Combined element (H and C) stable isotope ratios of methane in carbonaceous chondrites

Anna L. Butterworth,[1]★ Olivier Aballain,[2] Jerome Chappellaz[2] and Mark A. Sephton[1]†

[1]*Planetary and Space Sciences Research Institute, Open University, Milton Keynes, Buckinghamshire MK7 6AA*
[2]*Laboratoire de Glaciologie et Géophysique de l'Environnement (CNRS-UJF), 54 rue Molière - Domaine Universitaire - BP 96, 38402 St Martin d'Hères Cedex, France*

ABSTRACT

We have performed the first ever combined-element stable isotopic measurements of extraterrestrial molecules. Methane from two carbonaceous chondrites, Murchison and Cold Bokkeveld, was measured for its hydrogen and carbon isotopic compositions. The combined isotopic composition of meteoritic methane reveals information about the indigenous nature of volatile aliphatic organic matter in meteorites and its probable extraterrestrial source environment. Deuterium enrichments relative to the solar nebula 4.6 Gyr ago reflect a contribution from low-temperature chemical reactions in interstellar space. Similar carbon but different hydrogen isotopic compositions for methane in the two meteorite samples probably represent comparable primary origins but varying levels of secondary processing and exchange with isotopically light hydrogen. Our high precision laboratory-obtained measurements provide valuable reference points for observational spectroscopists undertaking astronomical investigations of the stable isotopic composition of extraterrestrial methane.

Key words: astrochemistry – molecular data – methods: laboratory – meteors, meteoroids – Solar system: formation – ISM: molecules.

1 INTRODUCTION

Methane has been detected in several extraterrestrial environments by ground-based and space-based observations. Interstellar clouds, high- and low-mass protostellar objects, comets and the atmospheres of gaseous giant planets and moons in our outer Solar system all contain significant amounts of this simple organic molecule (e.g. see reviews by de Bergh 1995; Ehrenfreund & Charnley 2000). It is possible that, to some extent, the methane and other volatiles in these environments may share a common origin. Substances that comprised the interstellar cloud may not have been completely reprocessed during the formation of the Sun and planets and may have survived to contribute to the volatile inventory of primitive Solar system objects. Establishing the nature and fate of presolar methane is useful for constraining models of chemical evolution of the early Solar system.

Ground-based and space-based observations of methane in extraterrestrial environments can be supplemented by laboratory-based analyses. Extraterrestrial methane is available on Earth contained within certain primitive meteorites (Yuen et al. 1984), termed

carbonaceous chondrites. As fragments of ancient asteroids they have escaped extensive geological recycling experienced on larger planet-sized bodies. Methane in carbonaceous chondrites is part of a significant amount of carbon- and hydrogen-bearing organic matter that represents a valuable and tangible record of the inputs and processes that contributed to the early Solar system environment (Sephton 2002).

In well-characterized carbonaceous chondrites such as the Murchison meteorite, approximately 25 per cent of organic matter is present as solvent-soluble or free compounds, which comprise a wide variety of compound classes including aliphatic hydrocarbons, aromatic hydrocarbons, amino acids, carboxylic acids, hydroxy acids, sulphonic acids, phosphonic acids, alcohols, aldehydes, ketones, sugar-related compounds, amines, amides, nitrogen heterocycles and sulphur heterocycles. The remaining 75 per cent or so is a complex solvent-insoluble macromolecular material consisting of aromatic cores connected by aliphatic and ether linkages with various functional groups attached. Methane is reported to represent approximately 0.016 per cent of free organic inventory in Murchison.

The most fruitful laboratory-based approaches to reading the record in meteoritic organic matter involve the use of stable isotopes (Sephton & Gilmour 2001a). Early studies of this kind obtained information about a single-element isotope ratio of bulk fractions

★Present address: Space Sciences Laboratory, University of California at Berkeley, 7 Gauss Way, CA 94720-7450, USA.
†E-mail: m.a.sephton@open.ac.uk

representing either the separated whole, free or macromolecular organic assemblages (Becker & Epstein 1982; Belsky & Kaplan 1970; Krouse & Modzeleski 1970; Kvenvolden et al. 1970; Robert & Epstein 1982; Smith & Kaplan 1970; Yang & Epstein 1983). Later work achieved higher resolution by utilizing more preparative chemistry to achieve similar measurements for isolated fractions that contained compounds with broadly similar chemical structures (Cronin et al. 1993; Epstein et al. 1987; Krishnamurthy et al. 1992; Pizzarello et al. 1994, 1991). More recently, stable isotopic analyses have progressed to the stage where determinations of single-element isotope ratios for individual compounds are being achieved (Engel, Macko & Silfer 1990; Engel & Macko 1997; Gilmour & Pillinger 1994; Naraoka, Shimoyama & Harada 2000; Pizzarello et al. 1991, 2001; Pizzarello & Huang 2002; Sephton & Gilmour 2001a; Sephton, Pillinger & Gilmour 1998, 2000, 2001; Yuen et al. 1984).

Currently, compound-specific isotopic analysis techniques have developed to the extent where it is now possible to measure two different elemental isotope ratios of the same compound. Such methods provide simultaneous isotope ratio determinations for hydrogen and carbon (Morse et al. 1996), carbon and nitrogen (Rennie et al. 1996), oxygen and hydrogen (Begley & Scrimgeour 1997), and carbon and oxygen (Hener et al. 1998). If the different elements that make up a compound are transformed to distinct analytes before isotope ratios are determined then the technique is termed dual-element isotope ratio analysis. If the compound is measured in its entirety and single isotope ratios of the constituent elements calculated by subtraction then the technique is known as combined element isotope ratio analysis. To date, no laboratory-based dual element or combined isotope ratio measurements have been achieved for any extraterrestrial organic compound.

In this paper we report the combined element (H and C) stable isotopic composition of methane from two carbonaceous chondrites, Murchison and Cold Bokkeveld. The combined isotopic composition of meteoritic methane reveals valuable information about the indigenous nature of the volatile aliphatic organic molecules in meteorites, their probable extraterrestrial source environment and history of secondary processing during Solar system formation and evolution. Furthermore, the data provide high precision laboratory-obtained references for observational spectroscopists investigating the isotopic composition of methane before, during and after the birth of the Solar system.

2 EXPERIMENTAL WORK

2.1 Freeze–thaw disaggregation

For samples of each of the meteorites, Murchison (107 mg, 271 mg), Cold Bokkeveld (200 mg, 314 mg) and Orgueil (352.5 mg), the volatile component was extracted from chips using freeze/thaw cycling. A 10-ml internal volume Pyrex vessel (Fig. 1) was pre-roasted at 450°C before adding 0.5 ml of triple distilled reverse osmosis water. The water was degassed by combining a method of ultrasonic vacuum degassing (Schmitt et al. 1991) with a freeze (ethanol–ice slush, −20°C), pump, and thaw cycle. The ground glass base of the sample vessel (Fig. 1) allowed ice to form slowly from the base up, so that the vessel did not break. Meteorite chips were outgassed in the evacuated side arm (1), then tipped into 0.5 ml water (2). The 10-ml volume was closed before the sample was subjected to extended periods of the freeze–thaw cycling described above.
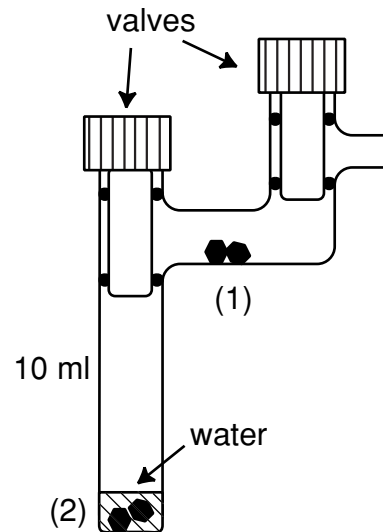

Figure 1. Schematic of the purpose-built freeze–thaw disaggregation apparatus designed to release volatile organic compounds from carbonaceous chondrites.
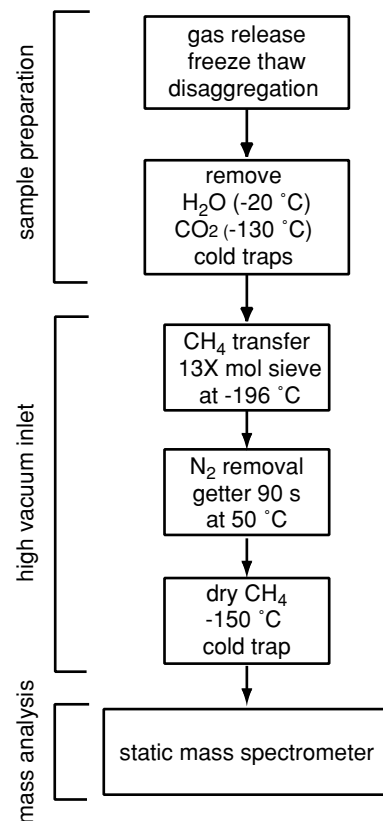

Figure 2. Schematic of the inlet and mass spectrometer system developed for the combined element (H and C) isotope analysis of methane.

2.2 Combined-element stable isotopic analysis

Any methane contained in the headspace gases was analysed using a purpose-built static mass spectrometer system (Fig. 2; Morse et al. 1996). The meteorite/water mixture was held at −20°C (ethanol bath cooled by liquid nitrogen) to trap H_2O, while CO_2 was trapped on to a cold finger (*n*-pentane/liquid nitrogen) slush −130°C.
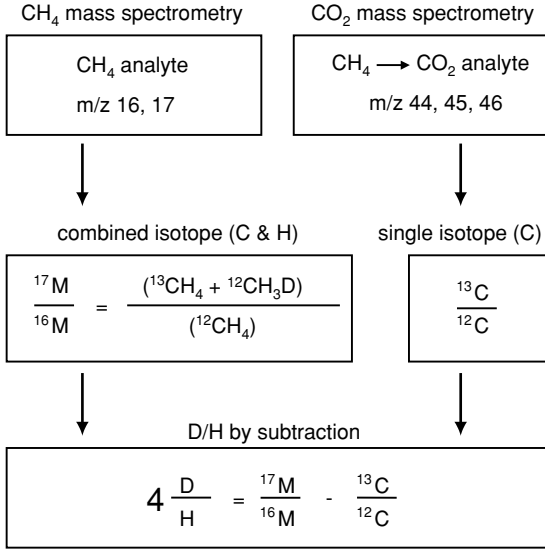
Figure 3. Analytical flow chart illustrating how combined-element stable isotope ratios are obtained.

Meanwhile methane was collected on a 13X molecular sieve trap, which was then heated to 150°C to release the methane into a static high vacuum volume. The gas was gettered (0.89 g of St172, SAES Ltd[1]) leaving only methane and noble gases. A final drying stage (cryogenic trap at $-150°$C) provided a pure methane analyte for mass spectrometric analysis. Methane was then measured as a single analyte for its combined (H and C) isotopic composition. The minimum sample size for isotope ratio measurements was 0.1 nmol, however the detection limit is ten times lower before background and isobaric interference may mask a methane signal. If methane was detected and successfully measured, freeze–thaw disaggregation was performed on a second sample of the meteorite for carbon isotope ratio determination as below.

The combined stable isotope ratio was resolved into the elemental isotope ratios for methane by measuring the carbon isotope ratio and calculating the hydrogen isotopic composition by subtraction (Fig. 3). The carbon isotope ratio of methane was measured with a Finnigan gas chromatograph–combustion interface coupled to a Finnigan MAT 252 isotope-ratio mass spectrometer in continuous flow mode as in Bräunlich et al. (2001). Owing to the small sample size and the difficulty in determining internal reproducibility from replicates, we conservatively estimate the uncertainty of carbon isotopic ratios to be ~ 1‰ (the routine reproducibility is ~ 0.05‰ on 3 nmoles of CH_4).

The abundances of stable isotopes are expressed in two forms. Simple ratios (D(^{2}H)/^{1}H and ^{12}C/^{13}C) as used in astronomical studies and δ values (δD and δ^{13}C) as used in geochemistry. δ values indicate the difference, in per mil (‰), between the relevant ratio in the sample and the same ratio in an international standard as follows:

$$\delta‰ = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000,$$

where $R = D/H$ for hydrogen and ^{13}C/^{12}C for carbon. Standards were Vienna Standard Mean Ocean Water (VSMOW) for hydrogen ($D/H = 0.0001557$) and Vienna Peedee belemnite (VPDB) for carbon (^{13}C/^{12}C = 0.0112372$). Carbon isotopes were measured

against a pure CO_2 standard with a δ^{13}C value of -45.98 ± 0.02 ‰ versus VPDB. Comparisons with an isotopically heavier standard with a δ^{13}C value of -6.47‰ indicate no significant linearity effects. Procedural blanks (44 freeze–thaw cycles) were less than 0.009 nmol methane.

3 RESULTS AND DISCUSSION

3.1 Methane from freeze–thaw disaggregation of carbonaceous chondrites

Table 1 lists the abundances of volatile products released by freeze–thaw disaggregation. The data indicate that while methane is common to CM2 meteorites such as Murchison and Cold Bokkeveld it is absent from CI1s such as Orgueil. The 2.3 nmol g^{-1} abundance of methane in Murchison is less than found in previous work by Yuen et al. (1984) who used freeze–thaw disaggregation methods to release 8.9 nmol g^{-1} from this meteorite. Presumably, the difference in abundance between this and the Yuen et al. (1984) studies is due to heterogeneity of volatile contents within the Murchison meteorite. Earlier work by Belsky & Kaplan (1970) employed a crushing technique combined with a vacuum system and gas chromatograph detector to detect methane in 11 meteorites including eight carbonaceous chondrites. However, the ever-present nature of methane following the crushing procedure raises the possibility that the detected gases may have been analytical artefacts.

The different number of freeze–thaw cycles required to completely disaggregate CI1 and CM2 meteorites (Table 1) may provide a clue as to why their methane contents are dissimilar. Orgueil rapidly disaggregates whereas Murchison and Cold Bokkeveld require multiple cycles to achieve the same effect. The reduced resistance of CIs is related to the more extensive levels of pre-terrestrial alteration experienced by these meteorites. Therefore, the greater cohesion of the CM2s may help to occlude and retain gaseous organic components such as methane.

3.2 Methane stable isotopes

Table 1 lists the combined isotopic composition of methane from Murchison and Cold Bokkeveld. Fig. 4 displays this data alongside ranges of carbon and hydrogen isotopic composition of methane from several cosmic settings. Excluding the possibility of terrestrial contamination is an imperative first step in the analysis of meteorites. The meteoritic methane data in Fig. 4 are distinct from terrestrial sources of methane (Wahlen 1994) and, therefore, the molecules extracted by our procedure are not laboratory artefacts or the result of terrestrial contamination and must be indigenous extraterrestrial molecules.
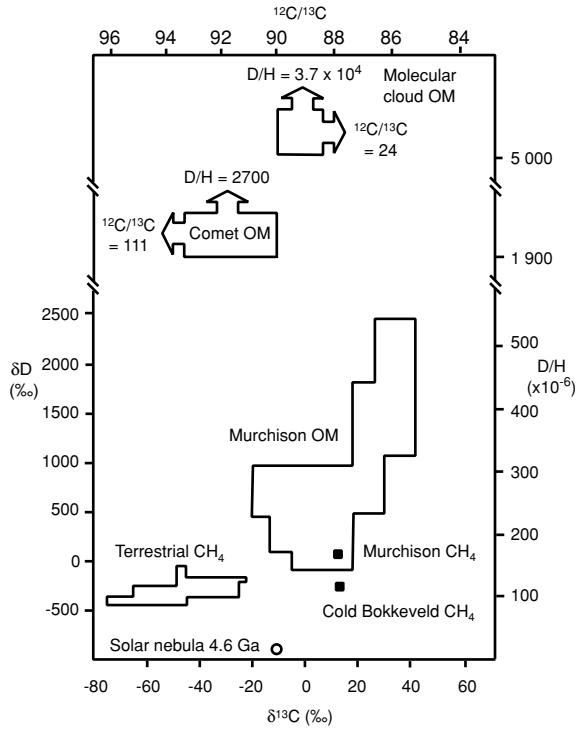
The hydrogen isotopic composition of various extraterrestrial materials (Table 2) was reviewed recently (Robert, Gautier & Dubrulle 2000). Briefly stated, all deuterium originated in the big bang and since then has been continually destroyed in stars causing a reduction of the overall deuterium content of the cosmos. However, in interstellar environments deuterium is concentrated when organic molecules take part in low temperature (10–20 K) reactions (e.g. Sandford, Bernstein & Dworkin 2001). In higher density and temperature environments such as solar nebulae, deuterated molecules become progressively isotopically lighter owing to exchange reactions with isotopically light hydrogen. Yet owing to the extreme deuterium enrichments associated with interstellar molecules, their ultimate contribution to organic matter can often be recognized even after extensive exchange has occurred. Comparing the data

---

[1] SAES Getters (G.B.) Ltd., Heritage House, Vicar Lane, Daventry NN11 5AA.

Table 1. Abundances and stable isotopic compositions of methane released from carbonaceous chondrites by freeze–thaw disaggregation. Value for cycles reflects number required for complete disaggregation of sample.

Meteorite	Type	Cycles	nmol g^{-1}	ppm C	Dv H $\times 10^{-6}$	δD	$^{12}C/^{13}C$	$\delta^{13}C$
Orgueil	CI	6	<0.2	nd	nd	nd	nd	nd
Murchison	CM2	35	2.3	28	167.75 ± 7.78	+77 ± 50	87.82 ± 0.11	13.3 ± 1
Cold Bokkeveld	CM2	45	1.8	21	113.39 ± 7.78	−272 ± 50	87.83 ± 0.11	13.2 ± 1

Note. nd: not determined.

Figure 4. The combined C and H stable isotopic composition of methane (boxes) from the Murchison and Cold Bokkeveld meteorites compared alongside the hydrogen and carbon stable isotope ranges for several relevant extraterrestrial environments and materials. OM: organic matter. References to data can be found in Table 2.

for methane in Murchison and Cold Bokkeveld with that for molecular clouds and the solar nebula in Table 2 and Fig. 4 suggests at least a small contribution from interstellar material.

The heavy stable isotope of carbon is produced in low- and intermediate-mass asymptotic giant branch stars and expelled into the interstellar medium. Hence, over time, the $\delta^{13}C$ value of interstellar space is increasing. Based on observations of organic matter in comets and methane in the outer Solar system it is estimated that the local interstellar medium had a $^{12}C/^{13}C$ value of around 89 ($\delta^{13}C$ = 0 ‰) immediately prior to Solar system formation 4.6 Gyr ago and has risen to approximately 57 ($\delta^{13}C$ + 560 ‰) at the present day (Langer & Penzias 1990). The $\delta^{13}C$ value for methane from Murchison and Cold Bokkeveld is consistent with other meteoritic material which partly predates the formation of the Solar system and has avoided extensive chemical reprocessing in the solar nebula or on planets, or biological fractionation on the Earth (Table 2, Fig. 4).

As the Murchison methane abundance in this work is less than that obtained in a previous study, it is prudent to consider whether

incomplete extraction of methane has introduced any isotopic fractionation. The isotopic consequences of partial recovery would be lighter $\delta^{13}C$ values in the analyte. However, as the $\delta^{13}C$ values for Murchison methane in this study are heavier, not lighter, than those obtained by Yuen et al. (1984), incomplete extraction is an unlikely cause of the different methane abundances in the two investigations.

3.3 Meteoritic methane in a cosmic context

It is possible, by recourse to previously published data, to bolster the interpretation that meteoritic methane has a partly interstellar origin. The combined-element stable isotopic composition of methane in Murchison lies within the range occupied by other volatile aliphatic compounds. The volatile aliphatic hydrocarbons, carboxylic acids, amino acids and sulphonic acids with identical numbers of carbon atoms exhibit similar $\delta^{13}C$ values (see Sephton 2002) indicating that their carbon skeletons were formed by the same type of process. It is likely, therefore, that these compound classes originated from the same extraterrestrial environment. Mass-independent sulphur isotope fractionations within sulphonic acids, brought about by gas phase reactions on a carbon monosulphide precursor (Cooper et al. 1997), and enantiomeric excesses in chiral amino acids, possibly resulting from ultraviolet circularly polarized light (Cronin & Pizzarello 1997), are best explained if this source environment is interstellar space.

The stable isotopic composition of methane allows us to assess the plausibility of certain hypotheses invoked to account for the organic matter in meteorites. For instance, it has been proposed that meteoritic organic matter is the result of the polymerization of simple organic compounds in the Solar nebula by high-temperature gas-phase pyrolysis (Morgan et al. 1991) or catalytic reactions on mineral surfaces (Studier, Hayatsu & Anders 1968). In this context, the methane in carbonaceous chondrites would represent leftover starting materials from such reactions. However, the stable isotopic composition of methane, and in fact the majority of other meteoritic compounds, is different from the solar nebula values (Table 2, Fig. 4). Hence theories that rely on nebular synthesis for the production of meteoritic organic matter appear unsatisfactory.

In detail, the carbon isotopic compositions of Murchison and Cold Bokkeveld methane are similar, yet the hydrogen isotopic compositions are not (Table 1). The simplest explanation for the isotopic differences is that the Cold Bokkeveld methane has had greater opportunity to exchange with Solar system normal hydrogen than that in Murchison. If this scenario is correct the combined-element stable isotope data contain two types of information: the carbon isotopic composition of methane is revealing its primary source, while the hydrogen isotopic composition reflects the degree of secondary alteration. The different susceptibilities of these two elements to secondary processing enhance their combined diagnostic value as molecular probes of extraterrestrial environments.

Table 2. Stable isotope ratios and δ values for terrestrial and several extraterrestrial environments.

Environment	D/H (10^{-6})	δ D	Ref	$^{12}C/^{13}C$	$\delta^{13}C$	Ref
Terrestrial						
Atmospheric	144 ± 2	-78 ± 10	(1)	93.4 ± 0.1	-47.2 ± 0.5	(1)
Biomass burning	148 ± 3	-50 ± 20	(1)	91.3 ± 0.3	$-25 \pm 3.$	(1)
Methanogenic	109 ± 8	-300 ± 50	(1)	94.7 ± 1.5	-60 ± 15	(1)
Thermogenic	132 ± 2	-150 ± 100	(1)	93.2 ± 2	-45.0 ± 20	(1)
Extraterrestrial						
Big bang	50	–	(2)	–	–	
Molecular cloud OM	5000 to 45 000	–	(3)	89	–	(8)
Comet OM (Hale–Bopp)	2300 ± 400	–	(4)	90 to 111	–	(9)
Solar nebula	25 ± 5	–	(7)	90.0	–	(10)
Meteoritic insoluble OM	380 to 620	1440 to 2980	(5)	90.5	-16.7	(11)
Murchison soluble OM	185 to 545	188 to 2500	(6)	85.2 to 90.2	-13.4 to $+36$	(12)

References: (1) Wahlen (1994), (2) Schramm (1998), (3) Guelin, Langer & Wilson (1982), (4) Meier et al. (1998), (5) Robert et al. (2000), (6) Pizzarello et al. (1991), (7) Geiss & Gloeckler (1998), (8) Langer & Penzias (1990), (9) Wyckoff et al. (2000), (10) de Bergh (1995) (11) Robert & Epstein (1982), (12) Krishnamurthy et al. (1992).

3.4 The utility of dual-element stable isotopic analysis for extraterrestrial materials

Determining the stable isotope ratios of more than one element for the same compound acts as a powerful constraint on the possible sources of organic entities. The successful application of combined-element stable isotopic analysis to meteoritic methane can now be extended to other compounds and a number of meteorite samples. The extremely small sample required for our method ensures that sample-size restrictions should be no barrier to the analysis of important specimens. With several sample-return missions to asteroids, comets and planets planned or underway, recovered extraterrestrial materials can now be examined for their methane contents. Effective characterization of methane in primitive objects can improve our understanding of the volatile content of the local interstellar medium as the Solar system was forming.

Data obtained from laboratory analyses will also provide valuable limits on interpretations from observational data for planetary atmospheres. Methane is the second most abundant deuterated species in the gas giant planets (after molecular hydrogen) and comparing combined element isotope ratios of primitive Solar system materials with observational data for atmospheric methane can reveal the role of late accreting planetesimals in atmosphere generation.

4 SUMMARY AND CONCLUSIONS

We have performed the first ever the combined-element (H and C) stable isotopic measurement of extraterrestrial molecules, namely methane in two carbonaceous chondrites. The data produced from the experiments designed to obtain these high-precision laboratory measurements reveal a number of important conclusions. These include the following.

(1) Methane is a component of the volatile inventory in CM2 carbonaceous chondrites but appears to be absent in the less coherent CI1 chondrites.

(2) The combined-element (H and C) stable isotopic composition of methane in carbonaceous chondrites reveals enrichments in the heavy isotopes compared with terrestrial values.

(3) Deuterium enrichments suggest at least a partial origin by interstellar reactions prior to the formation of the Solar system.

(4) Similar δ^{13}C but different δD values indicate that two types of information are available: the δ^{13}C values revealing a common primary source while δD values reflect different levels of secondary processing and secondary exchange.

REFERENCES

Becker R. H., Epstein S., 1982, J. Geochim. Cosm. Acta, 34, 257
Begley I. S., Scrimgeour C. M., 1997, An. Chem., 69, 1530
Belsky T., Kaplan I. R., 1970, J. Geochim. Cosm. Acta, 34, 257
Bräunlich M. et al., 2001, J. Geophys. Res., 106, 20465
Cooper G. W., Thiemens M. H., Jackson T. L., Chang S., 1997, Sci, 277, 1072
Cronin J. R., Pizzarello S., 1997, Sci, 275, 951
Cronin J. R., Pizzarello S., Epstein S., Krishnamurthy R. V., 1993, J. Geochim. Cosm. Acta, 57, 4745
de Bergh C., 1995, Adv. Space Research, 15, 427
Ehrenfreund P., Charnley S. B., 2000, ARA&A, 38, 427
Engel M. H., Macko S. A., 1997, Nat, 389, 265
Engel M. H., Macko S. A., Silfer J. A., 1990, Nat, 348, 47
Epstein S., Krishnamurthy R. V., Cronin J. R., Pizzarello S., Yuen G. U., 1987, Nat, 326, 477
Geiss J., Gloeckler G., 1998, Space Sci. Rev., 84, 239
Gilmour I., Pillinger C. T., 1994, MNRAS, 269, 235
Guelin M., Langer W. D., Wilson R. W., 1982, A&A, 107, 107
Hener U., Brand W. A., Hilkert A. W., Juchelka D., Mosandl A., Podebrad F., 1998, Z. Lebensmittel-Untersuchung Und-Forschung a-Food Research and Technology, 206, 230
Krishnamurthy R. V., Epstein S., Cronin J. R., Pizzarello S., Yuen G. U., 1992, J. Geochim. Cosm. Acta, 56, 4045
Krouse H. R., Modzeleski V. E., 1970, J. Geochim. Cosm. Acta, 459
Kvenvolden K., Lawless J., Pering K., Peterson E., Flores J., Ponnamperuma C., Kaplan I. R., Moore C., 1970, Nat, 228, 928
Langer W. D., Penzias A. A., 1990, ApJ, 357, 477
Meier R. et al., 1998, Sci, 279, 1707
Morgan W. A. Jr, Feigelson E. D., Wang H., Frenklach M., 1991, Sci, 252, 109
Morse A. D., Morgan G. H., Butterworth A. L., Wright I. P., Pillinger C. T., 1996, Rapid Comm. in Mass Spectrometry, 10, 1743

Naraoka H., Shimoyama A., Harada K., 2000, Earth Planet. Sci. Lett., 184, 1

Pizzarello S., Huang Y. S., 2002, Meteor Planet. Sci., 37, 687

Pizzarello S., Krishnamurthy R. V., Epstein S., Cronin J. R., 1991, J. Geochim. Cosm. Acta, 55, 905

Pizzarello S., Feng X., Epstein S., Cronin J. R., 1994, J. Geochim. Cosm. Acta, 58, 5579

Pizzarello S., Huang Y. S., Becker L., Poreda R. J., Nieman R. A., Cooper G., Williams M., 2001, Sci, 293, 2236

Rennie M. J., MeierAugenstein W., Watt P. W., Patel A., Begley I. S., Scrimgeourt C. M., 1996, Biochem. Soc. Trans., 24, 927

Robert F., Epstein S., 1982, J. Geochim. Cosm. Acta, 46, 81

Robert F., Gautier D., Dubrulle B., 2000, Space Sci. Rev., 92, 201

Sandford S. A., Bernstein M. P., Dworkin J. P., 2001, Meteor. Planet. Sci., 36, 1117

Schmitt M., Faber E., Botz R., Stoffers P., 1991, An. Chem., 63, 529

Schramm D. N., 1998, in Prantzos N., Tosi M., v. Steiger R., eds Primordial Nuclei and their Galactic Evolution. Kluwer, Dordrecht, p. 3

Sephton M. A., 2002, Natural Product Reports, 19, 292

Sephton M. A., Gilmour I., 2001a, Planet. Space Sci., 49, 465

Sephton M. A., Gilmour I., 2001b, Mass Spectrometry Rev., 20, 111

Sephton M. A., Pillinger C. T., Gilmour I., 1998, J. Geochim. Cosm. Acta, 62, 1821

Sephton M. A., Pillinger C. T., Gilmour I., 2000, J. Geochim. Cosm. Acta, 64, 321

Sephton M. A., Pillinger C. T., Gilmour I., 2001, Prec. Res., 106, 47

Smith J. W., Kaplan I. R., 1970, Sci, 167, 1367

Studier M. H., Hayatsu R., Anders E., 1968, J. Geochim. Cosm. Acta, 32, 151

Wahlen M., 1994, in Lajtha K., Michener R. H., eds, Stable Isotopes in Ecology and Environmental Science. Blackwell Scientific Publications, Oxford, p. 93

Wyckoff S., Kleine M., Peterson B. A., Wehinger P. A., Ziurys L. M., 2000, ApJ, 535, 991

Yang J., Epstein S., 1983, J. Geochim. Cosm. Acta, 47, 2199

Yuen G., Blair N., Des Marias D. J., Chang S., 1984, Nat, 307, 252

This paper has been typeset from a TEX/LATEX file prepared by the author.