MOLECULAR AND COMPOUND-SPECIFIC ISOTOPIC STUDY OF MONOCARBOXYLIC ACIDS IN MURCHISON AND ANTARCTIC METEORITES. Y. Huang, Y. Wang[1], M. De'Rosa[1], M. Fuller[1], and S. Pizzarello[2]
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Introduction: Low molecular weight monocarboxylic acids are the most abundant soluble organic compounds in the Murchison (10 to 100 times more abundant than amino acids) [1,2] and other CM carbonaceous chondrites [3,4]. Carboxylic acids, albeit of longer chain length, are the essential components in the cell membranes of living organisms on Earth. Since carbonaceous meteorites may have seeded early earth with pricursor organic molecules [5], understanding the formation mechanisms of the monocarboxylic acids is central to understanding the prebiotic organic synthesis and origin of life.

Compared with the extensive studies on meteoritic amino acids, monocarboxylic acids in Murchison meteorite have received considerably less attention. Characterization of molecular distributions of monocarboxylic acids in Murchison was conducted in 1970's using gas chromatography equipped with stainless steel capillary GC columns [1,2]. Only 13 monocarboxylic acids were reported in Murchison [1,2]. The stainless steel capillary column has a limited resolution compared with modern fused silica capillary GC column, especially for the complex mixture of straight chain and branched hydrocarbons in the Murchison meteorite. Later studies of Antarctic carbonaceous meteorites using fused silica capillary GC column revealed a much larger suite of more than 35 monocarboxylic acids. Given that Murchison has been demonstrated to contain the most extensive series of extraterrestrial organic compounds [5], it is surprising that the composition of the monocarboxylic acids in Murchison would have been relatively simple.

Additional concerns for the early studies on the Murchison monocarboxylic acids come from the experimental procedures used to isolate these compounds for GC and GCMS analyses. The procedure involves a water-CH_2Cl_2 partitioning step to extract the monoacids, followed by solvent evaporation prior to GC and GCMS analyses. Because the low molecular weight acids are misible with water and also volatile, the procedure is likely to casue significant loss of these compounds and result in bias in molecular distributions. Later study [6] using cryogenic distillation and ion chromatography indeed demonstrate that a loss in acetic acid in the ealier reports [1,2] must have occurred.

The goals of the present study are: 1) to re-examine the monocarboxylic acids in Murchison using an improved and direct sample introduction technique, solid phase microextraction (SPME) recently developed for water soluble organic compounds [7], and modern GC capillary column for GC and GCMS analyse, in order to eliminate possible procedural compound losses and resolve complex structural isomers; 2) to determine the carbon and hydrogen isotopic ratios of individual monocarboxylic acids in the Murchison and Antarctic carbonaceous meteorites using SPME coupled with GCIRMS [8], in order to better define the origin, genetic relationship and synthetic paths of these important compounds. Although previous studies have reported carbon isotopic compositions for bulk monoacid fractions [9,10], as well as 6 individual monoacids in Murchison using a lengthy isolationn procedure [6], majority of the individual acids have not been characterized isotopically. No compound-specific hydrogen isotope characterization of monoacids in Murchison has been performed.

Results and discussions: Using SPME coupled with GC, GCMS, we found a much larger suite of more than 50 straight chain and branched monocarboxylic acids in Murchison meteorite (see Fig.1a for a partial chromatogram). About 30 compounds were identified by coinjection with authentic standards (12 acids), or by comparing mass spctra using computer library search, aided by comparing with published GC retention times [3,4]. The other compounds were identified by interpretation of mass spectra, which is relatively straight forward for these simple compounds. The monocarboxylic acids are comprised of both straight chain and branched acid isomers with a complete structural diversity. The straight chain mono acids range from C_1 to C_{10}. Notably, it is the first time that formic acid is reported in Mruchsion (identified by coninjection with a standard). We also analyzed an Antarctic carbonaceous meteorite (EET96029.20, type C2) for its monocarboxylic acid composition, but found majority of the mono acids are straight chain compounds, including formic acid (Fig.1b).

The carbon and hydrogen isotopic values of mono acids in our Murchison sample show several consistent characteristics: 1) there is a general trend of decreasing $\delta^{13}C$ and δD values with chain length for the straight chain acids; 2) acetic acid has abnormally low $\delta^{13}C$ and δD values that are attributed to contamination during the room temperature storage at Smithonian Institution for the last 30 years; 3) branched acids are enriched in C-13 by 7 to 30 ‰, or D by 500 to 1500 ‰ relative to the straight chain acids, and do not show a trend with

increasing carbon numbers; and 4) majority of compounds have isotope ratios (particularly hydrogen isotope ratios) in the positive δ range and outside the range for biological compounds produced on earth.

The molecular and isotopic data are in accord with an abiotic synthesis of monoacids in Murchison involving radicals and ions at the low-temperature interstellar environments [1,2,7,8]. A kinetically controlled carbon addition reaction involving one-carbon moieties during the abiotic synthesis may be responsible for the depletion of heavier isotope analyses of straight chain acids. The consistent enrichment in the heavy isotopes in the branched compounds relative to the straight chain counterparts, on the other hand, may suggest more involvement of interstellar species during their synthesis. Alternatively, formation of branched acids may have been favored at lower temperatures that would allow more incorporation of heavy isotopic species. The higher stability of branched acids than the straight chain counterparts may have affected the species involved and synthetic locales, and could also directly allow incorporation of more heavy isotopic species.

The EET96029.20 Antarctic meteorite that we examined contain exceptionally high amount of formic acid, which is a known interstellar molecule [11]. The δD value of the formic acid confirms its exterrestrial origin and incorporation of the interstellar D/H ratio (Fig.1b). Our results indicate that Antarctic meteorites are also a valuable, overlooked source of information for understanding the distribution and formation of meteoritic organic compounds.

Our study also demonstrates that SPME coupled with GCIRMS is an effective approach for compound-specific carbon and hydrogen isotopic analyses of low molecular weight, water soluble, and volatile organic compounds such as monocarboxylic acids in carbonaceous meteorites.

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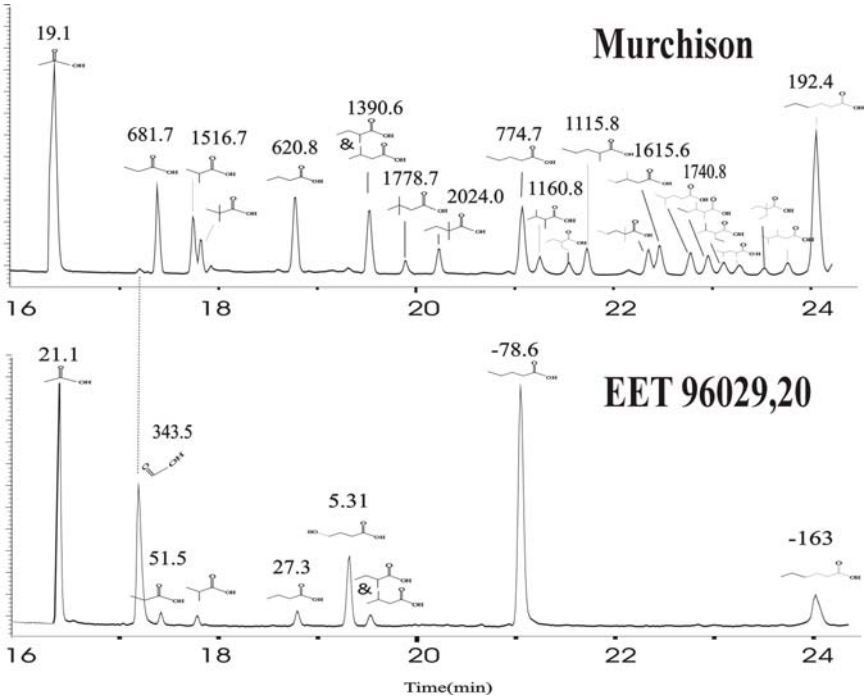

Fig. 1. a) Partial chromatograms showing the straight chain and branched monocarboxylic acids in Murchison, and the hydrogen isotope compositions of individual acids; b) Monocarboxylic acids in Antarctic carbonaceous meterorite EET96029,20. Note the high abundance of formic acid in EET96029.20, which is only in trace amount in Murchison.