

Pyrite biooxidation surface processes: morphological, chemical and isotopic signatures

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Though the interactions between *Acidithiobacillus ferrooxidans* (*A.f.*) and sulfides minerals are extensively studied, the details of the processes taking place at the surface of the pyrite crystals are still poorly understood. This study aimed at improving our knowledge of pyrite oxidation at the micrometric scale by combining surface morphological (CLSM), chemical (Raman spectroscopy) and isotopic (SIMS) techniques. One obvious goal of this study was to investigate whether reliable biosignatures on mineral surfaces can be identified. A pure natural pyrite has been bio-oxidized (*A.f.*) and compared to abiotic oxidations (Fe^{3+} , H_2O_2 , $\text{O}_{2,\text{atm}}$).

Bacteria attached to pyrite surfaces (principally on the walls of deep and geometric corrosion holes) act mostly as direct electron pumps, regulating electron fluxes within the mineral lattice and avoiding surface passivation. The “biotic oxidation layer” is made of sulphates or oxides micrometric mounds, that have specific molecular conformation and Raman signatures. At variance, abiotic chemical oxidation of pyrite results in a mixture of several oxidation phases associated at the micrometer scale.

The dissolution of pyrite appeared to be either nonstoichiometric (during the first days) or stoichiometric (with increasing time) with a slightly positive (+0.4‰) or negative (-1.3‰) S isotopic fractionation between sulphates and pyrite, respectively. Dissolved sulphates $\delta^{18}\text{O}$ reflect the range of the $\delta^{18}\text{O}$ of the two oxygen sources (H_2O and dissolved $\text{O}_{2,\text{atm}}$) and the associated kinetic isotopic fractionations. The observed range for the $\delta^{18}\text{O}$ of the oxidation products attached to pyrite surfaces (SIMS analyses) is wider and presents: (i) sulphates that incorporate dissolved $\text{O}_{2,\text{atm}}$ (from +20 to +25‰), (ii) products similar to the dissolved sulphates with $\delta^{18}\text{O}$ from 0 to +10‰ and (iii) compounds with a negative $\delta^{18}\text{O}$ ($\approx -15‰$) made of a mixture of oxides and sulphates formed on local less acidic surface environments. Natural abiotic air-oxidation produces sulphates and oxides with low $\delta^{18}\text{O}$ (from -15 to -10‰) suggestive of direct oxidation by water vapor.

These results show that, though the mineralogy and isotopic composition of oxidation products cannot be taken as direct simple biosignatures, bio-oxidation is more local and more intense with deeper corrosion morphologies, dispersed monophase oxidation compounds having typical Raman signatures and a strong isotopic heterogeneity at microscale.