

# SEM-EDS Study of a Mine Pit Lake Turbidity Layer: Biogeochemical and Environmental Aspects

/ JAVIER SÁNCHEZ ESPAÑA (1,\*), IÑAKI YUSTA (2), MARTA DÍEZ ERCILLA (1)

(1) Instituto Geológico y Minero de España, c/Ríos Rosas, 23. 28003, Madrid (Spain)

(2) Departamento de Mineralogía y Petrología, Universidad del País Vasco, Apdo 644. 48080, Bilbao (Spain)

## INTRODUCTION AND SCOPES.

The use of Scanning Electron Microscopy (SEM) coupled with analyses by Electronic Dispersive System (EDS) represents a valuable tool for the study of complex mineral assemblages where highly crystalline minerals coexist with nearly amorphous phases. The SEM resolution often results in a significant progress with respect to standard XRD, XRF or optical microscopy. This work reports the main mineralogical features of suspended mineral particles (SMP) which form a turbidity layer (TL) below the redoxcline of Cueva de la Mora acidic mine pit lake (AML) (Figs. 1-2). This transitional zone is highly reactive and constitutes a redox boundary where complex microbial reactions take place.

## ENVIRONMENTAL FRAMEWORK.

The small lake which presently exists in the old mine pit of Cueva de la Mora (Huelva, Spain; Fig. 1) was formed after its abandonment and flooding in the early 1970s. The lake contains a volume of 0.2 Mm<sup>3</sup> of highly acidic (pH 2.2-4.5) and metal-rich water, surface area of 17800 m<sup>2</sup> and a max. depth of 40 m. The hydrochemical and limnological features of this lake have been reported in Sánchez-España et al. (2009). In short, this lake presents a 10 m-deep, oxygenated mixolimnion, and a 30 m-deep, anoxic monimolimnion (Fig. 2).



fig 1. Field view of Cueva de la Mora pit lake.

## HYPOTHESIS AND PREVIOUS WORK.

One of the most remarkable features of the AML of Cueva de la Mora consists in a 8 m-thick TL situated below the redoxcline (between 10 m and 18 m in depth; Fig. 2a). It is hypothesized that this turbidity layer represents a "reaction front" in which complex, microbially-catalyzed reactions and precipitation of different chemical compounds is taking place throughout the entire year. Previous geochemical calculations suggested precipitation of different Fe<sup>III</sup> compounds of variable crystallinity, including schwertmannite, jarosite and goethite (Sánchez-España et al., 2009). However, conventional examination (XRD, XRF) of sediments and SMP collected at different depths did not allow to distinguish any mineral product of microbial metabolism, which are usually nanocrystalline to nearly amorphous, and relatively minor in proportion with respect to detritic pyrite, silicates (quartz), and aluminosilicates (chlorite, illite, K-feldspar).

Another intriguing aspect in the limnology of this pit lake deals with the behaviour of copper and sulphur (Figs.

2b and 2c). Copper drastically decreases in concentration to near-zero values near the oxidic-anoxic boundary (shaded area in Fig. 2), and subsequently shows a relative concentration peak below the redoxcline at a depth of around 20 m, to decrease again near the lake bottom (Fig. 2b). Such anomalous behaviour could be related with sorption-desorption and/or precipitation-dissolution reactions. Reduced sulphur is present at around 10-11 m depth in the form of H<sub>2</sub>S (Fig. 2c). This gas is clearly distinguished on site by its characteristic "rotten-egg" odour.

## METHODS.

The SMP studied in this work were taken from two sediment traps installed in 2009 at depths of 7 m (ST-7) and 19 m (ST-19). These solids were removed from the trapping cylinder in September 2009, and subsequently transported to the laboratory, air-dried, optically inspected with a binocular microscope, and further studied by SEM-EDS at UPV/EHU. The pictures and EDS analyses were carried out in graphite-coated samples in a JEOL JSM-7000F electron microscope.

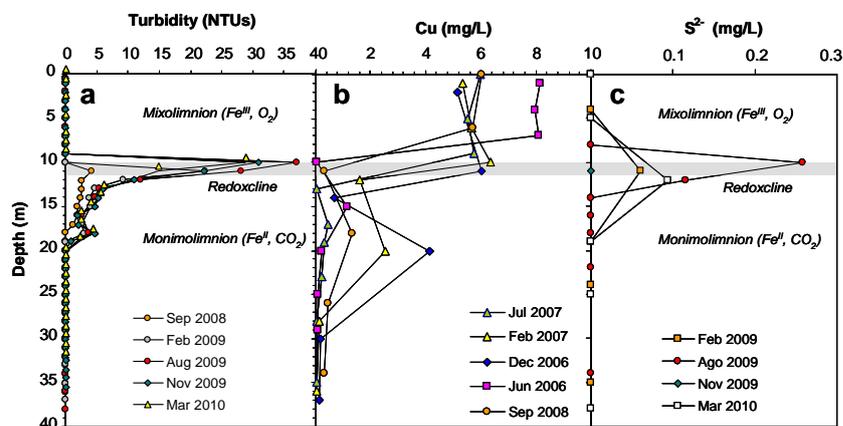


fig 2. Vertical profiles of turbidity (a), Cu (b) and sulphide (c) measured in different seasons in the acidic pit lake of Cueva de la Mora (Huelva, Spain) (from Sánchez-España et al., 2009, and Díez-Ercilla, 2010).

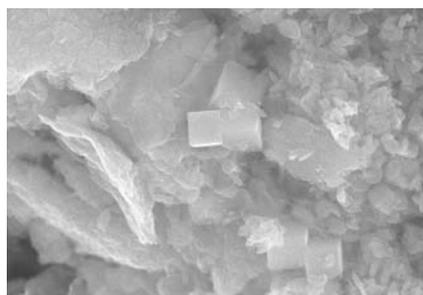
**palabras clave:** Meromixis, Bacterias, Fe<sup>I</sup>, Fe<sup>III</sup>, Ciclo Biogeoquímico, Minería Metálica, Sulfuros.

**key words:** Meromixis, Bacteria, Fe<sup>I</sup>, Fe<sup>III</sup>, Biogeochemical Cycling, Metal Mining, Sulphides.

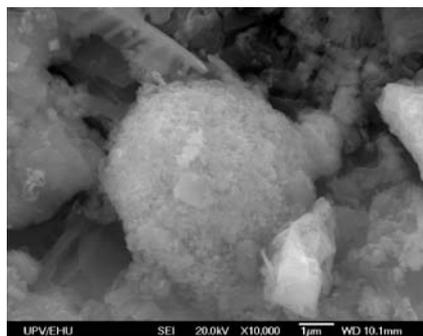
## RESULTS AND DISCUSSION.

### *Iron Precipitation and Pyrite Oxidation.*

Sample ST-7 showed abundant jarosite crystals scattered in the sample (Fig. 3), in agreement with the pH measured in the lake during 2009 (pH 2.2-2.5). Evidences of jarosite transformation to globular goethite are frequent (Fig. 4), suggesting transformation of jarosite to goethite during particle settling.

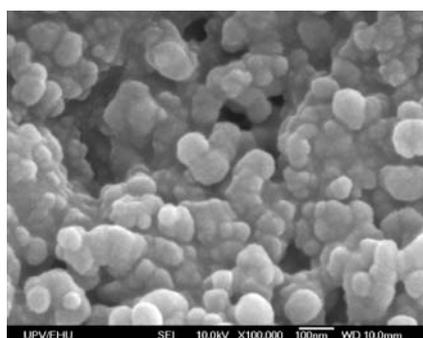


**fig 3.** SEM image of pseudo-cubic crystals of jarosite formed in the mixolimnion of the pit lake (sample ST-7).



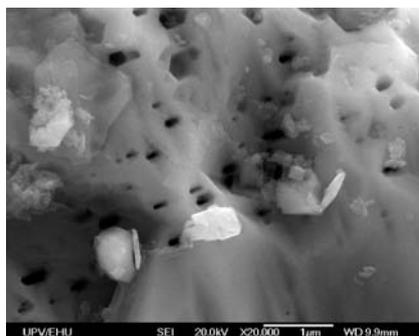
**fig 4.** SEM image of globular goethite replacing former jarosite crystals (sample ST-7).

Schwertmannite was not identified in the sediment samples. However, laboratory works have demonstrated that this mineral actually forms in this lake at pH 2.8-3.2, during the winter season (Fig. 5).



**fig 5.** Synthetic schwertmannite obtained in the laboratory after titration of Cueva de la Mora pit lake surface water up to pH 3.0-3.5.

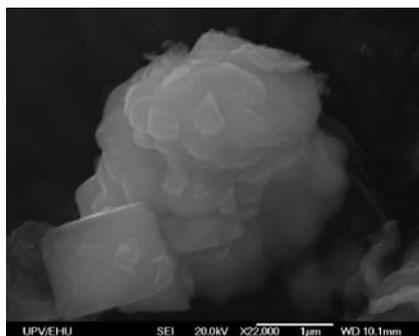
The fragments of detrital pyrite show abundant etch-pits indicative of abiotic (chemical) oxidation (Fig. 6). These pyrite fragments are commonly associated with jarosite crystals which would be a secondary product of pyrite oxidation.



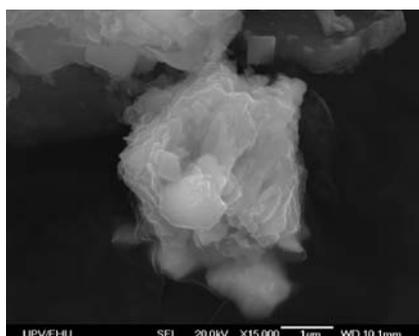
**fig 6.** SEM image of etch-pits in a detrital fragment of pyrite which is being oxidized and partly dissolved (direct chemical attack by  $Fe^{III}$ ). Jarosite crystals formed near the pyrite surfaces are also visible.

### *Precipitation of CuS and FeS.*

The most striking feature observed in the studied anoxic sediments taken at 19 m depth is related with the presence of amorphous precipitates of copper and iron sulphide (Figs. 7 and 8). This finding is of prime environmental interest and implies direct evidence of biogeochemical cycling of Fe and S.



**fig 7.** SEM image of amorphous CuS precipitate aside of a cubic Cu-sulphate crystal (sample ST-19).



**fig 8.** SEM image of amorphous FeS precipitate.

### *Biogeochemical-Environmental Aspects.*

An evident conclusion emerging from this study and other field and laboratory works carried out in Cueva de la Mora is that a substantial microbial activity seems to exist which, coupled to a number of abiotic (chemical, mineralogical) processes, affects to a great extent the water chemistry and limnology of this lake.

The mineralogical and textural features of the studied SMP are in accordance with our geochemical knowledge, as well as with recent microbiological studies which have identified the presence of different Fe- and S-related bacteria (including sulphur-oxidising and sulphate-reducing bacteria, as well as iron oxidizers and iron reducers) at different depths in the water column and in sediments (Wendt-Potthoff et al., *in prep.*). Overall, the investigations point to the existence of biogeochemical cycling of iron and sulphur through the redoxcline of this lake. The anoxic layer supplies the oxygen-rich mixolimnion with dissolved ferrous iron, which is bacterially oxidized and, given the pH of this layer (2.8-3.2), immediately reprecipitated in the form of nanometric particles of (chiefly) schwertmannite, forming the turbidity layer in the oxic-anoxic boundary. Copper is adsorbed onto the schwertmannite surfaces, and directly precipitated as CuS. Both CuS and FeS are products of microbial activity. The TL geometry suggests a probable microbial reduction of  $Fe^{III}$  mineral particles during settling.

### *ACKNOWLEDGEMENTS.*

We thank Gabriel López (Sgiker, UPV/EHU) for his kind help during the SEM-EDS analyses. This work has been funded by MICINN through research project number CGL2009-09070, and Gob. Vasco (Grupo Invest. IT-446-07).

### *REFERENCES.*

- Diez-Ercilla, M. (2010): Estudio biogeoquímico del lago minero de Cueva de la Mora, Faja Pirítica. Diploma de Estudios Avanzados, Universidad Autónoma de Madrid, 55 pp.
- Sánchez-España, J, López-Pamo, E., Diez-Ercilla, M., Santofimia E. (2009): Physico-chemical gradients and meromictic stratification in Cueva de la Mora and other acidic pit lakes of the Iberian Pyrite Belt. *Mine Water Environ*, **28**, 15-29.
- Wendt-Potthoff, K., Koschorreck, M., Diez-Ercilla, M., Sánchez-España, J. (*in prep.*) High microbial activity in a nutrient-rich, acid meromictic pit lake.