

# Modeling the behavior of the rare earth elements in acid drainages

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**Key Words:**lanthanides, yttrium, scandium, surface complexation, basaluminite, schwertmannite | **Palabras clave:**lantánidos, irio, escandio, complejación superficial, basaluminita, schwertmannita

## INTRODUCTION

Lanthanide series (from La to Lu) plus scandium (Sc) and yttrium (Y) are referred to as Rare Earth Elements (REE) according to recommendation by the International Union of Pure and Applied Chemistry (IUPAC). REE are essential raw materials for modern technological applications. In mining environments, the dissolution of Fe sulfides generates acidic solutions with  $\text{H}_2\text{SO}_4$ , and dissolution of rocks are much more intense in Acid Mine Drainage (AMD) than in the rest of weathering profiles. Once in solution, REE form sulfate complexes, which inhibit their sorption in clays and stabilizes them in the solution. Consequently, REE concentrations in AMD are orders of magnitude higher than in the rest of natural waters. Since AMD is expected to run for hundreds of years, the total reserves are virtually unlimited, and then, AMD could become a small but continuous source of REE. Moreover, due to their common use in modern industry, some toxicological studies suggest that REE could have a significant pathogenic potential. Therefore, knowing the mobility constraints of REE in natural waters and particularly in AMD is a target of interest.

REE geochemistry in AMD is strongly linked to pH, and therefore to AMD neutralization processes. Thus, when AMD effluents mix with the alkaline river water or are neutralized with limestone addition, its pH increases leading to schwertmannite (Schw) ( $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_2$ ) and basaluminite (Bas) ( $\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5(\text{H}_2\text{O})$ ) formation. At pH higher than 4.5, however, REE concentrations in the water decrease below detection levels, indicating that these elements are trapped in these two solid phases.

## SAMPLING

Water and precipitate samples were collected from several mixing points of the Odiel river catchment where an alkaline stream received an acid discharge (PO, AG, DB, TO). The Rio Tinto (RT) locality corresponds to

the reverse situation, where a small alkaline stream discharged into the Rio Tinto main stream. Finally, three solid samples of white precipitates (ES) were collected in different days at the outflow of treatment plant of Mina Esperanza, where Bas formed.

Water samples were taken with a syringe and filtered with 0.45 and 0.1  $\mu\text{m}$  filters (Millipore), stored in 125 mL-polyethylene bottles, acidified down to  $\text{pH} < 2$  with  $\text{HNO}_3$ , and cooled during transport. The solid samples were collected with a syringe from the suspended precipitates clouds and left to decant in the bottle, dried and digested. The sampling campaigns were always carried out in February-Mars, the humid season. When possible, ochre and whitish precipitates were taken separately. Water samples and the solid digested in  $\text{HNO}_3$  were analyzed by ICPMS and ICPAES.

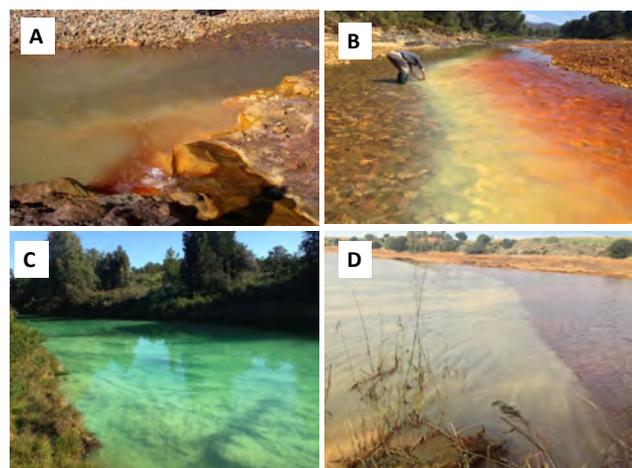


Figure 1. Pictures of the sampling points: A) precipitation of ferrhydrite (reddish) and Bas (whitish) at the mixing point of Mina Poderosa (PO) acid discharge and Odiel river; B) Precipitation of Schw (reddish) and Bas (whitish) mixing point of Agrio acidic discharge (right hand of the picture) and Odiel river (AG); C) Bas covering the bed of Debesa Boyal stream (DB); D) Bas precipitation at the mixing an alkaline stream (left-low corner) and the Tinto river (RT).

## MODEL

Sorption experiments of Sc, Y and lanthanides on Bas and Schw show that the sorption occurred at pH from 4 to 7, and increased with SO<sub>4</sub> concentration in the solution. A thermodynamic model is proposed where the formation of monodentate surface complexes of sulfate-REE aqueous species MSO<sub>4</sub><sup>+</sup> (M accounting for REE), together with the species Sc(OH)<sub>2</sub><sup>+</sup> for scandium explained the measurements. Moreover, fractionation to the solid phase increased from La to Lu, with Y in an intermediate heavy REE position. Scandium sorption occurred at lower pH (Fig. 2A) as bidentate surface complexes of both sulfate and hydroxide-REE aqueous species. Similar sorption experiments were conducted with Schw. Here, REE sorption was occurring at pH similar to Bas, although Sc was retained at one unit lower pH (Fig. 2B). The aim of the present work is to test the validity of the thermodynamic models to predict the REE behavior in AMD environments, and discuss the main limitations and uncertainties.

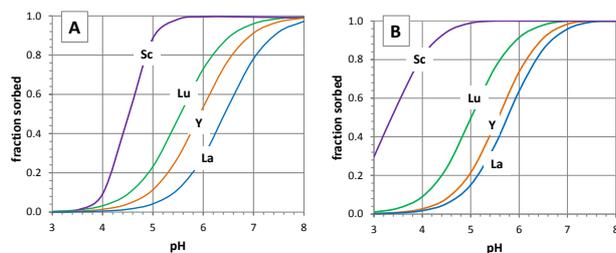


Figure 2. Variation of the fraction sorbed in Bas (A) and in Schw (B) with pH for four selected REE.

## RESULTS AND DISCUSSION

The precipitates formed at the mixing waters are made up of a mixture of Fe(III) and Al hydroxide-sulfates. When Fe and Al phases can be distinguished, they are formed by Schw and Bas, respectively. Schw does not contain REE, whereas these elements are entirely retained in Bas.

According to laboratory sorption experiments, both Schw and Bas adsorb REE at pH between 4 and 7. Therefore, the lack of REE in Schw is attributed to the formation of this mineral at pH below 4, whereas Bas precipitation occurs at pH higher than 4.5. This pH values are consistent with those measured in the pore water of the two zones, Schw and Bas, measured in neutralization columns of AMD with limestone (Ayora et al., 2016).

The surface complexation model onto the Bas surface has been used to predict the REE removal in mixing waters. The model is able to anticipate the main trend of the REE distribution pattern observed in the solid phase, regardless the AMD sulfate concentration (Fig. 3). This distribution pattern confirms the selective partition of medium and heavy REE and Y with respect to light REE.

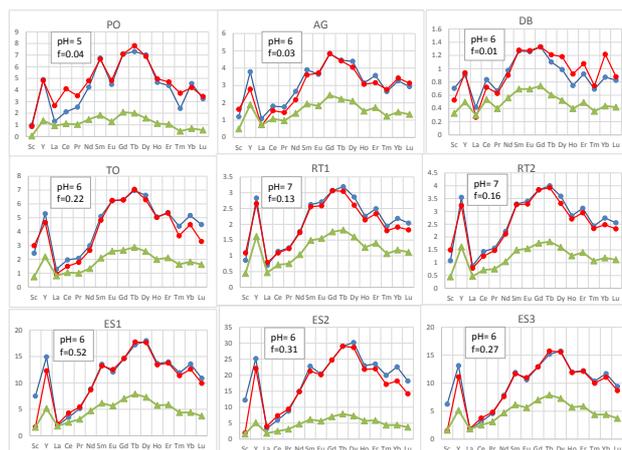


Figure 3. REE patterns of solid precipitates from the study area: analyzed (red) and predicted (blue). The concentrations of the parent AMD (green triangles) are also plotted for comparison. All the solid concentrations are normalized to the North American Shale Composite (NASC) and scaled to the same Gd value by multiplying them by a factor f.

There are, however, some uncertainties in the modeling. First, the dilution of the REE content in AMD occurring in the mixing at the same time as precipitation precludes an accurate prediction of the REE concentration in the solid. Nevertheless, the dilution factor caused by water mixing can be independently estimated from other conservative solutes, at least within the order of magnitude. A second uncertainty is the estimation of the pH at which sorption occurs. This final pH of the mixture is obviously in the range between the two mixing end members, and could be approached from the geochemical modeling of the major element chemistry and flow proportions of these two end members. However, even so, this calculation assumes that all the reactions occur instantaneously. As deduced from the sorption breakthrough curves, a sub or overestimation of the sorption pH would lead to an over or underestimation of the heavy REE with respect to light REE, as deduced from Fig. 2. Finally, an inconsistency was observed in the Sc behavior. Whereas Sc is predicted to sorb in Schw at pH between 3 and 4, the field samples of this mineral formed at pH higher than 3 shown Sc concentration below detection level (<0.4 µg/L). More research is needed to confirm or not the possible segregation of Sc from the rest of REE at low pH.

## REFERENCES

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