A visual guide to the interpretation of methane stable isotopologue data– application to deep carbon cycles

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Making CH_4

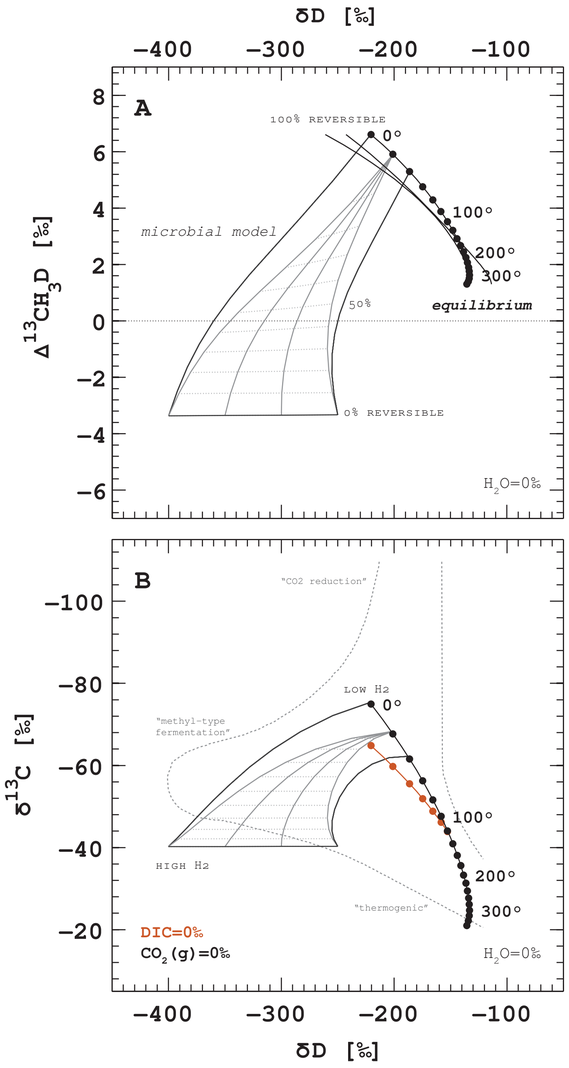

Figure 1. Model of isotopologue abundances in CH_4 produced during microbial methanogenesis from CO_2+H_2 [*Wang et al., 2015*]. The underlay in (B) is the outline of the "Whiticar plot" [*Whiticar, 1990*].

Breaking CH_4

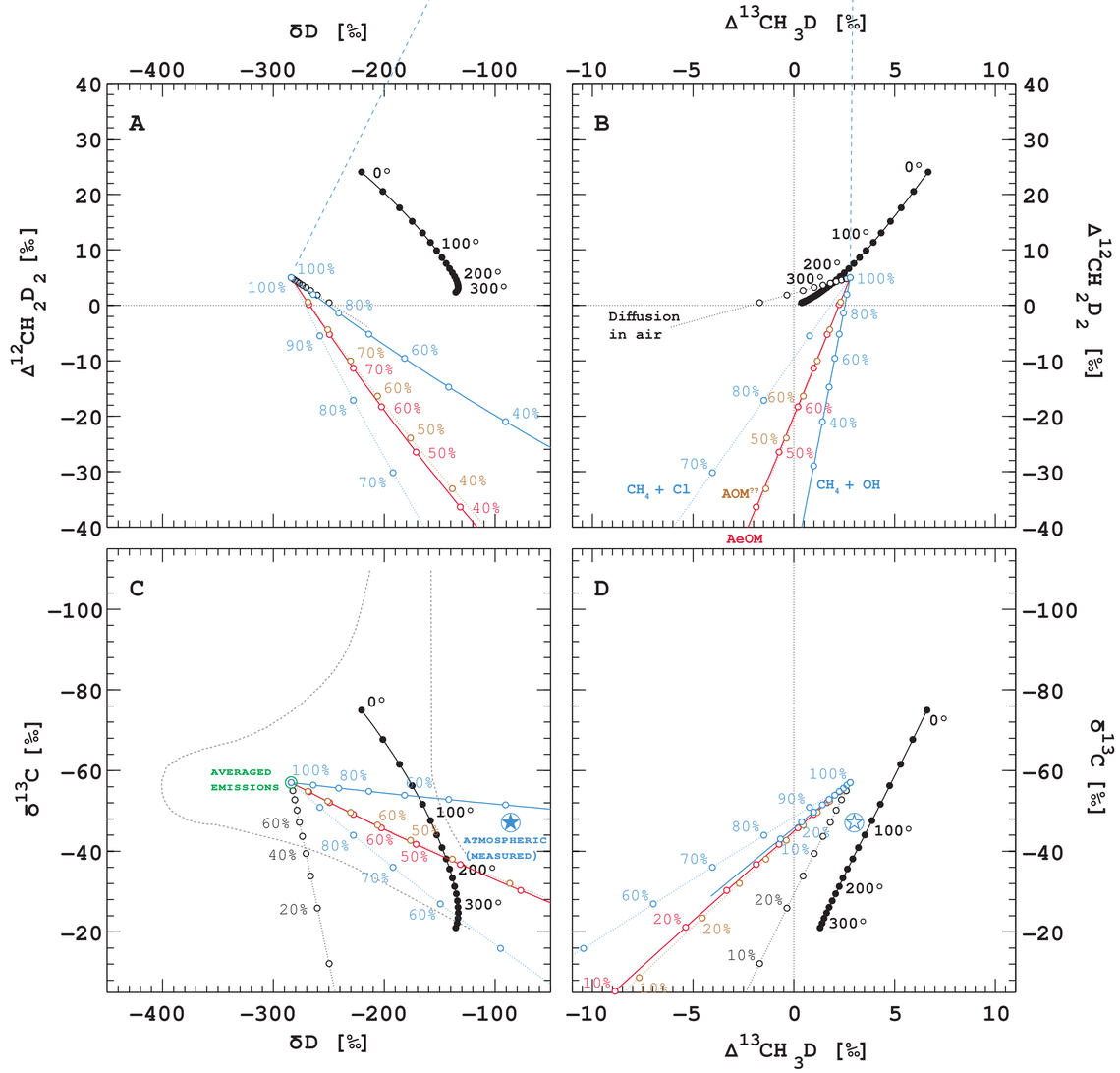

Figure 2. Evolution of CH_4 isotopologue ratios in closed-system, unidirectional bond-breaking processes. Predictions are derived from models and/or data presented by the MIT and UCLA teams [*Wang et al., 2016*; *Whitehill et al., 2017*; *Young et al., 2017*]. Calculations used the estimated weighted average of modern sources of atmospheric methane as the starting point. Trajectory labels indicate the fraction of remaining CH_4. Predictions of atmospheric $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ assume an open system in steady-state.

Swapping Atoms

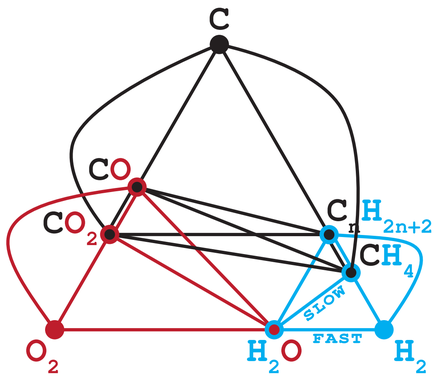

Figure 3. Pathways for isotopic exchange between major species in the system C–O–H. The core & ring of nodes with two colors represent the central & outer atoms, respectively. Each line in this diagram represents a geothermometer comprising the isotope ratios of the corresponding element in the species at the connected nodes.

Attainment of equilibrium in CH_4 clumped isotopologue abundances requires reordering of the C–H bonds within molecules. This may occur by homogeneous (direct) exchange of H between two CH_4 molecules, or by all CH_4 molecules independently exchanging H with a second species (heterogeneous). Understanding the mechanisms enabling exchange in various environments is vital for correct interpretation of classical and novel stable isotope geothermometers.

(*Not shown:* H_3COOH, H_2CO, CH_3OH)