Cometary dust analogs exposed to solar UV radiation on the International Space Station

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Comets are made of ...

ICES: H$_2$O, CO, CO$_2$, CH$_3$OH, CH$_4$, N$_2$, NH$_3$, ...

CARBONACEOUS MATERIALS

SILICATES
Laboratory investigation aims to study the processes which drive the evolution of cometary materials

**Energetic processing**
- Galactic cosmic rays
- UV photons
- Solar wind
- Solar energetic particles

**Thermal processing**
- Warm-up phase during star formation
- Variation of distance from the Sun
Laboratory for Experimental Astrophysics
INAF - Catania

Ion beam (100-400 keV)  Vacuum chamber  FTIR spectrometer
Vacuum chamber

Analysis:

IR spectroscopy

Raman spectroscopy

$P \sim 10^{-9} \text{ mbar}$
In situ Raman spectroscopy

Laser Ar$^+$ (514.5 nm)
IR and Raman spectroscopy

Experimental procedure

Substrate (Si, KBr, CsI)
T=10-300 K

Background (mid-infrared) at 16 K (KBr substrate)
Experimental procedure

Sample
T=10-150 K

IR beam

Mid-IR spectrum of the sample as deposited (CH₃OH at 16 K)
Experimental procedure

Bombardment or irradiation of the sample
T=10-150 K

Ions (keV - MeV)
UV photons
Experimental procedure

Processed sample
$T=10\text{-}150\text{ K}$

Mid-IR spectrum of the sample after irradiation
($\text{CH}_3\text{OH} + 200\text{ keV H}^+\text{ at }16\text{ K}$)

CO$_2$, CO, H$_2$CO, CH$_4$
Experimental procedure

Continuum normalization

\[ \tau = - \ln \left( \frac{I}{I_0} \right) \]
$\text{H}_2\text{O}:\text{CO}$
$H_2O:CO$
$\text{H}_2\text{O} : \text{CO}$
H₂O:CO

Mixture after processing
H₂O:CO:CO₂:H₂CO:CH₃OH = 100:15:15:1.5:1.5
Organic refractory residue

Energetic processing modifies the chemical composition of the sample forming volatile species and a refractory residue.

Palumbo, Ferini, Baratta, 2004, Ad Sp Res 33, 49
Baratta et al. 2015, PI Sp Science 118, 211
Complex molecules trapped in the residue

\[ \text{N}_2: \text{CH}_4 = 1:1 \]
\[ \text{N}_2: \text{CH}_4: \text{CO} = 1:1:1 \]
\[ \text{N}_2: \text{CH}_4: \text{H}_2\text{O} = 1:1:1 \]
\[ \text{N}_2: \text{C}_8\text{H}_{18} = 1:1 \]
\[ \text{N}_2: \text{C}_8\text{H}_{18} = 9:1 \]
\[ \text{Ar}: \text{C}_8\text{H}_{18} = 10:1 \]
\[ \text{CO}: \text{CH}_4 = 1:1 \]

Accolla et al., 2018, A&A 620, A123
Complex molecules trapped in the residue

Accolla et al., 2018, A&A 620, A123
Complex molecules trapped in the residue

Accolla et al., 2018, A&A 620, A123
Ultra Carbonaceous Antarctic micrometeorites probing the Solar System beyond the nitrogen snow-line

Dartois et al. 2013, Icarus 224, 243; Baratta et al. 2015, Pl. Sp. Sci., 118, 211
Do complex molecules survive in the interplanetary medium?

✓ Complex molecules formed after cosmic-ray bombardment of simple ices remain trapped in the refractory residue;

✓ Nitriles are thought to be key intermediates to form amino acids providing one of the basic ingredients for life;

✓ Infrared spectra of micrometeorites show the presence of astrobiologically relevant chemical bonds;

✓ Formation of organic refractory material could have occurred in comets and TNOs and/or during the protostellar phase;

✓ It has been suggested that comets, asteroids, and micrometeorites could have delivered organic material on the early Earth;

How long complex molecules trapped in the residue survive in the interplanetary medium exposed to UV solar photons?
Photochemistry on the Space Station

This is an international project related to ASTROBIOLOGY. This project is approved by ESA (European Space Agency). The Italian participation is funded by ASI (Agenzia Spaziale Italiana). The aim is to study the survival of organic material exposed to solar UV radiation. We prepared organic refractory residues that remained exposed for about 16 months.
Photochemistry on the Space Station

Residues after 200 keV He$^+$ on N$_2$:CH$_4$:CO at 16 K

3 different thicknesses of the residue
(180 nm; 135 nm; 50 nm)

10 samples for each thickness

Baratta et al. 2015, Planet. Space Science 118, 211
Baratta et al. 2019, Astrobiology 19, 1018
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Photochemistry on the Space Station

2 samples “exposed” on the ISS
2 samples “not exposed” on the ISS
2 samples exposed to UV lamp and temperature cycles (-20-60 °C) at DLR
2 samples suffered the same temperature cycles as those on ISS
2 samples stored at DLR at constant temperature (5 °C) under vacuum

Baratta et al. 2015, Planet. Space Science, 118, 211
Baratta et al. 2019, Astrobiology 19, 1018
Photochemistry on the Space Station

24 July 2014 launch of rocket "Soyuz-U" to transport cargo ship "Progress M-24M" from Baikonur (Kazakhstan)

18 August 2014
Expose-R facility placed outside the ISS on the Universal Platform D of the Russian module Zvezda

22 October 2014
Removal of protective cover

3 February 2016
Expose-R facility returned inside the ISS

2 March 2016 samples landed at Karaganda (Kazakhstan), on-board the Soyuz 44S return capsule

Exposure to space vacuum lasted 531 days
Exposure to solar UV photons lasted 469 days
Samples stability
Photochemistry on the Space Station

All control samples do not show any significant spectral modification
Photochemistry on the Space Station

Spectral modifications observed after exposure to UV solar photons
Photochemistry on the Space Station

\[ \text{-C≡N nitrile} \quad \text{-N≡C isonitrile} \]

Baratta G., Accolla M., Chaput D., Cottin H., Palumbo, M.E., Strazzulla G. 2019, Astrobiology 19
Photochemistry on the Space Station

Effective absorption coefficient

\[ \alpha_{\text{eff}}(\text{UV}) = 5.1 \, \mu\text{m}^{-1} \]

Destruction rate

\[ \Gamma = 10.6 \, \text{yr}^{-1} \]

Baratta et al. 2019
Survival time of CN bonds in a particle made of 50% silicates and 50% organic matter placed at 1 au (Baratta et al. 2019)
Investigate the effects of solar wind ions and solar energetic particles (SEP)

Summary

Nitriles contained in Interplanetary Dust Particles as large as 20-30 µm can survive their journey in the interplanetary medium;

Nitriles contained in Interplanetary Dust Particles could have reached the prebiotic Earth providing one of the basic ingredient for life.
Acknowledgments
Solar Irradiance
Interaction of ions with matter

J.F. Ziegler: SRIM (Stopping and Range of Ions in Matter); TRIM (TRansport of Ions in Matter)
# Energetic processing in the Solar System

<table>
<thead>
<tr>
<th>Energy</th>
<th>Fluxes (cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solar Photons</strong></td>
<td></td>
</tr>
<tr>
<td>2 eV Visible</td>
<td>2.0·10(^{17})</td>
</tr>
<tr>
<td>4 eV NUV</td>
<td>1.5·10(^{16})</td>
</tr>
<tr>
<td>6 eV FUV</td>
<td>3.0·10(^{13})</td>
</tr>
<tr>
<td><strong>Solar Wind (1 AU)</strong></td>
<td></td>
</tr>
<tr>
<td>1keV H(^{+})</td>
<td>3.0·10(^{8})</td>
</tr>
<tr>
<td>4keV He(^{2+})</td>
<td></td>
</tr>
<tr>
<td><strong>Solar Flares (1 AU)</strong></td>
<td></td>
</tr>
<tr>
<td>&gt;1 MeV H(^{+})</td>
<td>10(^{10}) (cm(^{-2}) yr(^{-1}))</td>
</tr>
<tr>
<td>&gt;1 MeV He(^{2+})</td>
<td></td>
</tr>
<tr>
<td><strong>Galactic cosmic rays</strong></td>
<td></td>
</tr>
<tr>
<td>&gt;1 MeV H(^{+})</td>
<td>1-10</td>
</tr>
<tr>
<td>&gt;1 MeV He(^{2+})</td>
<td></td>
</tr>
</tbody>
</table>
\[ dN_{CN} = N_{CN}^0 e^{-\phi_{UV}(x)t\sigma(CN)} \, dx \]

\[ \phi_{UV}(x) = \phi_{UV}(0)e^{-\alpha(UV)_{\text{eff}} \cdot x} \]

\[ n_{CN} = \int_{x_1}^{x_2} dN_{CN} = N_{CN}^0 \int_{x_1}^{x_2} e^{-\Gamma \cdot t \cdot e^{-\alpha(UV)_{\text{eff}} \cdot x}} \, dx \]
constant of the composite medium \( \varepsilon_{av} = \tilde{N}_{av}^2 \) (where \( \tilde{N} \) is the complex index of refraction) is given by the relation

\[
\varepsilon_{av} = \varepsilon_m \left[ 1 + \frac{3F_v}{\varepsilon + 2\varepsilon_m} \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon - \varepsilon_m} \right) \right]
\]

where \( \varepsilon_m \) is the dielectric constant of the matrix, \( \varepsilon \) and \( F_v \) are the dielectric constant and the volume fraction of the inclusions, respectively. We assume that the organic material is the matrix and the inclusions are made of crystalline forsterite in Eq. 5. By

with \( F(R_{sph}, \tilde{N}_{av}, r) \) the fraction of the incident radiation field transmitted within a sphere of radius \( R_{sph} \) down to a distance \( r \) from the center. For a sphere Eq. 4 can be modified in:

\[
n_{\text{CN}} = \int_0^{R_{sph}} dN_{\text{CN}} = V_{\text{or}} N^{0}_{\text{CN}} 4\pi \int_0^{R_{sph}} e^{-\frac{1}{4} \Gamma \cdot t \cdot F(R_{sph}, \tilde{N}_{av}, r) } r^2 dr
\]

(6)
fraction $F_{CN}$ of survived $-\text{C}≡\text{N}$ units, within a sphere of radius $R_{\text{sph}}$ at 1 AU after a time $t$, is given by

$$F_{CN} = \frac{n_{CN}}{V_{or}N_{CN}^0 \frac{4}{3} \pi R_{\text{sph}}^3} = \frac{3}{R_{\text{sph}}^3} \int_0^{R_{\text{sph}}} e^{-\frac{1}{4} \Gamma \cdot t \cdot F(R_{\text{sph}}, \tilde{N}_{av}, r)} r^2 dr$$

(7)

The time of flight of an IDP evolving inward (spiraling) under Poynting-Robertson (P-R) drag force from a heliocentric distance $R$ down to 1 AU is given in the work of Pepin et al. (2000):

$$\tau = 1.1 \cdot 10^{14} \delta \rho (R/R_0)^2 \text{ (seconds)}$$

(8)

where $\delta$ and $\rho$ are the diameter and the density of the particle in c.g.s units, respectively, $R$ is the starting heliocentric distance, and $R_0$ is the distance that corresponds to 1 AU. found that the fluence suffered by an IDP during its P-R drag from a heliocentric distance $R$ down to 1 AU is the same as that the IDP would suffer at 1 AU in a $\chi$ times shorter period, where $\chi = 2 \cdot \ln(R/R_0) \cdot (R/R_0)^{-2}$. This relation can
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\[ \text{C}=\text{O} \quad \text{C}+\text{C} \quad \text{C}=\text{N} \]

\[ \begin{align*}
\text{O-H} \\
\text{N-H} \\
\text{C-H} \\
\text{-C}+\text{N} \\
\text{-N}=\text{C}=\text{O} \quad ?
\end{align*} \]

- Carbons and Nitrogen (N)

**Table: Mass Flux and Total Amount of Carbon**

<table>
<thead>
<tr>
<th>OBJECT</th>
<th>MASS FLUX (KG/YEAR)</th>
<th>TOTAL AMOUNT OF CARBON (KG/YEAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBONACEOUS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHONDrites</td>
<td>190</td>
<td>8.5</td>
</tr>
<tr>
<td>INTERPLANETARY DUST PARTICLES</td>
<td>3,200,000</td>
<td>112,300</td>
</tr>
<tr>
<td>MICROMETEORITES</td>
<td>2,700,000</td>
<td>34,700</td>
</tr>
</tbody>
</table>
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