

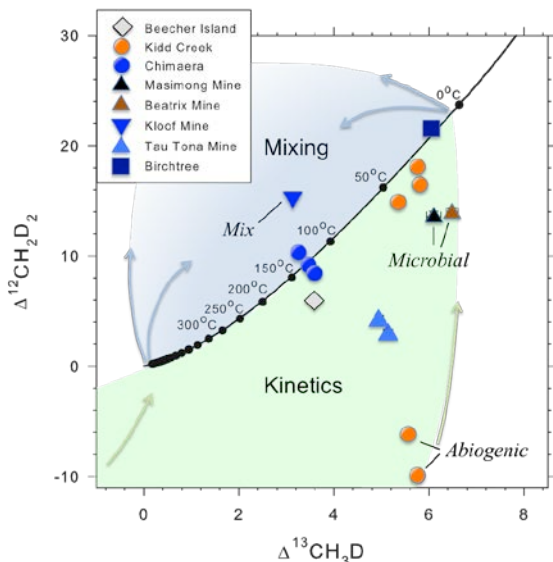
## A survey of methane $\Delta\text{CH}_2\text{D}_2$ vs. $\Delta^{13}\text{CH}_3\text{D}$ in nature and in the laboratory

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We use a large-geometry gas-source isotope ratio mass spectrometer operating at a mass resolving power up to  $\sim 60,000$  to measure resolved ion beams of  $\text{CH}_4$ , including  $^{13}\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$ , in gases from around the globe and from laboratory experiments. Our high-precision (e.g.,  $< 0.4$  ‰ std error for  $\Delta\text{CH}_2\text{D}_2$ ) measurements of  $\Delta^{13}\text{CH}_3\text{D}$  vs.  $\Delta\text{CH}_2\text{D}_2$  show deviations from thermodynamic equilibrium in many gases (Fig. 1).



We have identified two causes for the departures from equilibrium: 1) kinetic limitations on  $\text{CH}_2\text{D}_2$  formation during abiotic synthesis of methane; and 2) mixing. Our simulations of the kinetics of  $\text{CH}_4$  formation on surfaces suggest a temperature-dependent barrier to  $\text{CH}_2\text{D}_2$  formation both in natural samples (e.g., Kidd Creek, Fig. 1) and in  $\text{CH}_4$  synthesis experiments; e.g., the Sabatier reaction at  $90^\circ\text{C}$  produces  $\Delta\text{CH}_2\text{D}_2$  values of  $-56$  ‰. Post-formation isotopic bond re-ordering may be an important process.