

CARBON ISOTOPIIC COMPOSITION OF INDIVIDUAL, LOW MOLECULAR WEIGHT HYDROCARBONS AND MONOCARBOXYLIC ACIDS FROM MURCHISON METEORITE. G. Yuen, Chemistry Department, Arizona State University, Tempe, AZ 85287; N. Blair, D. Des Marais, S. Chang, NASA Ames Research Center, Moffett Field, CA 94035

Knowledge of the variation in C,N,H-isotopic composition with the chemical structures of organic compounds in meteorites can provide insight into the mechanisms responsible for the syntheses and, thus, their source regions, as these processes are expected to leave in their products a recognizable isotopic signature. Although carbon isotopic measurements of total carbon and solvent-soluble and acid-insoluble organic fractions have been made (1-4), measurements of individual compounds have not been reported prior to this work, with the exception of several amino acids (3).

In a closed, evacuated 700 ml pyrex apparatus, 3 interior pieces (23.5g) of Murchison were disaggregated by 40 freeze-thaw cycles in water (50 ml) assisted by sonication. After a 20 ml aliquot of the head space gas was removed for analysis of the predominant constituent, CO<sub>2</sub>, (Table 1, column I), the apparatus was partially immersed in liquid nitrogen; and the non-condensable gases were transferred with the aid of a toepler pump to a gas chromatograph-combustion (GCC) system where CO and CH<sub>4</sub> were separated and converted directly to CO<sub>2</sub> (Table 1, column I). The remaining head space gases were cryogenically transferred, along with several ml of water, to a KOH trap cooled with liquid nitrogen, while the freeze-thaw apparatus was maintained at 40°C by a water bath. Abundances and carbon isotope values for the individual hydrocarbons first collected in the KOH trap, then analyzed by GCC the system, are listed in Table 1 (column II). The solution in the freeze-thaw apparatus was separated from the meteorite solid, neutralized with KOH, and evaporated to dryness by lyophilization. The resulting residue was redissolved in water, acidified with H<sub>3</sub>PO<sub>4</sub> and distilled. The volatile carboxylic acids in the distillate were separated by ion suppression chromatography and converted to CO<sub>2</sub> in the GCC system (Table 1, column II). Treatment of the solid Murchison residue with 50 ml of 2N H<sub>3</sub>PO<sub>4</sub> generated another suite of hydrocarbons (Table 1, column III).

With few exceptions, notably benzene, the volatile products are substantially isotopically heavier than their terrestrial counterparts, signifying an extraterrestrial origin. The abundances of both carboxylic acids and saturated hydrocarbons decrease with increasing carbon number, and acids exceed hydrocarbons of the same carbon number by factors of 10 (C<sub>5</sub>) to 100 (C<sub>2</sub>). The carbon in acids is systematically heavier than that in hydrocarbons. Generally, for both classes of compounds, increasing carbon number is also associated with decreasing <sup>13</sup>C-abundance, and branched isomers are isotopically heavier than their normal (straight-chained) counterparts. When the isotopic composition of the saturated, normal isomers of each class is plotted versus carbon number - taking CO<sub>2</sub> as the C<sub>1</sub>-acid counterpart to CH<sub>4</sub> and assuming -7.9‰ (Table 1, footnote a) to be representative of pentane - two roughly parallel curves

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result with the hydrocarbon curve displaced by an average of  $14 \pm 2$ ‰ to lower values at each carbon number.

Although these data alone do not give clear indications of the origin(s) of the hydrocarbons and acids, some general conclusions are warranted. Both classes of compounds are the products of kinetically-controlled processes rather than thermochemical equilibrium. The variation of isotopic composition with carbon number is consistent with formation of higher molecular weight species from lower homologues. This parallel variation between both classes implies some aspects of their histories were similar. The carbon monoxide and acid-insoluble carbon (both isotopically light,  $< -10$ ‰) are unlikely to have supplied the source carbon for most, if not all, the compounds analyzed. Multiple production mechanisms are not yet excluded by the data.

In principle these compounds may have been synthesized in interstellar clouds, the pre-solar nebula or parent bodies (or some combination). This uncertainty in origin may be diminished as more systematic study is directed at elucidating the variations of C,N,H-isotopic composition with chemical structure in the organic constituents of meteorites, on the one hand, and in the organic compounds produced by model processes, on the other. When the patterns of isotopic variation with chemical structure in the natural and synthetic products are compared, similarities may come to light that are diagnostic of common production mechanisms and, thus, attributable to specific source regions.

Table 1. Abundance (umoles) and Isotopic Composition ( $\delta^{13}\text{C}_{\text{PDB}}$ ) of Hydrocarbons and Monocarboxylic Acids in Murchison Meteorite.

Compound	I	II	III
CO	57.4 (+29.1 ± 0.2)		
CO <sub>2</sub>	0.05 (-32 ± 2)		
Methane	0.09 (+8 ± 2)	0.12 (+10.2 ± 0.5)	0.45 (+15.6 ± 0.4)
Ethane		0.2 (+3.7 ± 0.1)	0.18 (+9.6 ± 0.2)
Propane		0.21 (+1.2 ± 0.1)	0.13 (+5.1 ± 0.2)
isoButane		0.1 (+4.4 ± 0.1)	0.04 (+14 ± 0.1)
Butane		0.13 (+2.0 ± 0.1)	0.04 (-20.5 ± 0.2)
Pentane		a	0.02
Ethane		0.03 (-0.1 ± 0.4)	0.01
Butenes		a	0.02
Benzene		0.66 (-28.7 ± 0.2)	0.92 (lost)
Acetic Acid	40 (+22.7 ± 0.2)		
Propionic Acid	15.2 (+17.4 ± 0.2)		
isoButyric Acid	5.9 (+16.9 ± 0.2)		
Butyric Acid	4.2 (+11.0 ± 0.3)		
isoValeric Acid	2.4 (+8.0 ± 0.2)		
Valeric Acid	1.1 (+4.5 ± 0.2)		

a) Analyzed together: 0.3 (-7.9 ± 0.05).

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2. Smith and Kaplan (1970) *Science*, 167, 1367.

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4. Becker and Epstein (1982) *Geochim. Cosmochim Acta* 46, 81.