2.1.P11

Direct nanoscale observations of mixed REE phosphate crystal growth on the dissolved surface of REE fluorocarbonate minerals

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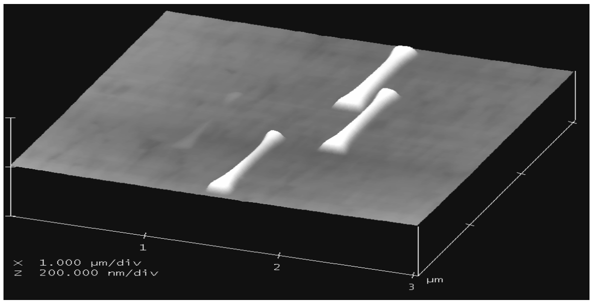
Mixed REEPO$_4$, being investigated for lighting applications and for long-term storage of nuclear wastes, are related to the important mineral monazite. Previous works indicated macroscopically the low-temperature crystallisation of various REEPO$_4$ [e.g. 1,2] exhibiting very low solubillity products (log $K_{sp}^{REEPO_4}$ <-25) [e.g. 3]. We demonstrate herein the first *in-situ* microscopic investigation regarding growth of mixed REEPO$_4$ crystals onto fluorocarbonate mineral surfaces acting as the source of REE during dissolution. The substrates used were natural parisite (Ca(REE)$_2$(CO$_3$)$_3$F$_2$) and bastnäsite (REE(CO$_3$)F)) interacted with H$_3$PO$_4$ aqueous solutions into an AFM fluid cell, at room temperature under atmospheric P_{CO_2}. In H$_2$O, the {0001} surface of the above minerals is progressively dissolved on a nanoscale revealing triangular hillocks. After injection of H$_3$PO$_4$ random aggregates of mixed REEPO$_4$ are promptly developed on the surface of parisite, while individual crystals in parallel array are grown on the dissolved surface of bastnäsite. Thus the crystal growth process, leading to characteristic epitaxy, is slower and it takes place through “connection” of former adjacent triangular hillocks.



In-situ AFM image of REEPO4 crystals (~30 nm in height) epitaxially overgrown on the {0001} surface of bastnäsite

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2.1.P12

Study on the surface chemistry and oxidation mechanism of pyrite mediated by *Thiobacillus ferrooxidans* in the supergene environment

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The surface properties of pyrite and mediation of bacteria may play important roles in oxidation of pyrite in the supergene environment. As the XPS spectra discovered, there is a significant amount of Fe^{3+} distributed on the the surface of pyrite from the Tongling copper ore district of Anhui province, China (see Fig.1), whereas Fe^{2+} is the dominant species. By integrating with the previous researches[1], two-stepped oxidation mechanism of pyrite in the acidic supergene environment is proposed.

In the first step, the Fe^{2+} on the surface of pyrite enter the cells of *thiobacillus ferrooxidans*, which attach on the pyrite surface[2] , and is oxidized into Fe^{3+} subsequently. In the second step, the metabolized Fe^{3+} interacts with the Fe^{2+} on the pyrite surface to induce oxidation of pyrite. The S produced by the reaction between Fe^{3+} and pyrite can be progressively oxidized by oxygen in the air through *thiobacillus ferrooxidans.* The two reactions are given as following equations :

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S$$

$$2S + 3O_2 + 2H_2O \xrightarrow{Thiobacillus\ \ ferrooxidans} 2H_2SO_4$$

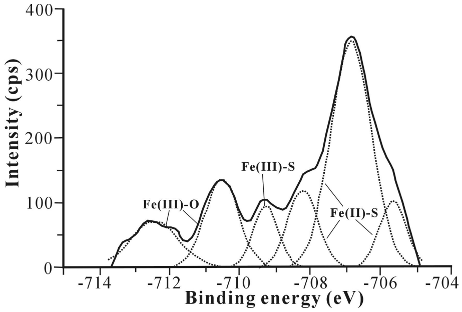

Fig. 1 . The XPS spectra of pyrite surface.

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