Nano-scale interactions of fungi with mineral surface

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Classical studies of biotic weathering have mainly focussed on solution phase interactions with minerals and on the ability of plants and microorganisms to influence soil solution composition. Only recently, has the relevance of direct (contact) interactions between fungi and minerals been recognized as an important driver in weathering environments. This can be examplified by the fungal components of lichen symbioses or the ectomycorrhizal association between plants and fungi.

For ectomycorrhiza, the distal tree roots are closely interconnected with a dense fungal mycelium network in which hyphal strands interact directly with soil organic and/or mineral surfaces. These fungal extensions are sustained by the photosynthate of the trees, and in return, they solubilize minerals and directly aid the mass transfer of a large array of elements (e.g. P, N, K, Zn, Fe, Cu etc) towards the tree roots. The exudation of protons, ligands and siderophores by hyphae tips has been suggested as the main factor controlling the weathering of minerals. However, the fungi are in close contact with the mineral surface and therefore may destabilize the lattice structure of the mineral surface, yet this dissolution processus has been largely overlooked and our contribution intends to fill that gap.

In this study, we investigated the weathering of biotite induced by *Sullus bovinus* hyphae grown in symbiosis with *Pinus sylvestris* trees grown on biotite substrates within agar-perlite systems. The fungal-mineral systems were maintained under sterile conditons and fungal hyphae were allowed to colonize the biotite surface (around one cm^2) for about ~ three months before removal of the mineral substrate for analysis. Half of the biotite sample was treated with a detergent to remove the fungal material and expose the weathered surface. This exposed surface was subsequently analysed by Vertical Scanning Interferometry (VSI) to quantify any changes in the biotite surface microtopography and to determine the weathered biotite volume. The other half of the biotite sample, was used for Focus Ion Beam (FIB) sections (~ 100 nm thick, 15 µm long by 5 µm wide) with sections cut across several mature filaments or across terminal hyphae segments. These sections were transferred onto TEM grids and characterized using Electron Energy Loss Spectroscopy (EELS), Energy Dispersive Spectrosopy (EDS) and Energy-filtering TEM (EFTEM). These techniques allows (i) the determination of the mass loss upon hyphae-mineral surface interaction (ii) the quantification of chemical bonds between hyphae and the biotite surface, (iii) the imaging of secondary mineral phases at the interface and (iv) quantification of uptake of elements from mineral to fungi at the molecular scale.

Dolomite nucleation on extracellular polymeric substances

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Research in natural environments, in conjunction with laboratory culture experiments, has demonstrated that microbes can induce low-temperature dolomite formation. Nevertheless, the exact mechanism and the ecological significance of the process remain unclear.

Here, we present a laboratory experiment designed to determine whether dolomite nucleation is an active microbial process at the cell wall or a passive process associated with microbially produced organic compounds. Pure strains of *Desulfovibrio brasiliensis*, a dolomite producing bacterium, were initially grown at 30°C under anoxic conditions in a medium whose chemical composition prevents dolomite formation. The cultures were subsequently sterilized and the chemical composition of the medium modified to permit carbonate precipitation. At this time, nucleation of Ca-dolomite occurred in the absence of living bacteria, but in the presence of fresh extracellular polymeric substances (EPS) previously produced by *D. brasiliensis*.

Our results suggest a key role for EPS in dolomite formation. In contrast, excretion of metabolites and nucleation on the cell wall appear less important for the process. We propose that EPS acts as a structural template at the molecular scale which, absorbing and ordering ions in a preferential way, promotes dolomite formation at 30°C. Our experiments show how microbial activity may induce biomineralization through the excretion of specific organic molecules in the environment. The occurrence of such biominerals may be unexpected if only the inorganic chemistry of the solution were considered.