

Accurate μ Raman characterization of reaction products at the surface of (bio)oxidized pyrite

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ABSTRACT

Biotic and abiotic oxidation experiments were performed on ground pyrite grains. MicroRaman (μ Raman) spectroscopy was used to characterize and statistically analyze the reaction products formed at the pyrite surface. Reaction compounds consist of iron and sulfur-oxy species for all experiments including various amounts of sulfates, iron oxi-hydroxides, polysulfides, and elemental sulfur as well as scarce amounts of thiosulfate. These compounds are distributed as micrometric to submicrometric bumps. μ Raman spectroscopy allowed for clear recognition of four phases of iron oxi-hydroxides and, without any correlation, four molecular structures of sulfate groups. Peaks associated with the oxidation products were assigned and are discussed according to hydration and to most probable chemical bonds with pyrite surfaces. Sulfates formed in solution (T_d local symmetry) are distinguished from anhydrous sulfates (C_{3v} to 0 local symmetries) formed directly at the surface of pyrite grains. Proposed structures are related to the surrounding chemical properties (e.g., local acidity) and to the heterogeneous electronic properties of pyrite grains. The distribution and combination of oxidation compounds at the surface of pyrite grains provide clues that distinguish bio-oxidized from chemically oxidized pyrite surfaces. Bio-oxidized surfaces are characterized by the exclusive presence of C_{3v} sulfates that reflect active electronic circulations within the pyrite lattice. In contrast, air-oxidized pyrite surfaces exhibit a high proportion of 0 symmetry sulfates adsorbed on hematite bumps indicating a strong passivation of the mineral surface.

Keywords: Pyrite oxidation, μ Raman spectroscopy, biosignatures, sulfates, iron oxi-hydroxides, electronic circulation