2.3.P11

Alteration of phyllosilicates studied in situ by hydrothermal AFM

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The investigation of phyllosilicate surfaces in aqueous solutions at nanometer-scale is significant for industrial applications and for the understanding of fundamental natural processes such as rock formation and weathering. In this work the behaviour of apophyllite and vermiculite was investigated.

Applying various analytical methods [1, 2], changes in chemical composition, structure, and surface morphology were detected on apophyllite at different pH. The changes at low pH were explained by the protonation of the terminal oxygens at the silicate tetrahedra and the removal of the interlayer cations. This causes an increase of interlayer spacing and the formation of a distinct morphological pattern on the surface (Fig. 1a). Here we show that at low pH the pattern are formed discontinuously comprising a multi-step protonation. The reactivity of these surfaces and the formation of different reaction products were studied by in situ pH-jump-experiments.

The reactivity of vermiculite basal surfaces at hydrothermal acidic conditions was found to be much slower than that of apophyllite. At hydrothermal acidic conditions a complex pattern of swelling channels (Fig. 1b) inducing dissolution was observed, reflecting a different reaction mechanism.

Present results stress the reactivity of the basal surfaces of phyllosilicates and provide new details about their swelling behaviour in aqueous solutions.

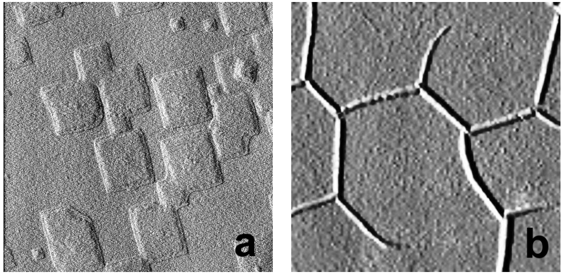

Figure 1. Morphological pattern observed at acidic conditions on a) apophyllite and b) ver miculite (001) surface.

References

[1] Aldushin, K., Jordan, G., Rammensee, W., Schmahl, W.W., and Becker, H.-W. (2004) *GCA*, **68**, 217.
[2] Aldushin, K., Jordan, G., Fechtelkord, M., Schmahl, W.W., Becker, H.-W., and Rammensee, W. (2004) *Clays Clay Miner.*, in review.

2.3.P12

Formation of poorly crystalline iron monosulfides: Surface redox reaction on high purity iron

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The interface between 99.99% pure iron and 0.1 M $NaHCO_3$ deoxygenated solution with $3.1*10^{-5}$ to $7.8*10^{-3}$ M Na_2S*9H_2O added was studied. The surface processes were characterised by the ex-situ techniques X-ray Diffraction, X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy, Energy Dispersive X-ray, and Normal Raman Spectroscopy (NRS). Open Circuit Potential (OCP) was monitored during in-situ NRS measurements, and potentiodynamic anodic polarization measuremtents were also carried out.

OCP-time transients indicated that the native oxide is unstable in deaerated bicarbonate solution and undergoes reductive dissolution leaving the metallic Fe covered by $Fe(OH)_2$, adsorbed OH^-, and patches of 'magnetite-like' oxide. Immidiately upon injection of the Na_2S-solution the iron interface undergoes complex redox surface processes and a poorly crystalline FeS film forms. Potentiodynamic anodic polarization measurements indicated a mechanical breakdown of the FeS film. The origin and initiation of this breakdown process is not clear but is probably a result of internal strees developed during film growth. Based on surface studies supported by electrochemical measurements, a conceptual model for the cmplex redox processes occuring at the iron interface is proposed. This model describes the structural development of a poorly crystalline FeS, which breaks down, allowing further dissolution of the Fe and formation of FeOOH at the interface.