

# Isotopic Fractionation of Sulphur During Precipitation of Iron Sulphate Minerals from Acid Mine Drainage (San Miguel Mine, IPB)

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*Sulphur isotope composition of the dissolved sulphate and acid drainage minerals in abandoned mine environments (efflorescences and ochreous precipitates) can reflect the evolution paths of the sulphide oxidation processes. This study presents some preliminary results of the isotope fractionation observed in these sulphate minerals and we try to explain the complex processes that cause isotope effects in sulphur during mineral precipitation.*

## INTRODUCTION

The occurrence of efflorescent sulphate minerals in mine-drainage setting are widely reported in the Iberian Pyrite Belt (IPB). However, little is known about the relationship between isotope composition and the progress of crystallization of these minerals, particularly taking into account that isotopes provide valuable information about the history of the weathering in terms of origin and chemical conditions of waters and solids. The mineralogy of the mine-drainage environments is the result of different processes including oxidation, dehydration and neutralization reactions, and the typical evolution from ferrous sulphate minerals to iron oxyhydroxide minerals is always controlled by the proportion of these reactions (Jerz et al., 2003). Thus, the knowledge of mineral assemblages is important to estimate the evolution paths of the oxidation processes during weathering.

Stable isotopes of sulphur should be a useful tool for the interpretation of those operative processes that affect the pyrite oxidation. Although stable isotope geochemistry of acid mine drainage (AMD) has been the subject of several investigations in many other impacted mine sites elsewhere, its application in the sulphate minerals from the IPB is scarce. In this study, isotopic composition of sulphates and dissolved  $\text{SO}_4$  are used to improve the understanding of the sulphide alteration processes and to provide detailed information about the environmental conditions.

## AREA OF STUDY

The San Miguel mine was exploited for copper from 1859 to 1960, primarily by

underground works and later in an open pit. During that time, 1.29 Mt of pyritic ore with an average grade of around 2–3% Cu and 46% S were produced. In addition, there are evidences of Roman mining and other excavations in the area. One of the most remarkable features of this deposit is the occurrence of a mature gossan over the sulphide mineralization. This gossan is ~12 m thick and is the result of the intense weathering and oxidation underwent by the exposed mineralization.

The mining area of San Miguel has several mine-waste piles which contain high concentrations of sulphide minerals that are constantly producing acidic waters. At the Open pit site, partially filled with mine-waste rocks and stockpile ores, impressive crusts of efflorescent salts episodically "bloom" on the bottom surface associated to ochreous growth. During rainfall, the surface runoffs in this zone are stored in ephemeral ponds within depressed areas (showing a characteristic vivid red colour). However, during the dry periods these mine areas are partially desiccated with formation of great variety of yellowish and whitish Fe-rich sulphate crusts, whereas at the bottom of the ephemeral ponds polygonized muds are developed. The shrinkage of the wet muds is also accompanied by the development of massive yellow coarse-grained crystal aggregates, appearing as extruded efflorescences through the cracks. These areas act as reservoirs of the metals and the dissolved sulphate remaining in solution.

## METODOLOGY

Surface efflorescences and surface water were collected from the San Miguel open pit. Efflorescence salts

were selectively sampled from the soils and waste piles, while ochreous precipitates were collected from the desiccated pond areas. Sulphur isotope data were obtained separately from dissolved  $\text{SO}_4^{2-}$  in surface waters and sulphate hydrated and hydroxysulphate minerals. Sulphate minerals and hydroxysulphates were selectively dissolved in order to separate new formed minerals from the large quantities of detritic grains. The solutions were reprecipitated as  $\text{BaSO}_4$  by addition of a  $\text{BaCl}_2$  solution to perform the sulphur isotopic analyses using a VG Isotech SIRA-II spectrometer (Laboratorio de Isótopos Estables, Universidad de Salamanca). Laboratory techniques for isotopic analyses of jarosite and dissolved sulphate have been summarized by Wasserman et al. (1992) and Carmody et al. (1998), respectively.

## RESULTS

The  $\delta^{34}\text{S}$  values of the dissolved sulphate and sulphate minerals match broadly with those reported for the sulphides from the San Miguel mineralization (-3.85 a +10.1‰) (e.g. Arnold et al., 1977; Routhier et al., 1978). These results confirm that supergene oxidation of sulphide minerals produce minor or negligible sulphur isotope fractionation. The lack of substantial isotope fractionation between sulphides and sulphates, suggest that oxidation of sulphides is the principal source of  $\text{SO}_4^{2-}$ , without contribution of primary sulphates (e.g., barite) or microbial sulphate reduction (described for the Tinto ecosystem by González-Toril, 2003).

In the waste piles the most common efflorescent sulphates are rozenite,

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hexahydrite, copiapite and coquimbite. The first products of the pyrite decomposition show lower  $\delta^{34}\text{S}$  values with respect to those precipitated in the second stage in waste piles. By contrast, the hidroxysulphates precipitated at the bottom of the red pond shown  $\delta^{34}\text{S}$  values higher than the earlier precipitated sulphates, with the exception of schwertmannite. In general, these S-isotope compositions describe a trend which seems to follow the stages of precipitation of secondary minerals. According to Velasco et al. (2005), sulphide weathering at the San Miguel area takes place in three stages. Firstly, the pyrite oxidation produces melanterite and/or their dehydration products (rozenite, szomolnokite) together with hexahydrite and sulphuric acid (first stage); lately, tertiary minerals precipitate as hydrated salts from the acid solutions (copiapite, coquimbite), or as result of the dissolution and oxidation of primary sulphates (second stage). These salts are successively dissolved by the rain and by the pore waters and then partially reprecipitated as hydronium jarosite, schwertmannite and/or halotrichite-pickeringite rich aggregates (third stage). In these assemblages jarosite usually appears as the cementing material of mud detritic particles, whereas schwertmannite developed as tick gelatinous layers (up to several mm) indicate long times of water supersaturation. The isotopic fractionation of sulphur of the studied sulphate minerals during the precipitation from the saturated solutions is relatively small (1.8‰), in agreement with the fractionation values estimated by Thode and Monster, (1965). These results could indicate a possible dependence between sulphur signature and the observed paragenesis of sulphate minerals, but there are other factors that could affect to the isotope value too.

In any case, the oxidation of sulphide minerals is a complex process (Seal, 2003) that is affected by several factors such as crystallinity, rate of precipitation, intermediate sulfoxyanions, precipitation-redissolution, temperature, etc., that change the isotopic values of the involved sulphates. As an illustration we found the isotope values for the ochreous precipitates. Although these sulphate minerals are developed from complete oxidized solutions, sulphate minerals formed in the pools show different fractionation rates (e.g. schwertmannite compared with hydronium jarosite, or halotrichite). Thus, in this case, differences in fractionation probably owing to rates of precipitation, relative stability, composition, crystalline structure (weaker or stronger bonds), etc. In term of  $\delta$ -values, the schwertmannite (a hydroxisulphate with poor crystallinity and low S content;

10.36%  $\text{SO}_3$ ) show the lower isotopic difference between the solution and the mineral ( $\Delta\delta^{34}\text{S}_{\text{Schwertmannite-sulphate}}=0\text{‰} - 0.05\text{‰}$ ). In contrast, hydronium-jarosite, as a member of the family that typically has good-developed crystallinity and higher S content (33.31%  $\text{SO}_3$ ), reveals a poor but significative isotopic fractionation of S between the mineral and the solution ( $\Delta\delta^{34}\text{S}_{\text{Hjarosite-sulphate}}=+0.3\text{‰} - +1\text{‰}$ ) during the precipitation process. Finally, the largest observed difference between the  $\delta^{34}\text{S}$  values of the mineral and the solution was for halotrichite-pickeringite minerals ( $\Delta\delta^{34}\text{S}_{\text{Halotrichite-sulphate}}=+1.2\text{‰}$ ). Briefly, isotopic analyses shown that poorly crystallized minerals like schwertmannite, quickly formed during long period of supersaturation, exhibit the lower values compared to the recorded for the hydronium-jarosite. This indicates that no or very scarce isotope fractionation of S has occurred during the precipitation of schwertmannite. These results agree the proposal by Prietzel and Meyer (2005), by which the extension of isotope fractionation during the precipitation of solids in supersaturated inorganic solutions is influenced by the rate of precipitation. According to Bigham and Nordstrom (2000), metastable phases such as schwertmannite and ferrihydrite may form more readily than stable phases (such as jarosite and goethite). Consequently, isotope fractionation should be larger when well-crystallized solids are formed (like jarosite), whereas for rapid formation of colloidal quasi-amorphous solids (like schwertmannite) is expected a negligible isotopic fractionation.

### CONCLUSIONS

The dissolved  $\text{SO}_4$  formed from the alteration of the pyrite is the principal source of sulphur and appears with an isotopic signature almost identical to that of the parent sulphides; no other complementary sulphur source has been identified. Sulphur isotope data from iron sulphate minerals formed from mine waters at the San Miguel open pit suggest the existence of a discreet fractionation that rarely reach 2%. All the sulphur isotope data shift the  $\delta^{34}\text{S}$  value of the dissolved  $\text{SO}_4$  in acid waters to a heavier value of less than +1.8‰.

These changes in the isotopic composition could be explained with a trend of mineral precipitation that likely would be illustrated by different stages of dissolution and reprecipitation of the dissolved sulphate and salts. Briefly, sulphur isotope values could reflect the order in which the minerals are likely to form. Thus, these changes typically would describe the evolution of the observed paragenetic sequence with the lower  $\delta^{34}\text{S}$  values for the rozenite (1<sup>st</sup> stage) and the heavier for the copiapite

(2<sup>st</sup> stage), hydronium jarosite, and halotrichite-pickeringite (3<sup>rd</sup> stage). Although this conclusion agrees with field observations we cannot rule out other mechanisms.

In short, this research confirms that the extent of isotopic fractionation is a very complex process which depends on several factors. These processes are likely to cause non-equilibrium isotope effects in sulphur but for the moment it is very difficult to define exactly the importance of these mechanisms during sulphate precipitation. These preliminary results evidence that more analyses and research are needed.

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