

Measurement of intact methane isotopologues, including $^{13}\text{CH}_3\text{D}$

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Methane (CH_4) is both a significant greenhouse gas and resource. Its present and past cycling can be studied through measurements of concentration and/or bulk isotopic ratios ($^{13}\text{C}/^{12}\text{C}$, D/H , and $^{14}\text{C}/^{12}\text{C}$). Currently, isotope ratios are measured by mass spectrometric analysis of H_2 and CO_2 produced from CH_4 , or by spectroscopy of CH_4 . However, the interpretation of bulk isotopic variations of CH_4 are often equivocal, necessitating additional tracers.

We have developed a technique for mass spectrometric analysis of several isotopologues of intact CH_4 , including $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$, and $^{13}\text{CH}_3\text{D}$ (and the method can be extended to others). Our most novel capability is the analysis of the multiply substituted isotopologue $^{13}\text{CH}_3\text{D}$, which is expected to differ relative to a random isotopic distribution due to kinetic isotope effects, mixing processes, and as a function of temperature at equilibrium. Measurements of $^{13}\text{CH}_3\text{D}$ concentrations (along with the singly substituted species) could elucidate the formation temperatures of thermally generated CH_4 , discriminate between sources of CH_4 to the atmosphere (e.g., microbial vs thermogenic gas), and help to characterize CH_4 chemistry in the atmosphere where potentially large enrichments are expected (e.g., [1], [2], [3]).

Measurement of intact CH_4 requires a mass spectrometer capable of separating CH_4 species both from water and from internal isobars (CH_4 adducts, fragments, and isotopologues). We show here the initial results and capabilities of such measurements using the MAT 253 Ultra prototype high-resolution gas-source mass spectrometer. We reproduced δD values of known samples to within 0.2 ‰ (1 s.e. = 0.1‰). In addition to demonstrating accuracy, this result reveals that the method may result in improved precision for δD measurements of CH_4 relative to conventional techniques. We have measured ratios of $^{13}\text{CH}_3\text{D}$ to mass 17 species ($^{13}\text{CH}_4$, $^{12}\text{CDH}_4$, and $^{12}\text{CH}_5$) to better than ± 0.4 ‰ (1 s.e.); this value reflects counting statistics and should be improved with longer counting times. The critical enabling feature of our mass spectrometer is the ability to cleanly separate a portion of the $^{13}\text{CH}_3\text{D}^+$ peak from that of $^{13}\text{CH}_5^+$ (shown in Figure 1.)

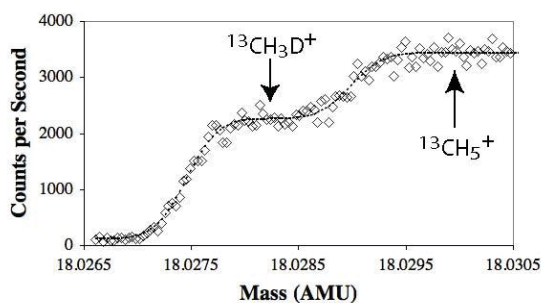


Figure 1: Peak scan of mass 18 CH_4 with a model fit through the data. Water is sufficiently resolved as to not appear at this scale.

[1] Ma et al., (2008) *GCA* **72** 5446-56. [2] Mroz et al., (1989) *GRL* **16**, 677-678. [3] Kaye and Jackman (1990) *GRL* **17**, 659-60.

The Unsaturated (Vadose) Zone—the Where of Weathering

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The unsaturated zone (UZ), that portion of the Earth's crust between land surface and the regional water table—the latter being defined as the surface below which pore-water pressure is persistently above atmospheric—is the vital bio-geochemical reactor that sustains the planetary critical zone. Weathering reactions in the UZ sustain life by releasing bioessential elements such as potassium, calcium, and magnesium that are mostly locked up in solid mineral phases during the bioaccessible parts of the rock cycle. The UZ sits at the intersection of the lithosphere, atmosphere, and terrestrial biosphere, acting as a highly non-linear regulator of water, carbon, and nutrient dynamics. It is the key interface controlling hydrospheric influences on land based life. UZ water is the mobile solvent that delivers aqueous reactants and removes aqueous products from the sites of weathering reactions. It also partitions the pore space within the evolving geometry of soil structure, thereby controlling crucial pore-geometric relations including proximal and long-range connectedness (topology) of gas and liquid phases. The resulting dynamics mediate residence times, redox states, complexation, and chemical activity, along with fluid permeabilities and solute dispersivities. Hysteresis in the relations between water content θ and matric pressure ψ acts to partially constrain fluxes of water (and heat) to the uppermost UZ. This provides plant-root microcosms more opportunity for water and nutrient extraction and moderates weathering reactions by controlling equilibrium versus kinetic control of chemical processes. UZs may be classified according to water-table depth, water balance, and water-flux variability in time and space. These determine whether UZs act as (1) rapid, disequilibrium pass-through conduits with little opportunity for weathering reactions, (2) equilibrium controlled static reservoirs of water and solutes where not much is happening, or (3) totally happening places essential for oxygen-intensive life.

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Vive la Weathering. Vive l'UZ Science. Vive l'Art!