

# INTERFEROMETRIC STUDY OF PYRITE DISSOLUTION IN ACIDIC CONDITIONS

M.P. ASTA <sup>(1)</sup>, J. CAMA <sup>(1)</sup>, A. LÜTTGE <sup>(2)</sup>, P. ACERO <sup>(1)</sup>, C. TORRENTÓ <sup>(1)</sup> Y C. AYORA <sup>(1)</sup>

<sup>(1)</sup> *Institute of Earth Sciences «Jaume Almera»-CSIC, Lluís Solé i Sabarís s/n, Barcelona 08028, Spain.*

<sup>(2)</sup> *Department of Earth Sciences and Department of Chemistry, Rice University, Houston, Texas 77005, USA.*

## INTRODUCTION

The oxidative dissolution of sulfide minerals produces acid mine drainage (AMD) with release of high concentrations of toxic elements such as Fe, As, Pb, Cu, Zn and sulfates. Resulting waters, with high concentrations of dissolved solids, can infiltrate to the aquifers or can be incorporated into rivers, causing considerable damage to the environment.

The most common sulfide mineral is pyrite ( $\text{FeS}_2$ ). The dissolution of  $\text{FeS}_2$  has been widely studied using several experimental methodologies (e.g., batch and flow-through experiments, ex situ AFM, etc.) that contributed to the existing knowledge of the pyrite disintegration. In this study we try to elucidate on the surface mechanism(s) that control the pyrite dissolution by means of vertical scanning interferometry (VSI) in acidic conditions and oxygen saturated atmosphere. Using this technique it is possible to quantitatively map changes in mineral surface topography at the sub-nanometer-scale vertical and micrometer-scale lateral resolutions (Luttge et al. 1999; 2003; Arvidson et al. 2003).

## EXPERIMENTAL METHOD

We have used a scanning white light phase shift interferometer (MicroXam, ADE-Phase Shift Technology) with 10x and 50x Mirau objectives to quantify a pyrite

surface dynamics during dissolution. The lateral resolution of the system is 0.5-1.2 microns depending on the objective used and the vertical resolution is better than 2 nm (see details in Lüttge et al., 1999; 2003).

A pyrite fragment of approx. 1.5 cm x 0.5 cm x 1 cm from La Rioja (Spain) was used in this study. Before the fragment dissolution took place, a cleaved surface was picked out to be scanned. Images of this pristine, unreacted surface were used to compare variations in surface topography before and after dissolution.

The pyrite fragment was suspended in a 10 L polypropylene bottle containing a pH 1 (HCl) solution and allowed to dissolve for several weeks. This low solid/solution ratio ensured pyrite dissolution to occur under highly undersaturated conditions with respect to pyrite. After 13 days the pyrite fragment was retrieved from the solution, immediately dried at room temperature, and the initially surface selected was examined by VSI. As the surface examination concluded (2 hours), the fragment was placed back into the bottle with the same solution to continue its dissolution. Using SPIP software digitized interferograms of the pyrite surface were converted to height-mode and three-dimensional images.

## RESULTS AND DISCUSSION

The pristine surface of pyrite consisted of «flat» terraces that were limited by steps of 0.2-3 microns in height,

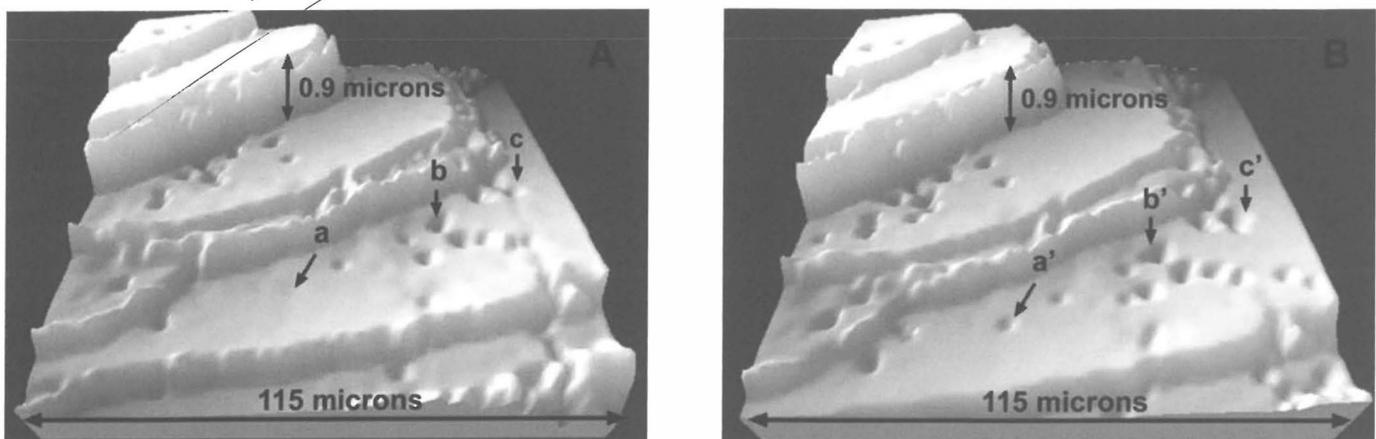


Figura 1: Three-dimensional image of the pyrite surface region: (A) initially pristine surface that shows the presence of terraces, steps and scattered pits over the surface area; B) after 13 days of dissolution in HCl solution (pH 1) at room temperature and oxygen saturated atmosphere. A comparison of the images allows to observe the formation of new etch pits (a and a') and the changes in the shape of some pits (b, c and b', c') during dissolution.

yielding a low surface roughness (Fig. 1A). Also, initial nano-pits distributed all over the cleaved surfaces were observed. A comparison of the images of the same surface area before and after dissolution showed some changes in topography and surface morphology (Fig. 1B).

The dissolution of the pyrite surface yielded little variation in the height of the steps during dissolution. Noticeable dissolution features observed were the formation of new etch pits, the coalescence of some of the previously existing, as well as the increase in depth of the existing pits and the change in original shape with time (Fig. 1B). Hence, the etch pit development seems to play an important role in the control of the dissolution mechanism(s). These observations may be explained as heterogeneous dissolution occurring all over the pyrite surface as is described in the literature of sulphide dissolution (Cama and Acero, 2005; Cama et al., 2005; De Giudici and Zuddas, 2001).

Furthermore, a detail inspection of the reacted surface showed that small protrusions formed during the dissolution process. This might be interpreted as the result of the reorganisation of the surface at the nanometric scale as was described in previous studies of sulphide dissolution (De Giudici et al. (2002) in the sphalerite dissolution and De Giudici and Zuddas (2001) and Cama et al. (2005) for galena dissolution). Nevertheless, ongoing work is warranted to provide the necessary information to validate the occurrence of the described type of surface mechanism(s).

## REFERENCES

- Arvidson R.S., Ertan I.E., Amonette J.E., and Lüttge A. (2003). Variation in calcite dissolution rates: A fundamental problem? *Geochimica et Cosmochimica Acta*, 67, 1623-1634.
- Cama J. and Acero P. (2005). Dissolution of minor sulphides present in a pyretic sludge at pH 3 and 25°C. *Geologica Acta*, 3 (1), 15-26.
- Cama J., Acero P., Ayora C., and Lobo A. (2005). Galena surface reactivity at acidic pH and 25°C based on flow-through and in situ AFM experiments. *Chemical Geology*, 214, 309-330.
- De Giudici G. and Zuddas P. (2001). In situ investigation of galena dissolution in oxygen saturated solution: evolution of surface features and kinetic rate. *Geochimica et Cosmochimica Acta*, 65, 1381-1389.
- De Giudici G., Voltoni M., and Moret M (2002) Microscopic surface processes observed during the oxidative dissolution of sphalerite. *European Journal of Mineralogy* 14, 757-762.
- Lüttge A., Bolton E.W., and Lasaga A.C. (1999). An interferometric study of the dissolution kinetics of anorthite: the role of reactive surface area. *American Journal of Science*, 299, 652-678.
- Lüttge A., Winkler U., and Lasaga A.C. (2003). An interferometric study of the dolomite dissolution: A new conceptual model for mineral dissolution. *Geochimica et Cosmochimica Acta*, 67, 1099-1116.