized in the context of a research contract from the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR; German Federal Institute for Geosciences and Natural Resources). We appreciate the help of D. Meissner and J. Mawick in the Geochemistry Lab at Jacobs University Bremen.

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3. Application of Siderophores in Hydrometallurgical Extraction of Critical Metals
4. Conclusion

4.1. General conclusion

The first goal of this thesis was to investigate the influence of the siderophore desferrioxamine B on the mobilization and fractionation of ‘immobile’ HFSE Zr, Hf, Th, U and REY from igneous rocks during weathering and in aqueous solutions containing colloids and lithic particles such as river- and seawater. The second goal was to elucidate to what extent siderophores can be used to extract certain high technology metals not only in trace amounts, but in sufficiently large quantities and with a high selectivity so that siderophores might be used for economic extraction of metals from complex oxide-bearing ores in hydrometallurgical applications.

The data presented in chapter 2 show that the presence of the DFOB siderophore significantly leaches REY from igneous rocks and even ash particles present in river water. Further, the presence of the DFOB siderophore considerably increases the dissolved concentrations of the REY. This study indicates that siderophore complexation can lead to partial dissolution of igneous rocks and lithic particles and releases ‘immobile’ HFSE to ambient waters. Siderophores are important for controlling the fate of HFSE during chemical weathering of rocks. The presented data suggest that leaching in presence of siderophores creates distinct REY patterns typical for the siderophore desferrioxamine B. These patterns develop irrespective of the mineralogy, the textural and/or chemical composition of the rocks that are leached. The depletion of the LREY, the enrichment of the MREY and HREY over LREY and the decoupling of Ce are characteristic patterns for leaching in presence of siderophores. These patterns were produced during all siderophore experiments presented in chapter 2 and could not be produced with other abundant organic and inorganic reagents. Furthermore, the siderophore leachates are significantly enriched in Zr, Hf, Th, and U. These elements are usually considered as very immobile during water-rock interaction, but as shown here are mobilized to considerable extents when the siderophore DFOB is present during leaching. Desferrioxamine B facilitates the mobilization of these elements by ligand complexation (REY(III), Th, Zr, Hf) and the observed mobilization largely agrees with published thermodynamic data. Ce and U are oxidatively solubilized due to significantly higher stability constants with Ce(IV) and U(VI) compared to Ce(III) and U(IV). Oxidized Ce$^{4+}_{aq}$ and U$^{6+}_{aq}$ are immediately bound and removed as Ce(IV) DFOB and U(VI) DFOB complexes and in the attempt to maintain the redox equilibria, additional Ce$^{4+}_{aq}$ and U$^{6+}_{aq}$ are
produced. The overall effect of this “siderophore redox pump” is the preferential enrichment of dissolved Ce and U relative to dissolved LREY and Th, respectively. The observed high mobility of the pairs Zr-Hf and Th-U can help to explain certain geochemical observations made in nature. In estuaries, the aggregation and subsequent sedimentation of colloidal and nanometer-sized particles causes a removal of particle-reactive elements like the REY and Hf from the dissolved element pool (Elderfield et al., 1990). Particle-reactive HFSE solubilized and bound as very stable siderophore complexes might circumvent this and these elements might be able to enter the ocean without being trapped in the mixing zones by coagulation and sorption.

In Earth’s (near-)surface systems, ‘immobile’ U(IV) is oxidized to ‘mobile’ U(VI) during oxidative weathering of minerals and rocks (Choppin, 2006). Soluble U(VI) compounds such as uranyl (U(VI)O₂^{2+}), therefore, predominate over less soluble U(IV) species (Wilkins et al., 2006) and modern oxic seawater shows dissolved Th/U ratios below unity (e.g., Asmerom and Jacobsen, 1993). These low Th/U ratios are transferred to marine chemical sediments which act as archives of the Th/U ratio of seawater. Therefore, coupled or decoupled Th-U behaviour may be used as a paleo-redox-proxy for tracking the evolution of the redox level of a geochemical system such as the Earth’s atmosphere and oceans (e.g., Rosing and Frei, 2004; Bau and Alexander, 2009). Similarly, presence or lack of Ce anomalies in chemical sediments and precipitates, and in paleosols and paleoweathering profiles is used as a paleo-redox proxy (see e.g., German and Elderfield, 1990; Möller and Bau, 1993; Pattan et al., 2005). The experimental results in this thesis suggest that the presence of strong organic ligands such as siderophores is sufficient to promote oxidation and mobilization of U and Ce. If there is ample reason to believe that significant amounts of siderophores or other strong ligands were present during the deposition of a rock, the use of proxies such as U and Ce might be severely hampered.

Furthermore, we demonstrated that complexation by siderophores can efficiently modify the particle-reactivity of REY during scavenging on manganese (hydr)oxides and alter the trace metal signal in (hydr)oxide particles. Because of their high surface charge and large surface area, (hydr)oxide minerals efficiently scavenge particle-reactive trace metals such as the REY from ambient water (e.g., seawater). In scavenging experiments performed within this thesis, fractionation of HREY and Ce from LREY was observed, contrary to what was observed in the past for solutions without siderophores. In nature, redox-sensitive Ce is oxidized at the Mn-(hydr)oxide mineral surface. Our results suggest that the minute amount of
Ce\(^{4+}\) oxidized and present in solution is preferentially bound by the siderophore ligand. The resulting redox disequilibrium between Ce\(^{3+\text{aq}}\) and Ce\(^{4+\text{aq}}\) promotes continuous oxidation by the siderophore, so that with time more and more Ce(IV) is complexed by the siderophore and hence ‘shielded’ from scavenging by precipitating Mn (hydr-)oxides by the siderophore due to significantly higher complex stabilities of Ce(IV)-DFOB than Ce(III)-DFOB. Ce(IV) thus stays in solution, whilst the neighboring redox-‘insensitive’ REY are almost completely scavenged. Loges et al. (2012) showed concentration data for surficial secondary Mn oxides veins, which exhibit strong negative Ce anomalies and an enrichment of HREE over LREE. These and similar features might be explained by the presence of siderophores or strong organic complexing agents comparable with respect to binding sites.

The work presented in chapter 3 on hydrometallurgical applications showed that siderophores can leach and mobilize significant amounts of valuable metals from oxide ores like oxidized PGE ores or ferromanganese nodules and crusts. The data on the siderophore-promoted extraction of Pt and Pd from oxidized PGE ores demonstrated that both metals are significantly mobilized in DFOB solutions buffered to a pH of around 9, indicating preferential complexation of Pt and Pd at basic conditions with (Pt,Pd)HDFOB and/or (Pt,Pd)H\(_2\)DFOB\(^{+}\). Siderophores also represent viable reagents for the hydrometallurgical extraction of high technology metals from ferromanganese nodules and crusts. We showed that Li, Mo, Zr, Hf, Nb and Ta are significantly extracted (up to 80%) from the host phases whilst ‘major’ constituting metals like Fe and the base metals Mn, Ni, Cu, Co and Zn are not extracted to large extents (mostly <<5%).

This study highlights the importance of siderophores for the mobility and fractionation of certain high technology metals in the environment and provides first data for the application of siderophores in the field of extractive hydrometallurgy. The data presented in this study shows that siderophores like desferrioxamine B not only enhance the solubility and mobility of Fe(III), but also enhance the mobility of ‘immobile’ high field strength and highly siderophile elements like rare earth elements, Zr, Hf, Th, U and Pt and Pd. The observed fractionation patterns and the decoupling of Ce and U by siderophore-induced oxidation might be helpful in constraining the presence of siderophores or chemically similar organic chelating agents present during weathering and may potentially be used as a bio-proxy for paleoenvironmental research. The typical REY in combination with HFSE patterns that developed are unique for the presence of the siderophore DFOB and can be used to deduce the influence of siderophores on weathering and/or sedimentation/precipitation of a rock.
Additionally, the siderophore-promoted oxidation of U from rocks as a uranyl siderophore complex as demonstrated in this study might cause significant mobilization of U in the environment and therefore cause environmental problems in areas with high bioproductivity, i.e. where siderophores are likely to be produced in high amounts, and in areas where siderophores might be used for remediation of contaminated sites as suggested by (Rajkumar et al., 2010; Ahmed and Holmström, 2014). The significant mobilization of HFSE by siderophores might also complicate the interpretation of trace metal data from a variety of rocks, because some methods rely heavily on the fact that HFSE are immobile during water-rock interaction and are in contrast to large ion lithophile elements not leached during chemical weathering.

4.2. Prospective Research

This study deepened the understanding of the role of biogenic siderophores on immobile trace elements during water rock interaction and elucidated the potential applicability of siderophores in the hydrometallurgy of high tech metal ores. To further this and to better understand the consequences of siderophore-mediated HFSE mobilization, research should be fostered and more data are needed on the siderophore-promoted mobility of high field strength elements in the environment. Future research should not only be focused on broadening the database by leaching other rock types, but should also be focused on other abundant but structurally different siderophores like mugineic acid, rhizoferrin or others. Whilst many of these facilitate the dissolution of mineral particles and enhance the solubility of Fe(III) and other polyvalent trace metals, the actual mode of binding and the extent of mobilization and/or fractionation may differ significantly.

In order to better understand the fate of Hf in estuarine systems and during scavenging on (hydr)oxide particles, scavenging experiments could be conducted with Zr(IV) and Hf(IV) in siderophore-bearing solutions similar to the REY scavenging experiments conducted in this study. Furthermore, the variation in Zr/Hf elemental ratios during scavenging on (hydr)oxides in presence of siderophores could complement this and represents an interesting approach for future research. To better quantify the influence of siderophores during scavenging of REY and other particle-reactive HFSE onto (hydr)oxide particles, scavenging experiments should be conducted with naturally occurring Mn-rich spring waters. These have been reported to occur e.g. in Hokkaido, Japan (M. Bau, Jacobs University Bremen, pers. comm., 2014) and in
the Western Cape region (N. J. Beukes, University of Johannesburg, pers. comm., 2013). Comparing experimental results with actual in-situ Mn precipitates is of significant interest and should be complemented by geochemical modelling, as thermodynamic data for REY-DFOB complexation is readily available in literature. Such a follow-up study could shed light on the influence of siderophores on the scavenging behavior of ‘naturally occurring’ REY and other HFSE in ‘natural’ Mn-rich solutions, especially as these waters contain significant amounts of other cations and anions which were not considered in the lab-scale experiments with artificial solutions in this study. Extended X-ray Absorption Fine Structure (EXAFS) analysis or X-ray Absorption Near Edge Spectra (XANES) obtained by synchrotron radiation could provide useful information on the actual siderophore-metal binding mechanism and could also provide oxidation states and information on neighboring atoms of the coordinated metal. Synchrotron radiation might also help to distinguish if siderophore-metal complexes are subject to binary or ternary sorption on (hydr)oxide particles or not (e.g. scavenging of LREY-DFOB complexes instead of completely dissolved LREY).

With regard to soil processes and mineral deposit formation, an interesting study following up on this thesis would be the role and importance of siderophores on laterite formation and element fluxes before, during and after lateritisation. Laterites are intertropical to tropical soils enriched in iron and aluminium (oxides) and depleted in silica, which formed by intense, hot and humid weathering of rocks. Laterite soils host a number of either ‘conventional’ deposits (Ni-Co laterites, weathering crusts of banded iron-formations, manganese deposits) as well as deposits for certain critical metals, like PGE, REY and Cr (Evans, 2009). Next to laterites representing modern – or geologically young – well-weathered soil horizons, many fossilized paleosols are thought to be of lateritic origin (see e.g. Gutzmer and Beukes, 1998). From a geochemical perspective, especially lateritic paleosols of Precambrian age are of interest, as they represent records of mobilized iron in the transition from an anoxic to an oxygenated atmosphere and first terrestrial life (Gutzmer and Beukes, 1998). While plant and microbial activity definitely had a certain impact on lateritisation in recent geological times, the function and influence of ‘life’ on the formation of Precambrian laterites (‘paleosols’) is still rather unclear. Siderophores, produced by plants and microbes alike to solubilize iron from (hydr)oxidic mineral structures, may play a significant role in controlling the (HFS) element fluxes during formation of laterite horizons (and paleosols).
Most studies to date, the presented one included, focused on the influence of siderophores on trace metal behavior. Apart from some studies on the isotopic fractionation of Fe by siderophore leaching (Brantley et al., 2001; Liermann et al., 2011), there has been no study dealing with the influence of siderophores on stable isotope geochemistry of HFSE. As siderophores and similarly strong biogenic organic ligands have probably been produced in a wide range of environments since the dawn of biological life on earth, a highly interesting question is thus the extent to which these ligands fractionate, actively or passively, stable isotopes of HFSE during ligand-promoted dissolution or oxidative solubilization. Stable isotope systems of trace metals are in the focus of many ongoing research efforts and have a tremendous impact on the understanding and reconstruction of past and present geological systems. However, if siderophores alter isotopic signals and if there is ample reason to believe that significant amounts of siderophores were produced during the deposition of a studied rock (e.g. during cycles of very high bioproductivity or during oxygen ‘highs’ of e.g. the Carboniferous), the potential use of isotope systems like εNd-εHf or $^{138}\text{Ce}/^{142}\text{Ce}$ as proxies may be significantly confined due to siderophore-promoted isotope fractionation.

This study assessed the siderophore-promoted mobilization of high technology metals from rocks, ores and aqueous solutions. However, given the high affinity of DFOB towards these metals, developing mechanisms for ‘immobilization’ of high-tech metals by using siderophores might be equally important and promising. An interesting approach is to incorporate siderophores into the interlayers of clay minerals like smectite, illite or montmorillonite (H. Dong, Miami University, pers. comm., 2014). The thus fixed siderophore may be able to bind and complex metals from solution and may ‘immobilize’ them by being itself attached to and fixed in the interlayer of clay minerals. Such a technique might be useful in bioremediation of heavy-metal contaminated sites or, given the high affinity towards the actinides, in research related to nuclear waste repositories.

The experiments conducted in chapter 3 on the hydrometallurgical extraction of PGE with siderophores have been conducted as batch leaching, or incubation experiments at variable physicochemical conditions to simulate tank or reactor leach operations. Percolation leach experiments are considered to be a good approximation for simulating heap leach conditions on a lab-scale because of longer reaction times of the fluid with the ore. To further assess the applicability of siderophores during heap leaching, percolation experiments involving siderophores should be conducted over time ranges and at temperature ranges typical for heap leach operations. Percolation leach experiments have been conducted by (Mwase et al., 2014)
4. Conclusion

on pristine Platreef PGE ores from South Africa, which involved a bio-leach with microbes and a subsequent cyanide leach over a time range of several weeks. The results of this study were promising. Using siderophores in percolation experiments with oxidized PGE ores might show interesting results on whether siderophores can be used in heap leach operations or if their use is restricted to tank or reactor leach operations as simulated in this study. Because of the high amount of fines and clay minerals present in the here investigated oxidized PGE ores, agglomeration might be considered in combination with siderophore percolation leach experiments to avoid solution channeling and the formation of impermeable zones (Dhawan et al., 2013).

One of the most severe problems faced with processing the oxidized PGE ores are the different extents in oxidation of the material. The term ‘oxidized PGE ore’ is not clearly defined and may mean anything from ‘nearly fresh’ over ‘oxidized’ to ‘completely weathered’ and further rock material bare of any primary features (i.e. soils in a wider sense). Mine geologists and geoscientists seem to have a quite diverging understanding of the term ‘oxidized’, a problem often encountered in the course of this study. However, the problems in processing lie within the mineralogical heterogeneity of these special ores. Studies on oxidized Platreef from the Bushveld, South Africa, showed that flotation successfully separates relic ‘pristine’ (base metal associated-) PGMs from ‘oxidized’ portions and might be an important pretreatment of the oxidized ore (see e.g. Schneiderhöhn and Moritz, 1939; Becker et al., 2014). Flotation pulps, i.e. the residue of flotation operations, containing country rock, non-floating gangue as well as the ‘oxidized portion’ of the PGE hosting phases in the form of Fe and Mn (hydr)oxides, probably provides better primary material for batch and percolation leach experiments with siderophores than untreated ore material. This may be readily available for heap leach operations due to the fact that much of this material is already crushed, milled and stockpiled (du Toit, Zimplats, pers. comm., 2012; Roberts, Anglo American, pers. comm., 2014).
5. Related scientific works

5.1. Research project “Experiments on carboxylic-acid and siderophore-promoted dissolution of supergene, oxidized PGE ores from the Great Dyke, Zimbabwe”

Jacobs University Bremen has been contracted by the “Bundesanstalt für Geowissenschaften und Rohstoffe” (BGR) to conduct selective leaching experiments on PGE ores of the oxidized main sulphide zone of the Great Dyke in Zimbabwe. The focus on this study was on assessing the carboxylic-acid and siderophore-promoted leaching behavior of Pt and Pd from these ore matrices. Whilst the tested carboxylic acids provided dissatisfactory results with regard to Pt and Pd mobilization, we eventually established a promising leach route consisting of a hydrochloric acid pretreatment and a subsequent siderophore leach. Parts of this study are published in the peer-reviewed publication in chapter 3.2.

5.2. Research project “Experiments on siderophore-promoted dissolution of supergene, oxidized PGE ores from the Great Dyke, Zimbabwe and the Bushveld Complex, South Africa”

As a follow-up study, Jacobs University Bremen was contracted again in 2013 to further assess the siderophore-promoted dissolution of oxidized PGE ores from the Great Dyke, Zimbabwe, and to also extend the sample database for leaching to oxidized PGE ores from the Platreef formation of the Bushveld Igneous Complex in South Africa. Because the established siderophore leach route from the previous year’s study produced low recoveries for Pt and Pd from Platreef ores, the study was extended and alternative anorganic and organic leaches were tested on the material with very promising results with regard to Pt and Pd recoveries and selectivities.

5.3. Co-supervised BSc Projects

Katharina Wortberg (2013): Impact of siderophores on mobilization of REY, Zr, Hf, Th and U from fresh and weathered igneous rocks. Jacobs University Bremen.
5. Related scientific works

5.4. Conference proceedings

Note that some abstracts were (co-)authored under my birth name “Dennis Mohwinkel”.


Mohwinkel, D., Bau, M., 2012. Siderophore-enhanced extraction of Pt from oxidised PGE ores from the Great Dyke, Zimbabwe. First European Mineralogical Conference (emc) 2012, Frankfurt/Main, Germany


6. References

The references in this thesis are formatted according to the guidelines of the journal *Hydrometallurgy*.


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