



A morphochemical and isotopic approach of pyrite oxidation by autotrophic bacteria : evidence of biosignatures ?

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Biom mineralization and fossilization of microorganisms are still in strong debate for topics like the study of pristine traces of life on Earth or Exobiology. With the development of new technologies and space missions, it is of first importance to find reliable direct or indirect criteria of biogenic processes. The aim of this study was to characterize compounds produced during experimental pyrite bioleaching at the mineral/bacteria interface which could be identified as fossilisable biosignatures. Those experiments have been compared with abiotic oxidations (by O₂, H₂O₂ or Fe(III)_{aq}). Bioleached grains were characterized *in situ* by : Confocal Laser Scanning Microscopy (CLSM) allowing *in vivo* observation, X-ray Photoelectron Spectroscopy, Infra-Red or Raman spectroscopies for molecular identification of secondary products and Secondary Ion Mass Spectrometry for oxygen isotopes measurements.

Oxidation of ferrous sulfides by autotrophic bacteria like *Thiobacillus ferrooxidans* was chosen because it is a well-known system, which can be compared to similar Archean biotopes in which microorganisms were living in sulfur-rich environments. This type of autotrophic bacteria interact strongly with sulfides and could attack the mineral lattice by inducing drastic and permanent chemical and structural changes (pitting and surface oxidation products).

A 1 to 5% statistical surface coverage of bioleached pyrite by bacteria was determined by CLSM. The observed secondary oxidation products at the pyrite surface include (i) sulphates precipitated from the solution (characteristic Raman band ν_1 at 980cm⁻¹)

or directly formed at the mineral surface (μl at 1020cm^{-1}), (ii) ferrous and ferric-oxides, (iii) polysulfides (S_nS^{2-}), (iv) elemental sulfur (S_8) and (v) polythionates. The oxidation layer is composed of micrometric isolated bumps containing one or a mixture of those chemical species.

This chemical and spatial heterogeneity of secondary products is also noticed for oxygen isotopic measurements. A typical $\delta^{18}\text{O}$ of 2.41‰ (± 0.26) is observed for soluble sulphates at the end of bioleaching experiments ($\delta^{18}\text{O}$ of water = -5.5‰) that is in good agreement with literature (Van Everdingen and Krouse, 1985). At variance, the surface oxidation products show large $\delta^{18}\text{O}$ variations at a micrometer scale (from ≈ -40 to $\approx +40\text{‰}$). Such a range is a priori not compatible with known equilibrium isotopic fractionation for sulphates species in solution. The observation may imply : (i) that large isotopic fractionation result from oxidation taking place in a closed system isolated from the solution by bacterial cells, or (ii) that sulphates incorporate oxygen isotopically fractionated during microbial respiration, or (iii) non equilibrium fractionation takes place between water and intermediate species.

Thus, it seems important to identify simultaneously, at a local scale (*i.e.* a few μm), the chemistry of oxidized products, their $\delta^{18}\text{O}$ and their origin to be able to argue in favour of chemical traces of biogenic processes.

Van Everdingen R. O. and Krouse H. R. (1985) Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature* **315** (30), 395-396.