Bacterial Oxidation of Pyrite Surface

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Abstract. The article considers the study of the role of bacteria in the surface oxidation of pyrite. The experiment provided the data on characteristic morphological changes of the surface and the first data on influence of a non-autonomous phase (NP) on bacterial oxidation.

Keywords: Pyrite · Iron-oxidizing bacteria · SEM-EDAX · Non-autonomous phase · Surface

1 Introduction

For many years, extensive studies have been conducted on the processes of diagenetic redistribution of ore-forming components in the Earth’s lithosphere and the formation of iron-containing nodules and ores, aimed at their prospective industrial use. Most researchers believe that the earliest microbial ecosystems were based on sulfur transformations – sulfate-reduction and disproportionation (Wacey et al. 2011). The choice of pyrite as the object of study is geochemically justified by the close connections of iron sulfides with organic matter in various environments, including hydrothermal conditions (Lindgren et al. 2011).

Although the chemistry of the processes has been studied in principle, there remains a number of unresolved issues. The most important are proof of paleobacterial processes and determination of their role in the formation of mineral deposits. Here the range of opinions is very wide: from complete denial to recognition of their leading character at the sedimentary-hydrothermal stage of ore formation (Vinichenko 2007). The morphological effects of the interaction of mineral surfaces with bacteria have not been sufficiently investigated, which complicates interpretation of natural observations. In particular, it is unclear what effect non-autonomous phases located within the surface layer of the crystal have on the interaction of bacterial communities with the pyrite surface (Tauson et al. 2008, 2009a). Non-autonomous phases (NP) are nanocrystalline objects formed in the surface layer of the crystal through interaction with its surface of the growth medium components or contacting autonomous (classical) phases. The experiment within the framework of present research used specially synthesized pyrite crystals with different degrees of NP development on the surface (Tauson and Lipko 2013), with the aim to study the process of interaction between bacteria and NP and to establish the role of surface phases in the oxidative processes initiated by the acidophilic iron bacteria.
2 Methods and Approaches

The culture of acidophilic iron-oxidizing bacteria isolated from natural habitats (sulfide occurrences) of the Baikal area of the Irkutsk region was used for research on the bio-oxidation of the pyrite surface. This bacterial culture was provided by the laboratory № 7 of Irkutsk scientific-research Institute of rare and precious metals and diamonds, JSC “Irgiredmet”. Iron-oxidizing bacteria are used in laboratory tests for bacterial oxidation of resistant iron-sulfide ores containing gold.

The synthesis of pyrite crystals was performed according to the standard technique of hydrothermal thermogradiient synthesis in titanium inserts at T = 450 °C and 500 °C and a pressure of 1 kbar (Tauson et al. 2008). In the synthesis of pyrite Fe⁺S charge was used, the composition of the surface non-autonomous phase was regulated by the activity of sulfur depending on Fe/S ratio. The obtained crystals were up to 5 mm in size. Pyrite, obtained at high sulfur activity, contains virtually no NP on the surface. At lower sulfur activity, a layer of NP up to ~ 500 nm thick with a base composition similar to pyrrhotite, but with different forms of sulfur, is formed: Fe²⁺ [S, S₂, Sn]²⁻ (Tauson et al. 2008). These surface formations are able to absorb cationic impurities and oxysulfide anions.

To conduct research on pyrite bio-oxidation, a mixture of acidophilic iron bacteria was grown on a liquid 9 K medium at room temperature and constant stirring within 5 days. In eight 250 ml conical flasks with 50 ml of 9 K medium (without FeSO₄) there were placed pieces of polished pyrite (4 flasks) and 5–6 pieces of pyrite with nonautonomous phases (4 flasks). The medium and pyrite flasks were sterilized at 0.5 atm. for 10 min to minimize pyrite oxidation. After cooling the medium, 6 flasks were inoculated with 5-day bacterial culture. Previously, the culture was centrifuged and washed from the medium residues with iron in 0.01 m H₂SO₄. The concentration of iron bacteria cells added to the medium with pyrite was about 1*10⁷ cells/ml. The remaining two flasks with polished pyrite and NP on the pyrite surface were used as a control, without bacteria. Cultivation took place at room temperature and constant stirring on a shaker (about 110 rotation/min) for three weeks. Every week 2 flasks with different samples of pyrite were selected for further research. The flasks with control samples were examined after 3 weeks of cultivation. The bacterial film from the pyrite samples was washed with 2% aqueous solution of Polysorbate Tween 80. Pyrite crystals washed after the experiment were dried in air and analyzed on the scanning multi-microscope SMM 2000 in atomic force mode, scanning electron microscope FEI Quanta Company (USA) 200 with energy dispersive device EDAX for X-ray microanalysis.

3 Results and Discussion

The experiment on pyrite bio-oxidation established that the surface of polished pyrite is less susceptible to bacterial oxidation as compared with NP-containing pyrite. Microphotographs show the surfaces of polished pyrite (roughness less than 5 nm) and NP-containing pyrite (roughness more than 300 nm) after two weeks of bacterial cultivation (Fig. 1).
The surface with NP exhibits bacteria and characteristic traces of interaction between bacteria and pyrite in the form of holes of different size comparable to the sizes of bacteria. For polished pyrite, these traces are almost absent and are observed only on the borders of scratches left from polishing. A similar result was obtained for the pyrite surface with minimal NP development synthesized at high sulfur activity. Therefore, the activity of bacteria is associated with the structure of pyrite surface. Similar formations, but significantly smaller (nano-holes) were discovered earlier, in the study of pyrites from the Sukhoi Log gold deposit (Irkutsk region) (Tauson et al. 2009b). This confirms the affinity of processes occurring in nature and in the experiment.

4 Conclusions

The research resulted in acquisition of data on pyrite bio-oxidation taking into account the structure of crystal surface under the given conditions. For this purpose, crystals with different degrees of non-autonomous phases development on the surface controlled by growth conditions were synthesized and used in the experiment for the first time. It was found that the surface of polished pyrite is less susceptible to bacterial oxidation, as compared with pyrite containing a non-autonomous phase. The resulting characteristic morphological changes in the surface will further be instrumental in addressing the issues of ore genesis, as well as identifying minerals that were formed at the initial or final stage of growth involving bacteria.

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