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DUAL ISOTOPIC COMPOSITION OF METHANE IN MURCHISON METEORITE. A. L. Butterworth, M. A. Sephton and I. Gilmour, Planetary and Space Sciences Research Institute, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (email: a.l.butterworth@open.ac.uk)

Introduction: Examining the record contained within the organic matter in meteorites can reveal the nature of the inputs and processes that contributed to the early solar system environment. Specifically, isotopic measurements for individual organic compounds can reveal the reaction mechanisms and possible source environments from which the organic constituents were formed. Hydrogen isotopic measurements have become valuable indicators of the contributions from interstellar environments [1] and carbon isotopic measurements have been used successfully to indicate bond formation and destruction in a variety of meteoritic organic molecules [2,3]. Here, for the first time, we present dual isotopic data (H and C) for methane, the fundamental building block implicated in the stepwise formation of meteoritic hydrocarbons [2].

D/H measurement of methane. The D/H ratio of methane has been accomplished previously by a direct method involving the catalytic combustion of methane to CO₂ and H₂O and subsequent reduction of the water to hydrogen gas for measurement by mass spectrometric analysis. In this way, several D/H measurements of atmospheric methane have been made using 70 μmol methane, *e.g.* [4]. This large sample requirement has prevented the direct method being used for the D/H measurements of extraterrestrial methane.

An alternative approach to obtaining D/H ratios of methane is by an indirect method [5]. By measuring the combined isotopic composition of methane (mass 17/16 ratio) and the ¹³C/¹²C ratio (by combustion to CO₂), the D/H ratio may be calculated by the following relationship:

$$\frac{{}^{17}\text{M}}{{}^{16}\text{M}} = \frac{{}^{13}\text{C}}{{}^{12}\text{C}} + 4 \frac{\text{D}}{\text{H}}$$

where ¹⁷M and ¹⁶M represent the intensities of methane species (¹³CH₄ + ¹²CH₃D) and ¹²CH₄ respectively. A NIST standard methane, NGS#3, has been defined as having δ¹⁷M 0.0 ‰ (¹⁷M/¹⁶M = 0.0109351) [5] so that the combined isotopic composition of a methane sample may be represented similarly to the Urey delta notation as follows:

$$\delta^{17}\text{M} = \left[\frac{({}^{17}\text{M}/{}^{16}\text{M})_{\text{sample}}}{({}^{17}\text{M}/{}^{16}\text{M})_{\text{reference}}} - 1 \right] \times 1000$$

The dual isotopic composition of methane may be resolved from the combined isotopic signature using the equation:

$$\delta\text{D} = (17.5528 \cdot \delta^{17}\text{M}) - (18.043 \cdot \delta^{13}\text{C}) - 1490.6$$

The advantage of using methane itself as the analyte for mass spectrometric analysis is that chemical conversions involving water are avoided, the associated memory effects are eliminated and the required sample size is reduced.

A further reduction in sample size is achieved by analysing the methane in a static mass spectrometer. All of the sample is admitted to the mass spectrometer at once and compared to an identically sized aliquot of reference methane, which is analysed immediately after the sample has been pumped away. The mass spectrometer developed for methane isotope analysis (MIRANDA) has been used to investigate the properties of small samples (in 10 ml air) of atmospheric methane [6]. In addition, the instrument has been used to measure the combined isotopic composition of methane evolved during the stepped pyrolysis of some lunar soils [7].

Method: In an evacuated 3 ml Pyrex vessel, the volatile component was extracted from a powdered sample of Murchison interior (76 mg) in 0.2 ml water using freeze/thaw cycling assisted by sonication at 25 °C. The vessel was then attached to the vacuum inlet system of the static mass spectrometer (MIRANDA), allowing several hours for the joining volume to be evacuated.

The water was then frozen in liquid nitrogen and the headspace expanded into the high vacuum inlet for sample clean-up. There were two main purification stages; the first was to remove any water, since water cracks in a mass spectrometer source to produce isobaric interference at mass 17. The second stage was to minimise adverse pressure effects by removing almost all other gases present. Nanomole quantities of nitrogen were very difficult to avoid, but are too small to make gas chromatographic separation necessary, since the static system requires all carrier gas to be removed

before the sample may be admitted to the mass spectrometer. Fortunately active gases may be gettered using SAES St172 at 50 °C without affecting the isotopic composition of the methane. Only traces of noble gases remained in the analyte, which do not affect the m/z 17/16 ratio.

A “blank” of the entire procedure was carried out which resulted in 7 pmol methane detected in the mass spectrometer.

Results: A total of 0.266 nmol methane was recovered from the sample, which equates to 3.5 nmol/g, a lower yield than 8.9 nmol/g achieved by Yuen et al. [2].

As shown in Fig.1, assuming $\delta^{13}\text{C} +9.2 \pm 1.0$ ‰ (V-PDB) from [2], a δD value of $+906 \pm 50$ ‰ (V-SMOW) was calculated from the measured $\delta^{17}\text{M}$ of $+148 \pm 2$ ‰ (NGS#3).

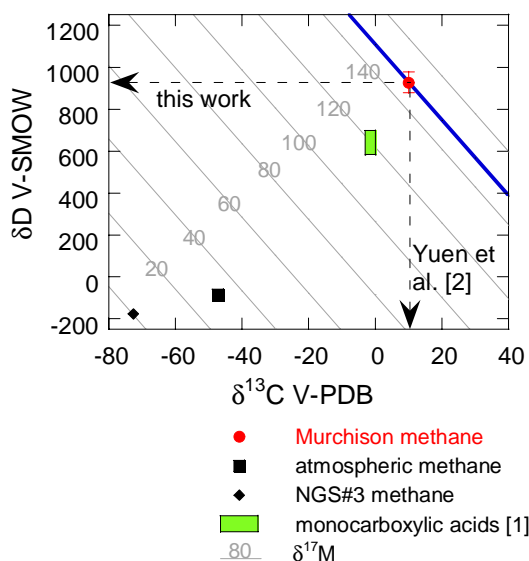


Figure 1: The plot of δD against $\delta^{13}\text{C}$ shows possible isotope combinations that result in particular $\delta^{17}\text{M}$ values plotted in steps of 20 ‰. Atmospheric methane and the reference NGS#3 (defined as having $\delta^{17}\text{M} = 0.0$ ‰) are shown for comparison.

Discussion: The δD value obtained for Murchison methane is significantly higher than bulk measurements of dried, solvent extracted aliphatic fractions from this meteorite but is comparable with bulk measurements for more polar dried organic fractions [2]. The apparent discordance between methane and aliphatic fractions from Murchison is unsurprising since bulk measurements are averages of a wide range of isotopically and structurally different molecules, including contri-

butions from terrestrial contaminants. Furthermore, the bulk fractions will have had their most volatile components, such as methane, removed by drying prior to analysis.

The high δD value of Murchison methane suggests the presence of some interstellar hydrogen in the molecule. D-enrichments are thought to result from gas phase ion-molecule and other reactions in the interstellar medium [8]. As methane is a building block of at least one class of organic molecule [2] and is also a common cracking product of high molecular weight organic matter, its $\delta^{13}\text{C}$ value may reflect the degree of carbon-carbon bond destruction that has occurred within the organic inventory of a meteorite. Additionally, as methane that has originated from a cracking process can be expected to contain less D than inherited material due to the high abundance of solar system normal hydrogen on meteorite parent bodies, the δD values may also be an indicator of the level of secondary processing.

It should be noted that the mass spectrometry technique has a tendency for a possible stretching of the $\delta^{17}\text{M}$ scale, a problem heightened by the use of a D-depleted methane standard for calibration for this work. Further work will address these calibration issues which may produce a slightly higher than true δD value. By disaggregating chips of meteorite, rather than a ground sample, we hope to increase methane yields.

In essence, this work is a study of the possibilities for measurements of the dual isotopic composition of very small samples of methane. Since Yuen et al. [2] analysed 209 nmol CH_4 to obtain $\delta^{13}\text{C}$, advances in continuous flow mass spectrometry have reduced the sample size needed (to ~ 0.4 nmol) [9]. The optimum sample size for $^{17}\text{M}/^{16}\text{M}$ measurement is 0.3 nmol (cf. methane D/H sample $70\mu\text{mol}$ [4]). For the first time it is possible to measure the dual isotopic composition of methane from less than 1 nmol total sample (120 mg Murchison).

References: [1] Krishnamurthy R. V. et al. (1992) *GCA* 56, 4045-4058. [2] Yuen G. et al. (1984) *Nature* 307, 252-254. [3] Sephton, M.A., et al. (1998) *GCA* 62(10), 1821-1828. [4] Levin I. et al. (1993) *Chemosphere* 26(1-4) 161-177. [5] Morse A. D. et al. (1996) *Rapid Commun. Mass Spectrom.* 10, 1743-1746. [6] Jackson et al. (1999) *Rapid Commun. Mass Spectrom.* 13, 1329-1333. [7] Lécluse C. et al. (1995) *Meteoritics* 30, 534 [8] Sandford, S.A. (1996) *Meteorit. Planet. Sci.* 31: 449-476. [9] Merritt et al. (1995) *J. Geophys. Res.* 100, 1317.