

Combined ^{13}C -D and D-D clumping in CH_4 : Preliminary results

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Methane is a key component of natural gas reservoirs, biogeochemical cycles and greenhouse gas emissions. Its cycle is often studied with stable isotopes (e.g., δD and $\delta^{13}\text{C}$), which help to distinguish between various environmental sources (e.g., thermogenic vs biogenic) and sinks [1]. However, as many of these processes generate methane with similar isotopic compositions, new measurements can aid in understanding various aspects of the methane cycle.

We present a new mass spectrometric technique that allows for the measurement of isotopologues of methane with more than one rare isotope ('clumped' isotopologues) at natural abundances. Specifically, we simultaneously measure $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ without interferences from water [2] and with external errors of 0.25-0.3‰ (in the Δ_{18} notation [3]).

Clumped isotopologues can serve as geothermometers for equilibrated systems, quantify kinetic processes and fingerprint different sources and sinks. To better understand the information recorded by the clumped isotopes of methane, we experimentally generated a high-temperature (200-500°C) calibration of equilibrium clumping, including approaches to equilibrium from multiple starting points. Application of this calibration to thermogenic methane samples from natural gas fields generally yields high temperatures ($\sim 190 \pm 65$ °C), which span the range of nominal natural gas formation temperatures, though with one high temperature outlier. The same calibration applied to biogenic gases gives lower temperatures (~ 45 -60°C) that are consistent with their inferred or known formation temperature.

Preliminary results indicate that the temperatures derived from combined $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ clumping are, in most cases, reasonable formation or storage temperatures. This suggests that methane may achieve internal isotopic equilibrium in both high and low temperature processes and retain that signature during storage. If so, then measurements of methane clumped isotopes will serve as a straightforward way to distinguish sources of methane in nature and give insight into the physics and chemistry of how methane forms.

[1] MJ Whiticar, *Chemical Geology* **161** (1999). [2] JM Eiler *et al.*, *IJMS* **335** (2012). [3] JM Eiler, *EPSL* **262** (2007).

The petrochemistry of Jake_M: A martian mugearite

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Jake_M (JM), the first rock analyzed by the APXS instrument on the Curiosity rover, is an alkaline igneous rock ($\sim 13\%$ normative nepheline). It differs significantly in composition from other known martian rocks and it is fractionated relative to typical martian igneous rocks (MgO ~ 3.5 wt%; Mg# ~ 0.37 ; Ni < 50 ppm; normative oligoclase and orthoclase [$\sim 13\%$]). JM is compositionally similar to terrestrial mugearites, a magma type typically found on ocean islands and in continental rift zones; indeed, were JM found on earth, we would be hard pressed to tell from its composition that it is a martian rock.

The discovery of this rock type on Mars likely indicates an origin by significant fractional crystallization of a primary alkaline or transitional magma generated by melting a region of the martian mantle compositionally distinct from the sources of other known martian basalts. JM's chemical composition (especially its high Al_2O_3 and low FeO contents) suggest that this fractional crystallization occurred under conditions that suppressed plagioclase crystallization relative to crystallization at 1 atm. Although non-unique, MELTS calculations indicate that a reasonable match to JM's composition can be achieved at 2 kbar (~ 15 km depth on Mars) after $\sim 50\%$ fractional crystallization of an estimated parental composition from St. Helena island containing 1.5 wt% H_2O . This result suggests a possible role for elevated pressure and/or water content in JM's petrogenesis.

The discovery of JM has implications for magmatic and eruptive processes on Mars, for the possibility of primary hydrous minerals in martian igneous rocks and for encountering even more fractionated alkaline magmas such as phonolites and trachytes. JM is also distinctly richer in potassium than other martian basalts, consistent with a metasomatized mantle source, perhaps characteristic of the mantle beneath the Gale Crater region.