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IDENTIFICATION OF TRACE ORGANIC COMPONENTS IN THE CR CHONDRITES BY 4D TOFMS.

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Introduction: The CR chondrites encompass some of the most primitive extraterrestrial materials available for analysis. Recent work [1, 2] has attempted to characterize their organic inventory and assess the influence of parent body alteration. The identification of GRO95577 as a unique CR1 chondrite [3, 4, 5] establishes a spectrum of alteration for the CRs from relatively unprocessed (Renazzo) to highly hydrated (GRO95577) [4, 5]. The relationships between these chondrites are important to our understanding of CR parent body structure, alteration history and composition.

The 4D-TOFMS technique has been used previously in [6]. This technique employs two serial columns of different polarities for two dimensional separation (molecular weight and polarity) and subsequent rapid detection by TOFMS. The sensitivity and resolving power of such an instrument is ideal for the analysis of extraterrestrial materials, particularly those of limited availability or that contain complex organic networks, such as the chondritic macromolecular material. The techniques' application to studying CR chondrites allows the identification of low-abundance organic constituents that are indicative of systematic changes brought about by alteration. Here we present the initial results of a survey of the CR chondrite organic inventory using 4D-TOFMS.

Samples: Four samples were chosen for analysis: Renazzo, Al Rais, EET87770 which we have previously characterised by traditional Py-GCMS methods [1], and GRO95577. Crushing of whole rock meteorite samples was carried out using an agate pestle and mortar within a Class 100 clean room.

Method: 1-2 mg of each sample was subjected to thermal desorption at 300°C to remove labile organic species, then flash pyrolysis at 610°C. Exact temperatures were recorded for each step using filament resistance (<600°C) and a photodiode (>600°C). Sample heating was undertaken using a Pyrola 2000 (Pyrolab, Sweden) for 2s in a total flow of He at 1ml/min. The interface was held at 200°C and coupled to the injector of a Pegasus 4D (GCxGC) TOFMS (LECO Corporation) maintained at 250°C. The Pegasus 4D system comprises an Agilent 6890 Gas Chromatograph, a LECO GCxGC module and a Pegasus IV time-of-flight mass spectrometer.

The primary (first dimension) column was a 30m×250µm×0.25µm BPX5 column connected to the secondary GC column (1.5m×100µm×0.1 µm BPX50).

The secondary column was installed in its own oven inside the main GC oven. The carrier gas was helium (99.9999%) supplied at a column flow rate of 1ml/min. Samples were analysed under the following GC oven program: The primary GC oven was held at 35°C for 1 min and then raised to 300 °C at a rate of 5°/min and held for 5 mins. The secondary oven was offset +15°C from the primary oven temperature. A liquid N cooled modulator was used with a temperature offset of +30°C above the primary oven temperature for modulation on the second column. Modulation frequency was 4s. Acquisition rate was 133 spectra/sec for a mass range of 33-400amu. Data processing was performed on LECO ChromaTOF software.

Results: *Renazzo:* Figure 1 shows the total ion chromatogram (TIC) for Renazzo presented as a contour map. Each point on the map represents an organic component within the pyrolysate, with abundant components displaying larger contour profiles. Benzene, toluene, naphthalene and C₁-C₄ alkyl benzenes are pronounced in the pyrolysate in addition to numerous volatile components. Volatile species that are masked in traditional analyses by low molecular weight aromatic species have been positively identified, e.g. acetone, hexane and acetonitrile.

However, the pyrolysate also displays abundant organic species at lower yields. These compounds include high molecular weight polycyclic compounds such as 3-ring phenanthrene and anthracene with C₁ methyl equivalents and the 4-ring species fluoranthene and pyrene. C₁-C₄-alkyl naphthalenes are also evident, along with biphenyl, C₁-biphenyls and dibenzofuran. Selected ion monitoring indicates the presence of trace amounts of aliphatic hydrocarbons up to C₁₀ and *n*-alkyl benzenes up to at least C₁₁. The abundant species identified in this study are consistent with previous pyrolytic degradation studies, however the increased sensitivity on the 4D-TOFMS technique has enabled low abundance species to be positively identified for the first time. For example, 4 ring species have previously been undetected in Renazzo due to their low abundances.

Al Rais: The TIC of Al Rais also shows benzene, toluene, and naphthalene in the pyrolysate. Thiophene is also abundant in the TIC contrary to previous studies [1]. *n*-alkyl-thiophenes up to C₁₂ and dibenzothiophene have also been identified in trace amounts. Aromatic cores extend to 4-rings as seen in Renazzo. Alkyl species are common in Al Rais: C₁-C₄ naphthalenes, C₁-C₂ phenanthrenes and up to C₁₃ *n*-alkyl benzenes. O-

heterocycles have also been identified in Al Rais including benzaldehyde, acetophenone and furenone.

EET87770: The TIC of EET87770 shows benzene, toluene, thiophene and naphthalene present within the pyrolysate. Previous studies [1] have been unable to identify benzene in EET87770, however the resolving power of the 4D-TOFMS is able to separate the two components readily. Past work [1, 2] has also identified naphthalene as the dominant aromatic component however this study does not support that. Lower abundances of methylthiophenes, C₁-C₂ alkylbenzenes, dibenzothiophene and phenanthrene are also present in the TIC. Selected ion monitoring identifies up to C₅ alkyl benzenes (although *n*-alkyl benzenes are as yet undetected), C₁-C₃ alkylnaphthalenes but no alkylated phenanthrenes. The *n*-alkane response for EET87770 is the same as in Renazzo, however at lower relative abundances, and the presence of some isoprenoid hydrocarbons (e.g. farnesane) indicates there is some contribution from terrestrial material that has not been removed by thermal desorption.

GRO95577: GRO95577 presents a much different TIC than the other CR chondrites analysed here. Fewer organic components are evident and relative abundances are much lower. Only benzene and toluene can be seen at appreciable levels in the TIC, with some C₁-

C₄ benzenes, biphenyl, naphthalene and C₁-methylnaphthalenes, benzothiophene and benzonitrile. Unlike the other CRs, phenanthrene is at relatively low abundance. *n*-alkanes extend up to C₁₀.

Discussion: Several organic components have been identified in this study that have previously been unresolved by conventional techniques, including low molecular weight volatiles and components at trace levels. These low-level organics reveal subtle differences in macromolecular structure and may shed light on the true structural diversity of primitive organic material. For example, the 4D-TOFMS technique has identified a lower diversity of organic species in GRO95577 when compared with other CR chondrites, particularly Renazzo. This may lend credence to the suggestion that parent body alteration is responsible for the modification of organic precursors sourced from the interstellar medium.

References: [1] Pearson, V. K. et al., (2006), *MAPS*, 41, 1291-1303, [2] Wang, Y. et al., (2005) *GCA*, 69, 3711-3721 [3] Met Bull 82, *MAPS* 33, A221-240. [4] Weisberg and Prinz, 2000, *MAPS*, 35, A168. [5] Perronnet and Zolensky, (2006) *LPSC XXXVII*, A2402. [6] Watson et al., (2005) *LPSC XXXVI*, A1842.

Figure 1. Total Ion Chromatogram (TIC) of Renazzo displayed as a contour map. Key: B = benzene, N = naphthalene, MN = methylnaphthalene isomers, C₂-C₄-N = C₂-C₄ alkylnaphthalenes, P = phenanthrene, A = anthracene, MP = methylphenanthrene isomers.

