

Nanoscale imaging of ectomycorrhizal weathering processes on minerals

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The weathering of phyllosilicate minerals in soil is vital to the formation of clay minerals, e.g. vermiculite and smectite, and for the release of nutrients, such as K and Mg, into the soil solution for uptake by plants. It is postulated that the plants themselves, along with their associated symbiotic mycorrhizal fungi, may help to accelerate this process through the release of organic acid exudates.

In model experiments at the nanoscale using Atomic Force Microscopy (AFM), we have investigated the *in situ* dissolution of biotite (001) to acid solutions, quantifying dissolution rates at various temperatures, and characterizing the development of etch-pitting. For example, from AFM x,y,z datasets the calculated dissolution rate of biotite (001) in oxalic acid ranges from $4.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ at 283 K to $2.1 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ at 308 K, with an apparent activation energy (E_a) of $49 \pm 2 \text{ kJ mol}^{-1}$. Furthermore we have investigated the relative effects of both proton-promoted and ligand-promoted dissolution, using siderophores in conjunction with organic acids.

These model nanoscale measurements are complemented by the imaging of mineral samples that had been previously implanted into microcosm and mesocosm systems. Biotite, chlorite and hornblende samples have been colonised by ectomycorrhizal fungi (*Paxillus involutus*), and nanoscale alterations in mineral topography arising from the fungi and the associated exudates have been recorded; these post-colonisation images are correlated with topographs and force measurements from exactly the same area before insertion in the micro- and mesocosms. These observations show novel features not previously observed with ectomycorrhizal fungi.

Weathering of Chlorite studied at the nanometre scale using Atomic Force Microscopy (AFM)

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Dissolution of chlorite in batch and flow-through reactors has been investigated by various techniques, but only one Atomic Force Microscopy (AFM) study has been reported to date [1]. AFM is a powerful technique as it enables the topographical changes of dissolving minerals to be followed in real time, under natural, aqueous conditions. Here we report such an approach applied to an Mg-rich chlorite.

The brucite-like layer dissolves in pure water through the generation and expansion of triangular etch pits and the formation of dissolution channels (Fig. 1).

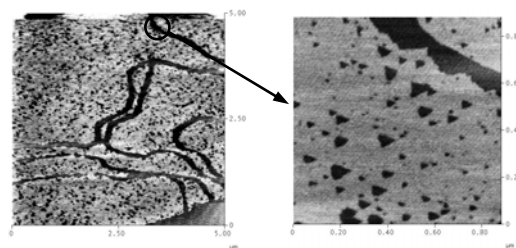


Figure 1: Formation of channels (left) and triangular etch-pits (right) in the brucite-like layer.

In contrast, the talc-like layer is very stable in neutral to acidic weathering solutions: in 200 mM oxalic acid, several hours are required in order to observe the effect of the attack of oxalic acid on the tetrahedral layer.

This work describes for the first time the dynamics of weathering-related features at the nanometre scale in a chlorite mineral.

[1] Brandt *et al.* (2003) *Geochimica et Cosmochimica Acta* **67**, 1451-146.