Stable Isotope Study in Iron-rich Sulphates from San Miguel Mine Wastes (Iberian Pyrite Belt, Spain)

/ ANA ALVARO GALLO (1,*), FRANCISCO VELASCO ROLDÁN (1)

(1) Departamento de Mineralogía y Petrología. Universidad del País Vasco. Barrio Sarriena s/n. 48940 Lejona (Vizcaya)

INTRODUCTION.

Stable isotopes provide important constraints on geochemical processes contributing to the knowledge of acid drainage chemistry, as they supply information on reaction pathways for sulphide oxidation. Due to sluggish kinetics of sulphate-water oxygen isotope exchange reaction, at low temperatures, the isotopic compositions of sulphate minerals may preserve a record of the sources concerning their origin (Seal et al., 2000). $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ are thus an efficient tool for tracing both the sources of dissolved SO_4^{2-} and the different oxidation mechanisms.

Stable isotope geochemistry of acid mine drainage (AMD) has been the subject of many investigations in affected mine sites elsewhere, although its application in sulphate minerals from the Iberian Pyrite Belt (IPB) is limited. In addition, no information seems to be available on the extent of S-isotope fractionation associated with the precipitation of Fe-hydroxysulphate minerals such us schwertmannnite and hydronium-jarosite. In this study we have determined the sulphur and oxygen isotope composition of various secondary sulphates, ochreous precipitates, and superficial acid waters. We also have compared the isotope ratios with values from ancient supergene minerals (gossan). The objectives of this study were (i) to evaluate the variability of S isotope in an acidic sulphate-rich environment and, (ii) calculate the extent of sulphur fractionation due to the formation of some Fe-hydroxysulphate minerals in ferric crusts.

SAN MIGUEL SULPHATES.

The mining area of San Miguel (IPB) has several mine waste piles that sporadically supply acid drainage. Schwertmannite (Sch), hydronium-jarosite (H-Jrs) and goethite are common minerals formed in the red pools and stream waters (pH ~2-3), with the ubiquitous presence of yellow to reddisbrown sediments. Efflorescences are usually found as powderish salts of variable colour around waste piles and river banks, and rarely occur as pure monomineralic phases. Whitish aggregates consist of mixtures of rozenite (Roz), hexahydrite (Hex) and halotrichite (Hal), and pickeringite (Pick) with halotrichite. On the other hand, the yellowish salts are mainly copiapite (Cop) and coquimbite (Coq).

METHODOLOGY.

Seven hydrated sulphate salts, six iron precipitates, four jarosite samples, one barite, and three acid mine waters were sampled at the San Miguel massive sulphide deposit. Efflorescence salts were selectively sampled from the open pit walls, pools and waste piles, while ochreous precipitates were collected from the desiccated pond located at the bottom of the open pit and stream areas (representative surface waters were also sampled). Jarosite (Jrs) and hypogene barite (Brt) were collected in the nearby gossan.

Bulk sulphate salts were dissolved, while schwertmannite, hydronium-jarosite and jarosite were selectively dissolved, followed by reprecipitation of the sulphate as $BaSO_4$, which was used for the sulphur and oxygen analyses. The sulphur isotope analyses were performed using a VG Isotech SIRA-II dual inlet mass spectrometer and the oxygen isotope ratios were measured using an on-line to a continuous flow helium ISOPRIME mass spectrometer, using He as a carrier gas (Lab. Isótopos Estables, Univ. Salamanca). Isotope ratios in acid waters, were measured in an IsoPrime CF mass spectrometer. For oxygen, the CO_2 equilibration method was used, while hydrogen was determined on an Elemental Analyzer by the Cr-reduction method.

RESULTS AND DISCUSSION.

The S isotope values obtained for iron sulphate minerals and dissolved SO_4^{2-} (+7.2 to +9.2‰) fall within the range of sulphide values from the San Miguel mineralization (Fig. 1A). These results agree with previous studies which establish that the aqueous sulphates produced by the oxidation of sulphides have a $\delta^{34}S$ values almost identical to that of the sulphide source.

Mineralogy	n	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$
Roz+Hex	2	8.2-8.5	2.8-5.3
Cop+Coq	4	8.8-9.0	2.3-3.2
Pick+Hal	1	9.2	2.5
Sch±H-Jrs	4	7.2-8.0	1.7-3.4
H-Jrs±Sch	5	7.7-9.1	1.8-4.3
Jrs	4	6.4-6.9	5.2-7.2
Brt	1	18.9	8.2

Table 1. Stable isotopic signatures from analyzed samples (efflorescence mixtures, barite and selectively dissolved hydroxysulphates) from San Miguel mine wastes.

This moderate variation contrast with the very limited change in $\delta^{34}S$ values observed for the jarosite from the gossan (Table 1). All these values are very similar to those for the ore mineralization, attesting to a process of gossan formation after intense oxidation and weathering of the sulphides without contribution of hypogene barite (Fig. 1A). It is apparent that the scarce occurrence of jarosite in the gossan clearly precludes a major SO_4 contribution to acid mine waters due to the dissolution of this mineral. Thus, sulphide oxidation appears to be the principal source of SO_4^{2-} in dissolved sulphate and recent iron sulphate minerals.

Although the $\delta^{34}S$ values of sulphate minerals are very similar, detailed analysis reveal slight differences. In the
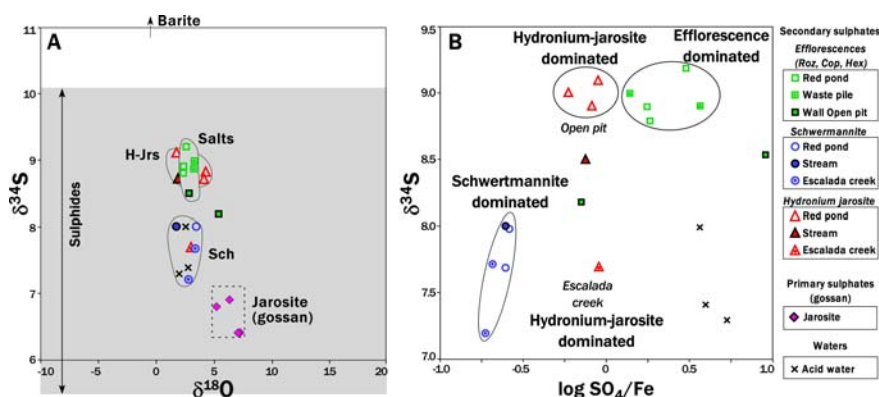
fig. 1 *A) Sulphur and oxygen isotopic compositions of sulphate minerals and dissolved SO₄ from San Miguel mine. B) Plot of the logarithm of SO₄/Fe wt. % content (EMPA analysis) vs. δ³⁴S values for sulphate mineral samples.*

red pools and creeks the schwertmannite $\delta^{34}S$ values (+7.2 to +8.0‰) are slightly lower than those for the hydronium-jarosite (+7.7 to 9.1‰). Ferrous iron efflorescents show statistically lower $\delta^{34}S$ values (+8.2 to 8.5‰) than those of the ferric iron which dominates the hydrated sulphates (+8.8 to 9.0‰). This deviation could be the result of geochemical and isotopic variations in acidic waters as the mineral were precipited. The changes in the geochemical parameters (such as pH, temperature, SO_4 and $Fe(III)$ concentration) and seasonal climatic variations could cause shifts in the isotope values of acidic waters.

Several groups are distinguished plotting the obtained $\delta^{34}S$ values vs. the logarithm of the SO_4/Fe in minerals and waters (Fig. 1B). The schwertmannite-dominated group shows a very similar sulphur isotopic composition regardless of the area in which they have been formed. Conversely, hydronium-jarosite-rich samples show different isotope sulphur values according to the features of the precipitation area. It is noteworthy that the efflorescent minerals also show different isotopic signatures depending on their location.

The $\delta^{18}O_{SO4}$ values of the analyzed samples draw two distinct populations depending on the main mineral phase. The $\delta^{18}O_{SO4}$ values of most of the recently precipitated minerals range from +1.7 to +5.3‰, whereas those of the ancient jarosites from the gossan show higher values, ranging from +5.2 to +7.2‰. On the first group, the similarity of $\delta^{18}O_{SO4}$ values among efflorescent sulphates (average of +3.1‰), hydroxides (average of +2.9‰) and dissolved sulphate (average of +2.4‰) suggests that there is no significant difference in the pyrite oxidation pathways operating at the mine site today. However, the variation between the isotopic values from acid mine drainage and the jarosite from the gossan could indicate differences in the supply of molecular O_2 between the process of gossan formation and the current evaporation-dissolution cycles in the waste piles.

CONCLUDING REMARKS.

This study ratify that the fractionation factors between sulphate minerals and water are relatively low (-0.2< $\Delta^{34}S_{mineral-sulphate}$ <+1.7‰), favouring the heavier isotope in the solid phase. In any case, the sulphate minerals formed in the pools with completely oxidized solutions (e.g. schwertmannite, hydronium-jarosite) suggest different fractionation factors. While schwertmannite typically poorly crystallized ($\Delta^{34}S_{Sch-sulphate}$ -0.2‰ - +0.3‰) supply no significant isotopic fractionation (Alvaro and Velasco, 2009), on the contrary, most of the hydronium-jarosite (usually showing good crystallinity) are enriched in the heavier isotope, if compared to parental acid water ($\Delta^{34}S_{H-Jrs-sulphate}$ +0.3‰ - +1.1‰).

According to Prietzel and Mayer (2005) and Balci et al., (2006) we know that isotope fractionation during the precipitation of solids in supersaturated solutions is influenced by the crystal structure of the precipitates, the precipitation rate, and crystal size of the products. Thus, the rapid formation of poorly crystalline solids (e.g. schwertmannite) should result in negligible isotope fractionation, whereas the better ordered structures with higher crystal sizes incorporate preferentially the heavy isotopes. Therefore, the isotope fractionation should be larger when well-crystallized solids and more stable phases are formed by through a slow reaction (such as occur with the hydronium-jarosite).

Briefly, acid mine drainage minerals at the San Miguel mine show slight but significative differences in their $\delta^{34}S$ value, ranging from +7.2 to +9.2‰. These slight variations in the isotopic composition suggest geochemical and isotopical changes in the acid solutions during mineral precipitation. In any case, the dissolved SO_4 is isotopically similar to the parent sulphides, and was originated from the oxidation of pyrite, which is obviously the principal source of sulphur. No other complementary sulphur source has been identified.

Summarizing, sulphur isotope data also suggest a discrete fractionation factor associated with the solid precipitation step that rarely reach +2‰. This fractionation is mainly controlled by kinetic effects, depending largely on the rate of precipitation and crystalline structure (Prietzel and Mayer, 2005; Balci et al., 2006). This research also confirms that the extension of isotopic fractionation is a very complex process that depends on a large number of factors demonstrating that further analyses and research are needed.

REFERENCES.

Alvaro, A. and Velasco, F. (2009): Stable isotope composition of acid mine drainage minerals from San Miguel massive sulphide mine waste. 8th ICARD, Skellefteå, Sweden, June 23-26, 1-10.

Balci, N., Bullen, TD, Witte-Lien, K., Shanks, WC., Motelica, M., Mandernack, KW. (2006): Iron isotope fractionation during microbially stimulated Fe(II) oxidation and Fe(III) precipitation. Geochim. Cosmochim. Ac., **70**, 622-639.

Prietzel, J. and Mayer, B. (2005): Isotopic fractionation of sulfur during formation of basaluminite, alunite, and natroalunite. Chem. Geol., **215**, 525-535.

Seal, RR II., Alpers, CN., Rye, RO. (2000): Stable isotope systematics of sulfate minerals. In: Alpers et al. (eds) Sulfate Minerals, Rev. Min. Geoch., **40**, 541-602.