Evolution of mineral surface during reaction: some constraints by coupling AFM and solution chemistry

G. B. De Giudici
P. Zuddas

Laboratoire de Géochimie des Eaux CNRS, Institut de Physique du Globe de Paris et Université Paris 7, 2, place Jussieu, case 7052, F75251 Paris Cédex 05, France

The reaction of galena (PbS) dissolution was investigated coupling *ex situ* AFM (Atomic Force Microscopy) observations to measurements of the kinetic rate. The nano-topography details of the (001) surface were observed in Tapping Mode after interaction with HCl solutions (pH = 2) at 303 K and room atmosphere. The kinetic rate was estimated by a set of experiments carried out in solutions at given constant pH (i.e. pH = 2, 3, 4).

At the atomic resolution, the AFM observations indicate that the unreacted (001) surface accords to the chess-board model, while, at the horizontal μmeter scale, is flat and regular with edges of 20 nmeters. Dissolution generates etch pits of 30, 50, 80 nm after, respectively, 3, 5 and 24 hours of interactions. The form of the etch pits is cubic and four new (110) faces are then generated by each etch pit.

Irrespective of pH, after the first 24 hours of reaction, the rate of dissolution reaches the constant value of 7 nanomoles/m^2/sec. The constancy of the rate of dissolution suggests that, after the initial evolution, the mechanism of the reaction should be constant.

Calculations based on the principle of mass balance have been applied to identify the face controlling the evolution of the surface shape. Using both microtopography and solution chemistry data, we estimated that the amount of dissolved matter is inconsistent with the simple translation of the (001) while is in agreement with the increase of the surface roughness if the chess-board model of etch pits distribution is assumed.

However, despite the assumption of the chess-board model, the evolution of galena surface is more properly described by the roughness coefficient. Since the shape of galena is controlled by the (110) external face, surface roughness coefficient can be represented by a function of the ratio of the (001) and (110) surface area. In such a conditions the roughness, that is independent on the size and distribution of the etch pits, remains constant when the residual (001) surface area is 20 times less than the initial (001) surface area. When this condition is verified, the shape of galena surface is expected to be a constant, as the relative amount of (110) and (001) surface area is constant. Consequently the density of reaction sites at galena surface is conservative and the dissolution rate is constant.

Concluding we propose that in a first stage the reaction of galena dissolution is controlled by the state of the surface, while in a second stage is the transport that controls the reaction.