

Rare Earth Element Adsorption onto Basaluminite

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INTRODUCTION

Rare Earth Elements (REE) are referred to Lanthanide series plus Scandium and Yttrium, according to recommendation by the International Union of Pure and Applied Chemistry (IUPAC) (Connelly et al., 2005). REE are considered critical raw materials because they are widely used in magnets for wind turbines, hydrogen batteries, as catalysts and many other technological uses. However, the global market of REE is controlled nowadays by China. Since the demand is steeply increasing, a problem of supply appears. To overcome with this situation, alternative resources of REE are necessary.

Acid Mine Drainage from the Iberian Pyrite Belt in the Southwest Spain are several orders of magnitude more concentrated in REE than natural waters. Moreover, passive remediation systems, which neutralize acid water with limestone dissolution, are proved to retain REE selectively into basaluminite, $(Al_4SO_4(OH)_{10} \cdot 5H_2O)$, an amorphous phase (Ayora et al. 2016). Therefore, the study of REE geochemistry in AMD becomes important in order to optimize the efficiency of REE recovery from passive treatments.

During the last 15 years, several authors have investigated REE mobilization in acid waters. There is no agreement neither at what pH REE are scavenged from water nor which precipitates are responsible for this. Whereas Verplanck et al., 2004 described that hydrous ferric oxides (HFOs) might be the responsible of REE retention from pH 5.1, Gammons et al., 2005 confirmed REE scavenging from water from at pH values 4.3 to 6.1 where a mixture of both hydrous Fe and Al oxides precipitated.

Before these studies, Bau 1999 performed laboratory experiments co-

precipitating REE with Fe oxyhydroxides at different pH, from 3.6 to 6.2. He confirmed the strong pH dependence in REE retention onto HFOs. Only around 10% REE retention was reached at pH 4.6 whereas more than 90% was found when $pH > 6$. This is in agreement with field studies that indicate a REE conservative behavior at low pH.

Since basaluminite was observed to concentrate REE in passive remediation systems, there is an interest to determine what pH is the most effective for REE retention. In this study REE sorption batch experiments onto synthetic basaluminite were performed at varying pH. The objective is to verify the pH dependence on REE sorption onto basaluminite, and to determine if partitioning among the different REE occurs.

MATERIALS AND METHODS

Basaluminite was synthesized following the method described by Adams and Rawajfih, 1977 by adding 0.214 L 0.015 M $Ca(OH)_2$ to 0.030 L of 0.05 M $Al_2(SO_4)_3 \cdot 18H_2O$; both commercial reagents. Precipitates were centrifuged at 4000 rpm for 10 minutes to remove supernatant, washed several times to remove $CaSO_4 \cdot 2H_2O$ and dried 2 days at maximum 40 °C.

Systematic XRD analyses were made for synthetic solid to dismiss impurities. Digestions of 0.1 g of solids in 5 mL HNO_3 65% were carried out for 12 h at 115 °C for chemical characterization.

A stock solution of 1 ppm REE was prepared with REE-mix in HNO_3 2% standard solution. Sorption experiments were carried out by mixing 10 mg of synthetic basaluminite with 10 mL of 1 ppm REE solution. Previously, pH of each solution was adjusted by adding NH_4OH 0.05M. After pH setting, REE

concentrations in initial solutions varied from 0.9 to 0.8 ppm. Suspensions were shaken for 6 hours at room temperature. Each pH was readjusted to the initial value in the middle of the experiment. Once the experiment finished, the suspensions were centrifuged 15 min at 4500 rpm. The supernatant was filtered through 0.2 μm nylon membranes into test tubes diluted 1:5 and acidified with 100 μL of HNO_3 20%. REE concentration in these solutions was determined by ICP-MS. Solids were dried at 40°C in the heater.

RESULTS AND DISCUSSION

Sorbed ratios were calculated as the difference between initial concentration in solution and equilibrium concentration in $\mu g/L$, compared to initial solution:

$$\text{Sorbed ratio} = \frac{([REE]_i - [REE]_{eq})}{[REE]_i} \quad (1)$$

REE adsorption onto basaluminite showed a clear dependence on pH: the higher pH the larger adsorption (Fig 1).

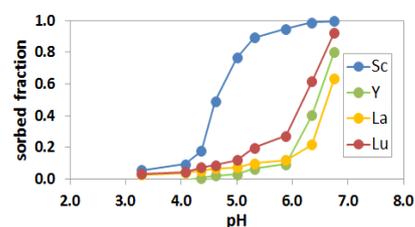


fig 1. REE sorption onto basaluminite depending on pH.

Scandium behaves totally different, starting sorption at pH lower than the other REE. Between pH 4.5 to 6.5 this element is totally adsorbed.

The rest of REE start to adsorb strongly at pH higher than 6 when only 10-20 % of REE is sorbed. Complete sorption of the group was not reached because basaluminite became unstable with pH,

palabras clave: Basaluminite, Tierras Raras, Adsorción, **key words:** Basaluminite, Rare Earth Elements, Sorption, Partitioning, Fraccionamiento.

as it will be discussed in the next section.

To describe the REE fractionation, an apparent partition coefficient (in L/Kg) is defined as:

$$D_{REE} = [REE]_s / [REE]_{eq} \quad (2)$$

where $[REE]_s$ is the difference between initial solutions $[REE]_i$ and equilibrium solutions $[REE]_{eq}$ in mg/L, normalized by sorbent (Kg) and volume of solution (L). Partition coefficients for 4 different pH values are plotted in Fig 2.

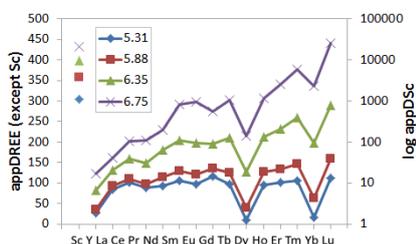


fig 2. D_{REE}^{app} values determined from experiments at pH 5.31 to 6.75.

From pH 5.88 patterns showed evident convex tetrad curves. It is also a clear partitioning, with enrichment in High Rare Earth Elements (HREE). However, negative anomalies are observed for Dy and Yb in all patterns which are not described in previous studies of REE sorption onto Fe and Al hydroxides (Bau, 1999; Gammons et al., 2005).

Basaluminite instability

The pH of initial solutions was always attempted by adding a different NH_4OH dose for each experiment. However, once adjusted and added basaluminite, pH slowly decreased towards a lower value. This is the reason why sorption at higher pH than 6.75 could not be obtained. Al and SO_4 amounts in solution at the end of experiments are plotted in Fig. 3.

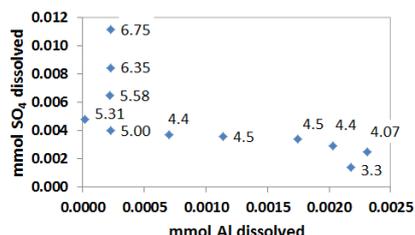


fig 3. Dissolved Al and SO_4 at the end of each experiment with its corresponding final pH.

At pH lower than 4, basaluminite was dissolved. Between pH 4.5 and 5 a

decreased in Al concentration was observed whereas SO_4 content remained constant. This suggests $Al(OH)_3$ precipitation. When pH increased above 5, Al was almost totally precipitated whereas SO_4 concentration in solution increased. At pH 6.75, about 50% of SO_4 initially present in basaluminite was removed. Carrero et al., 2017 described that 50% of SO_4 in basaluminite can be exchanged with $H_2AsO_4^-$. In our case, the release of SO_4 was closely related to the amount of OH⁻ supplied to the solution in order to reach the pH. Indeed, two moles OH⁻ were consumed to release one mol SO_4 , (Fig 4). This suggests that OH⁻ progressively exchanges with SO_4 groups weakly attached to the basaluminite structure.

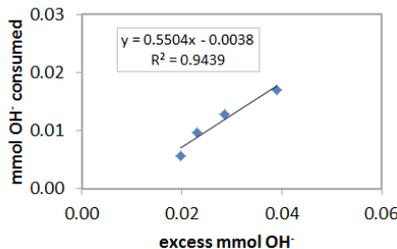


fig 4. Consumption of OH⁻ added to exchange with SO_4 from basaluminite at higher pH than 5.

With respect to REE, only 10-20% was scavenged from pH 4-4.5. If $Al(OH)_3$ precipitated along this pH range, it is not clear that REE were only adsorbed onto basaluminite. When pH was higher than 5, and SO_4 was released to the solution, REE adsorption increased significantly (Fig. 5). However REE retention is one order of magnitude smaller than SO_4 released. Therefore, REE sorption was linked to the increasing stability of REE-OH link when pH increases rather than SO_4 behavior.

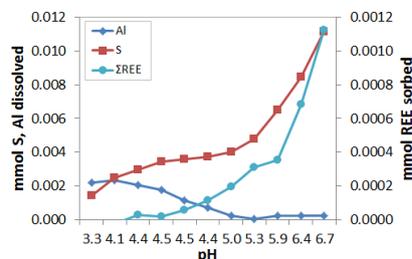


fig 5. Relationship between mass of total REE adsorbed and Al and S released to solution.

CONCLUSIONS

REE adsorbed onto basaluminite at pH higher than 5, suggest that this mineral could be responsible for the non-conservative behavior of REE in streams

at pH higher than 5. Scandium has different behavior from the rest of the group, starting to be sorbed at pH 4.5 and reaching total adsorption at pH 6.5. REE partitioning also occurred, and enrichment in HREE and MREE is confirmed.

REE sorption was closely related to the OH⁻/ SO_4 exchange into the basaluminite structure as pH increased. This could be so because the experiments were carried out with synthetic solutions with only REE and no SO_4 initial content. Since basaluminite seems to form from AMD, SO_4 appears to be critical to maintain basaluminite stable. Next step will be to perform the same experiments with SO_4 in solution.

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