Development of visualisation methodology for organic materials contained within carbonaceous chondrites

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DEVELOPMENT OF VISUALISATION METHODOLOGY FOR ORGANIC MATERIALS CONTAINED WITHIN CARBONACEOUS CHONDRITES. M. D Goodyear1, I. Gilmour1 and V.K. Pearson1,2 1Planetary and Space Sciences Research Institute and 2Department of Chemical and Analytical Sciences, The Open University, Milton Keynes MK7 6AA, United Kingdom (m.d.goodyear@open.ac.uk).

Introduction: Since their formation, many meteorites have experienced significant degrees of alteration, by heat, impact, and fluid-mediated processes on their parent bodies [1]. Carbonaceous chondrites contain significant amounts of organic materials; a small proportion is present as volatile or soluble compounds, but the majority comprises insoluble, macromolecular material (IOM) [2]. Using techniques developed for terrestrial materials [3], the location of organic materials within meteorites has been determined by treatment with osmium tetroxide and examination of the resulting pattern of osmium deposition by EDS [4]. Although that study was successful in showing the presence of organic materials, no work has yet been done to locate these materials at higher resolution within the meteoritic sub-structure, nor to relate their location to chemical class.

It is therefore of interest to determine if the organic materials are found in association with any specific mineral, or mineral sub-component of the meteorite [5], as the role any such association may have played during parent body processing is not known.

To identify the location of organic materials, it is necessary to employ methods to detect them in situ. In contrast, most methodology used to date involves removal of either the organic materials or the mineral matrix prior to analysis, thus losing any information concerning spatial arrangements.

Meteoritic organic materials are difficult to detect in situ, their concentration is relatively low [6] requiring sensitive methodology. Furthermore, the elements making up the organic materials (mainly CHON and S) occur in common minerals and inorganic compounds, thus their presence does not necessarily imply the occurrence of organic materials. To avoid this problem, it is necessary to introduce a tag, or marker, which can be fixed specifically to organic materials at the molecular level, thereby enabling detection above the background of the elements listed above.

Chemical modification:

IOM. IOM is believed to consist of small aromatic systems, linked together by short, branched aliphatic chains [7], and being composed of only common elements (CHON and S), cannot easily be detected against the mineral background. Furthermore, this structure would be unreactive to reagents suitable for introduction of molecular tags in situ. However, ozone reacts with double bonds (and aromatic rings) to form various oxygen-containing functional groups which, being more reactive, can be tagged, and it has been used to degrade organic materials present in coals and shales, as well as meteorites, but only after extraction from the mineral matrix [8]. Although the specific functional groups introduced by ozonolysis will depend on the exact structure and substitution of the IOM, carboxylic acids, ketones and quinones are likely to be formed [9].

Oxygen-containing functional groups. Several reagents have been used previously to derivatise organic materials in the solid state. Derivatisation enables the identification of functional groups [10], by the introduction of elements such as fluorine which are not indigenous at significant levels. Therefore, functional groups formed via ozonolysis can be further reacted, introducing marker or tag elements enabling their detection. As the structure of IOM is heterogeneous, the likely proportions of these functional groups cannot be predicted, so a range of methodology was developed to encompass the range of functionality expected. In addition, these oxygen-containing functional groups are present in a large fraction of the soluble organic component of carbonaceous chondrites [6], so this procedure will also be useful in determining the location of these compounds.

Experimental: To simulate the distribution of organic materials in meteorites, samples of inert substrate (crushed sandstone) were doped with solutions of standard organic compounds. Standards were prepared that would enable, on evaporation of the solvent, an organic content of ca. 1%, similar to that typically found for IOM in carbonaceous chondrites.

Polycyclic aromatic hydrocarbons (PAHs) were selected (Table 1) as analogues of the aromatic fragments of IOM [7]. These were exposed to ozone, to determine the conditions needed to decompose IOM.

<table>
<thead>
<tr>
<th>PAH</th>
<th>Rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>2</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>3</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>4</td>
</tr>
<tr>
<td>Perylene</td>
<td>5</td>
</tr>
<tr>
<td>1,12-Benzoperylene</td>
<td>6</td>
</tr>
<tr>
<td>Coronene</td>
<td>7</td>
</tr>
</tbody>
</table>
To investigate the conditions needed to react both pre-existing, oxygen-containing organic materials, and those introduced by ozonolysis, a range of compounds was selected (Table 2).

Compounds containing the functional groups listed in Table 2 were treated with various reagents known to react with that functionality. The chosen reagents are also given in Table 2.

Table 2. Functional groups investigated

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Model compound used</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>Cinnamyl alcohol</td>
<td>TFAA</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Benzaldehyde</td>
<td>HH-TFAA</td>
</tr>
<tr>
<td>Amino acid</td>
<td>Tryptophan, phenylalanine</td>
<td>TEA-TFAA</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>4-methoxybenzoic acid, Cinnamic acid</td>
<td>Py-DIC-TFE</td>
</tr>
<tr>
<td>Ketone</td>
<td>Benzophenone, Acetophenone</td>
<td>HH-TFA</td>
</tr>
<tr>
<td>Phenol</td>
<td>Naphthol</td>
<td>Py-TFAA</td>
</tr>
</tbody>
</table>

Key:
- DIC N,N-Diisopropylcarbodiimide
- HH Hydrazine Hydrate
- Py Pyridine
- TEA Triethylamine
- TFAA Trifluoroacetic anhydride
- TFE 2,2,2-Trifluoroethanol

Examples selected were typical of their class, and representative of those likely to be present in carbonaceous chondrites, both before and after ozonolysis. After doping and ozonolysis, the doped sample was exposed to the selected reagents in the vapour phase, and the reaction monitored by Thin-Layer Chromatography (TLC). The amount of material remaining was determined by extraction into a solvent, application of a known volume onto a TLC plate, and comparing with the spot sizes of solutions of known concentration, following elution with a suitable solvent, and visualization of the TLC plate (by UV). The reaction conditions were adjusted to maximize the extent of reaction.

Results:

PAHs. A range of reactivity of PAHs was observed towards ozonolysis. Although the larger, more condensed ring systems tended to react more slowly, all reacted to some extent, with 4-ring systems completely reacting in less than 24h.

Oxygen-containing functionality. All reactions progressed to >95% completion in less than 24h, with the exception of naphthol with pyridine-trifluoroacetic anhydride (which only gave ca. 90% reaction), with some (e.g. benzaldehyde and acetophenone) requiring less than 1h.

Summary and future work: A procedure has been developed for the introduction of oxygen-containing functional groups into IOM. The resulting products, or soluble oxygen-containing compounds already present in a meteorite can be further reacted to introduce molecular labels enabling their detection in situ, without the need to remove either them, or the surrounding minerals, from the body of a meteorite. Following this derivatisation, the presence, or otherwise, of organic compounds present in carbonaceous chondrites, in relation to the mineral features of the meteorites will be determined.

References: