

The intramolecular carbon isotopic composition of acetate in peatland porewaters

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The biogeochemistry of anaerobic porewaters is marked by obligate microbial syntrophy and complex ecological relationships. These *in situ* ecological properties are extremely difficult to probe either *in vitro* or *in situ* with specific inhibitors, since both of these treatments disrupt important microbial connections. Alternatively, stable carbon isotopic analysis of the gaseous substrates and products of methanogenesis can reveal the pathways of methane production. Carbon isotopic analyses of the methyl carbon of acetate provide us with the ability to relate laboratory derived fractionation factors between the acetate methyl and methane to natural systems in the field.

We hypothesize that isotopic estimates of methane production pathway that assume an acetate methyl isotopic composition similar to bulk organic matter can be significantly compromised during times when hydrogen concentrations are high. Such situations might occur when 1) pulses of fermentable substrates are applied or, 2) methanogen activity is limited by low temperatures.

We have adapted a pyrolytic technique for the intramolecular carbon isotopic analysis of acetate in natural samples via direct injection of an aqueous solution. This method capably measures the isotopic composition of the carboxyl carbon from injections of 1 nanomole of acetate in aqueous solution. Samples with acetate concentrations less than 1mM are preconcentrated via lyophilization and reacidified to an appropriate concentration. This technique is reliable down to 30 μ M acetate in the original sample.

Our analyses of the carbon isotopic composition of methane, CO₂, and the intramolecular values of acetate from an acidic peatland in central Pennsylvania challenge assumptions of acetate-methyl isotopic similarity to bulk organic matter. We find the carbon isotopic composition of acetate-methyl carbon in late-winter samples are 10 ‰ depleted relative to bulk organic matter. Using a laboratory determined fractionation factor for autotrophic acetogenesis, we find that a significant percentage of the acetate in acidic peatland porewaters may derive from CO₂.

Argon diffusion, solubility and mineral/melt partitioning in forsterite, enstatite, periclase, quartz and corundum

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Argon diffusivities and solubilities in single, gem-quality crystals of forsterite, enstatite, periclase, quartz and corundum were determined from experiments conducted between 1 and ~6000 bars Ar pressure and temperatures from 425°C to 1020°C. Polished single-crystal slabs were placed in open containers and exposed to an argon atmosphere either in a pressure vessel or in a gas-flow tube furnace at near-atmospheric pressure. Argon atoms from the pressure medium diffused into the crystals to produce near-surface concentration gradients, which were directly profiled using Rutherford backscattering spectrometry. There are no discernable differences in Ar diffusion along different crystallographic axes, and diffusivities do not vary as a function of the intrinsic oxygen fugacity of the experimental vessels. Argon diffusion is slow, and activation energies are low and similar even though crystal structures range from densely packed basic oxides to relatively open framework silicates.

In addition to diffusivities, the uptake gradients also yielded lattice solubilities of argon, as represented by the concentrations at the mineral surfaces. These solubilities are similar for the five minerals investigated and are very high, averaging ~2500 ppm. The solubilities are not well correlated with temperature or pressure: in fact, minerals from the lowest pressure experiments (~1 bar Ar) have essentially the same Ar solubilities as those from the highest pressure experiments (~6000 bar), suggesting that all sites capable of accommodating Ar atoms are filled at Ar pressures as low as 1 bar. These results imply that Ar atoms are hosted by a preexisting population of sites in the minerals, which we suggest are the point defects inherent to all crystalline materials. A series of validation experiments confirmed that diffusivities and solubilities are not complicated by adsorbed or heterogeneously distributed argon. Mineral/melt partition coefficients were calculated using mineral solubilities from this study and published Ar solubilities for basaltic melts. In all cases, Ar is compatible in the minerals investigated, although the degree of compatibility depends upon assumptions concerning the minimum Ar fugacity required to fully populate the available defects. Argon diffusivities and solubilities are used to model partial melting of a mantle reservoir to evaluate the efficiency of partial melting as a mechanism of Earth degassing and atmosphere formation.