Comprehensive Organic Analysis of Antarctic Micrometeorites

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COMPREHENSIVE ORGANIC ANALYSIS OF ANTARCTIC MICROMETEORITES. R. C. Wilson¹, E. Dobrica², V. K. Pearson¹, D. C. Turner¹ and I. Gilmour¹.¹Planetary and Space Sciences Research Institute, Open University, Milton Keynes, UK (r.c.wilson@open.ac.uk). ²CSNSM CNRS-Univ. Paris Sud, 91405 Orsay Campus, France.

Introduction: Micrometeorites (MMs) are thought to be significant contributors of organic material to the early Earth [1], and a variety of techniques have been employed to identify their organic composition [2-6]. These include the identification of key organic groups using combinations of infrared, energy dispersive X-ray, electron energy loss and Raman spectroscopy and scanning transmission X-ray microscopy [2-4], highlighting similarities between that of MMs and carbonaceous chondrites. Few studies, however, have focused on the characterisation of individual micrometeoritic organic components. Microscopic L²MS has been used to identify up to C₅ polycyclic aromatic hydrocarbons and their alkyl derivatives [5]. A combination of ion-exchange chromatography and fluorimetric detection has also been successful in identifying a number of protein amino acids including glycine and alanine [6].

We have previously reported a method to analyse µg-sized quantities of extraterrestrial materials, with prior application to assessing organic volatile release from MM atmospheric entry heating simulations [7]. In this study we utilise this technique to characterise the organic composition of Antarctic terrestrial particles and MMs collected in 1994 from Cap-Prudhomme [8].

Samples: Cap-Prudhomme sample #141 comprises of particles 100 - 400 µm grain size. Approximately 40 glacial sand (GS) particles were separated from sample #141, in addition to 24 dark particles (MM candidates). The dark particles were fragmented, enabling a portion to be analysed using scanning electron microscopy to confirm terrestrial (T) or extraterrestrial (ET) origin. The remainder was available for organic analysis. A batch of 18 particles of roasted sand (S) served as a control for the handling procedures.

Particles were divided into the following sample batches for organic analysis (Table 1) and were imaged under a light microscope to determine grain/fragment diameters.

Sample Handling: Samples were manipulated under a binocular microscope using a nylon brush (previously cleaned by sonication in methanol) and a drop of high grade methanol. The methanol was evaporated from the sample prior to pyrolysis.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>18 particles</td>
</tr>
<tr>
<td>GS1</td>
<td>18 particles</td>
</tr>
<tr>
<td>GS2</td>
<td>18 particles</td>
</tr>
<tr>
<td>T1</td>
<td>7 particles comprised of 15 fragments</td>
</tr>
<tr>
<td>T2</td>
<td>8 particles comprised of 15 fragments</td>
</tr>
<tr>
<td>ET</td>
<td>8 particles comprised of 21 fragments</td>
</tr>
</tbody>
</table>

Table 1: Description of sample batches

Experimental: Samples were pyrolysed using a Pyrola 2000 coupled to a Pegasus 4D GCxGC-TOFMS (LECO Corporation) for organic analysis. Experimental conditions were as described in [9] with a BP624 column (the primary column – 30mx250µmx1.4µm) and a BP20 column (secondary column – 1.8mx100µmx0.1µm). The injector was maintained at 200 °C with the primary GC oven held at 30 °C for 1 min, then raised to 230 °C at a rate of 5 °C/min and held for 10 mins. The modulation frequency was 3 s with the acquisition rate of 200 spectra/s for a mass range of 33-400 amu.

Results and Discussion: A number of organic species are identified in batch ET (Fig. 1). These include:

- Nitrogen and sulphur-nitrogen heterocycles – e.g. thiazole, methylthiazole and pyrrole
- Acids and alcohols e.g. acetic acid and phenol
- Nitriles e.g. acetonitrile, benzonitrile
- Aliphatics e.g. aliphatics, branched aliphatics, aliphatic alcohols, branched aliphatic alcohols
- Aromatics e.g. benzaldehyde, benzene, C₁₋₄ benzenes, thiophene, C₁₋₄ thiophenes, styrene and naphthalene
- Sulphur compounds e.g. sulphur dioxide, carbon disulphide, dimethylsulphide

These results are comparable with the organic inventory of Murchison, previously analysed using this technique [10] and is largely consistent with functional groups identified in MMs [2-4]. However, whilst there are noticeable similarities between the range of aromatic species, nitriles, alcohols and nitrogen heterocycles present in both the ET and T2 batches there are marked differences between the extraterrestrial and terrestrial organic pyrolysates, such as:

- a greater diversity of sulphur containing compounds in ET relative to terrestrial samples T1 and T2. These include SO₂, sulphur containing aromatics (alkylthiophenes) and heterocycles
(thiazole and alkylthiazole), previously identified in Murchison [7, 10] but none of which have been characterised in MM s prior to this study.

• an increased range of alkyl aromatics are identified in ET relative to T2, for example C₁–C₄ benzenes and thiophenes, consistent with analyses of Murchison [10] and unique to this study of MM s. Only C₁–C₂ benzenes were identifiable in T2.

• a number of branched aliphatics and branched aliphatic alcohols observed in Murchison [7] but not previously identified in MM s. A greater diversity was present in T2.

Conclusion: We have demonstrated a method enabling the detection of a range of organic species in micrometeorites. The organic inventory is analogous to that found in carbonaceous chondrites such as Murchison [7, 10]. However, there is a suggestion of significant contribution from terrestrial sources. The organic analysis of micrometeorites from more pristine Antarctic sources may yield improved results.


Acknowledgements: We would like to thank Jean Duprat, Cecile Engrand and Michel Maurette for providing samples from the Cap-Prudhomme site.

Figure 1: An annotated two dimensional total ion chromatogram of batch ET identifying key organic species. AN = acetonitrile, B = benzene, Th = thiophene, T= toluene, Thz= thiazole, BA= benzaldehyde, BN= benzonitrile, N=naphthalene.