

EXPERIMENTAL SIMULATION OF VOLATILE ORGANIC CONTRIBUTIONS TO PLANETARY ATMOSPHERES AND SURFACES R. C. Wilson, V. K. Pearson, G. H. Morgan, I. A. Franchi, D. C. Turner, I. P. Wright and I. Gilmour. Planetary and Space Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA. R.C.Wilson@open.ac.uk..

Introduction: The presence of organic molecules in extraterrestrial dust particles is well documented [1-3]. They have a high entry velocities in excess of 5 kms⁻¹ [4], but their energy is dissipated by aerodynamic breakdown in the upper atmosphere (80-100 km altitude). This results in particle heating to temperatures of 1700 °C [5]; however, peak temperatures experienced are dependent on a number of factors: heating duration, entry angle, entry velocity, particle size and particle density [5]. At the predicted entry heating temperatures, evaporation of organics and volatile materials is expected [6, 7] and these would be deposited in the Earth's atmosphere [8, 9] contributing to the inventory of organic and gaseous species. However, organic species are identified in extraterrestrial dust particles [1-2], suggesting that they can survive the effects of atmospheric entry heating. With the flux of total extraterrestrial material to the early Earth estimated to have been up to 10⁹x greater than that of present day [10], extraterrestrial dust particles were significant contributors of volatile and organic species to both the atmospheres and surfaces of planets throughout the history of the Solar System. This study seeks to characterise the nature of these evolved volatile species with a particular emphasis on those that may have influenced the development of planetary environments and potentially life.

Samples: Whole rock samples of the Murchison carbonaceous chondrite (grain size ≤30µm) were used as an analogue of a cluster of extraterrestrial dust particles because of similarities in mineralogy [11] and organic chemistry [7, 12, 13].

Experimental: Flash Heating and Py-GCxGC-TOFMS: Two simulation experiments are reported, both using a Pyrolya 2000 Filament Pulse Pyrolyser (Pyrolyab, Sweden) with the interface held at 175 °C. ~0.9 mg sample was flash heated in a He gas flow for 2-20 s to between ~400-1000 °C. The flash heating temperatures and durations were designed to be comparable to the entry heating conditions modelled by Love and Brownlee (1991).

One set of experiments was conducted offline to allow collection of the heated sample; heating steps were repeated until 10 mg of each residue was collected for evolved gas analysis. A second set of experiments, using the same heating regime, was conducted online, with the Pyroly 2000 coupled to a Pegasus 4D GCxGC-TOFMS (LECO Corporation). Experimental conditions were as described in [14] but

using a BP264 column (the primary column - 30mx250µmx1.4µm) and a BP20 column (secondary column - 1.8mx100µmx0.1µm). The injector was maintained at 230 °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.

Evolved Gas and Thermogravimetric Analysis: Flash heated samples were examined using a Netzsch STA 449C Jupiter thermo-gravimetric analyzer (NETZSCH-Gerätebau GmbH, Germany) coupled to a Hiden Analytical HPR20 RGA evolved gas analyzer (Hiden Analytical Ltd, UK). Volatile species of mass 18 (H₂O), 28 (N₂/CO), 32 (O₂) and 44 CO₂ were monitored throughout, to assess volatile and organic survival.

Results: Evolved Gas (EG) Analysis. Broad clusters occur at EG CO₂ peak positions 100-300 °C (indicative of volatile organic survival) and between 450-550 °C (suggesting the survival of less volatile organic species). There are pronounced clusters at 600 - 650 °C and ~700 °C (attributed to the survival of carbonate minerals). Less CO₂ was evolved from flash heated samples in the 100-400 °C and 700-750 °C peak positions than that of unheated Murchison, representing organic and inorganic carbon loss respectively. Samples flash heated to <600 °C contain extremely broad flat EG CO₂ peaks in the region of 100-600 °C, the areas/abundances of which were not calculable.

Thermogravimetric Analysis. Figure 1 displays the abundance (wt.%) of total volatiles remaining in samples heated to a range of temperatures for 2 s and 5 s. These abundances are substantially lower than that of unheated Murchison (indicated by the black dashed line). Total volatile abundance decreases rapidly as samples are flash heated to increasing temperatures, with just 0.24 wt.% and 0.09 wt.% total volatiles remaining in samples flash heated to temperatures of ~800 °C for 2 s and 5 s respectively. The abundance (wt.%) of inorganic carbon (bound within carbonate minerals) in samples flash heated up to ~600 °C is similar to the unheated Murchison value of 3.88 wt%. The decreasing abundance of the inorganic carbon in samples flash heated to temperatures >600 °C can be attributed to the thermal decomposition of carbonate minerals.

GCxGC-TOFMS Analysis. Organics lost during the simulation include a vast range of aliphatic and aromatic species. In particular, a number of aliphatic and aromatic alcohols, carboxylic acids and nitrogen containing compounds are identified such as amino acid derivatives, amines, amides, nitriles and nitrogen and sulphur-nitrogen heterocycles and their derivatives (Figure 2). These heterocycles include pyrrole, thiozole, methyl and dimethylthiozole, isothiozole, pyridine, a range of C₁ to C₃ alkylpyridines, C₁-C₂ alkylpyrimidines, pyrazine C₁-C₄ alkylpyrazines and triazine.

Discussion: Direct loss of water, dehydration of phyllosilicates, dehydration of alcohols and evaporation of organics account for the decrease in volatile abundance (wt. %) during flash heating simulations (Figure 1).

Evaporated organic species, such as those identified during our simulations (Figure 2), have the potential to condense in the upper atmosphere, eventually settling out on the planets surface [6]. Additionally, deposited organics may undergo further reactions within the atmosphere in the same manner as present day anthropogenic heterocyclic and volatile organic compounds [15]. Nitrogen heterocycles are constituents of essential biological molecules e.g. nucleobases cytosine, thymine and uracil are all pyrimidine derivatives and pyrrole is the building block of chlorins and porphyrins (from which chlorophyll and haemoglobin are derived respectively). The delivery of extraterrestrial dust particles was potentially a source of primitive organic matter, providing essential biological precursors and playing an influential role in the prebiotic chemistry and environmental modification of Earth and Mars.

The Pyrola 2000 has proved to be a versatile instrument, serving as an effective method of simulating the atmospheric entry heating of extraterrestrial dust, due to its capability to accurately heat samples to high temperatures for very short durations. Coupled to the Pegasus 4D GCxGC-TOFMS, we have been able to successfully characterise a broad range of volatiles released from relatively small samples during these simulations.

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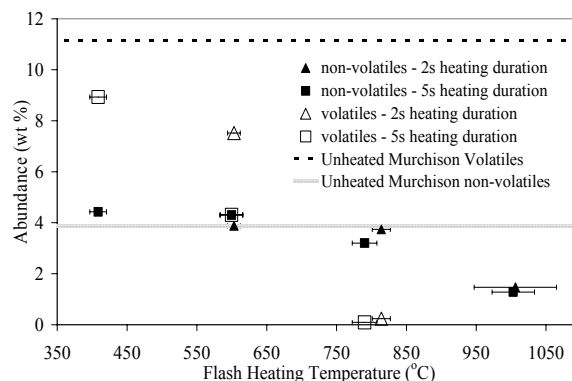


Figure 1: Total volatiles (wt. % water and organics) and non-volatile carbonate bound CO₂ remaining in flash heated samples.

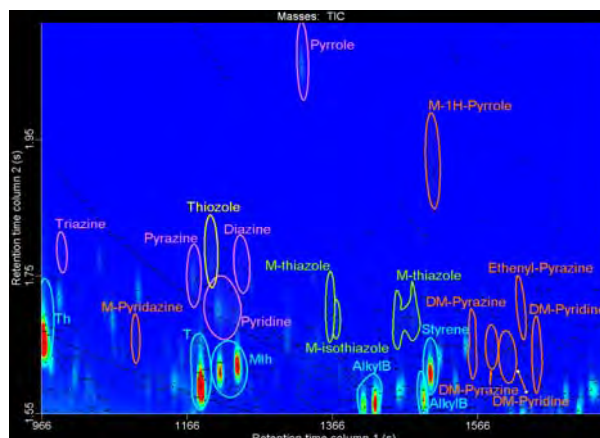


Figure 2: A 2D GC contour plot displaying nitrogen and nitrogen-sulfur heterocycles released from a sample heated for 2 s to ~1026 °C (B – Benzene; T – Toluene, Th – Thiophene; Mth – Methylthiophene; M- Methylene; DM – Dimethyl).