Methanogen variations related to hydrogeochemical conditions in organic-rich shales and coals in the Illinois Basin, USA

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Deep subsurface methanogens produce approximately 20% of the world's methane from organic-rich coals and shales, yet little is known about their metabolic and environmental requirements. Parameters influencing microbial methane generation include type of organic matter, and salinity and sulphate concentrations. In the Illinois Basin, two organic-rich units, Pennsylvanian coalbeds (~300m deep) and the New Albany Shale (~750m deep), support methanogenesis across a steep salinity gradient with variable sulfate concentrations. We hypothesize that 1) similar to other deep subsurface environments, the types of methanogens in the Illinois Basin are limited, and 2) methanogen variations reflect changes in hydrogeologic conditions. Using groundwater sampling results for solute chemistry, stable isotopes, cell counts, and terminal restrictive fragment length polymorphism, we find that methanogenic species numbers are low, and largely restricted to two groups for the coal and shale. Yet, substrate type has a significant correlation coefficient (>0.3) with species variation, indicating that type of organic matter influences methanogens. Also, chloride and stable isotope values of water have significant correlation coefficients (>0.3) with species variation. These conservative tracers are affected by meteoric water <50, 000 years old, indicating that deep recharge influences methanogenic diversity, and may have transported methanogens into the paleopasteurized subsurface.

Oxalic acid release in ectomycorrhiza mineral weathering

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The dominant trees of temperate and boreal regions have roots sheathed by symbiotic ectomycorrhizal fungi (EM) which use up to a third of the carbon fixed by the plant hosts. In return, the fungal mycelium enhances nutrient uptake by the plants, partially through secretion of low molecular weight organic acids that can accelerate mineral dissolution. EM weathering with pine trees plays a key role in carbon and nutrient cycling processes and pedogenesis, especially in the boreal forest. Here we report how carbon fixed by plants is passed to EM and drives the secretion of organic acids in response to fungal sensing of specific minerals in soil.

Pine seedlings (*Pinus sylvestris*) ectomycorrhizal with *Paxillus involutus* were grown in microcosms containing wells with a variety of mineral/rock grains. Pine shoots were exposed to $^{14}CO_2$. Photosynthetic fixing and transfer of this ^{14}C to the EM and through its mycelial network was traced for up to 35 hours. The quantity of ^{14}C translocated through the mycelium into wells containing mineral/rock grains increased in the order quartz < granite < basalt < limestone. On basalt and limestone, EM proximal to mineral grains was covered with white crystals with micro-Fourier Transform Infrared (FT-IR) spectroscopic characteristics identical to calcium oxalate. FTIR analysis of EM in contact with granite showed very low amounts of calcium oxalate, and none was detected on quartz. Scanning electron microscopy, X-ray analysis and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) confirmed high amounts of calcium in crystals on hyphae grown over basalt and limestone with much lower amounts of calcium found on hyphae grown over granite.

We conclude that trees fix carbon and provide it to EM fungi where it is used in the secretion of oxalic acid specifically targeted at calcium-rich minerals/rocks (e.g. basalt and limestone). Accumulation of calcium oxalate crystals as weathering products on the fungi occurs where EM generates enhanced mineral weathering. These findings emphasise the role of mycorrhizal fungi as environmental sensors and as agents of biological weathering – driven by the carbon energy supply from their plant hosts.