

# Partition of Scandium, Yttrium and Rare Earth Elements between Acid Mine Drainage and its evaporitic sulfates. Preliminary results

Carlos Ayora (1\*), Alba Lozano, (1), Francisco Macías (2), Carlos Ruiz-Cánovas (2)

(1) Instituto de Diagnóstico Ambiental y Estudios del Agua, CSIC, Jordi Girona 18, 08028 Barcelona

(2) Departamento de Ciencias de la Tierra, Universidad de Huelva, Campus El Carmen, 21071 Huelva

\*corresponding author: caigeo@idaea.csic.es

**Key Words:** REE, REY, SCYRE, alunogen, gypsum, melanterite, hexahydrate, factor analysis | **Palabras clave:** REE, REY, SCYRE, alunógeno, yeso, melanterita, hexahidrita, análisis factorial

## INTRODUCTION

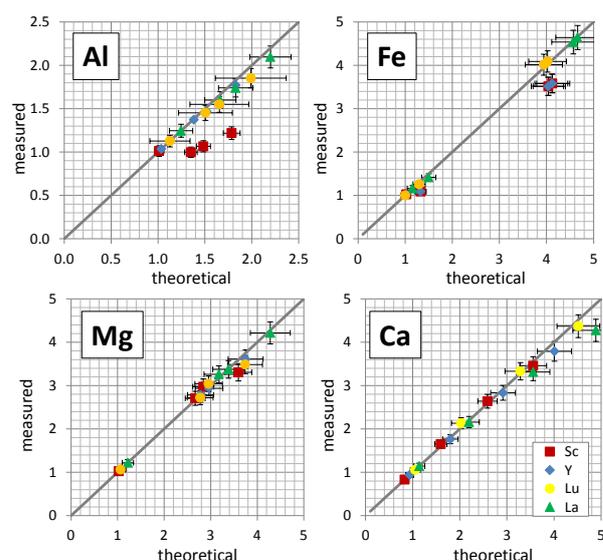
Scandium, Yttrium and Rare Earth Elements (SCYRE) are essential raw materials for modern technological applications. In mining environments, the dissolution of Fe sulfides generates acidic solutions with H<sub>2</sub>SO<sub>4</sub>, and dissolution of rocks and the release of solutes to the pore water are much more intense in Acid Mine Drainage (AMD) than in the rest of weathering profiles. Once in solution, SCYRE form sulfate complexes, which inhibit the sorption of SCYRE in clays and stabilizes them in the solution. As a consequence, SCYRE 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 SCYRE. Moreover, REE distribution patterns have been traditionally used to trace geochemical processes.

SCYRE 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 calcite addition, its pH increases leading to schwertmannite (Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>) and basaluminite (Al<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>10</sub>•5(H<sub>2</sub>O) formation. At pH's higher than 4.5, however, SCYRE concentrations in the water decrease below detection levels, indicating that these elements are trapped in basaluminite.

Significant amounts of AMD are not neutralized and are intensively evaporated during the dry season resulting in evaporitic Fe-Al-Ca-Mg-sulfates precipitation that cover the surface of soils and riverbeds in mining environments. These salts will be dissolved during the first rain event. However, the transference mechanism of SCYRE to these salts is not still properly understood. The aim of the present contribution is to describe for first time the partition patterns of SCYRE in such common surface processes. Moreover, a special attention will be paid to possible mechanisms of segregation of one element or group from the rest of SCYRE.

## MONOCOMPONENT SYSTEMS

As a first approach, four solutions with compositions slightly below the equilibrium with alunogen, hexahydrate, melanterite and gypsum were prepared. The solutions were evaporated in watch glasses at room temperature, and the aqueous and solid phases were progressively sampled. X ray diffraction (XRD) patterns confirmed the four referred minerals as the only phases present. The aqueous phase was analyzed by ICP-MS and ICP-AES. Lithium was assumed to be conservative along the precipitation of sulfates, and its concentration was used to calculate the evaporation extent, and the theoretical conservative concentration of SCYRE. The comparison from calculated and measured concentrations shows that most SCYRE behave conservatively within the analytical errors in the four studied evaporation experiments (Fig. 1).



**Fig 1.** Evolution of the concentration (mg/L) of some selected elements in the brines after progressive evaporation. The brines are in equilibrium with alunogen (Al), melanterite (Fe), hexahydrate (Mg) and gypsum (Ca).

The exception is Sc, which is strongly removed from the aqueous phase by the precipitation of alunogen. A slight removal of Sc by melanterite is also observed. Also, La is partially removed by gypsum in the most advanced evaporation stage recorded.

### MULTICOMPONENT SYSTEM

Sampling the aqueous phase became difficult after decreasing five times the initial volume. In order to study more advanced evaporation stages, a real multicomponent acid water from Poderosa mine (El Campillo, Iberian Pyrite Belt) was evaporated to dryness in a watch glass. The final precipitates were sampled in seven concentric rings aiming to obtain different mineral proportions. The samples were analyzed by XRD and SEM-EDS. An aliquot of each sample was dissolved and the major and trace elements by ICP-AES and ICP-MS. The statistical analysis of the aqueous phase concentrations was performed with the XLSTAT software (<https://www.xlstat.com/es/>).

The average solid phase is mainly composed by melanterite (70 mol %), alunogen (15 %) and gypsum (15 mol %), as calculated from the major solutes. Minor hexahydrate is also detected by XRD in some samples. From SEM-EDS observation, alunogen contains Si, hexahydrate contains variable amounts of Fe, Cu, Zn and Mn, melanterite contains Mg, Zn, Cu, Na and K, and gypsum does not contain other cations but Ca. No significant zonation in the concentric rings was observed, and no precipitation sequences could also be established from the SEM observation. Only the habitus of alunogen evolved from plate to needle-like crystals as the brine concentrated.

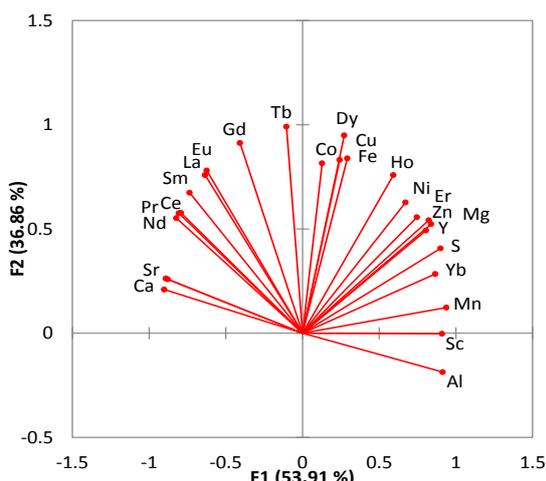


Fig 2. Factor analysis of the major and trace elements concentrations of seven precipitates from evaporation experiments of AMD from Poderosa mine

Although the proportion of the three main minerals is similar in the seven samples analyzed, there are still some differences that allow a statistical analysis of the trace element affinity for the different mineral phases. Thus, factor analysis of the major and trace

concentration of the different solid samples show two main factors that explain up to 91% of the variability observed.

Factor F1 (53.91% variability) is made up of highly positive (>0.75) factors of the variables Al, Mg, Zn, Mg, Sc, Y, and the heavy REE Yb and Er and highly negative (<-0.75) factors of the variables Ca, Sr, and the lighter REE Ce, Pr, Nd and Sm. On the other hand, Factor F2 (36.86 % of the variability) is constituted of highly positive (>0.75) factors of the variables Fe, Cu, Co, La, and the medium REE Eu, Gd, Tb, Dy, Ho, and no negative factors. No distinct association has been observed for the rest of factors (9.23 % of the variability).

A possible interpretation is to consider factor F1 as the substitution of Al with Sc, Y and heavy REE (Tb, Er) in alunogen. These trace elements share a similar Gd Yb ionic radius and valence with Al (Fig. 3). On the other hand, factor F2 would show the substitution of Ca with Sr and light REE (La, Ce, Pr, Nd, Sm) in gypsum. These lanthanides have different valence but very similar ionic radius than Ca. The intermediate lanthanides (Ho, Dy, Tb, Gd, Eu) are beautifully ordered in between Al and Ca following their ionic radius. As observed in SEM-EDS, transition metals were mainly included in melanterite and hexahydrate.

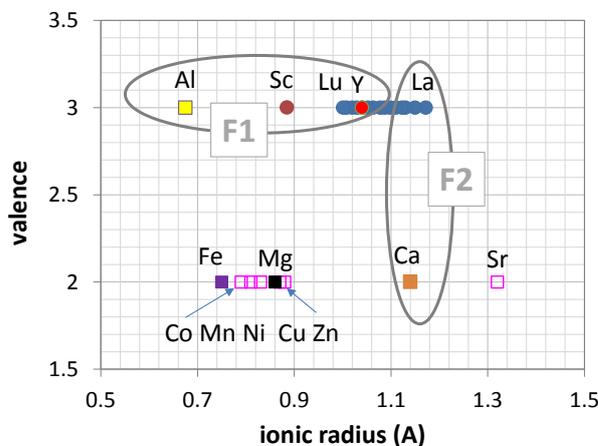


Fig 3. Ionic radius and valence of the major and trace components of the sulfates formed from evaporation of AMD from Poderosa mine.

### CONCLUSIONS AND FURTHER WORK

All the results confirm that Sc is fully incorporated in alunogen. Then, this element can be segregated from the rest by inducing the precipitation of alunogen from AMD (adding Al and SO<sub>4</sub>). The evaporation and precipitation of salts also induces a partition of Y and heavy lanthanides into alunogen and of light lanthanides into gypsum. The partition is strictly ruled by the similarity of ionic radii, and needs extreme evaporation to dryness. Further evaporation experiments of different AMD's, including Fe(III)-rich solutions are needed to build a robust statistics.