Mineralogy controls oxalic acid release in mycorrhiza weathering

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Symbiotic Fungal-Mineral Interactions

The roots of most plants support symbiotic mycorrhizal fungi by supplying them with sugars that can take up to a third of the total photosynthate carbon. In return, the fungal mycelium secretes copious amounts of low molecular weight organic acids that can accelerate mineral weathering [1] and promote plant growth. This is of particular importance in the boreal forest where pine trees form ectomycorrhizal associations which ensheath their roots in fungal mycelium. Nutrient uptake by the plant is consequently highly dependent on the ectomycorrhizal partner.

We cultivated *Pinus sylvestris* with the ectomycorrhizal fungus *Paxillus involutus* in sterile microcosms containing a variety of minerals and rock grains. When the fungus made contact with the minerals or rock grains we repeatedly observed the accumulation of crystals on the fungal mycelium. Micro fourier transform infrared resonance (FT-IR) spectroscopy revealed peaks characteristic of calcium oxalate crystals on the fungus when grown on basalt, apatite, olivine, gabbro, microcline and limestone. However, these peaks were not observed when the hyphae grew on granite or quartz, or when the fungus grew on apatite without a plant host. The presence of a plant host and calcium in the minerals/rocks were the key factors for calcium oxalate deposition on the hyphae.

Discussion

Recently, ectomycorrhizal fungi have been found to actively forage for minerals and favour the ones with the highest phosphorus content [1]. In this study we conclude that oxalic acid secretion by *P. involutus* is specifically targeted at certain minerals/rocks such as basalt and limestone that are rich in calcium. This generates localised enhanced weathering and accumulation of calcium oxalate crystals on the fungus. These findings emphasise the role of mycorrhizal fungi as environmental sensors and agents of biological weathering – driven by the carbon energy supply from their plant hosts.

[1] Leake *et al.,* (2008). *Min. Mag.* **72**, 85-89

An alternative approach for carbonate "clumped isotope" measurements and its application to lacustrine carbonates

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"Clumped isotope" thermometry is a method to determine the temperature of carbonate formation based on the excess abundance of ^{13}C-^{18}O bonds relative to the amount expected for a stochastic distribution of isotopes among all CO_2 isotopologues. Ghosh *et al*. (2006) have shown that this excess in abundance is temperature dependent and independent of the $\delta^{18}O$ of the ambient water.

We will present our approach in performing "clumped isotope" measurements on carbonates using a Kiel IV Carbonate Device autosampler and compare data of carbonate measurememnts carried out on on a Thermo Finnigan Delta V plus and on a MAT 253. In addition we will show a different calibration method for the correction of observed linearity effects of the mass spectrometer. This correction is based on measurements of several high-temperature carbonates of different isotopic composition. The use of these high temperature carbonates during sample runs reduces the need for frequent measurements of heated gases and adds an additional control to the quality of measurements.

We will also present new data from lacustrine carbonates from Lake Zurich. Lacustrine carbonates, because of their wide distribution, are important archives of continental climate change. However, the extraction of climatic information from carbonate oxygen isotope records is hampered by the dependency of $\delta^{18}O$ of carbonates from both the temperature and the isotopic composition of the lake water. Clumped-isotope thermometry has the capability to solve this long standing problem. We will compare a lake water temperature reconstruction for the past century from Lake Zurich with measured lake water temperatures. In addition we present data from authigenic carbonates, filtered from the top 10m of the water column of Lake Zurich during the summer of 2008.

[1] Eiler, J. M., (2007), *EPSL* **262**, 309-327. [2] Ghosh, P., *et al*., (2006), *GCA* **70**, 1439-1456.