

UNIVERSITAT DE BARCELONA

Rare earth elements, Yttrium and scandium retention in Fe- and Al-hydroxysulfates (basaluminite and schwertmannite) under the hydrogeochemical conditions of the Tinto River estuary (SW Spain)

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FACULTAT DE CIÈNCIES DE LA TERRA

RARE EARTH ELEMENTS, YTTRIUM AND SCANDIUM RETENTION IN Fe-AND AI-HYDROXYSULFATES (BASALUMINITE AND SCHWERTMANNITE) UNDER THE HYDROGEOCHEMICAL CONDITIONS OF THE TINTO RIVER ESTUARY (SW SPAIN)

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ABSTRACT

Rare-earth elements (REEs: lanthanides, yttrium and scandium) are scarce in mining concentrations in the Earth's crust, freshwater and seawater. In recent decades, REEs have become crucial to new technologies for computer chips (gadolinium), missile guidance systems (neodymium), nuclear reactor control rods (samarium), microwave emitters (yttrium), long-live missile batteries (promethium), electric vehicles (dysprosium) or in the glass industry (lanthanum). The need of REEs forces European manufacturing companies to invest in the exploration of alternative sources. An alternative source is the areas impacted by acid mine drainage (AMD), which display REE concentrations that are several orders of magnitude higher than those of freshwater and seawater. AMD neutralization as a result of mixing with seawater in estuaries prompts a spontaneous precipitation of Fe- and Al-oxyhydroxysulfate nanominerals (i.e., schwertmannite (Fe₈O₈(OH)₆SO₄) and basaluminite (Al₄(SO₄)(OH)₁₀·5H₂O), respectively), which play a significant role in the fate of Rare Earth Elements (REEs). The conditions for precipitating schwertmannite and basaluminite (pH 2.5-3.5 and 4.5, respectively) are not suitable to adsorb REEs, but when AMD mixes with the water of the estuary of Ría de Huelva (Spain), the pH increases up to between 4.5 and 8, yielding optimal conditions for REE adsorption on schwertmannite.

A geochemical study of this estuarine system is needed to shed light on the REE distribution. Earlier studies focused on the adsorption of REEs onto these Fe- and Al-oxyhydroxysulfates. However, two important aspects related to the affinity of REEs for these minerals remained unsolved and are necessary to comprehensible understand the distribution of REEs in the estuarine system. The first one is to know the capacity of schwertmannite to retain adsorbed REEs at a pH between 4.5 and 7. Desorption batch experiments in the presence of sulfate were performed to study this capacity at this pH range and room temperature. The solution chemistry was analysed to obtain the REE surface constants for the surface complexation reactions. Desorption of Lu-enriched schwertmannite at different pH values was investigated with High Energy X-Ray Diffraction (HEXD) and Extended X-ray Adsorption Fine Structure (EXAFS) to characterize the molecular structure of the surface complexes involved in the desorption reaction. The results indicate (1) that REE adsorption/desorption on schwertmannite is pH dependent and, as a consequence, schwertmannite retains adsorbed REE at pH > 6,

and (2) both monodentate and bidentate surface complexes are involved in the Ludesorption reaction.

The second aspect concerns the effects of an increase in pH and in ionic strength on the REE adsorption onto both nanominerals. In this study, REE adsorption onto schwertmannite and basaluminite has been studied in the pH range of 4.5-7 and ionic strength range of 0.25-0.5 M using batch experiments and EXAFS analysis to elucidate the behaviour of REEs under AMD impacted-estuarine conditions. The log K_{REE} values calculated for the adsorption of REEs onto schwertmannite and basaluminite were implemented in a non-electrostatic surface complexation model (NEM), which indicated that REE adsorption is both pH dependent and ionic strength independent. For schwertmannite, low pH resulted in a low retention (up to 10% at pH 4.5) in a monodentate coordination whereas high pH increased the adsorbed fraction (up to 99% at pH 6.5) in a bidentate coordination. For basaluminite, the REE affinity was affected by the REE atomic number, enhancing the adsorption of heavy REEs (HREEs, up to 90% at pH 6.5) with respect to light REEs (LREEs, up to 20% at pH 6.5). The agreement between the NEM calculations and the EXAFS analysis in Gd-basaluminite suggests that monodentate binuclear and mononuclear are probable REE coordination in basaluminite, although the presence of outer sphere complexes is also likely for LREE. Thus, the thermodynamic parameters provided in this study prove useful to predict the geochemical behaviour of REEs in AMD-impacted estuarine areas.

To shed light on the complex geochemistry of the overall estuarine system, a field campaign was carried out to collect samples of the estuarine sediment and water and to measure concentrations of relevant trace elements ((REEs) and metal(loid)s). This enabled to (1) better understand the elemental distribution in the sediments and water in the water-mixing area, (2) discern the elemental behaviour via mixing modeling, (3) reproduce the aqueous behaviour of REEs related to REE adsorption onto schwertmannite and basaluminite, and (4) evaluate the effect of the adjacent phosphogypsum stack on the estuarine geochemistry.

RESUM

Els elements de les terres rares (REEs: lantànids, itri i escandi) són escassos en les concentracions mineres de l'escorça terrestre, en l'aigua dolça i en l'aigua de mar. En les últimes dècades, les REEs s'han convertit en elements crucials per a les noves tecnologies de xips informàtics (gadolini), sistemes de guia de míssils (neodimi), barres de control de reactors nuclears (samari), emissors de microones (itri), bateries de míssils de llarga vida (prometi), vehicles elèctrics (disprosi) o en la indústria del vidre (lantà). La necessitat de disposar de REEs obliga les empreses manufactureres d'Europa a invertir en l'exploració de fonts alternatives. Una font alternativa són les aigües afectades pel drenatge àcid de mina (AMD), les quals tenen concentracions de REEs que són diversos ordres de magnitud superiors a les de les aigües dolces i de mar. En els estuaris, la neutralització de l'aigua dels AMD com a resultat de la barreja amb l'aigua de mar provoca la precipitació d'oxihidroxisulfats de ferro i d'alumini (és a dir, i schwertmannita $(Fe_8O_8(OH)_6SO_4)$ basaluminita $(Al_4(SO_4)(OH)_{10} \cdot 5H_2O),$ respectivament), els qual tenen un paper important en la distribució de les REEs. Les condicions per a la precipitació de schwertmannita i de basaluminita (és a dir, pH entre 2.5-3.5 i 4.5, respectivament) no són les adequades per a l'adsorció de REEs. No obstant això, quan l'aigua de l'estuari de la Ría de Huelva (Espanya) es barreja amb AMD, el pH augmenta entre 4.5 i 8, proporcionant les condicions òptimes per a l'adsorció de REEs.

Així doncs, ens cal un estudi geoquímic d'aquest sistema complex per conèixer com és la distribució d'aquests elements en l'aigua i sediments de l'estuari. Tot i que l'adsorció de REEs en ambdós oxihidroxisulfats s'ha estudiat, hi ha dos aspectes relacionats amb l'afinitat de REEs en aquests minerals que encara cal resoldre per entendre bé la distribució de REEs en aquest sistema aquàtic. El primer aspecte és determinar la capacitat de retenció de REEs de la schwertmannita a pH entre 4.5 i 7. En aquest àmbit, (1) s'han realitzat experiments "batch" de desorció amb la presència de sulfat en aquest rang de pH i a temperatura ambient i (2) s'han analitzat les solucions aquoses per obtenir les constants de complexació superficial de les REEs. A més a més, s'ha estudiat la desorció de Raig X d'alta energia (HEXD) i "Extended X-ray Adsorption Fine Structure" (EXAFS) podent caracteritzar l'estructura molecular dels complexos superficials involucrats en la desorció. Els resultats indiquen (1) que l'adsorció/desorció de REEs en schwertmannita depèn del pH i, com a conseqüència, la schwertmannita pot retenir les REEs adsorbides a pH > 6, i (2) que tant els complexos superficials monodentats com els bidentats estan implicats en la reacció de desorció de Lu.

El segon aspecte per resoldre está relacionat amb els efectes de l'increment del pH i de la força iònica en l'adsorció de les REEs en ambdós nanominerals. Així doncs, s'ha investigat l'adsorció de REEs en schwertmannita i basaluminita en els rangs de pH i de força iònica de 4.5-7 i de 0.25 M - 0.5 M, respectivament. S'han fet servir experiments "batch" i anàlisis EXAFS per dilucidar el comportament de les REEs en les condicions de l'estuari de la Ría de Huelva impactat per AMD. Els valors de log KREE calculats per a l'adsorció de REEs en schwertmannita i basaluminita s'han implementat en un model de complexació superficial no electroestàtic (NEM), amb el què es dedueix que l'adsorció de REEs depèn del pH, però no depèn de la força iònica. Per a la schwertmannita, un pH baix comporta una retenció baixa de REEs (fins a un 10% a pH 4.5) en una coordinació monodentada. En canvi, a pH alt, la fracció adsorbida és gairebé completa (fins a un 99% a pH 6.5) i té lloc en una coordinació bidentada. En el cas de la basaluminita, l'afinitat de les REEs està afectada per llur nombre atòmic, i s'incrementa l'adsorció de REEs pesades (fins a un 90% a pH 6.5) respecte a les REEs lleugeres (fins a un 20% a pH 6.5). L'acord entre els càlculs del NEM i dels resultat de l'anàlisi d'EXAFS en una basaluminita enriquida en Gd suggereix que les coordinacions monodentades binucleada i mononucleada de les REEs són probables en la basaluminita, tot i que la presència de complexos d'esfera exterior (outer-sphere complexes) no es pot descartar en el cas de les REEs pesades. Així doncs, els paràmetres termodinàmics obtinguts són essencials per predir el comportament geoquímic de les REEs en zones d'estuari impactades per AMD.

Per aclarir la geoquímica complexa de l'estuari de la Ría de Huelva, s'ha dut a terme una campanya de camp per recollir mostres del sediment i de l'aigua de l'estuari i per mesurar les concentracions rellevants d'elements traça (REEs, metalls i semimetalls). Amb aquestes dades s'ha pogut (1) discernir el comportament elemental mitjançant models de mescla, (2) comprendre millor la distribució elemental en els sediments i l'aigua a la zona de mescla d'aigua, (3) reproduir el comportament aquós de les REE relacionades amb l'adsorció de REE sobre schwertmannita i basaluminita, i (4) avaluar l'efecte de les piles adjacents de fosfoguix sobre la geoquímica de l'estuari de la Ría de Huelva.

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INTRODUCTION

Motivation and background

Rare Earth Elements (REEs) are considered as raw materials necessary for the development of new technologies. However, these materials are emerging pollutants that may pose a risk to the environment and human health (Chakhmouradian and Wall, 2012; Gwenzi et al., 2018). These elements are very mobile in acidic environments such as in acid mine drainage (AMD), which turn these waters into a secondary source of REEs, and provide a transport for these pollutants (León et al., 2021). The retention of REEs in the biggest AMD generating region in Spain, the Iberian Pyrite Belt (IPB), has been thoroughly studied because of the properties and the mobility of REEs in this environment (Ayora et al., 2013, 2016).

REEs are retained in passive remediation systems and in the confluence with natural streams, where water acidity is neutralized and Fe- and Al-precipitates with the capacity to adsorb lanthanides, Y and Sc (Ayora et al., 2016). However, not all the AMD-impacted streams can be treated with passive methods and the newly formed precipitates that occur in the confluence are redissolved downstream (Lozano et al., 2020b). In recent years, attempts have been made to model the mobility in passive treatment systems and in the confluence with natural streams (Lozano et al., 2020b). Nevertheless, with regard to the work of earlier authors on REE retention onto Fephases, some questions about the surface bindings that are formed at the surface of schwertmannite ($Fe_8O_8(OH)_6SO_4$) remain to be clarified (Lozano et al., 2020a).

In general, most of the REEs, along with other contaminants, are transported to the estuary of Ría de Huelva, where water acidity is neutralized as a result of mixing with seawater, thus decreasing the concentration of these elements in the aqueous phase (Elbaz-Poulichet and Dupuy, 1999). Studies on the mobility of REEs in this area conclude that pH plays an important role in the removal of REEs in this area and in the precipitation of secondary Al- and Fe- phases (Lecomte et al., 2017). However, an adsorption model that predicts the mobility of these REEs under estuarine conditions remains to be devised because of the lack of thermodynamic data related to the variability of the ionic strength of estuarine waters.

Objectives and methodology

The aim of this thesis is to provide a better understanding of the processes involved in the retention and distribution of REEs along the estuary of Ría de Huelva (SW Spain). To this end, the following tasks have been carried out:

- I) Batch experiments at the laboratory:
 Ia) Desorption experiments of REE-enriched schwertmannite at the pH range of 4.5-7 found in the estuary of Ría de Huelva.
- Ib) REE adsorption experiments onto schwertmannite and basaluminite at different pH (4.5-7) and ionic strengths (I = 0.25 M-0.5 M).
- II) Measurements at the European Synchrotron Radiation Facility (ESRF):
- IIa) Extended X-Ray Absorption Fine Structure (EXAFS) onto Lu-desorbed schwertmannite at different pH.
- IIb) Extended X-Ray Absorption Fine Structure (EXAFS) onto Gd enriched basaluminite at different ionic strengths.
- IIc) Pair Distribution Functions (PDFs) of REE enriched basaluminite and schwertmannite.
- III) Field campaign at the estuary of Ría de Huelva to sample estuarine waters, suspended material and surface sediments.
- IV) Modeling of the adsorption of REEs onto schwertmannite and basaluminite under estuarine mixing conditions.
- V) Discussion on the distribution of REEs and other trace elements in the estuary of Ría de Huelva.

The following objectives are to be accomplished in accordance with this approach:

- To provide a better insight into the mechanisms of REE retention onto schwertmannite by obtaining the thermodynamic constants for the desorption reactions and modeling the experimental results.
- To study the effect of ionic strength on the REE adsorption onto basaluminite and schwertmannite.
- To devise a model for the surface structure of Lu when adsorbed onto schwertmannite as a function of pH.
- Similarly, to propose a model for the surface structure of Gd when adsorbed onto basaluminite and to examine an ionic-strength dependence of the proposed model.

- To analyse the estuarine samples and describe the distribution of REEs and other trace elements in the sediments, waters, and suspended matter.
- To model the REE retention via adsorption onto basaluminite and schwertmannite using the thermodynamic data obtained in this thesis.

Thesis outline

This thesis consists of five chapters. In the **first Chapter**, I describe the scientific background of the AMDs in the Iberian Pyrite Belt and the REE retention experiments performed with different Fe- and Al-oxides and hydroxides. In addition, I introduce schwertmannite and basaluminite as the targets for REE retention in the estuary of Ría de Huelva.

The **second Chapter** presents (1) the methodology used for the synthesis of schwertmannite and basaluminite and for the desorption and adsorption batch experiments, (2) the methodology and characteristics involved in the synchrotron beamlines used for the EXAFS and PDF analyses, (3) the equilibrium constant values and databases used in the geochemical PHREEQC modeling and (4) the sampling procedure and analysis of sediments, colloids and waters collected at the estuary of Ría de Huelva.

In the **third Chapter**, I present the experimental and modeling results related to (1) the purity of the synthetic phases, (2) the analysis of the desorption and adsorption batch reactions, (3) the Ab-Initio Molecular Dynamic (AIMD) modeling concerning the geometry of the aqueous REE-sulfate molecule used in the EXAFS models and (4) the characterization of the sediments, colloids, and waters of the estuary.

The **fourth chapter** focuses on the knowledge gained from the retention mechanisms of schwertmannite and basaluminite using the results of (1) the desorption of REE from schwertmannite at different pH values together with the EXAFS models and PDFs, (2) the REE adsorption onto schwertmannite and basaluminite at different ionic strengths and pH values, together with the EXAFS models and PDFs results from the analysis of Gd-rich basaluminite sample, and (3) the REE distribution along the estuary of Ría de Huelva using a geochemical model with PhreeqC. The model includes the thermodynamic data of the REE adsorption obtained at different ionic strengths to predict the hydrogeochemical conditions suitable for the retention of these elements onto the newly formed phases.

The **fifth chapter** summarizes the main conclusions of this thesis and proposes further research.

Two appendixes (Appendix A and Appendix B) contain supplementary information

CHAPTER 1

SCIENTIFIC BACKGROUND

1.1 Acid mine drainage (AMD) in the Iberian Pyrite Belt

Acid Mine Drainages (AMDs) are highly polluted waters characterized by high acidity, high sulfate concentrations and high concentrations of metal and metalloids. Their presence is a result of the oxidative dissolution of iron sulphides, such as pyrite (FeS₂), chalcopyrite (CuFeS₂), arsenopyrite (FeAsS) and pyrrhotite (FeS). These minerals are generally associated with coal and metal-bearing mineral deposits. A series of chemical and biochemical reactions occurs when the iron-bearing sulphide minerals are exposed to water and oxygen (Singer and Stumm, 1970):

Aqueous oxidation of pyrite by oxygen:

$$FeS_{2(s)} + 7/2O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (1)

Oxidative dissolution of pyrite by ferric iron:

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (2)

Aqueous oxidation of ferrous iron in the presence of oxygen:

$$Fe^{2+} + 1/4O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O$$
 (3)

Precipitation of ferric iron:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$$
(4)

Reactions (1) and (3) can be catalysed by bacterial activity, accelerating the overall process up to six-fold when compared to abiotic conditions (Singer and Stumm, 1970). The drastic decrease of pH favours the mobility of an enormous quantity of trace elements, which are responsible for the degraded quality of streams, rivers, lakes and groundwater (Johnson and Hallberg, 2005).

The Iberian Pyrite Belt (IPB) is a large area located at the southwest of the Iberian Peninsula. Its extension comprises from the Seville Province to Huelva Province, into Portugal. This area has a length and a width of 200 km and 40 km, respectively, and estimated original reserves of 1700 mt of sulphide ore (Sáez et al., 1999). Therefore, it is considered one of the largest polymetallic massive sulphide deposits worldwide. From a geological point of view, the IPB belongs to the South Portuguese Zone of the Hercynian Iberian Massif and is subdivided into three main units (Fig. 1.1), the Devonian pre-volcanic sediments (PQ group), the volcanosedimentary complex (VSC), and the post-volcanic lower Carboniferous group (Culm



Figure 1.1. Geology of the IPB, modified from Sáez et al. (1999).

This area has been a target of mining activities from pre-Roman times to today (Pinedo Vara, 1963). Early mining activities targeted Au, Ag and Cu from oxidized ores. Later, in the last century, Cu, Ag, Au and base metals were mined along with pyrite (for sulphuric acid) having up to 80 mines with an approximate production of 300 million tons of polymetallic ores (Strauss and Madel, 1974). Mining activities in the past years were confined to five districts: Neves-Corvo (Cu-Sn); Sotiel-Migollas (Cu-Pb-Zn-S-Ag); Rio Tinto (Au-Ag); Caledonia (Au-Ag) and Tharsis (Pyrite) (Sáez et al., 1999). Today, Cobre las Cruces (Cu) forms part of the main mining districts.

As a result of thousands of years of mining activities, together with the unique geology of the region, there is an enormous presence of metal-rich wastes that seriously impact the Tinto and Odiel Basins (Olías et al., 2004; Sánchez España et al., 2005; Cánovas et al., 2007; Sarmiento et al., 2009, 2011; Nieto et al., 2013). First approaches estimated the net transport of dissolved contaminants as 7,922 t y⁻¹ of Fe, 5,781 t y⁻¹ of Al, 3,475 t y⁻¹ of Zn, 1,721 t y⁻¹ of Cu, 1,615 t y⁻¹ of Mn, 71 t y⁻¹ of Co, 27 t y⁻¹ of Pb, 35 t y⁻¹ of As and minor quantities of other elements (Olías et al., 2006).

AMDs can be treated by either active or passive methods. Active methods require from constant chemical reagents and energy to function whereas passive methods require a small maintenance and use natural energy sources (photosynthesis, dissolution reactions, gravity) (Johnson and Hallberg, 2005). In the past decades, a remediation system for highly-polluted AMD was used to reduce the extreme metal and acidity without the perks of having Fe- and Al-clogging and armouring for conventional passive treatment methods (Ayora et al., 2013). This system is known as Dispersed Alkaline Substrate (DAS) and consists of several decantation ponds filled with calcite/MgO and woodchips. While the dissolution of the reagents (calcite and MgO) neutralizes water acidity, woodchips ensure a sufficient specific surface area for newly formed precipitates to accommodate. The increase in pH decreases the mobility of the trace elements and successfully reduces the pollution of the water (Caraballo et al., 2009; M. A. Caraballo et al., 2011a; Caraballo et al., 2011; Macías et al., 2012a,b). However, since few AMD-impacted streams are remediated with passive systems and most of the newly-formed precipitates at the confluences are unable to retain the REEs, these elements remain dissolved in AMD (Lozano et al., 2020a). Under these circumstances, most of the REEs and other contaminants are transported to the estuary of Ría de Huelva, where AMDs are neutralized by seawater mixing and the aqueous concentration of REEs decreases (Elbaz-Poulichet and Dupuy, 1999).

1.2 The estuary of Ría de Huelva

The estuary of Ría de Huelva receives from both Odiel and Tinto basins (Fig. 1.2). The Odiel basin has a surface of 2300 km², its main river (Odiel) has a length of 140 km and the estimated annual flow is 500 hm³ year⁻¹. The Tinto basin has a surface

of 720 km², its main river (Tinto) is 100 km long and carries an average flow of 100 $hm^3 y^{-1}$. The confluence of both rivers occurs at the estuary, accumulating the pollutants from both rivers as they mix with seawater. The Mediterranean climate of this area is characterized by long periods of drought and intense rainy events. A 50% of the annual rainfall occurs form October to January, the total mean annual rainfall is 812 mm.



Figure 1.2. Location of the IPB and main water courses draining the area. The rivers in orange are affected by AMD pollution.

The concentration of dissolved metals is high in summer, but it is higher in autumn and early winter during rain events when dissolution of evaporitic salts precipitated in summer takes place (Cánovas et al., 2012). Major and trace elements dissolved in the estuarine systems have been studied by several authors (Grande et al., 2000, 2003; Olías et al., 2006; Cánovas et al., 2007, 2012; Lecomte et al., 2017). Cánovas et al. (2012) quantified the dissolved pollutant load of the Odiel river over the course of 8 days, resulting in a total of 226 t of sulfate, 13 t of Al, 5.3 t of Zn, 3.2 t of Mn, ~1.9 t of Cu, 1.7 t of Fe, and lesser amounts of other metals (92 kg of Co, 47 kg of Ni, 24 kg of Pb, 17 kg of Cd, etc.). Since the AMD-polluted waters mix with seawater in the estuary, most of the metals lose their mobility as a result of the increase in pH, yielding losses between the riverine and seawater concentrations of 76% Cu, 64% Zn, 45% Co, 14% Cd and 12% Ni (Braungardt et al., 2003). Despite having losses of these elements, the AMD-impacted system still produces an extensive plume of contamination with regard to Mn, Cu, Cd and Zn, extending south towards the Strait of Gibraltar (Elbaz-Poulichet et al., 2001).

1.3 Rare earth elements (REEs) and their distribution in the Tinto and Odiel Basins

The group of rare earth elements (REE, lanthanides, yttrium and scandium; Connelly et al., 2005) is scarce in mining concentrations at the Earth's crust. REEs are divided into light REE (LREE: La to Nd), medium REE (MREE: Sm to Gd) and heavy REE (HREE: Tb to Lu and Sc and Y). In the last decades, this group has been essential in new technologies, such as gadolinium for computer chips, neodymium for missile guidance system; samarium for nuclear reactor control rods, yttrium for microwave emitters, promethium for long-live missiles batteries, or lanthanum in glass industry. The scarcity and versatility of REEs becomes in their consideration as critical and strategic raw materials with an increasing global demand (Chakhmouradian and Wall, 2012). According to US Geological Survey, China hosts 42% of the world's total REE reserve base, and accounted the 58-70% of the total world production in between 2021 and 2022 (Fan et al., 2016; Mineral Commodity Summaries 2023). The increasing internal demand in China has reduced its REE exportation since 2010, leading to the European Union and manufacturing companies to invest onto the exploration of alternative sources (Alonso et al., 2012; European-Commission, 2017; Hatch, 2012).

Although sulphide ore deposits display low REE concentration, the weathering of sulphide minerals leach and concentrate the REEs in extremely acid drainage (AMD), with high sulfate, Fe, Al and other metal(loid)s (e.g., Cu, Zn or As) (Moses et

al., 1987; Nieto et al., 2013; Nordstrom, 2015). The average REE concentration in AMD is several orders of magnitude higher than other water reservoirs such as ocean (5 pmol L^{-1}), groundwater (53 pmol L^{-1}), rivers (71 pmol L^{-1}), or lakes (170 pmol L^{-1}) (Merten et al., 2005; Ferreira da Silva et al., 2009; Noack et al., 2014). Even though the REE concentration in AMD is still far below profitable concentrations, acid waters are an environmental concern worldwide which require the implementation of treatment plants, where REE accumulation can range economical value. For example, in the Iberian Pyrite Belt (SW Spain), around 100 abandoned mines generate an intense AMD (Sánchez España et al., 2005; Nieto et al., 2013) that annually releases around 10.7, 2.1 and 5.5 tons of LREE, MREE and HREE, respectively (León et al., 2021). Hence, AMD waters are a potential secondary source of REEs (Cravotta, 2008; Sahoo et al., 2012; Ayora et al., 2016; Stewart et al., 2017; León et al., 2021).

Preliminary research has focused on REE mobility in Huelva estuary. Borrego et al. (2005) focused on the distribution of REEs in three sediment cores of the Huelva estuary retrieved at pH between 2.5 and 5. These authors found that the estuarine sediments were depleted in REEs under acidic conditions and their concentrations increased as pH rose. Moreover, with regard to the North American Shale Composite (NASC) ratios, it was shown a depletion of LREEs with respect to MREEs and HREEs. Borrego et al. (2012) found that the high concentration of REEs in fluvial waters $(\Sigma[REE] = 1090 \ \mu g \ L^{-1})$ dropped about one order of magnitude $(\Sigma[REE] \le 199 \ \mu g \ L^{-1})$ after the AMD-impacted river mixed with seawater, providing evidence that dilution and precipitation reactions led to REE depletion. To date, however, the interaction between the solids and the supernatant solutions remains unknown. Experimental approaches in REE behavior during seawater-AMD mixing have shown that an increase in pH induced the precipitation of poorly and highly organized Fe-bearing phases (e.g. jarosite, goethite and schwertmannite), which concentrated REEs in their structure (Lecomte et al., 2017). These approaches considered two end-member solutions (one taken from pure AMD and another from the seawater), and by varying their respective volumes an attempt to reproduce the mixing processes in the estuary was made. However, no effect of the phosphogypsum wastes was considered, which is an important process that might affect the geochemical system of the estuary of Ría de Huelva.

1.4 Earlier studies of REE retention on Fe- and Al-phases

Few studies have focused on the surface complexation of REEs (e.g., La, Yb and Eu) adsorbed onto Fe- And Al-phases, such as hematite (Marmier et al., 1997; Rabung et al., 1998; Marmier and Fromage, 1999; Estes et al., 2013), iron hydroxides (Dardenne et al., 2001; Liu et al., 2017; Finck et al., 2019), or alumina (Marmier et al., 1997, Xiangke et al., 2000) under conditions similar to estuarine areas (Xiangke et al., 2000). These studies revealed that amorphous ferric hydroxide displays a high REEs absorption capacity, preferentially for light LREEs. This is relevant at a neutral-high pH range (\geq 7), in which the speciation of HREEs changes to carbonate complexes, preventing the HREE adsorption onto Fe-hydroxides (Bau, 1999; Ohta and Kawabe, 2001; Sholkovitz, 1995; Byrne and Sholkovitz, 1996; Kawabe et al., 1999a, b; Quinn et al., 2006a,b). With regard to Al phases, it was shown that adsorption of Yb(III) and Eu(III) onto alumina (Al₂O₃) is both pH dependent and salinity independent at a pH range of 4.4-5.7 and ionic strength between 0.01 M and 2M (Marmier et al., 1997, Xiangke et al., 2000). However, until recently, the REE affinity for basaluminite and schwertmannite as well as the complexation stability under estuarine conditions remained poorly studied.

1.5 Schwertmannite and basaluminite

Schwertmannite is a Fe-oxyhydroxysulfate (Fe₈O₈(OH)₆SO₄) (Bigham and Nordstrom, 2000), with a poorly-crystalline tunnel-like structure formed by double chains of iron octahedra with sulfate tetrahedra located at inner and outer spheres coordination (Fernandez-Martinez et al., 2010; Sestu et al., 2017; Wang et al., 2021). This phase precipitates at pH between 2.5 and 3.5 in streams affected by AMD. The high surface area displayed by schwertmannite is positively charged at acidic pH, making this phase a sink for oxyanions in solution such as arsenate (Regenspurg and Peiffer, 2005; Zhang et al., 2016; Khamphila et al., 2017) , antimonate (Manaka et al., 2007; Li et al., 2016), chromate (Regenspurg and Peiffer, 2005; Khamphila et al., 2017), phosphate (Schoepfer et al., 2019a), selenate (Carrero et al., 2017b), and molybdate (Antelo et al., 2012). For more information about this topic, an excellent review of the occurrence of this mineral has been written recently (Schoepfer and Burton, 2021).

Under AMD conditions, REE species in solution are cations, repelling the positively charged surface in schwertmannite. However, recent studies have shown the adsorption capacity of schwertmannite for lanthanides, Y and Sc in the presence of sulfate at pH values from 4 to 7 (Lozano et al., 2020a), below-to-near the zero charge point in schwertmannite surface (Jönsson et al., 2005). The tidal dynamic in estuaries impacted by AMD allows the presence of this phase in suspension at pH above 5, where the repulsion between the REE sulfate (which is the dominant aqueous complex) and the surface of schwertmannite is reduced, and thus ensuring the retention of the REE (Elbaz-Poulichet and Dupuy, 1999; Lozano et al., 2020a).

On the other hand, basaluminite $(Al_4(SO_4)(OH)_{10} \cdot 5H_2O)$ is the Al counterpart of schwertmannite. Reported for the first time in an iron mine as a white precipitate (Bannister and Hollingworth, 1948; Hollingworth and Bannister, 1950), this mineral has been widely found in acidic waters with high content of sulfate (van Breemen, 1973; Adams and Rawajfih, 1977; Nordstrom, 1982; Bigham and Nordstrom, 2000). It usually precipitates when the pH increases to 4.5 due to the mixing of the waters or the neutralization in passive remediation systems (Caraballo et al., 2011b; Ayora et al., 2016; Lozano et al., 2020a, b). Synchrotron radiation has been used to perform Extended X-Ray Absorption Fine Structure (EXAFS) and Pair Distribution Functions (PDFs) to provide better insights into the structure of this mineral (Carrero et al., 2017a; Lozano et al., 2018). These studies have concluded that (1) basaluminite is an amorphous phase that presents a similar structure to that of felsöbanyáite and (2) this mineral is metastable in aqueous environments, tending to undergo several transformations to other Al hydroxides that are more stable, the ageing process can be inhibited in the presence of sulfate. On the other hand, basaluminite has been proved to be a sink for silica and highly polluting elements such as P, U, As, Se, Mo, Cr, Pb, V and Sc (Nordstrom and Alpers, 1999; Bigham and Nordstrom, 2000; Manaka et al., 2007; Sibrell et al., 2009; Sánchez-España et al., 2016; Carrero et al., 2017b). Moreover, several studies have proved the affinity of this mineral for REEs using chemical analyses (Verplanck et al., 2004; Gammons et al., 2005; Lozano et al., 2019a) and synchrotron-based methods (Lozano et al., 2019b).

In AMD-impacted estuaries, such as the estuary of Ría de Huelva, the mobility of the REEs is different than in non-impacted ones, having higher concentrations of dissolved REE that drop as the mixing with seawater occur (Elbaz-Poulichet and Dupuy, 1999; Carro et al., 2011; Cánovas et al., 2020, 2021). In this geochemical system, the AMD is neutralized due to the mixing with seawater and thus, the conditions for the colloids schwertmannite and basaluminite to precipitate are met (Bigham et al., 1990; Bigham and Nordstrom, 2000). These minerals have been widely found in AMD treatment plants and in neutralization by mixing with natural unpolluted streams (Caraballo et al., 2011b; Ayora et al., 2016; Lozano et al., 2020b) and Coal Mine Drainages (CMD) (Stewart et al., 2017; Zhang and Honaker, 2018; Hedin et al., 2019, 2020) and have been proved to be a potential sink for REE sulfates (Lozano et al., 2019a, 2020a; León et al., 2021). Recent studies show that the formation of these minerals generate pH buffers on the estuarine environment, these buffered areas are generally critical for the adsorption some elements, including REEs (Pérez-López et al., 2023). However, the capacity of these colloids to adsorb the REEs under different ionic strengths has not been yet experimented, which is critical in order to predict the mobility of these elements under the estuarine conditions. Moreover, the previous data from REE adsorption onto schwertmannite left several incognita regarding to the type of surface bindings that are formed and the stability of these (Lozano et al., 2020a).

CHAPTER 2

MATERIALS AND METHODS

2.1 Synthesis and characterization of schwertmannite and basaluminite

Schwertmannite was synthesized following the standard procedure (Bigham et al., 1990), adding 10.8 g of FeCl₃·6H₂O and 3 g of Na₂SO₄ to 2 L of Milli-Q water at 333 K. This solution was kept at 333 K for 12 min and, subsequently cooled to room temperature (298 \pm 2 K). The solid was dialyzed (cellulose membrane: Spectra/Por® Dyalisis Membrane) in 15 L of Millipore Milli-Q water, which were renewed every 24 h until the specific conductance was less than 5 μ S cm⁻¹ for five consecutive days. Once dialysis was finished, precipitate was centrifugated for 15 min at 4500 rpm (4150 RCF), frozen and lyophilized in an Alpha 2-4 LD plus, to avoid solid recrystallization.

For the synthesis of basaluminite 214 mL of Ca(OH)₂ were added to 30 mL of Al₂(SO₄)₃·18H₂O. A white precipitate comprised of gypsum and basaluminite was observed during the reaction, gypsum was separated by washing it several times with Milli-Q water (Adams and Rawajfih, 1977). Then, the precipitate was separated and freeze-dried.

The sorption densities of schwertmannite and basaluminite were calculated from previous studies (Fernandez-Martinez et al., 2010; Carrero et al., 2017b). Powder X-ray diffraction (XRD) analysis was performed using a 2Θ goniometer Bruker D8 Advance diffractometer and the specific surface area was obtained by the BET-N₂ sorption method using a Micrometrics Gemini V analyzer; Micrometrics. Moreover, the stoichiometry of schwertmannite was calculated by digestion of 0.01 g in 5 ml HNO₃ 65%. The acid solution was evaporated and the obtained pellet was dissolved onto 10 ml of Millipore Milli-Q water, acidified, and stored at 277 K for later chemical analysis.

2.2 Experimental setup

2.2.1 Desorption experiments

2.2.1.1 REE enrichment in schwertmannite

Schwertmannite was enriched with REEs following the method described by (Lozano et al., 2020a). A REE stock solution was prepared by addition of ICP standard

mix of 16 elements (excluding Pm) (Merck) and Na₂SO₄ salt in Milli-Q water. The final concentrations of each REE and Na₂SO₄ were 1 mg L⁻¹ and 2840 mg L⁻¹, respectively. The pH in solution was adjusted to 6.5 by adding a desired volume of 0.05 M NH₄OH solution. A total of 500 mg of schwertmannite were added to 500 mL of stock solution (S/L ratio = 1 g L⁻¹). The resulting suspensions were shaken for 6 h and pH was periodically re-adjusted to 6.5 by addition of NH₄OH. After this stage, the suspensions were centrifuged, solid was washed several times with Milli-Q water and freeze-dried. The supernatants as well as the stock solution were filtered through 0.22 μ m nylon membranes, acidified, and conserved at 277 K for later chemical analysis.

A Lu enriched-schwertmannite was specifically prepared for synchrotron analyses to avoid overlapping between rare earth elements. The stock Lu solution was prepared following the same procedure described above using un ICP Lu-standard solution (Merck) with a final Lu and sulfate concentrations of 5 mg L^{-1} and 2840 mg L^{-1} , respectively.

The concentration of adsorbed REE by schwertmannite ([REE]_{min}) was calculated using the following expression

$$[REE]_{min} = [REE]_{initial} - [REE]_{final}$$
(5)

where $[REE]_{initial}$ and $[REE]_{final}$ are the concentration of each REE in the stock solution and after adsorption experiments, respectively. The units of all the terms were expressed as mg L⁻¹.

2.2.1.2 REE desorption from schwertmannite

Batch desorption experiments were performed at pH 4.5, 5.0, 5.25, 5.5, 5.75, 6.0, 6.25, 6.50, 6.75 and 7.0 to study the effect of pH on REE desorption. A mass (0.01 g) of REE-enriched schwertmannite was suspended in 10 mL of 2840 mg L^{-1} Na₂SO₄ solution and equilibrated for 36 h. To reach the target pH in the solution, small volumes of 0.05 M NH₄OH solution were periodically added. The same procedure was followed with Lu-enriched schwertmannite at pH 4.5, 5.5 and 6.5. Additionally, desorption-kinetics batch experiments were performed with REEs-enriched schwertmannite at pH 4.85, 5.47 and 6.32 for 2, 6, 12, 24 and 36 h in line with the procedure described above. All the experiments were run in duplicate to ensure reproducibility of the results. The
resulting suspensions from each experiment were centrifuged, and the supernatants were filtered through 0.22 μ m nylon membranes, acidified and maintained at 277 K for further chemical analysis. The remaining Lu-enriched schwertmannite was freeze-dried and stored for synchrotron analysis.

The desorbed REE fraction (%) was calculated according to this expression

desorbed REE fraction (%) =
$$\left(1 - \frac{[REE]_{sch} - [REE]_{solution}}{[REE]_{sch}}\right) \cdot 100$$
 (2)

where $[REE]_{sch}$ and $[REE]_{solution}$ are the concentrations of each REE in the initial schwertmannite and in the final solution (mg L⁻¹), respectively. REE concentration on schwertmannite was calculated with Eq. (1).

2.2.2 Adsorption experiments

Two solutions (solution 1 and solution 2) containing REEs and SO₄ were prepared adding an ICP standard mix (Merck) of 16 REEs (excluding Pm) and Na₂SO₄ salts in Milli-Q water. The chemical composition of the two solutions was 1 mg L⁻¹ of each REE and 2840 mg L⁻¹ of Na₂SO₄. The ionic strength was adjusted to 0.25 M and 0.5 M in solution 1 and 2, respectively, by addition of NaCl. A total of 56 aliquots (28 plus duplicates) of 10 mL were taken from each solution and used in adsorption experiments with basaluminite and schwertmannite (solid/liquid ratio = 1 g L⁻¹) at room temperature (23 ± 2 °C) and atmospheric pressure for 6 h. pH in the aliquots was adjusted to the desired value (4.5, 5, 5.25, 5.5, 5.75, 6 and 6.5 for basaluminite and 4.5, 5, 5.5, 5.75, 6, 6.25 and 6.5 for schwertmannite) by adding different amounts of 0.04 M NH4OH solution. The pH was maintained constant during the reaction.

Two additional solutions that consisted of 5 mg L^{-1} Gd (ICP Gd standard, Merck) and 2840 mg L^{-1} (0.45 M) Na₂SO₄ were prepared with two different ionic strengths (0.25 M and 0.5 M) for the adsorption experiments with basaluminite and later characterization with Extended X-ray Absorption Fine Structure spectroscopy (EXAFS). Both solutions were in equilibrium with respect to basaluminite for 12 h and 36 h at pH 6.5.

After the adsorption experiments, the suspensions were centrifuged for 15 min at 4500 rpm (4150 RCF) and the supernatants were filtered through 0.22 μ m nylon membranes, acidulated (1% HNO₃) and stored at 4 °C for subsequent analysis. The remaining solid was freeze-dried for later characterization. The concentration of adsorbed REE by the mineral ([REE]_{mineral}) was calculated using the following expression

$$[REE]_{mineral} = [REE]_{in} - [REE]_{fin}$$
(1)

where [REE] is the concentration of each REE. The initial REE concentration $[REE]_{in}$ was measured from the stock solution, and the final concentration $[REE]_{fin}$ was measured from the final solutions.

The structure of the Gd aqueous species (i.e., $GdCl^{2+}$ and $GdSO_4^+$) were studied by High Energy X-ray Diffraction (HEXD) in the liquid solutions of the basaluminite experiment. To this end, two Gd solutions (5 mg L⁻¹) were prepared from Merck ICP standards, one with 26.3 g L⁻¹ (0.45 M) of NaCl and the other with 2840 mg L⁻¹ (0.02 M) Na₂SO₄. Both solutions were filtered and stored at room temperature without acidulation before HEXD analysis.

2.3 Analytical techniques

A Crison glass electrode calibrated with buffer solutions at pH 1.68, 4 and 7 was used to measure the pH in solution with an accuracy of 0.02. Chemical analysis was carried out with inductively coupled plasma optical emission spectroscopy (ICP-OES) for mayor elements (i.e., Fe and S) using a Perkin-Elmer® Optima 3200 RL apparatus. The detection limits were 0.1 mg L⁻¹ for S and 0.02 mg L⁻¹ for Fe. The REE concentrations (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in all solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS) with a Perkin-Elmer®SciexElan 6000 analyzer. The detection limits were 0.2 μ g L⁻¹ for REEs. The analytical error was < 5 % for both the ICP-OES and the ICP-MS measurements.

Gd-rich basaluminite samples and Gd aqueous samples were analysed by HEXD and Pair Distribution Function (PDF) analysis at the ID22 beamline of the European Synchrotron Radiation Facility (ESRF). Solid samples were loaded onto Kapton capillaries sealed with wax and irradiated under continuous rotation using a mono chromatic X-ray beam with an energy of 70 keV ($\lambda = 0.1771$ Å) in Debye-Scherrer geometry at room temperature and atmospheric pressure. Liquid Gd samples were loaded in glass capillary and measured without rotation with an X-ray beam energy of 61.86 keV ($\lambda = 0.2004$ Å). The 2D diffraction patters were collected using a PerkinElmer flat-panel detector and then corrected and integrated with the pyFAI software package (Kieffer and Karkoulis, 2013). PDFs were obtained by Fourier transformation of the reduced structure factors F(Q) using a $Q_{max} = 18.2$ Å⁻¹ with a background scattering corrected employing the PDFGetX3 software (Juhás et al., 2013).

Calculations of the metal complexes were optimized using the Gaussian16 package (Frisch et al., 1998). The B3LYP exchange-correlation functional (Becke, 1993; Stephens et al., 1994) was used together with the def2-TZVP ECP basis set (Weigend and Ahlrichs, 2005) for the metals Ln, where Ln = Lu and Gd, and the sulphur and chloride atoms. The oxygen and hydrogen atoms were treated with the LANL2DZ basis set (Hay and Wadt, 1985; Wadt and Hay, 1985a, b). The calculations were performed without symmetry and geometry constraints in both the gas phase and continuum solvation model. The continuum solvation model used to describe the aqueous environment was the conductor-like polarizable continuum model (CPCM) (Cossi et al., 2003). In all calculations, the water molecules coordinated to the lanthanide metal center were treated explicitly and the implicit continuum model was describing the solvation around the nine coordinated lanthanide complex. For the metal complexes of the Gd atom, which contains 7 lone pairs, the octuplet was used for the optimizations. The molecular models of $[Ln(H_2O)]^{3+}$ were used to conduct the calculations. These models were created starting from a tricapped trigonal prism. A microsolvation-continuum description of the sulfate ion, $SO_4(H_2O)_n$ with n = 1-10, was considered to obtain an accurate evaluation of the solvation-free energy of doubly charged anion SO₄²⁻ (Pliego and Riveros, 2020).

EXAFS data of Lu-enriched schwertmannite solid samples were collected at BM30 beamline (ESRF). The solid samples were arranged as 5 mm diameter pellets and covered with polyamide (Kapton)-type adhesive on sample holders. Standard of Lu₂O₃ was included for energy calibration in Lu levels. The experiment was carried out at 12 K using a helium cryostat to reduce the thermal vibration. Samples were measured in fluorescence mode using a 30-element Ge detector. The EXAFS data were scanned in a range from 9.1 to 9.88 keV for Lu L3-edge.

EXAFS data of the Gd-rich basaluminite samples were collected at the BM16 beamline (ESRF). The solid samples were arranged as 5 mm diameter pellets and covered with polyamide (Kapton)-type adhesive on sample holders. The standard of GdCl₃·nH₂O was included for energy calibration in Gd levels. The experiment was carried out at 12 K using a Helium cryostat to reduce the thermal vibration. The Gd High Energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) spectra were recorded with a Crystal Analyser Spectrometer (CAS) using a set of Si (333) crystals in a Rowland geometry. The EXAFS data were scanned in the range from 7.14 keV to 7.55 keV for Gd L₃ edge. The EXAFS data reduction, Fourier transformation and modeling were performed with the Athena and Artemis software from the IFFEFIT package (Ravel and Newville, 2005) . Samples analysed were named Low-I-12, Low-I-36, High-I-12 and High-36; where Low-I and High-I reference ionic strength values of 0.25 M and 0.5 M, respectively, and the numbers 12 and 36 reference the time (in hours) that the basaluminite were equilibrating with Gd solution.

EXAFS data reduction was performed using the Athena and Artemis software from IFFEFIT package (Ravel and Newville, 2005) by fit shell-by-shell, implementing different hypothetical structural coordination (e.g., monodentate or bidentate binuclear coordination). Backscattering phases and amplitude functions of the scattering paths were estimated using the Artemis software (Ravel and Newville, 2005). Several atomistic models of adsorbed REESO₄⁺ aqueous complexes were deduced by molecular dynamics simulations. The K weighted EXAFS spectra were fitted in the range 2.5 -12.45 Å⁻¹ for Lu schwertmannite and 2.6 - 10.2 Å⁻¹ for Gd basaluminite. The interatomic distance (R), Debye-Waller factor (σ^2) and Fermi energy levels (ΔE_0) were fitted using a least-squares refinement algorithm, whereas the coordination number (N) was fixed according to the CPCM simulations.

F-test calculations (Joyner et al., 1987; Michalowicz et al., 1999) were performed to select the most suitable model for each sample (Downward et al., 2007). When the models to compare have the same degrees of freedom ($v_0 = v_1$), the F value is calculated as:

$$F = \frac{\chi_1^2 / \nu_1}{\chi_0^2 / \nu_0} \tag{7}$$

where χ_i^2 and χ_i^2/v_i represent the chi square and reduced chi square of the fitting, respectively. When the compared models have different degrees of freedom ($v_0 \neq v_1$), F is calculated as

$$F = \frac{(\chi_1^2 - \chi_0^2)/(\nu_1 - \nu_0)}{\chi_0^2/\nu_0}$$
(8)

2.4 Field campaign: sampling and analytical techniques

The field campaign took place during the wet season under low tide environment (January 2023). Samples were taken at the Tinto River before the confluence with Odiel River (Fig. 2.1) in a two-day interval. Samples from points RTI-0, RTI-0', RTI-1, RTI-2 and RTI-3 were taken during the first day, and samples from RTI-A, RTI-B, RTI-C, RTI-D and RTI-E were obtained in the second day.

Colloid samples were taken from RTI-0 and RTI-1 (Fig. 2.2). A total volume of 25 L of estuarine water was extracted from each of these points at a depth of 50 cm below the boat. Later, this volume of water was filtered through cellulose membranes, which were previously kept at 305 K for 24 h to and then weighted. Then, the colloid-saturated filters were lyophilized, kept at 305 K for 24 h and weighted again to see the mass of solid that was filtered in 25 L of each sample.

Cores no longer than 25 cm were taken from the sampling points RTI-0 to RTI-3. Sediments from the uppermost, the middle (if possible) and bottom parts were extracted from the cores, freeze dried and stored for later analysis. Interstitial water of the cores was sampled for physicochemical parameters. Water samples from the sampling points were extracted, to measure major, minor, trace elements and physicochemical parameters.



Figure 2.1. Estuary of Ría de Huelva (the Tinto river sub-estuary): a) schematic map and (b) Google Earth image indicating sampling points and the phosphogypsum stack.

A representative part of the solid samples (sediments and colloids) was selected for digestion and sequential extractions. For the digestions, 0.1g of sample was weighted in a Teflon pump PFA. Then, 2.5 mL of HNO₃ 65 % were added and the pumps were put it in the oven at 363 K for 24 hours. Every 1 h or 2 h for 3 or 4 times, the pumps were taken out of the stove to let them cool and were opened to reduce the pressure. The next day, pumps were taken out of the stove and cooled. For each pump, a 100 mL flask and a 50 mL plastic centrifuge tubes were marked and prepared the same way. After that, the pumps were taken and the residue cleaned with Milli-Q water. Without passing 50 mL of total volume, the liquid was introduced in the centrifuge tube, and centrifuged at 3000 rpm for about 25 min. When finished, with a Pasteur pipette, the supernatant liquid was placed in the 100 mL volumetric flask. The solid residue remained in the tube. This residue was passed from the tube to the pump that was used in the beginning. For this, I put 2.5 mL HNO₃ 65%, shook carefully and poured it into the pump. After the residue was poured from the tube, it was mixed with 7.5 mL HF 40% in three dosages of 2.5 mL. Then, the pump was closed and put on the stove 24 h at 363 K. The next day, pumps were removed from the stove and placed in a hotplate at 523 K. Before allowing evaporation, they were unplugged and 2.5 ml of 60% HClO₄ was added. When the bead already formed (totally solid residue), it was recovered with 2.5 mL HNO₃ 65%, once the bead was dissolved, it was added in the 100 mL flask and filled it to the marked volume.



Figure 2.2. Photographs of an extracted core (in-situ supernatant and sediment) at sampling point RTI-E (a) and sediment cores at RTI-E (b), RTI-0 (c), RTI-2 (d) and RTI-3 (e) (see Fig. 1.2) and two lyophilized slices from the RTI-3 core (f). The RTI-E sediment core is 50 cm long, and the diameter of the cores is 8 cm. pH, conductivity and ORP of the in-situ supernatant water extracted from each core are displayed.

A modified procedure of sequential extraction proposed by Dold (2003) was performed with the colloidal and sediment samples (Caraballo et al., 2009b; Lecomte et al., 2017). The sequential extraction consisted of a 5-step selective dissolution that involved 1) the water-soluble phase, 2) the carbonate and exchangeable phases, 3) the poorly ordered metal oxyhydroxides, oxyhydroxysulfates and Mn-hydroxides, 4) the highly ordered metal oxyhydroxides, 5) the organic matter and 6) the residual phase.

Half a gram (0.5 g) of each sample was used for the overall procedure. After each step, the sample and the corresponding solution were centrifuged for 15 min at 4500 rpm. The supernatant and solid samples were then separated, and the liquid was filtered through 0.22 μ m nylon membranes and acidified with 1% HNO₃ solution. In each step, a blank sample was subjected to the same procedure and analysed accordingly.

Step 1 consisted of stirring the sample in Milli-Q water for 1 h; in step 2, a total of 20 mL of 1 M ammonium acetate was added to residue of the first step and the solution was shaken for 2 h; in step 3, 20 mL of 0.2 M ammonium oxalate that was acidified to pH with 0.2 M oxalic acid solution were added to the residue of step 2 and shaken for 1 h in total darkness; in step 4, 20 mL of a 0.2 M ammonium oxalate solution were mixed with the residue of step 3 and shaken at 80 °C for 2 h in a water bath, and in step 5, the residue of step 4 was mixed with 10 mL of 30% w/v (8 M) H₂O₂, allowing evaporation until the volume reduced to 3 mL. Subsequently, another 10 mL of 8.8 M H₂O₂ were added and heated at 85 °C for 1 h to reduce the volume to 3 mL. After this, 10 mL of 1 M ammonium acetate solution acidified with acetic acid to pH 4.5 were added and shaken for 16 h at room temperature; the final step consisted of a regular digestion using HF and HClO₄ and HNO₃ for the residual matter.

A bulk extraction of all the materials was performed to calculate a REE recovery percentage according to the procedure by Quispe et al. (2012) and Lecomte et al. (2017). The recovery percentage was between $85 \pm 19\%$ and $112 \pm 19\%$ with a mean of 99.8 %.

pH from collected estuary suspensions was measured with an accuracy of 0.02 pH units at room temperature with a Crison[®] glass electrode calibrated with buffer solutions at pH 2, 4, 7 and 9. Concentrations of the trace elements in the sequential extraction fractions were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) with a Perkin-Elmer Sciex ELAN 6000 apparatus and major elements by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo Fischer ICAP 6000 series (6500 Radial) spectrometer. The analytical uncertainties of the ICP measurements were estimated to be 7% for ICP-OES and 5% for ICP-MS. Solid and aqueous internal standards were intercalated between samples to check the analytical accuracy. The deviation from the stipulated values was always lower than 5%.

Concentrations of the major elements of the estuarine water samples were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2). Concentrations of the trace elements of these samples were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with a Thermo Scientific iCAP TQ ICP-MS without any prior dilution using Kinetic energy Discrimination - Argon Gas Dilution (KED-AGD mode). For trace element determinations, an internal solution containing Be, Sc, Ge, Rh and Ir was added on-line to the samples to correct signal drifts. Estuarine and seawater reference materials for trace metals (SLEW-3 and CASS-6) were also analyzed to check the analytical accuracy. Detection limits were between 0.02 mg L⁻¹ and 0.2 mg L⁻¹ for major elements and ranged between 0.23 μ g L⁻¹ (Zn) and 3.44 pg L⁻¹ (La) for trace elements.

2.5 Model description

A non-electrostatic model (NEM) is used to account for REE adsorption/desorption on schwertmannite that is caused by exchange between the $LnSO_4^+$ complex (Ln represents lanthanides, Y and Sc) and *n* protons in *n* surface sites ((XO)_n) expressed as

$$LnSO_4^+ + nXOH \rightleftharpoons (XO)_n LnSO_4^{1-n} + nH^+ \qquad K_{Ln} \tag{9}$$

The equilibrium constant K_{Ln} for this reaction is calculated as

$$K_{Ln} = \frac{\{(XO)_n LnSO_4^{1-n}\} \cdot a_{H^+}^n}{a_{LnSO_4^+} \cdot \{XOH\}^n}$$
(10)

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where a_{LnSO4+} and a_{H+} are the activities for REE aqueous complex and proton, respectively, $\{(XO)_n LnSO_4^{1-n}\}$ is the molar fraction of the sorbed species $(\{(XO)_n LnSO_4^{1-n}\} = [(XO)_n LnSO_4^{1-n}]/T_{XOH})$, and $\{XOH\}$ is the molar fraction of free surface sites $(\{XOH\} = [XOH]/T_{XOH})$.

The concentration of free surface sites [*XOH*] is calculated as the difference between the total site concentration (T_{XOH}) and the sum of each occupied site:

$$[XOH] = T_{XOH} - \sum n[(XO)_n LnSO_4^{1-n}]$$
⁽¹¹⁾

Appling logarithms in Eq. (10) and rearranging, the following expression is obtained:

$$\log \frac{[(XO)_n LnSO_4^{1-n}]}{a_{LnSO_4^+}} - n \log[XOH] + (n-1)\log T_{XOH} = npH + \log K_{Ln}$$
(12)

in which the slope of the regression line is the number of occupied sites (n) in the reaction. Values of n close to 1 or 2 in desorption experiment indicates the cleavage of complexes in monodentate or bidentate coordination, respectively. Eq. (12) is similar to expressions for REE adsorption on basaluminite (Lozano et al., 2019a), in which the mass action expression for bidentate adsorption was described with greater detail (Wang 380 and Giammar, 2013).

2.6 Speciation of REEs and mixing/adsorption models

Aqueous REE speciation was calculated using PHREEQC (Parkhurst and Appelo, 1999) and the Donee Thermoddem_V1.10 database (Blanc et al., 2012). Equilibrium constants at zero ionic strength and 298 K for aqueous speciation of lanthanides, Y and Sc (Lozano et al., 2019a) were added to the database, as well as the solubility products for Sc(OH)²⁺, Sc(OH)² and Sc(OH)₃ (Wood and Samson, 2006), LnF^{2+} and LnF_2^+ (Luo and Millero, 2004) and $LnCl^{2+}$ (Luo and Byrne, 2001), $LnSO_4^+$ (Schijf and Byrne, 2004), $Ln(OH)^{2+}$ (Klungness and Byrne, 2000), $Ln(OH)^2_2$, $Ln(OH)^0_3$ (Lee and Byrne, 1992), $Ln(CO)^+_3$, $LnHCO^{2+}_3$, $Ln(CO_3)^-_2$ (Luo and Byrne, 2004) and $Ln(NO)^{2+}_3$ (Millero, 1992). Solubility constants for solid REE phases

(Ln(OH)₃ and Ln(OH)₃(am)) were included from the LNLL database (Johnson et al., 2000; Spahiu and Bruno, 1995). Equilibrium constants for aqueous inorganic speciation are listed in Table A1. A water-mixing model was formulated using two end-member waters: the most AMD-influenced water (RTI-A sampling point with pH = 2.98) and the most seawater-influenced one (RTI-3 sampling point with a pH = 7.86). The chloride ion (Cl⁻) was selected to balance solution charges. The mixing model used different percentages of the RTI-A and RTI-3 solutions to define intermediate solutions in order to emulate the estuarine mixing process without involving mineral precipitation or elemental sorption. Saturation indexes (*SI*) were calculated using the analysis data from the supernatant water of the cores. When SI > 0 the solid phase is saturated and therefore tends to precipitate, when SI = 0 the solid phase is in equilibrium with the water solution, and when SI < 0 the solid phase is undersaturated and therefore is dissolving.

After the mixing calculation, a REE adsorption model was implemented by taking into consideration the reactive surfaces of the main Al- and Fe-precipitates in AMD neutralization (i.e., schwertmannite and basaluminite). For schwertmannite, 4.75 sites nm^{-2} and a specific surface area of 200 $m^2 g^{-1}$ were selected (Regenspurg et al., 2004; Antelo et al., 2012; Lozano et al., 2020a; Schoepfer and Burton, 2021). For basaluminite, the specific surface area was 68 $m^2 g^{-1}$ and the number of surface sites was 4.6 sites nm^{-2} (Carrero et al., 2017a; Lozano et al., 2019a). The solid:liquid ratio was allowed to vary to check the conditions in which the model reproduced the field results. The REE adsorption data was taken from Lozano et al. (2019a, 2020a) and from the results of this thesis. The adsorption reactions (monodentate and bidentate surface complexes with schwertmannite and monodentate surface complexes with basaluminite) are listed in Section 3.6.

CHAPTER 3

EXPERIMENTAL AND FIELD RESULTS

3.1 Schwertmannite and basaluminite characterization

A site density of 4.75 sites nm^{-2} was used to calculate the concentration of schwertmannite surface sites (Lozano et al., 2020a), considering the number of single coordinated sites on each face of the unit cell (Fernandez-Martinez et al., 2010). The measured specific surface area for the synthetic schwertmannite (157 m² g⁻¹) was of the same order of magnitude as previously reported values (175-200 m² g⁻¹) (Regenspurg et al., 2004; Antelo et al., 2012; Lozano et al., 2020a). Thus, the final concentration of surface sites was 1240 µmol g⁻¹.

Likewise, a side density of 4.60 site nm⁻² was extracted from basaluminite unit cell (Carrero et al., 2017a; Lozano et al., 2019a). Together, this value and the specific surface area measured for the synthetic basaluminite (79 m² g⁻¹) were used to calculate the concentration of surface sites (600 μ mol g⁻¹). XRD of the samples are displayed in Fig. 3.1. The absence of impurities (e.g. gypsum and Na₂SO₄) confirms that no solid contamination affects the experiments.



Figure 3.1. XRD of synthetic basaluminite (orange) and schwertmannite (yellow) used in the experiments.

3.2 REE desorption experiments

REE concentrations measured in the pre- and post-adsorption and desorption solutions corroborated the REEs retention onto schwertmannite and the subsequent release to the solution (Table 3.1). The kinetic desorption experiments showed a sharp increase in the desorbed fraction of most of the REEs up to 6 h. Thereafter, a gradual increase occurred until the system reached equilibrium after 24 h (Fig. 3.2). As regards Sc, a slight desorption commenced after 12 h, reaching steady state at about 24 h.

Table 3.1. REE concentrations (mg L^{-1}) in stock solution (initial), after adsorption and desorption experiments (2840 mg· L^{-1} SO₄ solutions; 1 g L^{-1} ratio) at each pH.

solutions	initial	adsorption					desor	ption				
лШ		6 50	4.50 ±	$5.00 \pm$	$5.25 \pm$	$5.50 \pm$	$5.75 \pm$	6.00 ±	$6.25 \pm$	6.50 ±	6.75 ±	$7.00 \pm$
pn	-	0.30	0.07	0.02	0.04	0.03	0.08	0.02	0.11	0.04	0.02	0.06
Sc	1.040	0.000	0.027	0.010	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y	1.031	0.000	0.767	0.722	0.597	0.451	0.268	0.184	0.088	0.040	0.012	0.005
La	1.002	0.014	0.769	0.755	0.666	0.555	0.427	0.320	0.170	0.089	0.030	0.012
Ce	1.031	0.003	0.699	0.655	0.538	0.404	0.249	0.164	0.084	0.039	0.013	0.005
Pr	1.007	0.002	0.748	0.676	0.522	0.386	0.221	0.141	0.069	0.032	0.010	0.004
Nd	0.972	0.002	0.678	0.596	0.460	0.334	0.184	0.125	0.062	0.027	0.009	0.003
Sm	0.969	0.000	0.699	0.597	0.432	0.295	0.150	0.099	0.046	0.020	0.006	0.002
Eu	0.973	0.000	0.682	0.596	0.424	0.273	0.139	0.091	0.042	0.018	0.005	0.002
Gd	0.942	0.000	0.661	0.596	0.449	0.319	0.172	0.114	0.054	0.024	0.007	0.003
Tb	1.082	0.000	0.666	0.585	0.420	0.286	0.141	0.085	0.038	0.016	0.005	0.002
Dy	1.015	0.000	0.722	0.611	0.401	0.267	0.129	0.080	0.036	0.015	0.004	0.002
Но	1.122	0.000	0.716	0.621	0.435	0.294	0.145	0.087	0.038	0.016	0.005	0.002
Er	0.989	0.000	0.731	0.620	0.439	0.270	0.128	0.081	0.035	0.015	0.004	0.002
Tm	1.118	0.000	0.698	0.585	0.381	0.247	0.110	0.065	0.028	0.011	0.003	0.001
Yb	0.996	0.000	0.680	0.544	0.320	0.196	0.085	0.053	0.022	0.009	0.003	0.001
Lu	1.090	0.000	0.670	0.537	0.348	0.220	0.090	0.057	0.023	0.009	0.003	0.001

The digestion of the pure schwertmannite shown a chemical composition close to ideal values, with 7.91 mol_{Fe} mol_{Sch}⁻¹ (ideal stoichiometry 8 mol_{Fe}·mol_{Sch}⁻¹). However, REEand Lu-rich schwertmannite displayed a lower amount of Fe according to the ideal stoichiometry, 7.6 and 7.68 mol_{Fe} mol_{Sch}⁻¹, respectively. The REE concentration after adsorption experiments ranged between 0.0052 and 0.0064 mol·mol_{Sch}⁻¹ for lanthanides, 0.022 mol mol_{Sch}^{-1} for Sc and 0.0105 mol $\cdot mol_{Sch}^{-1}$ for Y in REE-rich schwertmannite, whereas Lu-rich schwertmannite contained 0.034 mol_{Lu} mol_{Sch}^{-1} . The results of the stoichiometry of the digestions are included in Table A2.

REE desorption experiments are displayed in Fig. 3.3. Desorption reactions were observed at pH \leq 6.75, 6.5 and 6.25 for LREE, MREE and HREE, respectively. The desorbed fraction gradually increased with pH decreasing until reach values between 86% and 73% from La to Lu at pH \approx 4.5. Different behaviour was observed in Sc, where desorption reaction started at pH below 5 and the desorbed fraction increased to 45% at pH 4.5.



Figure 3.2. Desorption kinetics in REE-rich schwertmannite (2840 mg L^{-1} SO₄ and pH = 4.85).



Figure 3.3. Desorbed fraction for REEs in solution with 2840 mg L^{-1} of sulfate. Error bars range between 1% and 7%.

3.3 REE adsorption experiments at different ionic strengths

Lanthanum (La), gadolinium (Gd) and lutetium (Lu) were selected as representative elements for light REEs (LREEs), middle REEs (MREEs) and high REEs (HREEs), respectively. Yttrium (Y) and scandium (Sc) were also analyzed owing to their divergent behavior with respect to the lanthanide series. The chemical composition of the initial and final solutions used in the adsorption experiments are shown in Tables 3.2a-d. As shown in Fig. 3.4 the solutions were undersaturated with respect to REE-hydroxides, and basaluminite and schwertmannite were stable at the studied pH range except at pH 4.5. Precipitation of REEs and dissolution of the solid phases were therefore discarded in this study.

Table 3.2a. REE concentrations (mg L^{-1}) in the initial stock solution (2840 ppm SO₄ in solutions) and after adsorption experiments for basaluminite (1 g L^{-1} solid/liquid ratio) at different pH and ionic strength of 0.25 M.

<i>I</i> = 0.25 M	Initial (mg L ⁻¹)			After a	dsorption (m	g L ⁻¹)		
pН		4.5 ± 0.15	5 ± 0.06	5.25 ± 0.03	5.5 ± 0.07	5.75 ± 0.03	6.00 ± 0.05	6.5 ± 0.07
Sc	1116.32	278.02	97.37	21.77	8.80	2.51	1.61	1.11
Y	1026.01	978.89	938.28	904.86	838.50	783.76	705.53	421.43
La	1087.64	1056.74	1046.34	1052.14	1021.49	1029.93	1011.90	905.11
Ce	1004.98	977.76	945.78	952.48	855.10	896.70	869.91	701.64
Pr	1062.69	1010.10	950.50	960.17	922.87	892.36	852.15	641.84
Nd	1020.79	985.45	989.27	955.74	907.50	886.19	842.61	638.49
Sm	1047.70	1038.37	987.67	976.64	894.21	809.92	759.78	466.31
Eu	1031.14	1000.32	963.91	906.46	837.05	796.05	720.05	422.77
Gd	956.72	927.85	890.91	887.86	831.65	747.01	691.13	434.52
Тb	1016.31	975.01	915.59	825.17	749.42	675.95	602.48	325.62
Dy	1047.66	1020.53	946.61	895.31	801.78	694.99	618.82	300.72
Но	1172.50	1117.13	1105.99	913.89	813.69	709.55	613.06	294.76
Er	924.59	880.32	802.72	767.39	672.53	559.44	489.53	222.07
Tm	1066.95	1040.19	985.10	794.10	655.71	526.19	419.96	168.30
Yb	977.58	920.30	847.89	703.56	591.53	422.12	344.57	114.97
Lu	913.21	817.71	740.99	625.52	507.54	367.32	290.02	101.25

Table 3.2b. REE concentrations (mg L^{-1}) in the initial stock solution (2840 ppm SO₄ in solutions) and after adsorption experiments for basaluminite (1 g L^{-1} solid-liquid ratio) at different pH and ionic strength 0.5 M.

$I = 0.5 \mathrm{M}$	Initial (mg	L ⁻¹)	_	After adsorption (mg L ⁻¹)							
pН		$\textbf{4.5} \pm \textbf{0.09}$	5 ± 0.02	5.25 ± 0.06	5.5 ± 0.08	5.75 ± 0.03	6.00 ± 0.02	6.5 ± 0.06			
Sc	1123.95	193.65	52.92	28.70	0.00	0.00	0.00	0.00			
Y	1016.03	948.63	914.93	867.47	825.91	796.98	647.69	327.10			
La	1066.40	1038.22	1005.57	975.56	974.78	977.08	930.69	812.77			
Ce	978.01	932.38	890.46	846.08	860.52	880.63	815.24	616.53			
Pr	996.49	949.23	925.71	897.75	900.34	880.07	794.49	549.01			
Nd	1004.29	971.38	927.08	906.27	868.12	848.84	771.26	503.26			
Sm	1038.94	956.86	937.53	885.50	861.47	847.11	688.82	344.99			
Eu	1008.48	965.73	895.31	875.47	817.41	782.82	653.58	310.06			
Gd	939.39	896.80	861.79	811.42	793.80	758.54	628.37	318.30			
Tb	994.05	866.82	807.92	763.14	711.80	675.31	529.00	229.79			
Dy	1035.16	969.31	904.84	851.04	798.02	734.59	541.92	204.53			
Но	1133.87	983.82	911.51	852.70	787.79	726.24	542.91	207.56			
Er	902.97	833.81	792.10	725.00	674.42	615.15	424.76	148.09			
Tm	1057.97	908.23	816.62	747.64	638.75	551.98	375.12	109.18			
Yb	945.33	872.96	771.48	683.44	595.38	481.71	286.01	68.77			
Lu	832.50	786.04	687.20	616.90	506.13	435.56	252.95	63.00			

Table 3.2c. REE concentrations (mg L^{-1}) in the initial stock solution (2840 ppm SO₄ in solutions) and after adsorption experiments for schwertmannite (1 g L^{-1} solid/liquid ratio) at different pH and ionic strength of 0.25 M.

<i>I</i> = 0.25 M	Initial (mg	L-1)		After	r adsorption	(mg L ⁻¹)		
pН		4.5 ± 0.01	5 ± 0.01	5.5 ± 0.03	$\textbf{5.75} \pm \textbf{0.04}$	6.00 ± 0.02	6.25 ± 0.05	6.50 ± 0.06
Sc	922.61	56.06	10.72	0	0	0	0	0
Y	944.26	893.32	826.81	692.21	415.93	154.48	80.29	50.74
La	1108.21	1046.36	994.59	912.96	678.95	312.15	189.70	126.91
Ce	1037.68	962.14	846.25	722.02	415.97	161.78	88.10	56.22
Pr	1062.74	963.19	830.01	663.57	372.16	126.15	68.57	44.99
Nd	961.09	884.11	741.80	601.18	311.37	106.63	56.17	36.31
Sm	965.57	852.95	702.02	508.26	251.52	76.14	39.97	25.82
Eu	970.20	877.73	714.28	528.05	249.91	79.06	39.47	24.90
Gd	886.61	800.02	680.92	522.09	282.40	88.66	47.14	30.22
Tb	925.98	831.61	691.50	507.48	238.54	72.64	37.16	22.85
Dy	1065.13	969.15	770.94	568.60	275.34	79.94	39.75	25.47
Но	1121.74	1035.70	866.38	637.77	309.97	87.80	45.57	28.94
Er	947.96	860.00	697.93	495.06	241.63	70.67	34.97	21.72
Tm	945.06	830.14	665.02	460.75	206.69	55.79	27.75	17.43
Yb	983.78	850.05	667.77	434.46	181.36	47.11	23.71	14.51
Lu	953.23	857.72	662.34	452.21	200.14	52.80	26.18	16.15

Table 3.2d. REE concentrations (mg L^{-1}) in the initial stock solution (2840 ppm SO₄ in solutions) and after adsorption experiments for schwertmannite (1 g L^{-1} solid/liquid ratio) at different pH and ionic strength of 0.5 M.

$I = 0.5 \mathrm{M}$	Initial (mg L ⁻¹)		After adsorption (mg L ⁻¹)									
pН		$\textbf{4.5} \pm \textbf{0.11}$	5.00 ± 0.03	5.50 ± 0.03	5.75 ± 0.05	6.00 ± 0.01	6.25 ± 0.03	6.5 ± 0.03				
Sc	1061.14	54.98	0	0	0	0	0	0				
Y	967.74	952.87	863.75	642.41	397.99	267.50	117.79	47.05				
La	1081.57	1099.46	1004.62	837.04	622.92	477.44	261.36	127.55				
Ce	1027.42	933.73	876.30	640.47	377.29	269.54	116.49	49.75				
Pr	1035.62	986.84	850.84	581.55	329.54	211.61	92.58	40.24				
Nd	955.86	901.04	765.15	512.85	279.42	189.61	79.22	32.62				
Sm	964.62	865.34	721.77	436.27	208.92	129.59	53.67	21.59				
Eu	946.04	893.51	725.08	436.24	209.93	134.37	53.18	21.17				
Gd	864.89	807.80	688.39	458.80	240.01	153.73	63.62	26.68				
Tb	884.06	824.26	694.07	436.76	204.44	125.80	51.16	15.15				
Dy	1024.20	985.00	807.32	483.73	225.81	144.98	54.84	21.25				
Но	1041.91	1036.45	859.26	540.41	265.08	161.14	64.64	24.12				
Er	905.56	842.12	707.84	442.41	203.85	130.00	49.30	15.15				
Tm	874.24	833.08	684.44	396.69	177.86	106.38	39.94	14.14				
Yb	927.89	853.66	676.03	380.32	159.02	93.11	32.75	13.13				
Lu	939.87	855.04	707.44	401.71	171.61	104.23	38.37	12.12				



Figure 3.4. Saturation indexes of (a) $REE(OH)_3$ and $Sc(OH)_3$ and (b) schwertmannite and basaluminite as a function of pH. The experimental pH range is within the vertical red lines.

With schwertmannite (Fig. 3.5), the adsorbed fraction is enhanced by the increase in pH. LREEs are less adsorbed ($\approx 85\%$ of adsorbed fraction at pH 6.5) than HREE ($\approx 98\%$ at pH 6.5), and Y and MREEs show an intermediate behavior ($\approx 90\%$ at pH 6.5). By contrast, Sc adsorbs nearly completely at lower pH (92% at pH 4.5). Similar adsorption capacity is observed at different ionic strengths (solution 1 in Fig. 3.5a and solution 2 in Fig. 3.5b), although the maximum adsorption capacity is reached at higher pH as ionic strength increases.

With basaluminite (Fig. 3.6), a lower adsorption capacity for LREEs and MREEs and a similar one for HREEs are distinguished when compared to schwertmannite. In addition, similar trends are observed as LREE are less adsorbed than HREE ($\approx 23\%$ versus $\approx 88\%$ at pH 6.5), MREE and Y show an intermediate behavior (67% at pH 6.5) and Sc is almost completely adsorbed above pH 5 ($\approx 90\%$). As with schwertmannite, no significant differences with ionic strength are observed.



Figure 3.5. REE adsorption fraction onto schwertmannite with a solution of 2840 mg L⁻¹ of sulfate and 0.25 M (a) and 0.5 M (b) of ionic strength. The vertical and horizontal error bars are between 1% and 7%, and \pm 0.1 pH units, respectively.



Figure 3.6. REE adsorption fraction onto basaluminite in a solution with 2840 mg L^{-1} of sulfate and 0.25 M (a) and 0.5 M (b) of ionic strength. The vertical and horizontal error bars are between 1% and 7%, and \pm 0.1 pH units, respectively.

3.4 Geometry of Lu-aqueous and Lu-surface complexes

Figure 3.7 shows the PDF analysis of the LuSO₄⁺ aqueous solution. Milli-Q water was used to extract the background of the PDF, yielding thus background-subtracted PDF. The PDF showed peaks at 1.45 Å and 2.33 Å, correlated to S-O interatomic distance inside the sulfate tetrahedra and Lu-O interatomic distance of the first coordination shell, respectively. Additionally, a peak at \approx 3.46 Å was associated to Lu-S distance. Density functional theory (DFT) calculations yielded a Lu-O coordination number (*N*) of 8 and a single share oxygen with the sulfate tetrahedron. A similar *N* in Lu-O path was also obtained for Lu in Lu³⁺- and LuCl²⁺-solutions (Kowall et al., 1995; Yaita et al., 1999; Allen et al., 2000) and Y in YSO₄⁺ solutions (Lozano et al., 2019b). DFT calculations suggest Lu-O distances are in the range between 2.30 and 2.33 Å, except for two oxygens located at \approx 2.20 Å. The observed Lu-O path distance was similar than values reported for free Lu³⁺ ion and its coordinated water molecules (i.e., 2.31(2) Å) (Persson et al., 2008; Finck et al., 2019) or Y-O interatomic distances in YSO₄⁺ specie (Lozano et al., 2019b).



Figure 3.7. PDF analysis of the $LuSO_4^+$ *aqueous solution and its molecule geometry calculated by CPCM. PDF is normalized with the* Lu-O *peak.*

3.5 Geometry of Gd-aqueous and Gd-surface complexes

Figure 3.8 displays the structural models for Gd-sulfates and Gd-chlorides and the PDFs, respectively. In regard to the REE-sulfate aqueous complex, the calculated coordination state of Gd–O is 9, sharing 8 and 1 oxygen atoms with water molecules and tetrahedral sulfate, respectively. For the REE-chloride aqueous complex the coordination state for Gd–O is 8. It is shown that Gd tends to form contact ion pairs with both Cl⁻ and SO₄²⁻. The interatomic distances of Gd–Cl in GdCl²⁺ and Gd–S in GdSO₄⁺ are 2.79 Å and 3.60 Å, respectively. The Gd–O interatomic distances in GdCl²⁺ vary from 2.458 to 2.494 Å, whereas in GdSO₄⁺ vary from 2.375 to 2.509 Å with a distal path of 3.285 Å.



Figure 3.8. PDF analysis of the $GdSO_4^+$ (blue) and $GdCl^{2+}$ (yellow) aqueous solutions and the molecule geometry of sulfate (a) and chloride (b) calculated by CPCM. PDF is normalized with the Gd-O peak.

3.6 Geochemistry of major and trace elements in the Ría de Huelva estuary

3.6.1 Distribution of major and trace elements in the supernatant water of

the cores

Table 3.3 lists the concentrations of relevant major and trace elements analysed at the different sampling points. The concentrations of REEs and Yttrium decrease towards the more seawater-influenced samples owing to an increase in pH, which triggers sorption and precipitation reactions, and a dilution process. This depletion is clearly observed in the NASC normalized REE patterns shown in Fig. 3.9, where the concentrations differ by several orders of magnitude from the AMD inlet to the less AMD-influenced samples. Concentrations of REEs obtained from our study and from previous experimental data provided by Lecomte et al. (2017) are of the same order of magnitude at their respective pH. The (La/Yb)_{NASC} ratios (Table 3.3) present values that range between 0.45 and 0.85, with the lowest value at the most acidic pH. An abnormal value (3.93) is obtained near the phosphogypsum stack (RTI-2 sample). Except for the

last point, there is a predominance of HREEs over LREEs in the estuarine water (Fig. 3). The (La/Gd)_{NASC} ratio ranges between 0.26 and 0.82 and shows the same increasing tendency with increasing pH, without any anomaly at RTI-2. This means that at the RTI-2 sampling point, phosphogypsum leaches more LREEs and MREEs than HREEs. This coincides with the heterogeneous REE distribution described for byproducts of this type of material (Borrego et al., 2004). The Eu/Eu* ratio (i.e., Eu_{NASC}/(Sm_{NASC} + Gd_{NASC})^{0.5}) shows a very slight negative anomaly (values from 0.78 to 0.95) at all sampling points except the RTI-2 sampling point, which presents a very slight positive anomaly (1.08). By contrast, the Ce/Ce* ratio (i.e., Ce_N /(La_N + Pr_N)^{0.5}) shows slightly positive anomalies (values between 1.01 and 1.12) in all samples except for RTI-2, which displays a very slight negative anomaly (0.79). Although RTI-0 is also close to the phosphogypsum stack, this pattern is only observed at RTI-2 sample.



Figure 3.9. NASC-normalized REE patterns of the water samples collected in the estuary.

	Concentration (mg·L ⁻¹)																					
Samp	ple p I	I	Na		Ca		K		Mg	g		S	B		Al	Р	Mn	Fe	Cu	Zn	L 5	Sr
RTI	-A 3.0	2 36	67.456	2	214.18	1 1	45.51	7	498.4	-40	651	.239	1.46	8 45	5.751	0.197	4.851	65.06	6 9.554	11.8	69 2.	883
RTI	- B 2.9	8 35	40.620	2	208.66	5 1	45.13	2	481.6	666	648	648.177 1.40		3 46	5.023	0.187	4.843	67.72	9 9.684	12.03	36 2.	672
RTI	-C 3.3	3 54	42.745	2	291.59	1 2	249.80	6	747.715		735	5.690	2.11	6 27	.797	0.080	3.192	27.04	6 6.135	7.52	4 4.	422
RTI	- D 3.3	5 70	44.763	3	34.38	1 3	322.06	8	884.752		786	5.447	2.51	2 22	2.712	0.081	2.634	12.61	3 4.998	6.03	1 5.	214
RTI	- E 3.6	9 72	33.778	3	38.90	3 3	321.16	2	906.732		786	5.977	2.60	4 15	5.965	0.082	2.104	6.575	3.941	5.00	9 5.	644
RTI	-0 5.2	2 72	86.768	3	357.17	1 3	352.85	1	968.6	31	806	5.171	2.72	9 10	0.415	0.090	1.766	3.094	3.073	4.17	1 5.	892
RTI	-1 5.4	4 83	21.507	3	376.52	5 3	898.30	0 1	1048.8	827	835	5.211	2.88	7 2.	.268	0.100	1.094	0.526	5 1.455	2.68	6 6.	472
RTI	-2 6.4	8 96	09.140		15.34	9 4	61.08	4	1186.8	886	908	3.034	3.37	$\begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}$.065	0.833	0.634	0.028	0.346	1.22	3 7.	225
<u></u> K11	-3 /.6	6 107	59.513	3 4	58.86	3 3	50.93	9.	1367.0	504	100	2.735	3.82	1 0.	.081	0.522	0.164	0.005	0.024	0.10	8.	434
Concentration (µg·L ⁻¹)																						
Sample	pH	V	Cı	r 🗍	Co		Ni	A	s	Rh)	Мо		Cd		Sn	Sb	Cs	Ba		TI	Pb
RTI-A	3.02	0.177	9.59	96 3	37.490	5 69	.159	14.1	48	37.3	68	0.435	5	44.33	1	0.051	0.102	0.29	9 13.09	92 3.	307	50.304
RTI-B	2.98	0.257	9.74	48 3	39.40	1 69	.560	13.7	30	34.4	55	<dl< th=""><th></th><th colspan="2">44.091</th><th>0.075</th><th colspan="2">0.138 0.25</th><th>12.25</th><th>53 3.</th><th>283</th><th>49.618</th></dl<>		44.091		0.075	0.138 0.25		12.25	53 3.	283	49.618
RTI-C	3.33	0.258	5.06	61 2	16.18	5 46	.242	4.5	4.501 57.1		26	<dl< th=""><th></th><th colspan="2">30.281</th><th>0.069</th><th>0.226</th><th>0.28</th><th>6 17.91</th><th>18 2.</th><th>300</th><th>42.470</th></dl<>		30.281		0.069	0.226	0.28	6 17.91	18 2.	300	42.470
RTI-D	3.35	<dl< th=""><th>3.32</th><th>21 1</th><th>77.160</th><th>5 39</th><th>.279</th><th>0.8</th><th>09</th><th>70.8</th><th>76</th><th><dl< th=""><th></th><th>24.76</th><th>1</th><th>0.266</th><th>0.2565</th><th>0.28</th><th>18.1</th><th>47 1.</th><th>968</th><th>39.050</th></dl<></th></dl<>	3.32	21 1	77.160	5 39	.279	0.8	09	70.8	76	<dl< th=""><th></th><th>24.76</th><th>1</th><th>0.266</th><th>0.2565</th><th>0.28</th><th>18.1</th><th>47 1.</th><th>968</th><th>39.050</th></dl<>		24.76	1	0.266	0.2565	0.28	18.1	47 1.	968	39.050
RTI-E	3.69	0.067	1.92	25 1	40.976	5 33	.113	1.6	72	70.0	76	<dl< th=""><th></th><th>21.71</th><th>7</th><th>0.057</th><th>0.348</th><th>0.25</th><th>1 18.37</th><th>76 1.</th><th>614</th><th>30.085</th></dl<>		21.71	7	0.057	0.348	0.25	1 18.37	76 1.	614	30.085
RTI-0	5.2	0.152	2 0.71	19 1	15.525	5 27	.756	3.7	22	75.1	29 84	<dl< th=""><th></th><th>18.81</th><th>7</th><th>0.170</th><th>0.396</th><th>0.25</th><th>4 19.26</th><th>55 1.</th><th>283</th><th>20.613</th></dl<>		18.81	7	0.170	0.396	0.25	4 19.26	55 1.	283	20.613
K11-1 DTI 2	5.4 6.40	0.080	0.23	55 i	/U.368	12	.604	1.2	9/	85.4	84 65	42.01	5	14.30	0	0.012	0.514	0.21	19.44	+0 0.	990 620	8.498
RTI-2 RTI-3	0.40	2.574		31 .	7 521	3	870	5.4	96	95.1	05 585	43.91	1	2 3 50	9	<dl 0.053</dl 	0.033	0.20	14.91	13 0.	174	0.005
	7.00	2.301	0.1	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	7.321	5.	.070	5.7	70	115	005	12.05	1	2.55	/	0.055	0.554	0.20	10.90	51 0.	1/4	0.217
sample	pН	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	(La/Yb)	NASC	(La/Gd) _N	ASC E	u/Eu*	Ce/Ce*
RTI-A	3.02	35.70	12.79	38.02	5.14	23.64	6.44	1.40	8.10	1.23	6.85	1.30	3.61	0.46	2.83	0.43	0.45	5	0.26		0.87	1.10
RTI-B	2.98	35.89	13.23	37.88	5.16	24.15	6.60	1.48	8.14	1.24	6.69	1.28	3.42	0.45	2.73	0.42	0.48	3	0.27		0.91	1.07
RTI-C	3.33	23.95	8.88	24.59	3.34	15.28	4.30	0.93	5.11	0.78	4.21	0.82	2.23	0.30	1.75	0.27	0.51	L	0.29		0.89	1.05
RTI-D	3.35	18.19	7.22	19.97	2.57	12.39	3.34	0.66	3.99	0.59	3.36	0.64	1.71	0.24	1.36	0.20	0.53	3	0.30		0.81	1.08
RTI-E	3.69	14.98	5.52	15.32	2.05	9.18	2.52	0.60	3.15	0.46	2.51	0.48	1.33	0.18	1.03	0.14	0.54	Ļ	0.29		0.95	1.06
RTI-0	5.2	10.54	4.08	10.67	1.32	5.77	1.45	0.30	2.03	0.29	1.58	0.33	0.89	0.12	0.66	0.10	0.62	2	0.34		0.78	1.07
RTI-1	5.4	4.40	1.91	4.38	0.54	2.56	0.65	0.14	0.78	0.11	0.57	0.12	0.35	0.03	0.23	0.05	0.85	5	0.41		0.89	1.01
RTI-2	6.48	0.42	0.33	0.42	0.05	0.14	0.04	0.01	0.07	<dl< th=""><th>0.03</th><th>0.005</th><th>0.01</th><th><dl< th=""><th>0.008</th><th><dl< th=""><th>3.93</th><th>3</th><th>0.82</th><th></th><th>1.08</th><th>0.79</th></dl<></th></dl<></th></dl<>	0.03	0.005	0.01	<dl< th=""><th>0.008</th><th><dl< th=""><th>3.93</th><th>3</th><th>0.82</th><th></th><th>1.08</th><th>0.79</th></dl<></th></dl<>	0.008	<dl< th=""><th>3.93</th><th>3</th><th>0.82</th><th></th><th>1.08</th><th>0.79</th></dl<>	3.93	3	0.82		1.08	0.79
RTI-3	7.66	0.14	0.01	0.03	<dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<></th></dl<>	<dl< th=""><th>-</th><th></th><th>-</th><th></th><th>-</th><th>-</th></dl<>	-		-		-	-

3.6.2 Distribution of major and trace elements in the surface sediment the cores

The element distribution in the sediment was studied using the results from the sequential extractions. Note that water soluble phases contained in the sediments released most of the elements from the salts formed during sample lyophilization. These elements, therefore, are not part of the sediment, but were originally dissolved in water. Hence, the distribution of the elements can be discussed by only considering the other phases involved.

In the estuarine sediments, Ni and Mn are mainly present in the residual phase, with smaller amounts related to the highly and poorly ordered metal oxyhydroxides phases (Fig. 3.10). Cd is mainly released by carbonate and exchange phases. The presence of Cd in the carbonates depends on pH such that the highest the pH the highest the Cd concentration in the sediment.

Zn, Cu and Co are the most reactive divalent elements with a high concentration in the exchange and both metal oxyhydroxide phases. Their concentrations in the sediment are distributed between the carbonate and exchange phase, and the poorly and highly ordered metal oxyhydroxide phases. Trivalent Tl is closely related to highly ordered metal oxyhydroxide phases and its concentration in the sediments lowers with the influence of seawater (Fig. 3.10).

Fe concentration in the sediment diminishes as pH increases, similarly to aqueous Fe in the estuarine waters (from 90% wt to 30 % wt in AMD to seawater, respectively). At pH < 6.5, Fe is found in highly ordered metal oxyhydroxide phases (jarosite and goethite) whereas at pH \geq 6.5 is present in amorphous metal oxyhydroxide phases (Fig. 3.11). Cr is mainly present in the residual phase though an important amount is related to the poorly ordered metal oxyhydroxides. Al is mostly released by the poorly ordered metal oxyhydroxide phases but is also present in the residual phase and highly ordered metal oxyhydroxide phases.



Figure 3.10. Concentrations of Ni, Mn, Tl, Cd, Zn, Cu and Co as a function of pH (low pH is associated with AMD-impacted water and high pH is influenced by seawater). Line colours: black = total concentration, blue = residual phase, turquoise = highly ordered Fe-oxide phase, orange = poorly ordered Fe-oxide phase, purple = carbonate and exchange phase and green = organic phase.

Pb is concentrated in the highly ordered metal oxyhydroxide phases (Fig. 3.12). Its concentration remains constant in the pH range of 3.5-6.5 and decreases at pH of 7.5 (RTI-3 sampling point). As is mainly found in the highly ordered metal oxyhydroxide phase at pH < 6. In contrast, at pH > 6 the As content is higher in the poorly ordered metal oxyhydroxide phases.



Figure 3.11. Concentrations of Cr, Fe and Al as a function of pH (low pH is associated with AMD-impacted water and high pH is influenced by seawater). Line colours: black = total concentration, blue = residual phase, turquoise = highly ordered Fe-oxide phase, orange = poorly ordered Fe-oxide phase, purple = carbonate and exchange phase and green = organic phase.

Concentrations of P are about 2-3 wt% at all sampling points except at RTI-2 with a 10 wt% (Fig. 3.12). At this point, P is mainly found in the poorly ordered metal oxyhydroxide phase and is associated with the phosphate precipitates (Caraballo et al., 2011b; Ayora et al., 2016; Lozano et al., 2020b) and schwertmannite (Fan et al., 2023). U shows a high affinity for the carbonate-exchange and poorly ordered metal oxyhydroxide phases (Fig. 3.12). U concentration in the sediment increases with pH and achieves a maximum at the RTI-2 sampling point.



Figure 3.12. Concentrations of Pb, As, P and U as a function of pH (low pH is associated with AMD-impacted water and high pH is influenced by seawater). Line colours: black = total concentration, blue = residual phase, turquoise = highly ordered Fe-oxide phase, orange = poorly ordered Fe-oxide phase, purple = carbonate and exchange phase and green = organic phase.

The REEs NASC normalized patterns display a pH dependence (Fig. 3.13). At acidic pH the sediments are depleted in REEs with respect to NASC whereas under neutral acidic pH the patterns approach the normalized values. At acidic pH, the depleted normalized REE patterns in the sediments contrast with the enriched REE patterns (compared with pH-neutral conditions) of the water analyzed at the sampling points (Fig. 3.9). Although REEs mainly concentrate in the residual phase, other phases are relevant as pH increases. The (La/Yb)_{NASC}, (La/Gd)_{NASC}, Eu/Eu* and Ce/Ce* ratios for the relevant phases in the sequential extraction and for the bulk sediment are listed in Table 3.4. In the bulk sediment, the (La/Yb)_{NASC} and the (La/Gd)_{NASC} ratios show an enrichment in LREEs with respect to HREEs and MREEs, respectively, which is pH dependent. The enrichment is higher at acidic pH (e.g., (La/Yb)_{NASC} = 2.5 and $(La/Gd)_{NASC} = 1.6$ in the RTI-E1 sample) than at circumneutral pH (e.g., $(La/Yb)_{NASC} =$ 1.27 and (La/Gd)_{NASC} = 1.15 in the RTI-3 sample). Carbonate, exchange and poorlyordered metal oxyhydroxide phases display low (La/Yb)_{NASC} and (La/Gd)_{NASC} ratios, suggesting an enrichment of MREES and HREEs with respect to LREEs in these phases. This is consistent with the sorption experiments of REE onto basaluminite and schwertmannite (Lozano et al., 2019a, 2020a), in which the sorbed fraction of HREEs and MREEs was higher than that of LREEs. By contrast, the (La/Yb)NASC and the (La/Gd)_{NASC} ratios of the residual and highly ordered metal oxyhydroxide phases are high, especially at acidic pH, indicating and enrichment of LREEs in these phases. The Eu/Eu* ratio in the sediments presents a slightly positive anomaly (1.09-1.20) whereas the Ce/Ce* ratio does not present any relevant anomaly (values between 0.81 and 0.98).



Figure 3.13. NASC-normalized REE patterns of the estuarine sediment samples: a) RTI-E, b) RTI-1; c) RTI-2 and d) RTI-3 (see Fig. 1.2).

Table 3.4. $(La/Yb)_{NASC}$, $(La/Gd)_{NASC}$, Eu/Eu^* and Ce/Ce^* ratios obtained from the sequential extractions of the sediment and colloidal-matter samples collected at each sampling point.

		total			carbonate and exchange phases						
sample	(La/Yb) _{NASC}	(La/Gd) _{NASC}	Eu/Eu*	Ce/Ce*	(La/Yb) _{NASC}	(La/Gd) _{NASC}	Eu/Eu*	Ce/Ce*			
RTI-E	2.52	1.63	1.16	0.91	-	0.15	-	-			
RTI-0	1.89	1.28	1.09	0.92	-	0.30	-	0.93			
RTI-2	1.11	1.11	1.20	0.81	0.86	0.50	1.17	0.75			
RTI-3	1.27	1.15	1.18	0.88	1.02	0.58	1.20	1.02			
colloids 4.5	1.06	0.91	1.10	0.97	0.56	0.36	1.20	1.04			
colloids 5.5	1.30	1.13	1.18	0.98	0.51	0.34	1.26	1.00			
	po	orly ordered Fe	e-oxides	hig	hly ordered Fe	e-oxides					
Simple	(La/Yb) _{NASC}	(La/Gd) _{NASC}	Eu/Eu*	Ce/Ce*	(La/Yb) _{NASC}	(La/Gd) _{NASC}	Eu/Eu*	Ce/Ce*			
RTI-E	0.31	0.21	1.30	1.00	-	3.27	1.21	1.04			
RTI-0	0.36	0.32	1.21	1.02	3.03	2.03	1.25	0.89			
RTI-2	0.30	0.54	1.30	0.82	0.37	0.64	1.23	0.71			
RTI-3	0.65	0.67	1.18	0.93	0.74	0.73	1.24	0.84			
colloids 4.5	0.58	0.45	1.29	1.09	1.61	1.08	1.40	0.95			
colloids 5.5	0.45	0.40	1.29	1.21	1.56	1.08	1.33	0.98			
		residual pha	se								
Simple	(La/Yb) _{NASC}	(La/Gd) _{NASC}	Eu/Eu*	Ce/Ce*							
RTI-E	1.68	1.74	1.21	0.78							
RTI-0	2.00	1.65	1.25	0.94							
RTI-2	1.75	1.58	1.23	0.86							
RTI-3	1.53	1.82	1.24	0.85							
colloids 4.5	1.66	2.16	1.40	0.91							
colloids 5.5	2.07	2.14	1.33	0.95							

3.6.3 XRD analysis of the sediments

XRD analyses of the solid samples confirmed the presence of amorphous phases in the colloidal and sediment materials (Fig. 3.14). The most highly ordered Fe-bearing phases were jarosite and hematite. Goethite was not present. Quartz, illite, chlinochlore and kaolinite were identified. Silicates were considered to be erosion products from the host rock with no influence on the geochemistry of the estuarine waters aside from adsorption or exchange of some elements, including REEs (Wu et al., 2023).







Figure 3.14. XRD patterns of (a) sediment collected under acidic conditions (*RTI-E*), (b) the colloidal matter (*RTI-0*) and (c) sediment collected under near-neutral conditions (*RTI-1*).

CHAPTER 4

INTERPRETATION AND DISCUSSION OF THE RESULTS

4.1 Desorption experiments

4.1.1 REE affinity to schwertmannite surface

It is well known that schwertmannite transforms into goethite over weeks or months (aging) depending on the pH and aqueous sulfate concentration (Schwertmann and Carlson, 2005; Regenspurg and Peiffer, 2005; Acero et al., 2006; Burton et al., 2009). XRD patterns of the solid samples before and after the REE adsorption/desorption experiments show only peaks of schwertmannite (Fig. 4.1). This indicates that schwertmannite aging did not occur in the short batch experiments. Moreover, PhreeqC-calculated saturation indexes (*SI*) of the final solutions (Fig. 4.2) indicate that the solutions were undersaturated with respect to REE-hydroxides and supersaturated with respect to schwertmannite. Therefore, schwertmannite aging or dissolution as well as precipitation of secondary REE-phases did not interfere with the adsorption/desorption reactions.

Desorption experiments showed that retention of lanthanides and Y on the schwertmannite surface is pH dependent (Fig. 3.3) as occurred for REEs-adsorption on both schwertmannite and basaluminite (Lozano et al., 2019a, 2020b). Desorption is most effective at the lowest pH (4.85), leaving 20-40% of REEs sorbed on the surface. REE aqueous speciation at the experimental pH of 3 to 8, 1 mg L⁻¹ of each REE and 2840 mg L⁻¹ of Na₂SO₄ shows that (1) the positively-charged aqueous REE-sulfate complexes dominate (87% for LaSO₄⁺ and 82% of LuSO₄⁺), (2) the free REE³⁺-ion species range between 12% (La³⁺) and 18% (Lu³⁺) and (3) the carbonate-REE complexes start to be relevant at a pH higher than the experimental conditions (Fig. 4.3). It has been established, therefore, that the REE-sulfate species are the main candidates to be adsorbed onto schwertmannite surface as indicated by Lozano et al. (2020b).


Figure 4.1. XRD patterns of (a) pure, (b) REE-enriched and (c) post-desorption experiments. Only peaks of schwertmannite are identified.



Figure 4.2. Saturation Indexes (SI) for Sc and Ln hydroxides (a) and schwertmannite (b) at 298 K and 1 ppm of each REE. Experimental pH conditions are delimited between red lines.

At pH < 7, the schwertmannite surface is positively charged and has a high affinity with aqueous oxyanions (molybdate, arsenate, chromate, phosphate, selenate and antimonate (Schoepfer and Burton, 2021). At pH > 7 (pH = 7 is the point of zero charge), the schwertmannite surface becomes negative, releasing the retained oxyanions and adsorbing cations (Jönsson et al., 2005; Antelo et al., 2012). Moreover, the zeta-potential studies on schwertmannite enriched with oxyanions as molybdate, selenate, phosphate and chromate revealed a shift of the point of zero charge to acidic pH (Khamphila et al., 2017). Given that the adsorption of REE-sulfate cations onto schwertmannite is optimal at pH 6.5, the synthetic schwertmannite of the present study probably has a point of zero charge shifted to acidic pH. This shift could be due to sulfate over-adsorption during the synthesis process (Carrero et al., 2017b). In addition, desorption experiments provided ample evidence that schwertmannite releases the previously sorbed REEs at pH < 6.5, below the point of zero charge.

Sc behaves differently (Fig. 3.3). Desorption happens when $Sc(OH)_n$ aqueous species are no longer relevant (Fig. 4.3). This makes Sc suitable for both Sc adsorption (Zhang and Honaker, 2018, Lozano et al., 2020b). The higher surface affinity for Sc is likely to happen due to its lower ionic radii, which facilitates its adsorption onto the structure of schwertmannite compared with other REEs. An alternative explanation is the formation of a different REE bond onto the mineral surface. Similar experiments of Sc adsorption on goethite, hematite and montmorillonite were run to characterize Sc bonding with EXAFS (Chassé et al., 2020). The results suggested a lack of adsorbed covalent bonds or a preference for a specific site. Therefore, Sc should be allocated at the outer shell of the mineral. This hypothesis, however, is not valid for goethite since Qin et al. (2021) found that Sc forms bidentate binuclear binding inner sphere complexes on goethite surfaces.



Figure 4.3. Aqueous speciation distribution with pH of (a) Y, (b) Sc, (c) La and (d) Lu in a 2840 mg L⁻¹ sulfate solution at 298 K and atmospheric pCO_2 .

4.1.2 Equilibrium constants for REE desorption

Figure 4.4 shows the linear correlation obtained by implementation of Eq. (12), for La, Gd and Lu as examples of LREE, MREE and HREE, respectively, as well as Sc due to its divergent behaviour (all elements shown in Fig. A2). The displayed slope values range between 1.3 and 1.7 from LREE to HREE, respectively, and 2 for Sc. Similar results have been described in REE adsorption experiments performed onto schwertmannite, where monodentate and bidentate surface bindings are possible for REE and Y, but only bidentate surface bindings are possible for Sc. Similarly, other REE adsorption experiments onto basaluminite described a different behaviour in Sc

when compared to other REE. REE and Y only formed monodentate bindings at the surface of basaluminite, whereas Sc only formed bidentate surface bindings (Lozano et al., 2019a, 2020a).

The desorption equilibrium constants (log K_{Ln}) for lanthanides and Y were obtained by Eq. (12) considering both i) desorption from monodentate surface complexes (slope and occupied sides n = 1), and ii) bidentate surface complexes (slope and occupied sides n = 2), and only bidentate surface complexes for Sc (Table 4.1). The equilibrium constants in desorption reactions assuming a bidentate complex were in the same order of magnitude than those obtained for adsorption reactions by previous authors (Lozano et al., 2020a), where K_{Ln} for monodentate coordination was not calculated. The implementation of calculated K_{Ln} on adsorption models could help to estimate the contribution of both surface coordination in REE desorption.



Figure 4.4. Linear regressions for the Sc, La, Gd and Lu experimental data using Eq. (12). Note that the slope values for lanthanides range between 1.3 and 1.67 whereas for Sc the slope is ≈ 2 .

Element	bidentate complex	log K	error (±%)	monodentate complex	log K	error (±%)
Sc	$(\mathrm{XO})_2\mathrm{ScSO}_4^-$	-4.92	1.88	-	-	-
Υ	(XO) ₂ YSO ₄ -	-7.62	1.63	$XOYSO_4$	-1.92	3.70
La	(XO) ₂ LaSO ₄ -	-7.98	2	$XOLaSO_4$	-2.28	2.18
Ce	$(\mathrm{XO})_2\mathrm{CeSO}_4^-$	-7.77	1.76	$XOCeSO_4$	-2.00	3.98
Pr	(XO) ₂ PrSO ₄ -	-7.60	1.73	$XOPrSO_4$	-1.90	3.67
Nd	(XO) ₂ NdSO ₄ -	-7.49	1.91	$\rm XONdSO_4$	-1.79	3.32
Sm	$(\mathrm{XO})_2\mathrm{SmSO}_4^-$	-7.39	1.61	$\rm XOSmSO_4$	-1.69	4.33
Eu	(XO) ₂ EuSO ₄ -	-7.37	1.41	$\rm XOEuSO_4$	-1.68	4.92
Gd	(XO)2GdSO4-	-7.47	1.58	$\rm XOGdSO_4$	-1.77	4.16
Tb	(XO) ₂ TbSO ₄ -	-7.34	1.68	$XOTbSO_4$	-1.62	6.29
Dy	(XO) ₂ DySO ₄ -	-7.37	1.13	$XODySO_4$	- 1.64	6.51
Но	(XO) ₂ HoSO ₄ -	-7.36	1.22	$XOHoSO_4$	-1.64	7.15
Er	(XO) ₂ ErSO ₄ -	-7.31	0.95	XOErSO ₄	-1.59	7.87
Tm	(XO) ₂ TmSO ₄ -	-7.21	1.18	$\rm XOTmSO_4$	-1.63	7.65
Yb	(XO) ₂ YbSO ₄ -	-7.08	0.86	$XOYbSO_4$	-1.58	10
Lu	(XO) ₂ LuSO ₄ -	-7.06	1.06	XOLuSO_4	-1.62	9.44

Table 4.1. Log K_{Ln} values and their respective errors for bidentate and monodentate complexes. Calculations were done assuming n = 2 and n = 1 for bidentate and monodentate complexes, respectively.

4.1.3 Model validation

Using PhreeqC (Model B1, Appendix B), the log K_{Ln} values obtained were used to calculate the desorbed fraction at the experimental conditions (T = 298 K, pCO₂ = 3.5 bar and [sulfate] = 2840 mg L⁻¹). First, the schwertmannite surface was equilibrated with a REE-rich solution at pH 6.5 in the presence of sulfate to enable the formation of monodentate and bidentate bindings. Thereafter, to simulate the desorption experiments, the surface was equilibrated with a REE-free solution with the same sulfate concentration and a pH ranging between 3 and 8. The model, in which monodentate and bidentate desorption equilibrium constants were implemented, reproduces satisfactorily the experimental desorption edges (Figs. 4.5 and A3), demonstrating a combination of bidentate and monodentate surface complexes for REEs and Y. However, only bidentate surface complexes take place for Sc. Lozano et al. (2020b) suggested lanthanide adsorption on schwertmannite via bidentate surface complexes, without discarding the presence of monodentate. In this study, however, desorption can only be represented by a combination of both monodentate and bidentate complexes, suggesting that REE-schwertmannite adsorption also requires the formation of both ligands. Considering monodentate and bidentate models separately, bidentate accounts better for the retention of REEs at a higher pH (up to \approx 6). However, monodentate desorption shows a greater influence on the desorbed fraction at pH < 6, suggesting that monodentate bindings are more stable during REE-schwertmannite desorption. This is related to the point of zero charge of schwertmannite (pH \approx 7); the surface is positively charged, resulting in negatively charged bindings (i.e. bidentate) that are less stable than neutrally charged bindings (i.e. monodentate).

The predominance of monodentate bindings contrasts with earlier conclusions (Lozano et al., 2020b) as their models predict REE-adsorption onto the surface of schwertmannite with only bidentate models. This discrepancy could be attributed to (1) a hysteretic behaviour of desorption and (2) a possible transformation of initial bidentate to monodentate surface complexes with subsequent desorption.

In order to better understand the presence and structure of both surface complexes, the surface of Lu-rich schwertmannite will be discussed below using the results from the EXAFS and F-test analysis.



Figure 4.5. Simulations of Sc, La, Gd and Lu desorption in the experiments using the complexation constants listed in Table 4.1. Models for only monodentate and only bidentate are shown as blue and green dashed lines, respectively.

4.1.4 Atomistic model of the LuSO₄⁺ surface complex

Given the decrease in Lu signal in the samples of adsorption and desorption experiments run at low pH, the k^3 range in the EXAFS spectra, which is used to implement the Fourier transform, was set between 2.5 Å⁻¹ and 12.45 Å⁻¹. In this range, only the samples retrieved from experiments run at pH 6.5 (LuA and Lu6.5,

respectively) displayed a good signal-to-noise rate up to a k^3 value above 10 Å⁻¹. Since samples from desorption experiments run at pH < 6.5 contained low Lu concentration for further XAS analysis, the analytical results were not used.

Three inner-sphere surface complexes (monodentate mononuclear, monodentate binuclear and bidentate binuclear; Fig. 4.6) were tested to model the coordination of the adsorbed LuSO₄⁺ molecule. The geometry of the LuSO₄⁺ molecule was obtained using DFT models, resulting in eight Lu-O first-shell paths (6 with R = 2.33 Å and 2 with R = 2.20 Å) and one Lu-S path (R = 3.64 Å). The bidentate binuclear surface complex shares two O atoms with two different octahedral Fe atoms (Fig. 4.6a), yielding a Lu-Fe path (N = 2 and R = 4.53 Å). The monodentate mononuclear surface complex shares one O with one octahedral Fe (Fig. 4.6b) leading to a single Lu–Fe path (N = 1 and R = 4.56 Å). In the monodentate binuclear surface complex, one O is shared with two octahedral Fe atoms (Fig. 4.6c), accounting for two Lu-Fe paths (N = 2 and R = 3.7 Å). Note that paths with a negligible effect on the model (e.g., Lu-O-O) were not included.

Table 4.2 lists the parameters of the Lu-EXAFS models. Overall, the distances for the Lu-O paths maintain their initial values (R = 2.26 Å and 2.38 Å), and the predicted Lu-S interatomic distance ranges between 3.58 Å and 3.62 Å in all the tested structural models. However, the model suggests N values of the Lu-S path higher than 1, indicating the role of sulphate in the stabilization of the REE at the schwertmannite surface. The fact that DFT models display a Lu-SO₄⁺ aqueous specie constituted by one sulphate molecule indicates that structural sulphate could be involved in REE adsorption onto schwertmannite.

Although a k^3 range of ≈ 10.2 Å⁻¹ limits the interpretation of Fe-Lu distal paths, EXAFS data is used to complement the chemical data obtained from the batch desorption experiments and the d-PDF analyses. The Lu-Fe path distances (*R*) in the bidentate binuclear and monodentate mononuclear models are very similar, ranging between 4.52 Å and 4.56 Å for Lu6.5 and LuA, respectively. The Lu-Fe path in the monodentate binuclear model yields R = 4.17 Å with $\Delta r = -0.57$. The high structural deformation needed to adjust the mineral surface to the LuSO₄⁺ molecule in the monodentate binuclear model is in accordance with the high χ^2 value obtained, which indicates an invalid geometry. Figure 4.7 shows the experimental and fitted curves of the k^3 weighted EXAFS spectra and their Fourier transform amplitude for both monodentate mononuclear and bidentate binuclear coordination. Both fittings are satisfactory for samples run at a higher pH (*i.e.*, LuA and Lu6.5). F calculations indicate that both bidentate and monodentate are alike and cannot be discarded at any sample (Table 4.3).



Figure 4.6 Atomistic representations of the three proposed models for $LuSO_4^+$ adsorption. The aqueous complex is attached to the octahedral Fe by different positions. The inner sphere surface complexes considered in this research are: (a) bidentate binuclear; (b) monodentate mononuclear, and (c) monodentate binuclear.

 Table 4.2a Results of the EXAFS fits for Lu6.5 sample. Model 1: Bidentate binuclear.

 Model 2: Monodentate mononuclear. Model 3: Monodentate binuclear. The error is

 expressed in parenthesis after de digit. Var = the number of independent variables.

Model	Neighbor	Path	Ν	σ^2	E ₀	R	Var.	χ^2
1	1st shell	Lu-O ₁	4(2)	0.0035(2)	8.10(3)	2.38(1)	8	108
		Lu-O ₂	4(2)	0.0035(2)	8.10(3)	2.26(4)		
	2nd shell	Lu-S	2(2)	0.0082(6)	8.10(3)	3.58(1)		
		Lu-Fe	$2_{\rm fix}$	0.00672(2)	8.10(3)	4.52(5)		
2	1st shell	Lu-O ₁	4(2)	0.0035(2)	8.10(3)	2.38(1)	8	111
		Lu-O ₂	4(2)	0.0035(2)	8.10(3)	2.26(4)		
	2nd shell	Lu-S	2(2)	0.0082(6)	8.10(3)	3.58(1)		
		Lu-Fe	$1_{\rm fix}$	0.00593(3)	8.10(3)	4.52(4)		
3	1st shell	Lu-O ₁	4(2)	0.0035(2)	8.10(3)	2.38(1)	9	135
		Lu-O ₂	4(2)	0.0035(2)	8.10(3)	2.26(4)		
	2nd shell	Lu-S	2(2)	0.0082(6)	8.10(3)	3.58(1)		
		Lu-Fe	2_{fix}	0.00152(2)	8.10(3)	4.17(8)		

Table 4.2b Results of the EXAFS fits for LuA sample. Model 1: Bidentate binuclear. Model 2: Monodentate mononuclear. Model 3: Monodentate binuclear. The error is expressed in parenthesis after de digit. Var = the number of independent variables.

Model	Neighbor	Path	Ν	σ^2	E ₀	R	Var.	χ^2
1	1st shell	Lu-O ₁	5(1)	0.00123(4)	9.83(2)	2.44(2)	8	113
		Lu-O ₂	3(1)	0.00123(4)	9.83(2)	2.30(5)		
	2nd shell	Lu-S	2(2)	0.0082(6)	9.83(2)	3.62(3)		
		Lu-Fe	$2_{\rm fix}$	0.00605(6)	9.83(2)	4.56(1)		
2	1st shell	Lu-O ₁	5(1)	0.00123(4)	9.83(2)	2.44(2)	8	115
		Lu-O ₂	3(1)	0.00123(4)	9.83(2)	2.30(5)		
	2nd shell	Lu-S	2(2)	0.0082(6)	9.83(2)	3.62(3)		
		Lu-Fe	$1_{\rm fix}$	0.00112(3)	9.83(2)	4.56(4)		
3	1st shell	$Lu-O_1$	5(1)	0.00123(4)	9.83(2)	2.44(2)	9	178
		Lu-O ₂	3(1)	0.00123(4)	9.83(2)	2.30(5)		
	2nd shell	Lu-S	2(2)	0.0082(6)	9.83(2)	3.62(3)		
		Lu-Fe	2_{fix}	0.00152(2)	9.83(2)	4.20(7)		



Figure 4.7 k^3 weighted EXAFS spectra (a, b) at the Lu L3-edge and their respective Fourier transform (c, d). EXAFS have been fitted considering bidentate binuclear coordination (a, c) and monodentate mononuclear coordination (b, d). Experimental data is plotted as purple lines and fit data as orange lines.

Similar results were observed in the d-PDF analysis, in which positive peaks at 2.33 Å, 3.6 Å and 4.55 Å correlate with the Lu-O, Lu-S and Lu-Fe distances, respectively. In addition, a higher Lu content renders more intense negative peaks at 3.4 Å and 5.45 Å, which correlate with the Fe-Fe distances in the octahedral structural frame (Fernández-Martínez et al., 2010; Wang et al., 2015, 2021) (Fig. 4.8). Therefore, LuSO₄⁺ incorporation leads to a structural deformation, which needs a rotated octahedral Fe to accommodate the adsorbed molecule. When Lu desorbs at lower pH

(e.g., pH = 4.5), distortion is reduced, becomes reversible and does not change the intrinsic properties of the schwertmannite structure.

A comparison with the results from earlier EXAFS experiments shows that the free Lu(III) formed monodentate and bidentate surface complexes in ferrihydrite (Dardenne et al., 2001), whereas Eu(III) was retained as bidentate surface complexes in hematite (Estes et al., 2013). The differences in REE coordination onto Fe-oxide minerals could probably depend on phase crystallinity. Minerals with low crystallinity (e.g., schwertmannite and ferrihydrite) could afford some deformation in order to adjust to sorbed molecules in more surface sites (Fig. 4.8; Carrero et al., 2017, 2021; Lozano et al., 2019b). Therefore, according to EXAFS and desorption models, a coexistence of bidentate and monodentate surface complexes is suggested at $pH \approx 6.5$.

Table 4.3 Results of the F-test analysis conducted on the EXAFS models. Monodentate and bidentate account for monodentate mononuclear and bidentate binuclear coordination, respectively.

Sample	LuA		Lu6.	5
Fitting	Monodentate	Bidentate	Monodentate	Bidentate
F-Test	49.12%	50.88%	48.63%	51.37%



Figure 4.8 d-PDF (schwertmannite-subtracted) of the Lu-rich schwertmannite after desorption reactions at pH 6.5, 5.5 and 4.5. the position of main atomic-pairs in schwertmannite structure (Fernandez-Martinez et al., 2010) and $LuSO_4^+$ are indicated by vertical dashed lines.

4.1.5 Environmental implications

The pH dependence of schwertmannite affinity for aqueous REEs has widespread environmental implications. AMD-affected rivers with a low pH (< 3.5) show a conservative REE behaviour as the schwertmannite surface cannot interact with aqueous REEs (Lozano et al., 2020a). By contrast, in the AMD-affected estuarine areas (e.g. the Tinto and Odiel river flowing to Huelva estuary; SW Spain), pH increases up to 7.5, schwertmannite colloids remain suspended owing to tidal effects, and aqueous concentrations of REEs, Al and Fe decrease (Elbaz-Poulichet and Dupuy, 1999). Carro et al. (2011) showed that REEs concentration (Σ [REE]) drops from 173 µg L⁻¹ at pH 2.73, to 0.83 μ g L⁻¹ at pH 6.22 in the estuary mixing zone, and that the water is not supersaturated with respect to REE-phases at this pH range (Fig. 4.2), suggesting that newly formed Fe and Al phases (*i.e.*, schwertmannite and basaluminite) intervene in the REE remobilization. This process of depletion of REE via adsorption happens simultaneously with the dilution of the AMD by seawater mixture (Elbaz-Poulichet and Dupuy, 1999; Carro et al., 2011). This is borne out by the fact that Σ [REE] in the estuarine sediments varies between 33.11 mg L⁻¹ and 79.62 mg L⁻¹ at a pH range between 5.2 and 6.22, respectively (López-González et al., 2012).

However, the strong dependence of REE-schwertmannite desorption on pH, which is related to the point of zero charge, indicates that the REEs retained on schwertmannite colloids would be released if tidal dynamics moves the colloids to areas with a lower pH. Likewise, sedimentary schwertmannite dragged downstream by the river flow could release previously sorbed oxyanions (e.g., arsenate), which would provide free sites to be occupied by $LnSO_4^+$. Moreover, oxyanion release and subsequent adsorption of $LnSO_4^+$ onto schwertmannite surface could also take place in AMD remediation systems, where concentrations of removed REEs by sorption processes would become profitable. However, REE recovery requires the removal of penalizing elements (e.g. arsenate; Alloway, 2013). A sound understanding of REE-schwertmannite sorption/desorption reaction is essential for the fate of toxic REEs in surface waters and their economic value. The thermodynamic data of our study can be useful in the prediction of REE distribution in estuary areas as well as in AMD-treatment plants.

4.2 Adsorption experiments

4.2.1 REE affinity to basaluminite and schwertmannite surface

Figure 4.9 displays the modelled speciation for La, Gd and Lu in the different solutions as representatives of LREE, MREE and HREE, respectively. At lower ionic strength (I = 0.25 M), the molar fraction of REE-SO₄⁺ is up to 64% (La), 53% (Lu) and 47% (Gd), that of REE-Cl²⁺ is 6% (La), 4% (Gd) and 9% (Lu) and that of the free cation REE³⁺ is 29% (La), 44% (Gd) and 39% (Lu). At higher ionic strength (I = 0.5 M), the molar fraction of REE-SO₄⁺ decreases to 44% (La), 22% (Gd) and 31% (Lu) whereas that of REE-Cl²⁺ increases to 18% (La), 10% (Gd) and 20% (Lu) and that of the free

cation REE³⁺ increases to 38% (La), 67% (Gd) and 49% (Lu). Thus, the REE-SO₄⁺ complex is the main aqueous species at low ionic strength. With a high chloride content, however, the REE-SO₄⁺ fraction decreases to promote the free cation REE³⁺, which becomes the main species for MREEs and HREEs. The high concentration of sulfate in solution prevents a high REE-Cl²⁺ fraction, even if this aqueous complex is relevant in seawater conditions (Schijf and Byrne, 2021). Conversely, high ionic strength conditions prevent sulfate from interacting with REE, enhancing the free ions REE³⁺ fraction. Model results indicate that the REE speciation fraction remains stable at the pH range of \approx 3.5 and \approx 7 (i.e., between the pH in AMD-impacted rivers and that of estuarine water).



Figure 4.9. Aqueous speciation distribution of La (a,d), Gd (b,e) and Lu (c,f) in a solution with 1 mg L^{-1} of REE, 2840 mg L^{-1} of sulfate and 0.25 M (a,b) and 0.5 M (c,d) ionic strength at 25 °C and atmospheric pressure.

4.2.2 K_{EQ} for REE adsorption onto schwertmannite at different ionic strengths

The *n* value in the schwertmannite adsorption experiment (Eq. 12) ranges between 1 and 2 (Fig. A3), indicating that both monodentate and bidentate complexes occur.

The effect of ionic strength on the log K_{REE} for both bidentate and monodentate REE coordination proved to be negligible in the schwertmannite adsorption experiments (Fig. 4.10a,b). Note that the calculated log K_{REE} values slightly increase with salinity but remain the same within error. Moreover, the log K_{REE} values for REE adsorbed in bidentate coordination in our experiment are similar to those obtained at lower ionic strength (I = 0.03 M) by Lozano et al. (2020a) (Fig. 4.10a) strongly suggesting a negligible effect of ionic strength on the REE adsorption onto schwertmannite.



Figure 4.10. Log K_{REE} values of the adsorption reactions for: a) bidentate and b) monodentate surface complexes in schwertmannite and their respective error bars (see Table A3). Log K_{REE} values at different ionic strengths obtained by Lozano et al. (2020a) were included.

Log K_{REE} values of both monodentate and bidentate adsorption reactions were included in NEM to model schwertmannite adsorption at different ionic strengths (Models B2.2 and B2.4, Appendix B) as a function of pH. Bidentate and monodentate complexation model matches the experimental results at high pH (pH > 5.25) and low pH (pH < 5.25), respectively (Figs. 4.11 and A4). The pH effect on the type of surface complexation could be due to the positively charged surface of schwertmannite under acid conditions, with a described zero charge point at pH 7 (Antelo et al., 2012). Monodentate complexation leads a neutral surface charge (XOREE-SO₄⁻), whereas bidentate complex displays a negative charge ((XO)₂REE-SO₄⁻). Therefore, REE-SO₄⁺ could find few negatively charged surface sites under acid pH, which prevent the formation of bidentate complexes in favour of none interaction or monodentate complexes formation (Ayora et al., 2016; Lozano et al., 2020b). However, near and above zero charge point, more negative adsorption sites are available, allowing bidentate complex formation.

In the adsorption model, bidentate sites have higher impact on reproduction of the experimental results, in contrast with the desorption experiments in section 4.1.3, where monodentate curve is more impactful than bidentate one to reproduce the experimental results. This adsorption/desorption difference gives strength to the theory proposed in this thesis, in which, rather than having the bidentate binuclear sites desorbed in one step, they instead break one bond with one surface XO⁻ site to form a monodentate mononuclear surface site, which is later desorbed.



Figure 4.11. Adsorption model (lines) and experimental results (orange triangles) of REE-schwertmannite adsorption for: (a,d) La, (b,e) Gd and (c,f) Lu at I = 0.25 M (a,b,c); and I = 0.5 M (d,e,f). The complexation constants listed in Table A3 were used in the modeling. Purple lines represent the best-fit model considering different proportions of bidentate and monodentate adsorption mechanisms. Green and blue dashed lines represent exclusively monodentate and bidentate adsorption model, respectively.

4.2.3 KEQ for REE adsorption onto basaluminite at different ionic strengths

In the basaluminite experiment, REE adsorption yields a n value that is closer to 1 (monodentate; Fig. A5) although the LREE linear regression range is < 1 (i.e., n = 0.6). This suggests a combination of monodentate inner sphere and outer sphere complexation.

The log K_{REE} values obtained for REE adsorption onto basaluminite surface display significant differences between LREE, which are affected by ionic strength, and HREE, where the log K_{REE} variation with ionic strength is within the error range (Fig. 4.12 and Table A4). Furthermore, comparing with earlier REE adsorption experiments (Lozano et al., 2019a), increments in ionic strength are not correlated with log K_{REE} (i.e.,

log K_{REE} (I = 0.25 M) < log K_{REE} (I = 0.50 M) < log K_{REE} (I = 0.03 M)). Likewise, NEM calculated from the obtained log K_{REE} (Models B2.1 and B2.3, Appendix B) can successfully reproduce experimental HREE adsorption onto basaluminite, although LREE and MREE significantly differ for models (Figs. 4.13 and A6). The low accuracy for the LREE adsorption model may be related to the formation of outer sphere complexes deduced from *n* values below 1 (Fig. A5). Outer sphere complexes are more unstable and highly affected by ionic strength where ions in solution may cover the charged basaluminite surface debilitating the ligands with LREEs in outer sphere coordination (Hu et al., 2013, Zhang et al., 2019). Thus, the proposed model that considers more stable ligands (i.e., monodentate coordination) overestimates the adsorbed LREE fraction.



Figure 4.12. Log K_{REE} values of the adsorption reactions for monodentate surface complexes in basaluminite and the respective errors bars (see Table A4). Log K_{REE} values at different ionic strengths obtained by Lozano et al. (2019) were included.

This fact prevents a success identification of LREE coordination onto basaluminite by chemical date, where synchrotron techniques, such as EXAFS, could bring a better approach. However, the low concentration of LREE on basaluminite surface prevents the implementation of these techniques, even in fluorescence mode with higher resolution. Lozano et al. (2019b) implemented EXAFS analysis to characterize the YSO₄⁺ complexation onto basaluminite as an equivalent of HREEs due to their similar chemical properties (Henderson, 1984), but with higher concentration. Likewise, Gd (MREE) displays a similar behaviour to some elements of the LREE group but with higher concentration on basaluminite surface. Hence, the EXAFS characterization of Gd surface complexation could be extrapolated to both LREEs and MREEs.

4.2.4 Structure of the adsorbed Gd onto basaluminite

Chemical analysis displayed above indicated that REE adsorption onto basaluminite is leaded through monodentate surface complexation (n = 1) in HREEs and a combination of both monodentate inner sphere and outer sphere complexation (n< 1) for LREEs and MREEs. These results agree with previous REE sorption experiments run onto basaluminite and characterized by EXAFS analyses, where Y (i.e., HREE) surface complexation was described as monodentate binuclear inner-sphere (Lozano et al., 2019b). To study LREE and MREE surface complexation on basaluminite, Gd L₃ edge EXAFS spectra were fitted. In the models, the GdSO₄⁺ species defined by CPCM were coupled to basaluminite structure (defined by Carrero et al., 2017a) in two possible coordinations (monodentate mononuclear and monodentate binuclear inner sphere, Fig. 4.14), and nine Gd-O paths and one Gd-S path, corresponding to the GdSO4⁺ species were included. In addition, one or two Gd-Al paths were added to the model for GdSO4⁺ monodentate mononuclear and binuclear coordination, respectively. As GdSO₄⁺ species displays a broad range of Gd-O distances, this path has been divided into 4 proximal paths (Gd-O₁ = 2.33 Å) and 5 distal paths $(Gd-O_2 = 2.45 \text{ Å})$. The Gd-S path was included in the model with an interatomic distance R = 3.60 Å. For monodentate binuclear coordination, two Gd-Al paths at R =

3.96 Å were added in the model with one O shared by two octahedral Al atoms that links the $GdSO_4^+$ molecule (Fig. 4.14a). Likewise, the monodentate mononuclear model only had one Gd-Al path at R = 4.29 Å in which the $GdSO_4^+$ molecule shared an apical O with an octahedral Al (Fig. 4.14b).



Figure 4.13 Adsorption monodentate model (purple lines) and experimental results (orange triangles) of REE-basaluminite adsorption for: (a,d) La, (b,e) Gd and (c,f) Lu at I = 0.25 M (a,b,c) and I = 0.5 M (d,e,f). The complexation constants listed in Table A4 were used in the modeling.



Figure 4.14 Atomistic models for $GdSO_4^+$ adsorbed onto basaluminite. The aqueous complex is attached to the mineral surface by monodentate binuclear (a) and monodentate mononuclear (b) inner sphere complexation.

Model parameters for Gd monodentate binuclear and monodentate mononuclear complexes at different ionic strengths are listed in Tables 4.4 and 4.5, respectively. The k^3 EXAFS spectra and the respective Fourier transforms for the experimental and model results are displayed in Fig. 4.15. Given the beamline detection limit, the spectra obtained from the Gd L₃ edge EXAFS display a satisfactory signal up to $k^3 \approx 8$ Å⁻¹. As a consequence, the proposed fits cannot be used to determine the distal Gd-Al paths.

For monodentate binuclear coordination, the coordination number for Gd-O₁ and Gd-O₂ paths (N_{Gd-O}) varied between 9 and 11 (9 in the sample Low-I-12; 10 in the samples Low-I-36 and High-I-12, and 11 in the sample High-I-36), whereas the interatomic distance (R_{Gd-O}) varied between 2.31 Å and 2.40 Å for the Gd-O₁ paths and between 2.47 Å and 2.58 Å for the Gd-O₂ paths. The Gd-S coordination number (N_{Gd-S}) was fixed to 1 in order to conserve the species structure characterized by CPCM, whereas the Gd-Al coordination number (N_{Gd-Al}) was 2 for most of the samples in the EXAFS fitting. The interatomic distances R_{Gd-S} and R_{Gd-Al} were fitted to values between 3.70 Å and 3.79 Å, and 3.87 Å and 4.07 Å, respectively. Samples Low-I-36 and Low-I-12 displayed a good fit with reasonable low χ^2 , whereas samples at high ionic strength differ from proposed models.

For monodentate mononuclear coordination, the fitted coordination number (*N*) and interatomic distance (*R*) for Gd-O₁, Gd-O₂ and Gd-S paths are coincident with those reported by CPCM model in GdSO₄⁺ species in solution. However, N_{Gd-A1} had to be fixed to 1 in all samples due to models it tends to values around 2, breaking the proposed monodentate mononuclear coordination. This fact could indicate that Gd adsorption by monodentate binuclear coordination is the best model (displaying a slightly lower χ^2 in most of the cases). These results would agree with previous Y adsorption coordination in basaluminite (Lozano et al., 2019b) as monodentate binuclear is the dominant coordination for HREEs and MREEs.

GdSO₄⁺ coordination with basaluminite surface shows a longer distance in comparison with that of HREEs ($R_{Y-Al} = 3.52$ Å; 3.87 Å $\leq R_{Gd-Al} \leq 4.07$ Å) (Lozano et al., 2019b). The Gd-O coordination number (between 9 to 11) that is higher than those of the YSO₄⁺ ($N_{Y-O} = 8$; Lozano et al., 2019b) and LuSO₄⁺ ($N_{Lu-O} = 8$) molecules, together with longer Gd-S interatomic distances (i.e., 3.70 Å $\leq R_{Gd-S} \leq 3.89$ Å vs. 3.33 Å $\leq R_{Y-S} \leq 3.50$ Å; Lozano et al., 2019b, or 3.58 Å $\leq R_{Lu-S} \leq 3.62$ Å, in this thesis) indicate that Gd-S bindings in GdSO₄⁺ are ~ 0.37 Å longer than YSO₄⁺ molecules and ~ 0.22 Å longer than LuSO₄⁺ molecules. Therefore, although EXAFS data are not conclusive for Gd-Al path, increments in molecular size with a decrease in the REE atomic number could explain the longer Gd-Al interatomic distance. Assuming that this trend prevails over the REE sequence, LREEs display the highest molecular size, and hence, the longest distances between the LREE-SO₄⁺ molecule and the basaluminite surface. This fact and the high ionic strength could account for the increasing proportion of outer

sphere complex in LREEs as layers of ions in solution could cover surface charges, complicating LREEs bonding the basaluminite surface, however due to analytical limitations, this hypothesis cannot be confirmed.



Figure 4.15 k^3 weighted EXAFS spectra (a,b) and Fourier transform amplitude at the Gd L₃-edge adsorbed onto basaluminite (c,d). Fitted curves for bidentate binuclear (a,c) and monodentate mononuclear coordination (b,d) are displayed in orange and experimental curves in purple.

Table 4.4 Modelling parameters for Gd L3-edge EXAFS in monodentate binuclear inner sphere coordination in basaluminite. The error is within brackets. Var. = number of independent variables.

Model	Neighbor	Path	N _{initial}	N _{final}	σ^2	E ₀	R	Var.	χ^2
Low-I-12	1st shell	$Gd-O_1$	4	4(1)	0.0001(3)	7.10(1)	2.36(1)	4	31
		Gd-O ₂	4	5(2)	0.0001(3)	7.10(1)	2.52(3)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.00112(1)	7.10(1)	3.79(2)		
		Gd-Al	2	2(2)	0.0032(3)	7.10(1)	4.07(5)		
Low-I-36	1st shell	$Gd-O_1$	4	6(8)	0.0048(2)	5.69(3)	2.36(1)	4	17
		Gd-O ₂	5	4(10)	0.0048(2)	5.69(3)	2.52(4)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.00002(15)	5.69(3)	3.70(7)		
		Gd-Al	2	2(5)	0.00332(2)	5.69(3)	3.89(6)		
High-I-12	1st shell	$Gd-O_1$	4	5(1)	0.0029(3)	4.22(1)	2.31(2)	4	74
		Gd-O ₂	5	5(1)	0.0029(3)	4.22(1)	2.47(3)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.01275(9)	4.22(1)	3.72(5)		
		Gd-Al	2	2(5)	0.00707(7)	4.22(1)	3.87(9)		
High-I-36	1st shell	$Gd-O_1$	4	5(3)	0.0053(8)	9.11(2)	2.40(2)	4	62
		Gd-O ₂	5	6(2)	0.0053(8)	9.11(2)	2.58(2)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.00562(6)	9.11(2)	3.79(5)		
		Gd-Al	2	2_{fix}	0.00827(2)	9.11(2)	4.02(7)		

Table 4.5 Modelling parameters for Gd L3-edge EXAFS in monodentate mononuclear inner sphere coordination in basaluminite. The error is within brackets. Var. = number of independent variables.

Model	Neighbor	Path	N _{initial}	N _{final}	σ^2	E ₀	R	Var.	χ^2
Low-I-12	1st shell	$Gd-O_1$	4	4(1)	0.0001(3)	7.10(1)	2.36(1)	4	29
		Gd-O ₂	4	5(2)	0.0001(3)	7.10(1)	2.52(3)		
	2nd shell	Gd-S	1	1_{fix}	0.00508(1)	7.10(1)	3.79(2)		
		Gd-Al	1	$1_{\rm fix}$	0.00736(5)	7.10(1)	4.08(2)		
Low-I-36	1st shell	$Gd-O_1$	4	6(8)	0.0048(2)	5.69(3)	2.36(1)	4	19
		$Gd-O_2$	5	4(10)	0.0048(2)	5.69(3)	2.52(4)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.0001(15)	5.69(3)	3.79(4)		
		Gd-Al	1	$1_{\rm fix}$	0.00271(4)	5.69(3)	4.21(8)		
High-I-12	1st shell	$Gd-O_1$	4	5(1)	0.0029(3)	4.22(1)	2.31(2)	4	76
		Gd-O ₂	5	5(1)	0.0029(3)	4.22(1)	2.47(3)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.00668(9)	4.22(1)	3.76(4)		
		Gd-Al	1	$1_{\rm fix}$	0.00761(10)	4.22(1)	4.28(4)		
High-I-36	1st shell	$Gd-O_1$	4	5(3)	0.0053(8)	9.11(2)	2.40(2)	4	64
		Gd-O ₂	5	6(2)	0.0053(8)	9.11(2)	2.58(2)		
	2nd shell	Gd-S	1	$1_{\rm fix}$	0.00787(6)	9.11(2)	3.82(5)		
		Gd-Al	1	1(6)	0.00541(3)	9.11(2)	4.26(7)		

PDF analysis of basaluminite samples loaded with Gd, in which the PDF signal from pure basaluminite has been subtracted (differential PDF (d-PDF)), shows the structural effects of GdSO₄⁺ adsorption (Fig. 4.16). Although d-PDF has proved to be a good technique to characterize the interaction between adsorbed molecules and mineral surfaces (Lozano et al., 2019a, Carrero et al., 2017a), none positive peaks were identify above the background. This indicates that Gd concentration on basaluminite surface was below detection limit for d-PDF. However, a negative peak at 1.49 Å relative to S-O distance was observed (Carrero et al., 2017a). The fact that the S-O peak intensity increases with adsorption time and with ionic strength could indicate that sulphate is released from basaluminite due to (1) ion exchange with GdSO₄⁺ (Carrero et al., 2017a; Lozano et al., 2019a) and (2) basaluminite instability and heterogeneous dissolution at higher ionic strength. However, the exchange reaction could be rule out due to both, negative S-O and positive Gd-O peak intensity should be correlated in an exchange reaction (Carrero et al., 2017b).

Ion exchange during Gd adsorption increases the sulphate concentration, which modifies the molar faction of the $GdSO_4^+$ species. d-PDF analysis indicated a S-O signal loss between 20 and 25 % during $GdSO_4^+$ adsorption. In the adsorption experiments, the S/L ratio was 1 g L⁻¹ and the sulphate concentration of the input solution was 51.88 mg L⁻¹. Considering a heterogenous sulphate dissolution of 25% from the stoichiometric of initial synthetic basaluminite (Al₄(OH)₁₀SO₄·4H₂O; Farkas and Pertlik, 1997), the equilibration between released sulphate and REE in solution increments REE-SO₄⁺ molar fraction between 1 and1.5%. This suggests that REE adsorption enhances the proportion of aqueous REE-SO₄⁺ species suitable to adsorb, favouring thus the REE stabilization onto basaluminite.



Figure 4.16 Differential PDF (pure basaluminite subtracted from Gd loaded basaluminite) of samples: Low-I-12 (gray), Low-I-36 (dark olive green), High-I-12 (blue) and High-I-36 (red) samples.

4.3 Geochemistry in the Ría de Huelva estuary

4.3.1 Water chemistry and speciation of REE

Speciation of REEs under estuarine conditions is dependent on pH and REE (Fig. 4.17). For the speciation of the REE carbonate complexes, water samples were in equilibrium with respect to atmospheric CO₂. In LREE (Fig. 4.17b), the predominant complex is $LnSO_4^+$ (Ln = lanthanide), followed by Ln^{3+} . However, from RTI-2 to RTI-3, the $LnSO_4^+$ and Ln^{3+} molar fractions drop and carbonate complexes ($LnCO_3^+$) start to be relevant. As regards HREEs (Fig. 4.17a), the $LnSO_4^+$ molar fraction is significantly

lower (20% less) whereas Ln³⁺ presents a higher molar fraction. As pH increases, the fractions of these aqueous complexes diminish in contrast to the increase in carbonate and hydroxide complexes. Chloride complexes (LnCl²⁺) present molar fractions between 4% and 18% (LREE to HREE, respectively). Note, however, that as Cl⁻ is used for the charge balance, this value may change slightly. It is significant to REE speciation that the aqueous sulfate complexes adsorb onto schwertmannite and basaluminite (Lozano et al., 2019a,b,c) as other complexes (e.g. Ln³⁺) are much less reactive. However, free ion species are reactive with other ferric oxides (Marmier et al., 1997; Rabung et al., 1998; Marmier and Fromage, 1999; Liu et al., 2017).



Figure 4.17. Aqueous speciation of the collected water samples calculated as a function of pH with PhreeqC: (a) Lu (representative for HREEs) and (b) Ce (representative for LREEs).

4.3.2 Solid characterization, stability of critical precipitates

The stability of the crystalline oxides, oxyhydroxysulfates and REE-phosphates, the *SI* for each solution are calculated and displayed as a function of pH (Fig. 4.18). Saturation indexes for K- and Pb-jarosites indicate that the minerals are saturated (SI > 0), Na- and H-jarosites are at equilibrium ($SI \approx 0$) or even undersaturated (SI < 0) (Fig. 4.18a), K- and Pb-jarosite are also undersaturated (SI < 0) at pH > 6. Thus, these precipitates will tend to form preferentially in the acidic parts of the estuary. The other relevant crystalline iron oxides (goethite and hematite) are saturated throughout the estuarine environment (Fig. 4.18b).

As regards the colloidal material, although hematite is the only crystalline metalbearing oxyhydroxide, the elevated background in the XRD patterns (Fig. 3.14) indicates the existence of amorphous phases (Fig. 4.18c). The model, however, suggests the presence of schwertmannite and basaluminite at pH > 3.3 and 4.5, respectively, but at pH > 6.5, basaluminite is undersaturated (SI < 0), which could result in basaluminite re-dissolution with the consequent remobilization of adsorbed As, Se and REEs (Carrero et al., 2017b; Lozano et al., 2019a). On the other hand, ferrihydrite shows a constant positive *SI* index under all estuarine conditions. Phosphates present different behaviours; LREE-phosphates show a positive SI at pH > 5 whereas HREE-phosphates only show negative *SI* values, and MREEs present an intermediate behaviour (positive *SI* as LREE-phosphates tend to precipitate). Our geochemical models suggest that LREEs and MREEs are stable in some of the estuarine conditions whereas HREEs are not. However, other phosphates present in the phosphogypsum leachates (e.g., hydroxyapatite and strengite) are saturated at pH 5.5-7 (Papaslioti et al., 2018).



Figure 4.18. Saturation indexes (SI) of the different phases that may be involved in the estuarine geochemistry as function of pH, calculated with PhreeqC using the measured estuarine-water chemistry. The studied phases are (a) jarosites, (b) hematite and goethite, (c) schwertmannite, basaluminite and ferrihydrite, and (d) REE-phosphates, hydroxyapatite and vivianite.

4.3.3 Mixing models and REE adsorption models

The match for the concentrations calculated with the mixing model and those measured in field samples is shown in Figs. 4.19-4.25. As *SI* values with respect to Nabearing phases (e.g. Na-jarosite) are negative, Na was considered to be a reference element, indicating when seawater mixing may affect the water chemistry of the estuary. In the model, the pH range for schwertmannite precipitation (i.e. pH between 3.3 and 3.5) were reached with a solution that contains a volume of 50% of each end-member. In contrast, to attain a pH of 6.2, the mixing solution needs to contain a volume of 95 % of seawater and 5% of AMD, i.e., AMD waters need dilution.

Concentrations of alkaline and alkaline earth metals (K, Rb, Ca, Mg, Sr) in the mixing model satisfactorily match the field data (Fig. 4.19). In contrast, Li and Ba concentrations are mostly overestimated and underestimated, respectively. This suggests that, except for Ba and Li, most alkaline and alkaline earth elements behave conservatively. Estuarine Ba concentrations might be tied to sulfate concentration as a depletion of sulfate, which is caused by newly formed Fe- and Al-oxyhydroxysulfates, could result in a Ba increase (Golding et al., 2018). However, an alternative source of Ba cannot be ruled out based on our mixing model.

For Co, Cu, Cd, Ni, Zn, Mn and Tl concentrations, the model and the field data show a good match (Fig. 4.20), although the measured concentrations show different trends at Na concentrations above and below 7000 mg L⁻¹ (pH 3.7 - 5.2), probably defining the onset of schwertmannite and basaluminite precipitations at the higher pH values. Thus, although sorption of divalent cations on estuarine Fe- and Al-phases occur (Swedlund and Webster, 2001; Acero et al., 2006; Jönsson et al., 2006; Antelo et al., 2013; Fitzpatrick et al., 2017; Zhang et al., 2018), the aqueous concentration of these cations is mainly controlled by seawater mixing and, with the exception of Cu, they become quasi-conservative (Pérez-López et al., 2023). Moreover, the good match between field and model data suggests that the reactivity of these metals follows a trend (Cd < Ni < Tl < Zn < Mn < Co < Cu; Fig. 4.20).



Figure 4.19. Measured (orange triangles) and mixing-model calculated (purple circles) concentrations of alkali and alkaline-earth metals vs. measured Na concentrations at the different sampling points.



Figure 4.20. Measured (orange triangles) and mixing model calculated (purple circles) concentrations of Cd, Ni, Tl, Zn, Mn, Co and Cu vs. measured Na concentrations at the different sampling points.



Figure 4.21. Measured (orange triangles) and mixing model calculated (purple circles) concentrations of Cr, Fe, Al and Pb vs. measured Na concentrations at the different sampling points.

As for trivalent elements (Fig. 4.21), Fe(III) is mostly depleted due to precipitation of Fe-bearing phases (e.g., schwertmannite, jarosite, goethite, hematite and ferrihydrite). Similarly, Al might co-precipitate with schwertmannite at pH \approx 3.5-4 (Carrero et al., 2022) and precipitate as basaluminite at pH \geq 4.5. Metals with different oxidation states (Pb and Cr) show different behaviours (Fig. 4.21). Dissolution of Pb-Jarosite (Fig. 4.18) might have a control over Pb concentration in the water at [Na] < 7000 mg L⁻¹, and the precipitation of schwertmannite and basaluminite might have an impact on the Pb concentration at [Na] > 7000 mg L⁻¹. Otherwise, Cr and Fe concentrations in the water show a similar tendency, suggesting a Cr sorption on Febearing phases (e.g. schwertmannite) (Regenspurg and Peiffer, 2005; Antelo et al., 2012; Wang et al., 2021; Fan et al., 2023).

Concentrations of B and As (metalloids) present different behaviours (Fig. 4.22). The model and the field concentrations of boron display a good match, i.e., [B] is controlled by seawater mixing (conservative element). In contrast, arsenic is depleted, which is probably due to arsenate incorporation onto Fe- and Al- bearing precipitates (Regenspurg and Peiffer, 2005; Loring et al., 2009; Antelo et al., 2012; Carrero et al., 2017b; Wang et al., 2021). The As distribution is discussed in the following section.

As for non-metals S and P (Fig. 4.23), the model concentration of sulphur is slightly overestimated because of the precipitation of sulfate-bearing minerals (e.g., schwertmannite and basaluminite). The phosphorus concentration is extremely high at RTI-2 (near the phosphogypsum stack) compared to normal seawater probably due to phosphopgypsum leachates (Millán-Becerro et al., 2023). It is worth mentioning that the water is undersaturated with respect to hydroxyapatite at RTI-0 and RTI-1 (Fig. 2.1), and is saturated at RTI-2 and RTI-3, resulting in hydroxyapatite precipitation. This phase could be retaining some of the REEs (Owens et al., 2019).


Figure 4.22. Measured (orange triangles) and calculated (mixing model, purple circles) concentrations of B and As vs. measured Na concentrations at the different sampling points.



Figure 4.23. Measured (orange triangles) and mixing model calculated (purple circles) concentrations of S and P vs. measured Na concentrations at the different sampling points.

Uranium is the only analysed actinide presenting depletion when compared with the model data (Fig. 4.24). It is known that dissolved and particulate uranium are controlled by adsorption–desorption processes and formation of carbonate complexes, both depending on pH (Hierro et al., 2013). At low pH, U tends to be dissolved and barely adsorbed by suspended particles. As pH increases, the adsorption onto Fe- and Al-particles occurs up to pH = 5.5, which is the pH of the minimum solubility. At pH > 5.5, dissolved uranium increases by carbonate complexation (Walter et al., 2003; Hierro et al., 2013; Mehta et al., 2015; Santofimia et al., 2022).



Figure 4.24. Measured (orange triangles) and mixing model calculated (purple circles) concentrations of U vs. measured Na concentrations at the different sampling points.

Field concentrations of REEs are lower than those of the mixing model (Fig. 4.25). As $[Na] < 7000 \text{ mg L}^{-1}$, the concentrations are slightly lower and influenced by seawater mixing. For $[Na] > 7000 \text{ mg L}^{-1}$, however, the field concentrations are much lower. This change occurs at pH 3.7 (RTI-E) and pH 5.2 (RTI-0). In the pH range of 3.5-

5.5, REEs adsorb onto precipitates of schwertmannite and basaluminite, making it evident the buffer effect of the precipitating phases. The modeling of the REE adsorption shows two tendencies (Fig. 4.26), which may be accounted for by different solid:liquid ratios (S/L). With lower S/L ratios (e.g., S/L = 14 g L⁻¹), *SI_{schwertmannite}* < 0 whereas for S/L = 50 g L⁻¹ *SI_{schwertmannite}* > 0 and *SI_{basaluminite}* > 0. This indicates that precipitation of schwertmannite and basaluminite play a major role in REE scavenging, even though pH is not totally optimal for REE adsorption onto these minerals (Lozano et al., 2019a, 2020a). The elevated S/L is much higher than that obtained by filtration of the suspended material (≈ 0.5 g L⁻¹), suggesting a reactive estuarine sediment. Moreover, if the model results do apply to the whole estuary, schwertmannite and basaluminite should be present in areas where it is not saturated, which is only possible if sediment remobilization via tidal dynamics takes place.



Figure 4.25. Concentrations of REEs vs. Na concentration: field data at the different sampling points (orange triangles) and mixing model data (purple circles).



Figure 4.26. Concentration of Y, Ce, Gd, Lu and total REE as a function of Na concentration. Purple dashed lines correspond to the mixing model, green and blue dashed lines correspond to the adsorption model with a solid/liquid ratio of 10 g L^{-1} and 50 g L^{-1} , respectively.

4.3.4 Element distribution in the sediment

Ni and Mn (Fig. 3.10) were found mainly in the residual phase, with lesser concentration among the poorly and highly ordered metal phases. Ni adsorbed onto schwertmannite is released back to solution as schwertmannite transforms (ages) to goethite (Acero et al., 2006), which could explain its mobility in the estuary. Mn is released from dissolution of precipitated manganite (γ -MnOOH) in amonium oxalate at 80 °C, suggesting the presence of this phase in the poorly crystalline metal oxyhydroxide phases (Lee et al., 2002). Cd is mainly released by otavite (CdCO₃) and

exchange phases. The presence of Cd in the carbonates depends on pH such that the highest the pH the highest the Cd concentration. Undersaturation with respect to otavite and calcite (CaCO₃) (Fig. 4.27) leads to Cd adsorption onto schwertmannite (Acero et al., 2006).



Figure 4.27. Saturation indexes (SI) with respect to Cd-, Ca-, Cu-, Ni-, Co-, Pb- and Zn-carbonates as a function of pH.

Regarding to Zn, Cu and Co (Fig. 3.10), under extreme drought conditions, the divalent cations are scavenged by schwertmannite formed in acidic, sulfate soils (Fitzpatrick et al., 2017). With the exception of Mn, however, Co, Zn and Cd adsorbed onto schwertmannite at high pH are totally or partially released back to solution as schwertmannite ages to goethite (Acero et al., 2006; Kumpulainen et al., 2008). During schwertmannite ageing only 20% of total Cu is released back to solution, suggesting its presence in the highly ordered metal oxyhydroxides phases (Acero et al., 2006).

Moreover, basaluminite can also retain some Cu and Ni at $5 \le pH \le 7$ conditions (Lu et al., 2021; Acero and Hudson-Edwards, 2022). Nonetheless, the scavenging of these elements by solid phases is not enough for a considerable alteration of the estuarine aqueous chemistry, apart from Cu (Fig. 4.20).

As for Fe, Cr and Al (Fig. 3.11), Fe is found in highly ordered metal oxyhydroxide phases (jarosite and goethite) whereas at $pH \ge 6.5$ is present in amorphous metal oxyhydroxide phases (Fig. 4.21). Although chromate can be preferentially sorbed onto schwertmannite at acidic pH (Regenspurg and Peiffer, 2005; Antelo et al., 2012; Wang et al., 2021), aqueous Cr in the liquid samples is rather scarce (< 10 µg L⁻¹). Al usually precipitates as basaluminite, which is a relevant sink for REEs and oxyanions (Carrero et al., 2017b; Lozano et al., 2019a), or may be incorporated in the structure of schwertmannite (Sánchez-España et al., 2016; Carrero et al., 2017b, 2022).

Regarding to Pb (Fig. 3.12) $SI_{Pb-Jarosite} > 0$ in the pH range of 3-6 (Fig. 4.18), Pb accumulates in the sediment as Pb-jarosite precipitates. Pb-jarosite can precipitate in the presence of sulfate and chloride (Dutrizac and Dinardo, 1983), showing a high capacity to retain Zn and Cu via coprecipitation. Partial dissolution of Pb-jarosite is possible under both alkali and acidic conditions (Smith et al., 2006), which could be the cause of the decrease in Pb concentration in the sediment at the RTI-3 sampling point in which $SI_{Pb-Jarosite} < 0$. The presence of Pb, therefore, could become environmentally problematic if estuarine tidal dynamics or sediment remobilization affects Pb-jarosite under alkaline conditions. Note that the Pb concentration in the adsorbed phase is 250 mg kg⁻¹. Earlier studies show that most of Pb remains in the solid as schwertmannite ages (Acero et al., 2006) leading to a lead accumulation in the sediment.

As (Fig. 3.12) is mainly found adsorbed in the highly ordered metal oxyhydroxide phase, suggesting a sorption process at acid conditions, followed by desorption from the oxyhydroxide minerals at high pH, in accordance with previous studies (Regenspurg and Peiffer, 2005; Burton et al., 2009; Antelo et al., 2012; Carrero et al., 2017b; Wang et al., 2021). Sorption of arsenate in highly and poorly ordered metal oxyhydroxide phases occurs mainly in goethite (Manning et al., 1998; Gimenez et al., 2007; Loring et al., 2009; Burton et al., 2009), schwertmannite (Regenspurg and

Peiffer, 2005; Antelo et al., 2012; Wang et al., 2021), basaluminite (Carrero et al., 2017b) and jarosite (Savage et al., 2005; Smith et al., 2006; Asta et al., 2009).

Phosphorous (Fig.3.12) is mainly found in the poorly ordered metal oxyhydroxide phase and is associated with the phosphate precipitates (Caraballo et al., 2011b; Ayora et al., 2016; Lozano et al., 2020b) and schwertmannite (Fan et al., 2023). The high concentrations of phosphate can stabilize schwertmannite by the formation of strong surface complexes, preventing thus schwertmannite ageing (Schoepfer et al., 2017, 2019b). Moreover, the increase in P occurs with an increase in Fe(III) in the poorly ordered metal oxyhydroxide phases (Fig. 4.21), indicating that schwertmannite ageing is inhibited in the presence of high concentrations of phosphate.

Uranium (IV) (Fig. 3.12) source of origin is the phosphogypsum stack, this element is immobilized by phosphate and carbonate precipitates (Hierro et al., 2013; Mehta et al., 2015; Millán-Becerro et al., 2023) and schwertmannite (Walter et al., 2003; Nishimura et al., 2009; Santofimia et al., 2022). Hence, phosphate enhances schwertmannite stability and may notably influence the U chemistry in the estuarine sediment. However, the forming of its own U-phosphate phase is also likely to occur.

Regarding to REE (Fig. 3.13), their concentrations are higher in the residual phase. However, as the pH increases, the relevance of the poorly ordered metal oxhydroxide phase in the immobilization of these elements increases, this coincides with what it has been observed in this thesis and confirms the role of schwertmannite and basaluminite on the chemistry of these elements. The estuarine conditions, especially the dilution of the REE due to the seawater mixing prevent higher accumulation of REE in the sediment via adsorption processes, resulting in standard NASC normalized patterns at high pH and depleted at low pH. However, our models highlight a high solid/liquid ratio that can be critical for sorption of REE and other elements if an unexpected increase of pollutants affect the estuary.

The studied Ce and Eu anomalies (Table 3.4) are not of relevant importance. The slightly positive anomalies of the Eu/Eu* ratios in the sediment contrast with the slightly negative anomalies in the aqueous phase, suggesting a preference for Eu to accumulate in the sediment. However, the oxic conditions of the surface waters of the estuary do not facilitate the formation of aqueous Eu^{2+} (Sverjensky, 1984). Moreover,

these anomalies could be related to the redox oscillations in the phosphogypsum waste (Papaslioti et al., 2020), this hypothesis needs further investigation.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions on REE desorption

Desorption of REEs on schwertmannite is pH dependent. At pH between 6 and 7 more than 80% of the adsorbed REEs are retained at the surface, whereas at pH between 4.5 and 6 REEs desorb to a large extent. LREEs desorb mor strongly than HREEs. Sc is more effective retained between pH \approx 4.75 and 7, with desorption only starting at pH < 5.5.

A non-electrostatic surface complexation model can reproduce the experimental results by implementing desorption reactions of monodentate and bidentate surface bindings, showing a significant influence of the monodentate desorption reactions at pH $6 > pH \ge 4.5$ and bidentate at $6 \le pH \le 7$. I, therefore, suggest a two-step desorption reaction, where adsorbed bidentate complexes are transformed onto monodentate and then desorbed. In the case of Sc only bidentate surface complexes were formed in contrast to other REEs. Further research on the relationship between the schwertmannite surface structure and Sc is warranted.

DFT simulations of the $LuSO_4^+$ solution confirm that the aqueous species has a coordination state of 8 and tends to contact ion pair with sulfate tetrahedra. The simulated structure was used in the EXAFS fittings of the Lu-schwertmannite samples.

Despite the analytical limitation of the signal, model structures of the complexes corroborate the co-existence of monodentate mononuclear and bidentate binuclear surface complexes on the schwertmannite surface. In both cases, the LuSO₄⁺ complex attaches to the most distant oxygens of the iron octahedra, leaving similar Lu-Fe distances in both fits ($R \approx 4.55$ Å). Lu-O distances are ≈ 2.33 Å for the ones with N = 6, $R \approx 2.20$ Å for those with N = 2, and Lu-S distances are ≈ 3.6 Å. Moreover, an additional Lu-S path increases the accuracy of the fitting, suggesting a role of the structural sulfate of schwertmannite on Lu stabilization at the surface.

The model distances match the peaks obtained in the d-PDFs of the Luschwertmannite samples. The same d-PDFs show that the distances of Fe-O, Fe-S and S-O remain stable after desorption. Nevertheless, the existence of some negative peaks at the Fe-Fe distance from octahedral edge-sharing (≈ 3.45 Å and ≈ 5.45 Å) suggests that the attachment of Lu sulfate modifies the Fe-Fe distances of schwertmannite. This is probably due to tweaking the octahedra to accommodate the adsorbed aqueous complex, suggesting a reversible distortion.

The results of this thesis confirm that under AMD conditions (pH < 5) REEs are poorly retained by schwertmannite. However, under estuary conditions (pH between 5 and 8), schwertmannite retains the adsorbed REEs in varying degrees. It is probable that the estuary of Huelva is a geochemically favourable system for REEs retention by schwertmannite. Nevertheless, although further field data are necessary to confirm these findings, it is necessary to study the interactions between REEs and oxyanions at the surface of schwertmannite to have a better understanding of REE retention in complex geochemical systems.

5.2 Conclusions on the effect of ionic strength on the adsorption of REE

The affinity of REEs for schwertmannite and basaluminite is affected by physicochemical parameters under the AMD-impacted estuarine conditions (pH = 3-7 and ionic strength = 0.25-0.5 M).

Bidentate and monodentate coordinations in REEs are observed on schwertmannite surface. At high pH, the REE adsorption is strong and characterized by bidentate ligands (between 80% and 100% at pH 6.5 for LREE and HREE, respectively), whereas at low pH the adsorption capacity is reduced and shows monodentate ligands (between 10% and 15% at pH 4.5 for LREE and HREE, respectively). However, the surface retention capacity of schwertmannite remains constant in a broad range of ionic strengths (mostly controlled by Cl^- concentration), even though a high Cl^- concentration reduces the relative proportion of REE-SO₄⁺ species.

Although pH affects the REE affinity for basaluminite, the adsorption is also affected by the REE atomic number, especially at high pH, where LREEs are significantly less adsorbed (18% at pH 6.5) than HREEs (90% at pH 6.5). Despite the limitations of the EXAFS analysis, best fittings indicate that the REE adsorption onto basaluminite is controlled by monodentate binuclear and monodentate mononuclear inner-sphere ligands, but also by outer-sphere coordination in the case of LREEs. The

size of the REE-SO₄⁺ molecule is the key parameter in the REE adsorption mechanism. A larger size of LREEs increases the distance between the molecule and the basaluminite surface, facilitating the formation of outer-sphere ligands which are more sensitive to ionic strength than covalent monodentate binuclear inner-sphere ligands.

The results of this thesis provide new insights into the behavior of REEs and their interaction with newly formed Fe- and Al-oxyhydroxysulfate nanominerals (i.e., schwertmannite and basaluminite) in areas affected by AMD. The affinity of REEs for schwertmannite and basaluminite surfaces indicates that colloids of these minerals in the estuary water could remove aqueous REEs, especially at pH of 6.5. Therefore, the thermodynamic parameters (Log K_{REE}) obtained in our study will be useful to predict the geochemical behavior of REEs during AMD neutralization in environments with high ionic strength (i.e., the estuary of Ria de Huelva). Further research is warranted to have a full mechanistic understanding of the effect of ionic strength on LREE adsorption onto schwertmannite and basaluminite as well as to correlate the REE atomic number with outer-sphere coordination.

5.3 Conclusions on the role of schwertmannite and basaluminite on the retention of REEs and other critical elements in the estuary of Ría the Huelva

According to the field and model data of this thesis, three processes that affect the geochemistry of the estuary of Ría de Huelva are identified:

i) Mixing between AMD-river water and seawater is responsible for the behaviour of pH and conservative elements (Na, Ca, B, K, Rb, Mg and Sr). Some mining-related heavy metals (e.g., Cd, Ni, Zn and Mn) may also be considered conservative since they present a similar behaviour. However, large volumes of seawater are required to neutralize the acidity of the river water (in 1 L of AMD-seawater mixture, 95% must be seawater to attain a pH of 6.2).

ii) Precipitation of iron and aluminium oxy-hydroxysulfates (colloids) occur as direct consequence of the increase in pH and the high concentrations of aqueous Fe and Al. These newly formed colloids, which consist of poorly ordered material, can retain other elements (i.e., Cu, Pb, Cr, As, P, REEs and smaller amounts of Zn, Co, Ni and Mn) via sorption and/or coprecipitation. As sorption is affected by pH, REEs are more abundant into these phases under high pH conditions. Other elements, such as As, are

more plentiful in the sediment at acidic pH and their concentration is reduced as pH increases. Our REE model, which combines mixing and adsorption processes, is able to reproduce the behaviour of the aqueous REEs, requiring high S/L ratios at pH \ge 3.5. At this pH, precipitation of schwertmannite occurs, which is later followed by basaluminite at pH = 4.5. The high S/L ratio in the model is necessary to match the field data and is only possible if also the sediment (in addition to the colloids) participates in the reactions. Below this pH some adsorption does occur but requiring a smaller S/L ratio. The smaller ratio could be brought about by sediment and/or colloid remobilization via tidal dynamics.

iii) The phosphogypsum stack from a nearby phosphate fertilizer plant has a notorious impact on the geochemistry of the surrounding estuarine environment. A characteristic feature of this process is that the release of high quantities of phosphate, which is shown in earlier works and observed in our sequential extractions, contributes to maintain the Fe stability in the poorly ordered oxyhydroxysulfate phases (schwertmannite). This in turn enhances the capacity of retaining other elements (U and REEs) released by the phosphogypsum or transported by the AMD-impacted river.

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APPENDIX A: Tables and Figures related to REE adsorption

Table A1. Equilibrium constants for aqueous speciation of Sc, Y and lanthanides (Ln) with different ligands at T = 298 K and I = 0.05 M.

reaction	log _L βn	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ref.
$Ln^{3+} + H_2O = Ln(OH)^{2+} + H^+$	log _{OH} β* ₁	-4.31	-7.8	-8.81	-8.34	-8.32	-8.18	-7.84	-7.76	-7.83	-7.64	-7.59	-7.56	-7.52	-7.39	-7.45	-7.27	а
$Ln^{3+} + 2H_2O = Ln(OH)_2^+ + 2H^+$	$\log_{OH}\beta *_2$	-9.7	-16.4	-18.14	-17.6	-17.27	-17.04	-16.51	-16.37	-16.37	-16.18	-16.1	-16.07	-15.96	-15.88	-15.74	-15.67	b, h
$Ln^{3+} + 3H_2O = Ln(OH)_3 + 3H^+$	$\log_{OH}\beta *_3$	-16.1	-25.99	-27.9	-27.23	-26.63	-26.4	-25.91	-25.41	-25.28	-25.08	-24.83	-24.56	-24.35	-24.18	-23.85	-23.85	b, h
$Ln^{3+} + CO_3^{2-} = LnCO_3^+$	$\log_{CO3}\beta_1$		7.48	6.73	7.06	7.23	7.28	7.46	7.48	7.39	7.46	7.56	7.55	7.61	7.68	7.81	7.75	с
$Ln^{3+} + HCO_3^- = LnHCO_3^{2+}$	$\log_{HCO3}\beta_1$		2.32	2.34	2.31	2.25	2.28	2.34	2.47	2.36	2.46	2.5	2.46	2.49	2.52	2.53	2.49	с
$Ln^{3+} + 2CO_3^{2-} = Ln(CO3)_2^{-}$	$\log_{CO3}\beta_2$		12.63	11.3	11.76	12.08	12.17	12.53	12.63	12.48	12.78	12.91	13	13.12	13.27	13.3	13.37	с
$Ln^{3+} + NO_3^- = LnNO_3^{2+}$	$\log_{NO3}\beta_1$			0.58	0.69	0.69	0.79	0.78	0.83	0.47	0.51	0.15	0.25	0.15	0.2	0.25	0.56	d
$Ln^{3+} + F^{-} = LnF^{2+}$	$\log_{F}\beta_{1}$		3.97	3.11	3.29	3.35	3.29	3.61	3.72	3.71	3.83	3.88	3.78	3.77	3.77	3.84	3.74	e
$Ln^{3+} + 2F^{-} = LnF_2$	$\log_{F}\beta_2$		6.35	5.16	5.48	5.66	5.66	5.99	6.11	6.07	6.24	6.29	5.98	5.96	6.09	6.31	6.31	e
$Ln^{3+} + SO_4^{2-} = LnSO_4^+$	$\log_{SO4}\beta_1$	4.18	3.5	3.61	3.61	3.62	3.6	3.63	3.64	3.61	3.59	3.57	3.54	3.51	3.48	3.46	3.44	f, h
$Ln^{3+} + Cl^{-} = LnCl^{2+}$	$\log_{Cl}\beta_1$		0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	g

a: Klugness and Byrne, 2000

b: Lee and Byrne, 92

c: Luo and Byrne, 2004

d: Millero, 1992

e: Luo and Millero, 2004

f: Schijf and Byrne, 2004

g: Luo and Byrne, 2001

h: Wood and Samson, 2006 (for Sc speciation).

Table A2 REE and Fe concentrations calculated from digestions of pure schwertmannite, after adsorption, and Lu-rich schwertmannite (2840 ppm SO₄ solutions; $1 \text{ g } L^{-1}$ ratio).

	Pure		Adsorption	l	Lu-schwertmannite			
	Concentration (mg kg _{sch} ⁻¹)	Mole Mole _{Sch} ⁻¹	Concentration (mg kg _{sch} ⁻¹)	Mole Mole _{Sch} ⁻¹	Concentration (mg kg _{sch} ⁻¹)	Mole Mole _{Sch} ⁻¹		
Fe	481696.81	7.91	462766.50	7.60	467728.23	7.68		
Sc	0.00	0.00	1088.84	0.02	0.00	0.00		
Y	0.00	0.00	1010.49	0.01	0.00	0.00		
La	0.00	0.00	970.50	0.0064	0.00	0.00		
Ce	0.00	0.00	969.23	0.0063	0.00	0.00		
Pr	0.00	0.00	1057.10	0.0069	0.00	0.00		
Nd	0.00	0.00	920.61	0.0059	0.00	0.00		
Sm	0.00	0.00	1007.61	0.0061	0.00	0.00		
Eu	0.00	0.00	994.66	0.0060	0.00	0.00		
Gd	0.00	0.00	899.43	0.0052	0.00	0.00		
Тb	0.00	0.00	918.66	0.0053	0.00	0.00		
Dy	0.00	0.00	1014.37	0.0057	0.00	0.00		
Но	0.00	0.00	972.49	0.0054	0.00	0.00		
Er	0.00	0.00	1014.11	0.0056	0.00	0.00		
Tm	0.00	0.00	1012.83	0.0055	0.00	0.00		
Yb	0.00	0.00	1027.24	0.0054	0.00	0.00		
Lu	0.00	0.00	970.97	0.0051	6663.00	0.03		

Table A3 Log K_{REE} values and the respective errors for bidentate and monodentate complexes at I = 0.25 M and I = 0.5 M. In calculations, n = 2 for bidentate complexes and n = 1 for monodentate complexes.

Element	Bidentate complexes	I =0.25 log K	Error	I=0.5 log K	Error	Monodentate complexes	I=0.25 log K	Error	I=0.5 log K	Error
Y	$(XO)_2 YSO_4^-$	-7.67	0.16	-7.61	0.12	$XOYSO_4$	-2.10	0.13	-2.08	0.15
La	(XO) ₂ LaSO ₄ -	-8.00	0.22	-7.97	0.15	$XOLaSO_4$	-2.43	0.11	-2.44	0.11
Ce	$(XO)_2CeSO_4$	-7.71	0.19	-7.60	0.22	$XOCeSO_4$	-2.15	0.11	-2.08	0.09
Pr	(XO) ₂ PrSO ₄ -	-7.57	0.18	-7.47	0.17	XOPrSO_4	-2.00	0.11	-1.94	0.11
Nd	(XO) ₂ NdSO ₄ -	-7.52	0.17	-7.39	0.17	XONdSO_4	-1.95	0.12	-1.86	0.10
Sm	$(XO)_2SmSO_4$	-7.37	0.17	-7.23	0.18	XOSmSO_4	-1.80	0.12	-1.71	0.10
Eu	(XO) ₂ EuSO ₄ -	-7.40	0.16	-7.27	0.15	$XOEuSO_4$	-1.83	0.13	-1.74	0.13
Gd	(XO) ₂ GdSO ₄ -	-7.34	0.18	-7.11	0.17	$\rm XOGdSO_4$	-1.77	0.12	-1.58	0.11
Tb	(XO) ₂ TbSO ₄ -	-7.39	0.16	-7.23	0.15	XOTbSO_4	-1.82	0.13	-1.71	0.14
Dy	(XO) ₂ DySO ₄ -	-7.36	0.16	-7.26	0.12	$XODySO_4$	-1.79	0.14	-1.73	0.15
Но	(XO) ₂ HoSO ₄ -	-7.45	0.15	-7.33	0.14	$XOHoSO_4$	-1.88	0.15	-1.94	0.24
Er	(XO) ₂ ErSO ₄ -	-7.25	0.14	-7.10	0.14	$XOErSO_4$	-1.69	0.15	-1.57	0.14
Tm	(XO) ₂ TmSO ₄ -	-7.32	0.17	-7.21	0.13	$XOTmSO_4$	-1.76	0.13	-1.68	0.15
Yb	(XO) ₂ YbSO ₄ -	-7.16	0.15	-7.04	0.14	$XOYbSO_4$	-1.59	0.15	-1.51	0.14
Lu	(XO) ₂ LuSO ₄ -	-7.18	0.14	-7.02	0.15	$XOLuSO_4$	-1.61	0.15	-1.49	0.14

Element	Complexes	I=0.25 log K	Error	I=0.5 log K	Error	_
Sc	$(XO)_2ScSO_4^-$	-5.23	0.12	-5.31	0.03	
Y	$XOYSO_4$	-2.77	0.05	-2.56	0.06	
La	$XOLaSO_4$	-3.4	0.13	-3.10	0.12	
Ce	$XOCeSO_4$	-3.19	0.1	-3.00	0.13	
Pr	$XOPrSO_4$	-2.95	0.1	-2.92	0.099	
Nd	$XONdSO_4$	-3.12	0.07	-2.84	0.07	
Sm	$XOSmSO_4$	-2.97	0.04	-2.67	0.08	
Eu	XOEuSO ₄	-2.86	0.03	-2.65	0.05	
Gd	$\rm XOGdSO_4$	-2.80	0.04	-2.45	0.05	
Tb	$XOTbSO_4$	-2.65	0.04	-2.35	0.08	
Dy	$XODySO_4$	-2.69	0.04	-2.45	0.03	
Но	$XOHoSO_4$	-2.59	0.05	-2.31	0.06	
Er	$XOErSO_4$	-2.53	0.03	-2.35	0.03	
Tm	$XOTmSO_4$	-2.44	0.09	-2.13	0.02	
Yb	$XOYbSO_4$	-2.30	0.04	-2.12	0.04	
Lu	$XOLuSO_4$	-2.17	0.01	-2.10	0.05	

Table A4 Log KREE values	and respective	e errors for mo	onodentate con	nplexes. In c	calculations n =	= 1.


6 pН

5.5

3.0

5

-5.1598 + 1.6729x R= 0.99836

6.5

7

7.5





Figure A3a. Linear regressions obtained from experimental REE adsorption onto schwertmannite at I = 0.25 M using Eq. 4.





and experimental results (orange triangles) of REEs-schwertmannite at I = 0.25 M. Green, blue and purple lines represent the model with only monodentate, only bidentate and including both surface complexes,

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and experimental results (orange triangles) of REEs-schwertmannite at I = 0.5 M. Green, blue and purple lines represent the model with only monodentate, only bidentate and







Figure A6a. Adsorption model (purple lines) and experimental results (orange triangles) of REEsbasaluminite at I = 0.25 M.



Figure A6b. Adsorption model (purple lines) and experimental results (orange triangles) of REEsbasaluminite at I = 0.5 M.

APPENDIX B: PhreeqC input files

Model B1: Desorption of REEs from schwertmannite

DESORCIO REE SOLUTION SPECIES SURFACE MASTER SPECIES Х ХОН SURFACE SPECIES XOH = XOHlog k 0.0 2XOH + YSO4 + = (XO) 2SO4Y - + 2H +log_k -7.62 2XOH + LaSO4 + = (XO) 2SO4La - + 2H +log_k -7.98 2XOH + CeSO4 + = (XO) 2SO4Ce - + 2H +log_k -7.77 $2XOH + PrSO\overline{4} + = (XO) 2SO4Pr - + 2H +$ log_k -7.60 $2XOH + NdSO\overline{4} + = (XO) 2SO4Nd - + 2H +$ log k -7.49 $2XOH + SmSO\overline{4} + = (XO) 2SO4Sm - + 2H +$ log k -7.39 $2XOH + EuSO\overline{4} + = (XO) 2SO4Eu - + 2H +$ log_k -7.37 $2XOH + GdSO\overline{4} + = (XO) 2SO4Gd - + 2H +$ log k -7.47 2XOH + TbSO4 + = (XO) 2SO4Tb - + 2H +log_k -7.34 $2XOH + DySO\overline{4} + = (XO) 2SO4Dy - + 2H +$ log k -7.37 $2XOH + HoSO\overline{4} + = (XO) 2SO4Ho - + 2H +$ log k -7.36 $2XOH + ErSO\overline{4} + = (XO) 2SO4Er - + 2H +$ log k -7.31 $2XOH + TmSO\overline{4} + = (XO) 2SO4Tm - + 2H +$ log k -7.21 2XOH + YbSO4 + = (XO) 2SO4Yb - + 2H +log k -7.08 2XOH + LuSO4 + = (XO) 2SO4Lu - + 2H +log k -7.06 #MONODENTATES XOH + YSO4 + = XOSO4Y + H +log k -1.92 XOH + LaSO4 + = XOSO4La + H +log k -2.28 XOH + CeSO4 + = XOSO4Ce + H+log k -2.00 XOH + PrSO4 + = XOSO4Pr + H+log k -1.90 XOH + NdSO4 + = XOSO4Nd + H +log_k -1.79

ХОН	+	SmSO4+ =	= XOSO4Sm + H+
хон	+	log_k EuSO4+ =	-1.69 = XOSO4Eu + H+
		log k	-1.68
ХОН	+	GdSO4+ =	= XOSO4Gd + H+ -1 77
ХОН	+	TbSO4+ =	= XOSO4Tb + H+ -1 62
ХОН	+	DySO4+ =	= XOSO4Dy + H+ -1 64
ХОН	+	HoSO4+ =	= XOSO4Ho + H+
ХОН	+	ErSO4+ =	= $XOSO4Er + H+$ = 1.59
ХОН	+	TmSO4+ =	= XOSO4Tm + H+
ХОН	+	YbSO4+ =	= XOSO4Yb + H+
ХОН	+	LuSO4+ = log_k	-1.38 = XOSO4Lu + H+ -1.62
SOLU	JTI	ON 1	
	te	emp	25
	рH	I	2.5
	pe	dorr	4 O2(g) -0.67
	Te	ite	pe
	de	nsitv	1
	C	(4)	1e - 0.17 CO2(a) - 3.4
	Na	/ L	459.79538
	S ((6)	1921.2 charge
	-w	ater	1 # kg
SOLT	דידינ	ON 2	
	te		25
	рH	[5.75
	pe	2	4 O2(q) -0.67
	re	edox	ре
	ur	its	ppm
	de	ensity	1
	С ((4)	1e-17 CO2(g) -3.4
	Се	e(3)	1
	Dy	7(3)	1
	Εr	(3)	1
	Εu	ι(3)	1
	Gc	1(3)	1
	Нc	(3)	1
	La	ı(3)	1
	Lu	ı(3)	1
	Na	L	459.79538
	Nc	1(3)	1
	Pr	(3)	1
	S (6)	1921.2 charge
	Sc		1
	Sm	l(J)	1
	тr) (J) (J)	1
	.T.U	1(3)	1
	í vl-	(2)	1
	_T.	ater	⊥ 1 # ka
	W	aler	т ш ку

```
SURFACE 1
-sites units density
-no edl
-equilibrate 2
       ХОН 4.75 100 1
PHASES
       Fix_H+
       H+ = H+
        log k 0.0
END
SELECTED OUTPUT 1
                        selected output Desorcio REE1.sel
   -file
    -molalities (XO)2SO4Y- (XO)2SO4La- (XO)2SO4Ce- (XO)2SO4Pr-
(XO) 2SO4Nd-
    -molalities (XO)2SO4Sm- (XO)2SO4Eu- (XO)2SO4Gd- (XO)2SO4Tb-
(XO) 2SO4Dy-
    -molalities (XO)2SO4Ho- (XO)2SO4Er- (XO)2SO4Tm- (XO)2SO4Yb-
(XO)2SO4Lu-
    -molalities XOSO4Y XOSO4La XOSO4Ce XOSO4Pr XOSO4Nd
    -molalities XOSO4Sm XOSO4Eu XOSO4Gd XOSO4Tb XOSO4Dy
    -molalities XOSO4Ho XOSO4Er XOSO4Tm XOSO4Yb XOSO4Lu
    -totals Sc Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -3.5
                      NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
      Fix H+ -3.75 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.00 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.25 NaOH
                             10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.5 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.75 NaOH
                             10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
```

Fix H+ -5.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -5.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix_H+ -6.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.25 NaOH 10.0

Model B2: Adsorption at different ionic strengths

B2.1 Basaluminite I = 0.25 M

ADSORPTION REE Bas 0.25 SOLUTION SPECIES SURFACE MASTER SPECIES X XOH SURFACE SPECIES XOH = XOHlog k 0.0 #MONODENTATES XOH + YSO4 + = XOSO4Y + H +log k -2.77 XOH + LaSO4 + = XOSO4La + H+log k -3.4 XOH + CeSO4 + = XOSO4Ce + H +log k -3.19 XOH + PrSO4 = XOSO4Pr + H+log k -2.95 XOH + NdSO4 + = XOSO4Nd + H +log k -3.12 XOH + SmSO4 = XOSO4Sm + H +log_k -2.97 XOH + EuSO4 = XOSO4Eu + H+log_k -2.86 XOH + GdSO4 + = XOSO4Gd + H +log_k -2.80 XOH + TbSO4 + = XOSO4Tb + H +log_k -2.65 XOH + DySO4 + = XOSO4Dy + H +log_k -2.69 XOH + HoSO4 = XOSO4Ho + H+log_k -2.59 XOH + ErSO4 + = XOSO4Er + H +log_k -2.53 XOH + TmSO4 + = XOSO4Tm + H+log_k -2.44 XOH + YbSO4 + = XOSO4Yb + H+log k -2.30 XOH + LuSO4 + = XOSO4Lu + H+log k -2.17 SOLUTION 1 25 temp 3 рΗ pe 4 O2(g) -0.67 redox pe units ppm density 1 C(4) 1e-017 CO2(g) -3.4 Ce(3) 1 Cl(-1) 0.038 mol/kgs Dy(3) 1 Er(3) 1 Eu(3) 1 Gd(3) 1 Ho(3) 1

```
La(3) 1
   Lu(3)
            1
           0.0001 charge
   N(5)
           0.078 Mol/kgs
   Na
   Nd(3)
            1
   Pr(3)
            1
   S(6)
           0.02 Mol/kgs
            1
   Sc
    Sm(3)
            1
   Tb(3)
            1
            1
   Tm(3)
    Y
             1
   Yb(3)
             1
    -water 1 # kg
SURFACE 1
-sites units density
-no edl
       XOH 4.6 87 1
PHASES
       Fix H+
       H+ = H+
       log_k 0.0
END
SELECTED OUTPUT 1
   -file
                        selected output REEbas0.25.sel
    -molalities XOSO4Y XOSO4La XOSO4Ce XOSO4Pr XOSO4Nd
    -molalities XOSO4Sm XOSO4Eu XOSO4Gd XOSO4Tb XOSO4Dy
    -molalities XOSO4Ho XOSO4Er XOSO4Tm XOSO4Yb XOSO4Lu
   -totals Sc Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -3.5 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -3.75 NaOH
                            10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.00 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.25 NaOH
                             10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.5 NaOH 10.0
END
```

USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix^{H+} -4.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -5.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix H+ -6.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix H+ -6.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.25 NaOH 10.0

B2.2 Schwertmannite I = 0.25 M

REE Lu

SOLUTION_SPECIES

SURFACE_MASTER_SPECIES X XOH

SURFACE_SPECIES

XOH = XOH log_k 0.0

#BIDENTATES

2ХОН	+	YSO4+ = (XO) 2SO4Y- +	2ŀ	I+
		log_k -7.66591		
2ХОН	+	LaSO4+ = (XO) 2SO4La-	+	2H+
		log_k -7.99606		
2ХОН	+	$CeSO\overline{4}+ = (XO) 2SO4Ce-$	+	2H+
		log_k -7.71477		
2ХОН	+	PrSO4+ = (XO) 2SO4Pr-	+	2H+
		log_k -7.57374		
2ХОН	+	NdSO4+ = (XO) 2SO4Nd-	+	2H+
		log_k -7.51567		
2ХОН	+	SmSO4+ = (XO) 2SO4Sm-	+	2H+
		log_k -7.37372		
2ХОН	+	EuSO4+ = (XO) 2SO4Eu-	+	2H+
		log_k -7.39742		
2хон	+	GdSO4+ = (XO) 2SO4Gd-	+	2H+
		log_k -7.3408		
2ХОН	+	TbSO4+ = (XO) 2SO4Tb-	+	2H+
		log_k -7.38733		
2ХОН	+	DySO4+ = (XO) 2SO4Dy-	+	2H+
		log_k -7.36126		
2ХОН	+	HoSO4+ = (XO) 2SO4Ho-	+	2H+
		log_k -7.45313		
2хон	+	ErSO4+ = (XO) 2SO4Er-	+	2H+
		log_k -7.25448		
2XOH	+	TmSO4+ = (XO) 2SO4Tm-	+	2H+
		log_k -7.3216		
2XOH	+	YbSO4+ = (XO) 2SO4Yb-	+	2H+
		log_k -7.15888		0 1
2ХОН	+	LuSO4+ = (XO) 2SO4Lu-	+	2H+
		log_k -7.17623		
#MON	יחר			
VOU .	ית ר ד	X = X = X = X = X = X = X = X = X = X =		
XOII	. 1	$\log k = 2.2$		
V∩u .	⊥ т	$\frac{1}{2} \sum_{n=1}^{\infty} \sum_{i=1}^{n-2} \sum_{i=1}^{\infty} \sum_{i=1$		
7011	· 1	log k = 2.52		
V∩H -	+ C	$\frac{1}{2} \sum_{k=1}^{\infty} \frac{1}{2} \sum_{k=1}^{\infty} \frac{1}$		
A011		2 = 2 = 2 = 2 = 2 = 1 = 2 = 1 = 2 = 1 = 2 = 1 = 2 = 1 = 2 = 2		

		log_k	-2.15		
ХОН	+	PrSO4+ =	XOSO4Pr	+	H+
		log_k	-2.00		
ХОН	+	NdSO4+ =	XOSO4Nd	+	H+
		log_k	-1.95		
XOH	+	SmSO4+ =	XOSO4Sm	+	H+
		log_k	-1.80		

XOH + EuSO4 + = XOSO4Eu + H+

log k -1.83 XOH + GdSO4 + = XOSO4Gd + H +log k -1.77 XOH + TbSO4 + = XOSO4Tb + H+log k -1.82 XOH + DySO4 + = XOSO4Dy + H+log_k -1.79 XOH + HoSO4 + = XOSO4Ho + H+log_k -1.88 XOH + ErSO4 + = XOSO4Er + H+log_k -1.69 XOH + TmSO4 + = XOSO4Tm + H+log k -1.76 XOH + YbSO4 + = XOSO4Yb + H+log k -1.59 XOH + LuSO4 + = XOSO4Lu + H+log_k -1.61 SOLUTION 1 25 temp 3 рН 4 O2(g) -0.67 pe pe redox units ppm density 1 C(4) 1e-017 CO2(g) -3.4 Ce(3) 1 Cl(-1) 0.038 mol/kgs Dy(3) 1 Er(3) 1 Eu(3) 1 Gd(3) 1 Ho(3) 1 La(3) 1 1 Lu(3) 0.0001 charge N(5) 0.078 Mol/kgs Na Nd(3) 1 Pr(3) 1 0.02 Mol/kgs S(6) Sc 1 1 Sm(3) 1 Tb(3) Tm(3) 1 1 Υ Yb(3) 1 -water 1 # kg SURFACE 1 -sites units density -no edl ХОН 4.75 100 1 PHASES Fix H+ H+ = H+log k 0.0

END

SELECTED OUTPUT 1 selected output sch0.25n1.sel -file -molalities (XO)2SO4Y- (XO)2SO4La- (XO)2SO4Ce- (XO)2SO4Pr-(XO)2SO4Nd--molalities (XO)2SO4Sm- (XO)2SO4Eu- (XO)2SO4Gd- (XO)2SO4Tb-(XO) 2SO4Dy--molalities (XO)2SO4Ho- (XO)2SO4Er- (XO)2SO4Tm- (XO)2SO4Yb-(XO)2SO4Lu--molalities XOSO4Y XOSO4La XOSO4Ce XOSO4Pr XOSO4Nd -molalities XOSO4Sm XOSO4Eu XOSO4Gd XOSO4Tb XOSO4Dy -molalities XOSO4Ho XOSO4Er XOSO4Tm XOSO4Yb XOSO4Lu -totals Sc Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -3.5 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -3.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix H+ -4.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.5 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1

```
Fix H+ -5.75 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix<sup>H+</sup> -6.00 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
     Fix_H+ -6.25 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
      Fix H+ -6.50 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
       Fix H+ -6.75 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
       Fix H+ -7.00 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
       Fix H+ -7.25 NaOH 10.0
```

B2.3 Basaluminite I = 0.5 M

```
SOLUTION SPECIES
SURFACE_MASTER_SPECIES
        Х ХОН
SURFACE SPECIES
XOH = XOH
      log k 0.0
#MONODENTATES
XOH + YSO4 + = XOSO4Y + H +
       log_k -2.56
XOH + LaSO4 + = XOSO4La + H+
       log_k -3.10
XOH + CeSO4 + = XOSO4Ce + H +
       log k -3.00
XOH + PrSO4 = XOSO4Pr + H+
       log k -2.92
XOH + NdSO4 + = XOSO4Nd + H +
       log k -2.84
XOH + SmSO4 = XOSO4Sm + H + log_k -2.67
```

REE Bas 0.5

3.4

PHASES

Fix_H+

```
H+ = H+
       log k 0.0
END
SELECTED OUTPUT 1
   -file
                        selected_output_REEbas0.5.sel
                        Sc Y La Ce Pr Nd Sm
   -totals
                        Eu Gd Tb Dy Ho Er Tm
                        Yb Lu
                        XOSO4Y XOSO4La XOSO4Ce XOSO4Pr
   -molalities
                        XOSO4Nd XOSO4Sm XOSO4Eu XOSO4Gd
                        XOSO4Tb XOSO4Dy XOSO4Ho XOSO4Er
XOSO4Tm XOSO4Yb XOSO4Lu
    -saturation indices
                       Basaluminite
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -3.0
                     NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
     Fix H+ -3.25 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
       Fix H+ -3.5
                     NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
    Fix H+ -3.75 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
      Fix H+ -4.00 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.25 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.5 NaOH 10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -4.75 NaOH
                            10.0
END
USE solution 1
USE surface 1
EQUILIBRIUM PHASES 1
       Fix H+ -5.00 NaOH 10.0
END
```

USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix^{H+} -5.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -5.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix H+ -6.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -6.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.5 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -7.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1

END

B2.4 Schwertmannite I = 0.5 M

REE Lu

SOLUTION_SPECIES

SURFACE_MASTER_SPECIES X XOH

SURFACE_SPECIES

XOH =	XOH		
	log k O.	0	
2XOH	$+ YSO\overline{4} + = ($	XO)2SO4Y- +	2H+
	log_k	-7.61	
2XOH	+ LaSO4+ =	(XO)2SO4La-	+ 2H+
	log_k	-7.97	
2XOH	+ CeSO4 + =	(XO) 2SO4Ce-	+ 2H+
01/01/	Log_k	-7.60	
ZXOH	+ PrSO4 + =	(XO) 2S04Pr-	+ ZH+
22011	LOG_K	-7.47	
ZXUH	+ NUSO4+ -	(XU)2504Nu-	т илт
2204	109_K	-7.39 (VO)290/9m-	
ZAUR	$+ \sin (304 + -)$	(XU)23043III-	т 2пт
2204	TOG_K T Engolt -	(VO) 2 CO (E) = -	
27011	log k	(XO)2304Bu-	1 2111
2⊻∩н	+ CdSO(+ =	(XO) 2SO/Cd-	+ 24+
27011	log k	-7 11	1 2111
2⊻∩н	$\pm Tbg_k$	(XO) 2SO/TTh-	+ 24+
27011	log k	-7 23	1 2111
2XOH	$\pm DvSO4 \pm =$	(XO) 2SO4Dv -	+ 2H+
271011	log k	-7 26	' 211 '
2XOH	$+ H_0 S_0 4 + =$	(XO) 2SO4Ho-	+ 2H+
211011	log k	-7 33	
2XOH	+ ErSO4 + =	(XO) 2SO4Er-	+ 2H+
-	log k	-7.10	
2XOH	+ TmSO4+ =	(XO)2SO4Tm-	+ 2H+
	log k	-7.21	
2XOH	+ YbS04+ =	(XO)2SO4Yb-	+ 2H+
	log k	-7.04	
2XOH	+ LuSO4+ =	(XO)2SO4Lu-	+ 2H+
	log_k	-7.02	
#MONO	DENTATES		
XOH +	YSO4+ = XO	SO4Y + H+	
	log_k	-2.08	
XOH +	LaSO4+ = X	OSO4La + H+	
	log_k	-2.44	
XOH +	CeSO4+ = X	OSO4Ce + H+	
	log_k	-2.08	
XOH +	PrSO4+ = X	OSO4Pr + H+	
	log_k	-1.94	
XOH +	NdSO4+ = X	OSO4Nd + H+	
	log_k	-1.86	

ХОН	+	SmSO4+ = XOSO4Sm + H+
ХОН	+	EuSO4+ = XOSO4Eu + H+
ХОН	+	$\log_{k} -1./4$ $GdSO4+ = XOSO4Gd + H+$
ХОН	+	\log_k -1.58 TbSO4+ = XOSO4Tb + H+
ХОН	+	$\log_{k} -1./1$ DySO4+ = XOSO4Dy + H+
ХОН	+	$\frac{109}{k} = \frac{1.73}{100} + H + \frac{1.04}{100}$
ХОН	+	$\frac{109}{k} = 1.94$ ErSO4+ = XOSO4Er + H+
ХОН	+	$\frac{109 \text{ K}}{1.37}$ $TmSO4+ = XOSO4Tm + H+$ $\log k = -1.68$
ХОН	+	$\frac{100 \text{ k}}{\text{YbSO4+}} = \frac{1.60}{\text{XOSO4Yb}} + \text{H+}$
ХОН	+	$log_k = 1.31$ LuSO4+ = XOSO4Lu + H+ $log_k = -1.49$
SOLU	JTI	ION 1
	te pH	emp 25 H 3
	pe	4 02(g) -0.67
	re	edox pe
	de	ensity 1
	С	(4) 1e-017 CO2(g)
	Се	e(3) 1
	C Dr	L(-1) 0.2 mol/kgs
	Dy Ei	(3) = 1
	Ει	1(3) 1
	Go	1(3) 1
	Нc	b (3) 1
	Lá	a(3) = 1
	ы N	(5) 0.001 charge
	Na	a 0.24 Mol/kgs
	No	d(3) 1
	Pı	(3) 1 (b)
	5	$(6) \qquad 0.02 \text{ MO1/kgs}$
	Sr	n(3) 1
	Τł	b(3) 1
	Tr	n(3) 1
	Y V	(3) 1
	-1	vater 1 # kg
SURI	FAC	CE 1
-sit	ze,	s units densitv
-no	ec	11
		XOH 4.75 100 1
	~	
PHAS	SES	S Fiv H+
		$H^+ = H^+$

-3.4

log_k 0.0

END

SELECTED OUTPUT 1 selected output_sch0.25n1.sel -file -molalities (XO)2SO4Y- (XO)2SO4La- (XO)2SO4Ce- (XO)2SO4Pr-(XO) 2SO4Nd--molalities (XO)2SO4Sm- (XO)2SO4Eu- (XO)2SO4Gd- (XO)2SO4Tb-(XO)2SO4Dy--molalities (XO)2SO4Ho- (XO)2SO4Er- (XO)2SO4Tm- (XO)2SO4Yb-(XO)2SO4Lu--molalities XOSO4Y XOSO4La XOSO4Ce XOSO4Pr XOSO4Nd -molalities XOSO4Sm XOSO4Eu XOSO4Gd XOSO4Tb XOSO4Dy -molalities XOSO4Ho XOSO4Er XOSO4Tm XOSO4Yb XOSO4Lu -totals Sc Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -3.5 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -3.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.5 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -4.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix^{H+} -5.50 NaOH 10.0

END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -5.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -6.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.25 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.50 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix H+ -6.75 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM_PHASES 1 Fix H+ -7.00 NaOH 10.0 END USE solution 1 USE surface 1 EQUILIBRIUM PHASES 1 Fix_H+ -7.25 NaOH 10.0

Model B3: Mixing and adsorption of REEs

```
SOLUTION_SPECIES

SURFACE_MASTER_SPECIES

X XOH

Xa XaOH

SURFACE_SPECIES

#SCHWERTMANNITE

XOH = XOH

log_k 0.0

2XOH + YSO4+ = (XO)2SO4Y- + 2H+

log_k -7.60527

2XOH + LaSO4+ = (XO)2SO4La- + 2H+

log_k -7.9654

2XOH + CeSO4+ = (XO)2SO4Ce- + 2H+

log_k -7.60436
```

2ХОН	+	P	rSC)4+	=	()	XO) 2	S	041	Pr-	+	2H+
			log	ſ_k		-	7.4	46	57	73			
2ХОН	+	N	dSC)4+	=	()	XO) 2	2S	041	Nd-	+	2H+
			log	ſ_k		-	7.3	39	91	1			
2ХОН	+	S	mSC)4+	=	()	XO) 2	2S	04:	Sm-	+	2H+
			log	ſ_k		_	7.2	23	34	93			
2ХОН	+	· E	uSC)4+	=	()	XO)) 2	S	041	∃u-	+	2H+
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			log	ſ k		_	7.()З	88	07			
2ХОН	+	· L	uSC	$\overline{4}+$	=	()	XO) 2	2S	041	Lu-	+	2H+
			log	ſ_k		-	7.(01	6	24			
ХОН	+	YS	04+	- =	X	OS	041	Y	+	Н·	+		
			log	ſ_k		-	2.0	30	3				
ХОН	+	La	SO4	+ =	= 2	XO	SO	4I	a	+	H+		
			log	ſ_k		-	2.4	44	ł				
ХОН	+	Ce	S04	+ =	= 2	XO	SO,	4 C	Ce	+	H+		
			log	ſ_k		-	2.(07	7				
ХОН	+	Pr	SO4	+ =	= 2	XO	SO,	4 E	r	+	H+		
			log	ſ_k		_	1.9	94					
ХОН	+	Nd	SO4	+ =	=]	XO	SO,	4 N	Id	+	H+		
		~	Log	ſ_k		-	1.8	36)				
хон	+	Sm	SO4	+ = ,	= ;	XO	50' 1 '	4 S	Sm	+	H+		
VOII			TOG	ſ_К		-	1.	/			TT 1		
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			loc	r k	-	-	1.	94	ł				
ХОН	+	Er	so4	/ + =	= 3	XO	SO4	4 E	lr	+	H+		
			loc	r k		_	1.0	66	5				
ХОН	+	Τm	so4	(= 3	xo	SO,	4 T	'm	+	H+		
			loc	ſk		-	1.0	68	3				
ХОН	+	Yb	SO4	+ =	= 2	XO	SO,	4 Y	ľb	+	H+		
			log	ſ k		-	1.0	63	3				
ХОН	+	Lu	SO4	+ =	= 2	XO	SO,	4I	Ju	+	H+		
			log	ſ_k		-	1.0	61	-				
#BAS	AI	UM	INI	ΤE									
ХаОН	=	X	aOH -	I .									
			Loc	ſ_k	0	.0							
ХаОН	+	Υ	SO4	+ = ,	=]	Xa	US(4ر -	ŀΥ	+	H+		
			τοč	ſ_k		-	2.	56)				

XaOH	+	LaSO4+	=	XaOSO4La + H+	
XaOH	+	CeSO4+	=	-2.95 XaOSO4Ce + H+	
		log_k		-2.81	
XaOH	+	PrSO4+	=	XaOSO4Pr + H+	
ХаОн	+	IOG_K NdSO4+	=	-2.92 XaOSO4Nd + H+	
14011		log k		-2.84	
ХаОН	+	SmSO4+	=	XaOSO4Sm + H+	
		_log_k		-2.67	
ХаОН	+	EuSO4+	=	XaOSO4Eu + H+	
XaOH	+	GdSO4+	=	-2.05 XaOSO4Gd + H+	
		log k		-2.45	
ХаОН	+	TbSO4+	=	XaOSO4Tb + H+	
VeOII		log_k	_	-2.35	
хаон	+	log k	=	-2 45	
XaOH	+	HoSO4+	=	XaOSO4Ho + H+	
		log_k		-2.31	
XaOH	+	ErSO4+	=	XaOSO4Er + H+	
Х⊃ОН	+	Log_k TmsO/+	_	-2.35	
14011		log k		-2.13	
ХаОН	+	YbS04+	=	XaOSO4Yb + H+	
		log_k		-2.12	
хаОН	+	LuSO4+	=	XaOSO4Lu + H+ -2 10	
		IOG_K		2.10	
SOLUI	ΓIC	DN 1			
t	cen	np	25	5	
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1 1		dox	pe	.	
ι	ıni	lts	mc	g/kgw	
C	der	nsity	1		
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Ē	3		1.	.4683274	
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E	Br	(-1)	5.	.94	
(2 (4 7 -	1)	16	e-17 CO2(g) 14 18063	-
(Cd		0.	.0443306	
C	Ce		0.	.0380182	
C	21		0.	.0001 charge	
(0.	.3374957	
(ls.		0.	.0095958	
(Cu		9.	.5542054	
Ι	Dу		0.	.0069579	
E	Er		0.	.0036054	
t F	su F		1.	.0014029	
I	Гe	(3)	65	5.066064	
(Gd		0.	.0080954	
H T	ło		0.	.0012953	
r T	La		14 0	.0127853	
I	Li		0.	.1438358	
I	Lu		0.	.0004266	

-3.4

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Mg Mn Mo N(5) Na Nd Ni O(0) P Pb Pr Rb Pr Rb S Sb Sm Sn Sr Tb Tl Tm U V Y Y Yb Zn -water	498.4402 4.8513466 4.353e-05 0.075 3667.4564 0.023641 0.0691591 1e-09 02(g) 0.1973862 0.0503037 0.0051394 0.0373675 651.23856 0.0001016 0.0064389 5.138e-05 2.8834573 0.0012329 0.0033068 0.0004574 0.0059504 0.0001771 0.0357047 0.0028264 11.869126 1 # kg	-0.67
SOLUTION 2 temp pH pe redox units density Al As B Ba Br(-1) C(4) Ca Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe(3) Gd Ho K La Li Lu	25 7.82 7 pe mg/kgw 1 0.0806354 0.005996 3.8206561 0.0109815 93.8 1e-17 CO2(g) 458.8632 0.00284 0.00003095 0.0001 charge 0.0075214 0.0001933 0.000284 0.0239335 0.000012881 0.0000001 0.0000001 7.15 0.0048448 0.0000001 7.15 0.0048448 0.0000001 0.0000001 0.0000009 550.93872 0.00001205 0.158743 0.0000001	-3.4
Mg Mn	1367.6042 0.1641914	

Mo N(5) Na Nd Ni O(0) P Pb Pr Rb S S B S m Sn Sr Tb Tl Tm U V Y Yb Zn -wate	0. 0. 10 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.	.012030 .075 .0759.51 .000010 .003870 .003870 .000218 .000003 .113584 .000003 .113584 .000003 .27e-05 .000003 .27e-05 .000000 .000173 .000000 .003552 .002361 .000135 .000002 .001529 # kg)9 3)67 2263 2(g) 51 39 3461 49 47 39 3035 5 20 6172 37 01 23 53 2758 96		-0.67
SURFACE 2	1				
-sites_ur -no edl	nits der XOH XaOH	nsity 4.75 4.6	200 100	25 25	

-no MIX 1 1 0.9 2 0.1 SELECTED OUTPUT 1 -file ESTUARIO MIX90.sel -totals Al As B Ba Br Ca Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn END MIX 2 1 0.8 2 0.2 SELECTED OUTPUT 2 -file ESTUARIO MIX80.sel -totals Al As B Ba Br Ca Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm

		Sb V	Sn Y	Sr Yb	Tb Zn	Tl	Τm	U
END								
MIX 3 1 0.7 2 0.3								
SELECTED_OUTPUT -file -totals	3	EST Al Cl Eu Li Sb V	TUAR As Co F Lu P Sn Y	IO M B Cr Fe Mc Pb Sr Yb	MIX70 Ba Gd J Mn Pr Tb Zn	.sel Br Cu Ho Mo Rb Tl	Cd Dy K L Na S S Tm	Ce Er a Nd m U
END								
MIX 4 1 0.6 2 0.4								
SELECTED_OUTPUT -file -totals	4	ESI Al Cl Li Ni Sb V	TUAR As Co F Lu P Sn Y	IO M B Cr Fe Mc Pb Sr Yb	IIX60 Ba Gd J Mn Pr Tb Zn	.sel Br Cu Ho Mo Rb Tl	Cd Dy K L Na S S Tm	Ce Er a Nd m U
END		v	-	1.0				
MIX 5 1 0.5 2 0.5								
SELECTED_OUTPUT -file -totals	5	EST Al Cl Eu Li Sb V	TUAR As Co F Lu P Sn Y	IO M B Cr Fe Mc Pb Sr Yb	IIX50 Ba Gd Gd J Mn Pr Tb Zn	.sel Br Cu Ho Mo Rb Tl	Cd Dy K L Na S S Tm	Ce Er a Nd m U
END								
MIX 6 1 0.4 2 0.6								
SELECTED_OUTPUT -file -totals	1	EST Al Cl	TUAR As Co	IO M B Cr	1IX40 Ba c Cs	.sel Br Cu	Cd Dy	Ce Er

	Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn
END	
MIX 7 1 0.3 2 0.7	
SELECTED_OUTPUT 7 -file -totals	ESTUARIO MIX30.sel Al As B Ba Br Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn
END	
MIX 8 1 0.2 2 0.8	
SELECTED_OUTPUT 8 -file -totals	ESTUARIO MIX20.sel Al As B Ba Br Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn
END	
MIX 9 1 0.1 2 0.9	
SELECTED_OUTPUT 9 -file -totals	ESTUARIO MIX10.sel Al As B Ba Br Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn
END	
MIX 10 1 0.05 2 0.95	
SELECTED_OUTPUT 10	

-file ESTUARIO MIX5.sel -totals Al As B Ba Br Cd Ca Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn END USE mix 1 USE surface 1 END USE mix 2 USE surface 1 END USE mix 3 USE surface 1 END USE mix 4 USE surface 1 END USE mix 5 USE surface 1 END USE mix 6 USE surface 1 END USE mix 7 USE surface 1 END USE mix 8 USE surface 1 END USE mix 9 USE surface 1 END USE mix 10 USE surface 1 END SELECTED_OUTPUT 10

-file ESTUARIO MIXADS.sel -totals Al As B Ba Br Cd Ce Cl Co Cr Cs Cu Dy Er Eu F Fe Gd Ho K La Li Lu Mg Mn Mo Na Nd Ni P Pb Pr Rb S Sm Sb Sn Sr Tb Tl Tm U V Y Yb Zn