

Methane $^{13}\text{C}/^{12}\text{C}$ isotope analyses with the SAM-EGA pyrolysis instrument suite on Mars *Curiosity* rover: A critical assessment

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The amounts of methane and $\delta^{13}\text{C}_{\text{CH}_4}$ evolving from pyrolysis of the Sample Analysis of Mars evolved gas analysis (SAM-EGA) instrument suite as reported in ref. 1 are inconsistent with fundamental observations of thermogenic formation of methane from organic matter precursors. In pyrolysis, samples with organic carbon are heated, whereby the carbon isotopic composition of the evolving methane ($\delta^{13}\text{C}_{\text{CH}_4}$) is depleted in ^{13}C compared to the organic carbon precursor and increases systematically with increasing temperature (e.g., figure 11 in ref. 2 and figure 5 in ref. 3). The pyrolysis setup of the SAM-EGA instrument suite is that of

the so-called open-system pyrolysis for which quantitative data are available (3).

In comparison to these laboratory calibrations (“T” and “C” in Fig. 1), the SAM-EGA $\delta^{13}\text{C}_{\text{CH}_4}$ values are erratic, and do not exhibit any relationship with temperature and/or the amount of evolved CH_4 (Fig. 1). Specifically, $\delta^{13}\text{C}_{\text{CH}_4}$ values in 10 out of 16 samples are either more negative than -100‰ or more positive than -25‰ , values never measured in pyrolysis; moreover, $\delta^{13}\text{C}_{\text{CH}_4}$ values of eight samples >20 nmol are similar to that of *N*-tert-butyltrimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA), a potential contaminant (Fig. 1).

Despite these serious analytical issues, the authors (1) conclude, from the 10 most-depleted $\delta^{13}\text{C}_{\text{CH}_4}$ values, that “biologically produced methane from the Martian interior could result in the deposition of ^{13}C -depleted organic material after photolysis,” thus inferring that ^{13}C -depleted methane from a high-temperature process is of biological origin! Finally, the authors offer “Martian methanotrophy” and infer the widespread existence of “methane [that] was already ^{13}C depleted because of its biological production during methanogenesis.” Again, biogenesis of methane based on 9 out of 24 depleted $\delta^{13}\text{C}_{\text{CH}_4}$ values from a high-temperature process to infer methane as a proven biosignature on Mars.

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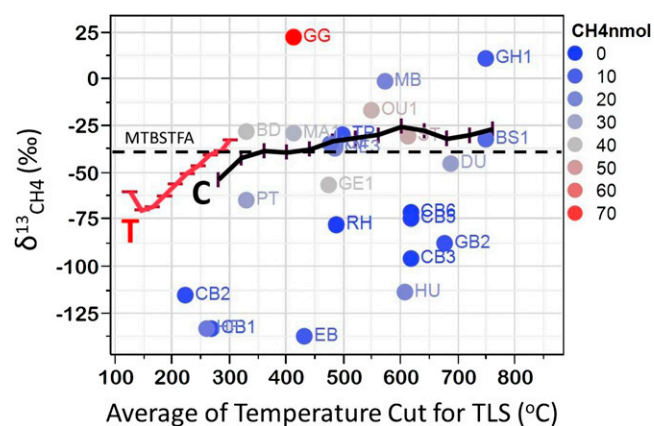


Fig. 1. SAM-EGA pyrolysis carbon isotopic composition of the evolved methane related to the pyrolysis temperature in comparison with laboratory data. The red line “T” is the trend for cumulative methane evolution in sealed gold tube pyrolysis from Tang et al.’s (2) figure 11. The black line “C” is from open-system pyrolysis with instantaneous methane formation (3). The SAM pyrolysis $\delta^{13}\text{C}_{\text{methane}}$ exhibit no correlation with temperature or methane concentration but rather plot randomly with an unrealistic range from -137‰ (EB) to $+11\text{‰}$ (GH1). Sample ID is from ref. 1. MTBSTFA is a potential contaminant from earlier wet chemistry experiments on the SAM instrument (1).

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