

THE FATE OF ORGANIC PHASES IN POROUS IDPS AND MICROMETEORITES DURING ATMOSPHERIC ENTRY: A PULSE-HEATING STUDY. G. Matrajt, *Department of Astronomy, University of Washington, Seattle WA, 98195 (matrajt@astro.washington.edu)*, D. Brownlee, *Department of Astronomy, University of Washington, Seattle WA, 98195*, M. Sadilek, *Department of Chemistry, University of Washington, Seattle WA, 98195*, L. Kruse, *Department of Chemistry, University of Washington, Seattle WA, 98195*.

Introduction:

Interplanetary dust particles (IDPs) and micrometeorites (MMs) are typically heated at temperatures higher than 500 °C for few seconds during their atmospheric entry [1,2]. They have been extensively studied with several techniques for their carbon content and for the nature of their carbonaceous phases [3, 4, 5, 6]. Several kinds of organic molecules have been found in IDPs and MMs: polycyclic aromatic hydrocarbons (PAHs) [3], hydrocarbons and a carbonyl group (C=O) which was mainly associated with a ketone [4,5], and amino acids [7,8].

Carbonaceous meteorites > 1 mm in size can have substantial interior gradients temperatures during atmospheric entry, which allows organic molecules in their interiors to survive with minimal or not heating. Smaller particles, however, should be uniformly heated unless porosity and sublimation processes allow formation of a thermal gradient over a few seconds timescales. Such thermal gradients may allow the survival of organic molecules. In order to investigate this survival we studied the fate of three different organic molecules (a PAH, a ketone and an amino acid) pulse-heated between 300-900 °C.

Although PAHs, ketones and amino acids are organic molecules which most of their members sublime or decompose at temperatures around 200 °C, there exist a few members of these families which have higher boiling or sublimation points and decompose between 200-550 °C: coronene (b.p.= 525 °C); 2-pentadecanone (b.p.= of 293 °C); lysine (m.p.= 215 °C). The boiling and melting points of these organic molecules, which have been directly or indirectly detected in IDPs and MMs, imply that IDPs and MMs cannot reach any temperature higher than 500 °C during their atmospheric entry. Yet, the models [1,2,9] and observations [10] suggest that unmelted IDPs and MMs, depending on their mass, size and density, reach peak temperatures between 400-1700 °C during atmospheric entry, indicating therefore that any low-boiling point (≤ 550 °C) organic molecule would be lost during such event. It is therefore paradoxical to observe in the matrices of IDPs and MMs, low-boiling point organic molecules such as PAHs, amino acids and ketones. We propose that the combination of porosity and a sublimable phase (such as organic material, water) which gets lost during heating, produces ablative cooling of the particle during its atmospheric entry, a process also known as "the heatshield effect". Although IDPs and MMs are heated on their surfaces to temperatures much higher than 500 °C, we think that porosity and ablative cooling result in poor heat transfer to the particle's interior and allow survival of organic compounds of intermediate volatility (boiling points ≤ 550 °C).

Samples and Methods:

To simulate the atmospheric entry processes we performed pulse-heating experiments of three solutions of organic molecules (coronene, 2-pentadecanone and lysine) adsorbed in a microporous medium: activated alumina (Al₂O₃). Alumina was ground down using a mortar and pestle to obtain a powder with grain size between 5 to 9 μm. To simulate the heating of ~10 μm porous IDPs we made a 10 μm thick layer of alumina loaded with the organic molecule on a 25 μm thick stainless steel substrate (which has very small thermal inertia). The heating was performed by insertion of the sample into a tube furnace, simulating atmospheric entry conditions (time=5 seconds, ram pressure=800 mTorr [2,9]). The survival of the organic molecules at different temperatures (ranging from room temperature up to 900 °C) was quantified by comparison of the heated sample to a control (not-heated) sample. The temperature inside the furnace was monitored using a thermocouple (Fluke). Two analytical instruments, GC-MS and ESI-MS, were used to analyze the solutions of the desorbed organic molecules after heating. The control samples were taken as the 100 % starting solution. The presence of organic molecules in the heated solutions was monitored and quantified. These were considered as the surviving molecules after the pulse-heating.

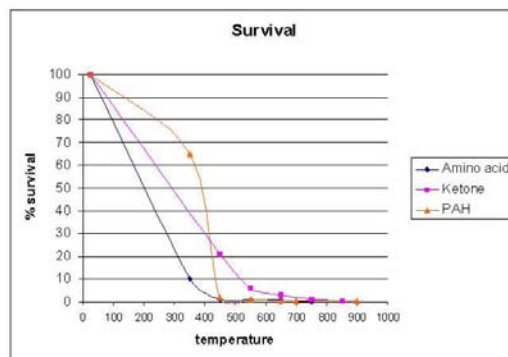


Figure 1: Survival of coronene, 2-pentadecanone and lysine (in %) as a function of temperature (in °C). The error bars are smaller than the symbols used to plot each value.

Results:

The area of the chromatographic peaks for each of the three organic molecules was integrated. Comparison of the control area versus the heated area allowed the quantification

Temperature (°C)	PAH (% of survival)	Ketone (% of survival)	Amino acid (% of survival)
Room temperature	100	100	100
350	65	n.d.	10.4
450	1.8	21	1.0
550	0.9	5.86	0.8
650	≤ 0.1	2.86	0.6
700	≤ 0.1	0.94	≤ 0.1
900	≤ 0.1	0.53	n.d.

Table 1:

Pulse-heating of coronene, 2-pentadecanone and lysine and % of survival. The temperature values are ± 25 °C due to a small gradient between the edge and the center of the foil. The instrumental error varied from 3.6 to 13 % for the three kinds of molecules.

of the % of surviving molecule after heating. Figure 1 plots the survival of each of the three organic molecules as a function of temperature. Table 1 shows the survival obtained for each molecule at each temperature. More than 90 % of the coronene is gone at 425 °C and only a few percent survives above 500 °C. However, even at very high temperatures such as 900 °C there is still a small survival of coronene. For the ketone, 80 % is already gone at 450 °C. At temperatures of 500 °C and higher only few percent survives. At very high temperatures such as 850 °C there is still a small survival. Finally, 90 % of the amino acid is gone at 350 °C and only few percent of the molecule survives at temperatures ≥ 450 °C. Surprisingly, at very high temperatures such as 750 °C there is still a small survival.

Discussion:

At room temperature there is 100 % survival of all the three molecules indicating that the only effect in the loss of the organic molecules is temperature. Nakano et al [11] conducted long term heating experiments on interstellar analogs composed of several organic molecules (ketones, alcohols, long chain carboxylic acids and PAHs). No substrate was used during these experiments. Temperatures varied from room temperature to 470 °C and the time of heating varied from 80 h to 200 h. The analysis of the organic mixtures showed that 95 % of the sample evaporated below 130 °C and all the sample was completely evaporated at temperatures greater than 260 °C, clearly showing that in the absence of a substrate, organic molecules do not survive at temperatures higher than 300 °C. Therefore, a porous substrate seems strictly necessary for the survival of organic molecules exposed to heat. The Al_2O_3 used in our experiments is microporous, and imitates the porous structure of IDPs and MMs. This porosity allows the molecule to be absorbed and thermoprotected, probably because the combination of microporosity with a sublimable phase produces ablative cooling, creating then a thermogradient inside the particle. In this way, the surface of the particles reaches peak temperatures higher than 500 °C, but not the interior where the organic phases remain thermoprotected. We observe survival at temperatures as high as 900 °C of PAHs and ketones, provided that they are absorbed in a microporous substrate. This demonstrates that ablative cooling is taking place and is the key for the survival of organic molecules in IDPs and MMs heated at temperatures ≥ 550 °C.

Implications for astrobiology:

Anders [12] suggested that the temperature at which organic molecules get totally destructed by pyrolysis is around

600 °C. In this work we have demonstrated that some organic molecules can survive up to 900 °C provided that they are absorbed in a porous medium. This indicates that IDPs and MMs that are heated less than 900 °C during their atmospheric entry can deliver intact organic molecules to the Earth's surface. This delivery was certainly increased during the heavy bombardment period (between 4.5-3.5 Ga), when the amount of extraterrestrial objects hitting the Earth's surface was much higher than today. Flynn [9] calculated that about 600 tons/y of particles being heated below 600 °C reach the Earth's surface. And Anders [12] calculated that about 0.2 tons/y of carbonaceous chondrites contribute organic molecules. The comparison of these numbers show that IDPs and MMs contribute ~ 3000 times more intact organic molecules than carbonaceous chondrites. From Flynn's calculations [9], about 50 % of the particles of cometary origin (entry velocity 14.3 km/sec) and of sizes ≤ 10 μm are not heated above 830 °C. This suggests that 50 % of the cometary particles smaller than 10 μm could also contribute to the delivery of intact organic molecules to the Earth's surface. Taken together, the asteroidal + cometary particles of ≤ 200 μm in size that were heated below 900 °C represent a major source of exogenous delivery of intact organic molecules of interest for the origin and evolution of life on Earth.

Conclusions:

In this work we have performed pulse heating experiments at different temperatures on three organic molecules absorbed on Al_2O_3 , to investigate the fate of the organic molecules in IDPs and MMs while entering the Earth's atmosphere. We have shown that some of the organic molecules can survive exterior particle temperatures up to 900 °C indicating that the combination of a microporous structure with a sublimable phase (organic material, water) leads to a heatshield effect, or ablative cooling, that protects organic phases from thermal degradation.

References:

- [1] Flynn et al (1989) *Icarus*, **77**, 287-310. [2] Love and Brownlee (1991) *Icarus*, **89**, 26-43. [3] Clemett et al (1993) *Science*, **262**, 721-725. [4] Flynn et al (2004) *Adv. Space Res.*, **33**, 57-66. [5] Keller et al (2004) *GCA*, **68**, 2577-2589. [6] Matrajt et al (2005) *A&A*, **433**, 979-995. [7] Brinton et al (1998) *Orig. Life Evol. Biosph.*, **28**, 413-424. [8] Matrajt et al (2004) *M&PS*, **39**, 1849-1858. [9] Flynn, G. (2001) in *Accretion of Extraterrestrial Matter Throughout Earth's History*, 107-127. [10] Sandford S. and Bradley J. (1989) *Icarus*, **82**, 146-166. [11] Nakano H. et al (2003) *Ap.J.*, **592**, 1252-1262. [12] Anders E. (1989) *Nature*, **342**, 255-257.