Sputtering analysis of astrophysical solids by Plasma Desorption Mass Spectrometry - PDMS


(Master Dissertation- 2015)
Sputtering analysis of astrophysical solids by Plasma Desorption Mass Spectrometry - PDMS

1- Optical Spectroscopies – the main source of information
2- How Mass Spectrometry can be used in Astrophysics?
3- MS of cosmic rays
4- Mass spectrometers in space
5- MS of cosmic samples (our data)
6- MS of analogues (our data)
7- Final Comments
Because sources are too distant, most of the information from the Universe comes by electromagnetic waves.
Thor's Helmet Nebula (near Sirius – Canis Major)

Ex.: image acquired by the Very Large Telescope, Chile

VLT image
The blue color reveals an oxygen cloud expanding

Thor’s Helmet Nebula (near Sirius – Canis Major)
Optical Spectroscopies are very important but, nevertheless,

Relevant cosmic information also comes via:
- gravitation (now: waves !)
- neutrinos
- electrons
- cosmic rays (ions)
- cosmogenic and cosmic materials
- space missions

More analytical techniques are necessary, in particular

Mass Spectrometry (MS)
How MS can be used in Astrophysics?

Direct use:

a) **cosmic rays**\(^*\) arriving on Earth and on artificial satellites
b) **secondary ions** produced by natural ionizing radiation
   impinging on planets, satellites, grains, asteroids and comets
c) **cosmogenic materials** (e.g. \(^{14}\text{C}\) produced in atmosphere)
d) **cosmic samples** (measurements in situ) and meteorites
   or material brought to Earth by missions

Indirect use:

study of **cosmic analogue samples** → laboratory data

* Primary CR: e\(^-\), H, He and heavy (C \(\rightarrow\) Fe) ions; Secondary CR: Li, mesons, e\(^+\)
How MS can be used in Astrophysics?

Mass Spectrometry →

mass determination of:
- elementary particles, atoms and molecules
- measurement of their abundance

How to get his?

- W. Wien 1898
- A. Dempster 1918
- F. Aston 1919

MS of the chemical elements in Universe

Thomson (1912) : first mass spectrum
Primary Cosmic Ray (CR) Species

Reminder:
Galactic cosmic rays
Solar wind

V_{SW} = 400c \text{ km/s}
V_s = 100 \text{ km/s}
V_{apex} = 16 \text{ km/s}
Solar wind on Earth orbit

- \[ \phi = A_1 \exp(-\eta E/m) + A_2 / (E/m)^2 \]
- \( \eta \sim 2600 \text{ (MeV/u)}^{-1} \)

Galactic cosmic rays

- MS easy
- MS difficult
- (very large spectrometers)

SW & GCR Energy Distributions
The knowledge of cosmic ray flux is crucial for planning life permanence in space.*

* Particularly for the long manned missions
The Viking Gas Chromatograph Mass Spectrometer (1971)

A gas chromatograph uses a thin capillary fiber known as a column to separate different types of molecules, based on their chemical properties.

→ Searching for Life on Mars

**b) Mass Spectrometers in Space**

**The Viking Gas Chromatograph Mass Spectrometer**

AMS: Searching for antimatter, dark matter and measuring cosmic rays

AMS: Alpha Magnetic Spectrometer: He / He

Mass: 8.5 ton

Launch: May 2011

AMS @ Internl. Space Station (ISS)
AMS: preparing for Mars mission. Measuring GeV cosmic rays

b) Mass Spectrometers in Space

antiproton / proton ratio
(2015 AMS-02 data)

antiproton secondary production
from ordinary cosmic ray collisions
(expected)

Alpha Magnetic Spectrometer: He / He

AMS @ Internl. Space Station (ISS)
AMS: 60 billion cosmic ray events after 5 years

b) Mass Spectrometers in Space

antiproton / proton ratio
(2015 AMS-02 data)

antiproton secondary production
from ordinary cosmic ray collisions
(expected)

Alpha Magnetic Spectrometer: p / p

AMS @ Internl. Space Station (ISS)
b) Mass Spectrometers in Space

**Time of Flight (TOF)**

AMS: a magnetic, TOF and position sensitive spectrometer

\[ \text{flux} = B \cdot r = m \cdot v / q \]

- Protons: higher flux at high energies
- Helium: data

PRL 110 (2013) 141102

TOF mass spectrometer

for masses

for trajectories (charges)

energy detector
b) Mass Spectrometers in Space

Mars Science Laboratory 2011

Analyzing the surfaces of rocks and other samples directly on Mars’ surface.
c) Cosmogenic materials

\[ n + ^{14}\text{N} \rightarrow ^{14}\text{C} + p \]

\[ ^{14}\text{C} \rightarrow ^{14}\text{N} + e^- + \bar{\nu}_e \]

\[ \tau_{1/2} = 5730 \text{ years} \]

Beta decay

The \(^{14}\text{C} / ^{12}\text{C}\) ratio gives the sample age
c) Cosmogenic materials

\[ n + {}^{14}\text{N} \rightarrow {}^{14}\text{C} + p \]

\[ {}^{14}\text{C} \rightarrow {}^{14}\text{N} + e^- + \bar{\nu}_e \]

\[ \tau_{1/2} = 5730 \text{ years} \]

Beta decay

The \(^{14}\text{C} / {}^{12}\text{C}\) ratio gives the sample age
d) Cosmic samples

Murchirson meteorite
(Australia – 28 Sep 1969)

mass 128: naphthalene
178: phenanthrene / antracene

IR + pulsed UV laser MS
(thermal desorption + ionization)

Carbonaceous chondrite type – Hanh et al., Science 239 (1988) 1523
**d) Cosmic samples**

**Apolo 11 - 1969**

- **Lunar Mission**
  - **Sample Returned**
  - **Year**
    - Apollo 11: 22 kg, 1969
    - Apollo 12: 34 kg, 1969
    - Apollo 14: 43 kg, 1971
    - Apollo 15: 77 kg, 1971
    - Apollo 16: 95 kg, 1972
    - Apollo 17: 111 kg, 1972
    - Luna 16: 101 g, 1970
    - Luna 20: 55 g, 1972
    - Luna 24: 170 g, 1976

**Moon rocks**

- **Regolith SiO$_2$ et al.**

**Mare Tranquillitatis**

- **maria** → **basaltic lava** → **olivine**
  - $\rho \approx 4$ g/cm$^3$

- **highlands** → **anorthosite**
  - $\rho \approx 2.6$ g/cm$^3$
  - **anorthite**

Armstrong's walk on the Moon (on the cat's eye)
main ion-solid mechanisms

1- Electron emission
2- Sputtering (neutrals and ions)
3- Chemical reactions
4- Structural modifications (compaction, amorphization, crystallization, phase transition, material stress, craters, ...)
5- Heating and Sublimation
TOF used in our measurements
Sputtering of silicates

- Analyzed by TOF mass spectrometer
- At room temperature

\[ ^{252}\text{Cf} \]

MCP detector (start)

sample

free field region

MCP detector (stop)

PDMS – Plasma Desorption MS
d) Cosmic samples

Silica / Quartz (from Apollo mission)

- 28Si: 92%
- 29Si: 5%
- 30Si: 3%

Positive ions:
- SiO₂⁻
- (SiO₂)₂⁻
- (SiO₂)₃⁻

Negative ions:
- SiO⁻
- SiO₂⁻
- SiO₃⁻

Color of Moon: PDMS
d) Cosmic samples

Silica / Quartz (brought by Apollo mission)
d) Cosmic samples

[Diagram showing mass spectrum with peaks for SiO$_2^-$, SiO$_3^-$, CaO$_2^-$, Al Si O$_4^-$, (SiO$_2$)$_2^-$, Al(SiO$_3$)$_2^-$, and Al(SiO$_3$)$_2^-$].

Anorthite (brought by Apollo mission)
Moon silicates

**Moon : 3.1 - 3.9 billion years ago**

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Mineral Name</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si O₂</td>
<td>Silica</td>
<td>2.2</td>
</tr>
<tr>
<td>Na₃ K Al₄ Si₄ O₁₆</td>
<td>Nepheline</td>
<td>2.6</td>
</tr>
<tr>
<td>Ca Al Si₃ O₈</td>
<td>Anorthite</td>
<td>2.7</td>
</tr>
<tr>
<td>Na Al Si₂ O₆</td>
<td>Jadeite</td>
<td>3.3</td>
</tr>
<tr>
<td>(Mg,Fe)₂ Si O₄</td>
<td>Olivine</td>
<td>4.0</td>
</tr>
</tbody>
</table>

ρ \(_{\text{moon}}\) = 3.3 g/cm³
e) Cosmic analogue samples

nepheline (20 nm) evaporated on a Si wafer (room temperature)

Counts (arbitrary units)

Hexagonal

FF-252Cf on nepheline (Na,K)AlSiO₄

$U_{\text{extraction}} = +18$ kV

$\text{Na}^+$

$\text{Na}_2^+$

$\text{NaLi}_2^+$

$\text{H}^+$

$39/41\text{K}^+$

$(\text{Na}_2\text{O})\text{H}_n^+$

$\text{Li}^+$

$\text{Na}_2\text{O}_n^+$

$\text{AlSiO}_n^+$

$\text{Al}_3\text{O}_n^+$

$n = 1, 2, 3, 4$
e) Cosmic analogue samples

FF-\textsuperscript{252}Cf on Na Al Si\textsubscript{2} O\textsubscript{6}

U\textsubscript{extraction} = +18 kV

Mass spectrum of positive ions

Mass spectrum of negative ions

Count (arbitrary units)

Counts (arbitrary units)

m/z

m/z

H\textsuperscript{+}

H\textsubscript{2}\textsuperscript{+}

H\textsubscript{3}\textsuperscript{+}

Na\textsuperscript{+}

39/41K\textsuperscript{+}

(Na\textsubscript{2}O)H\textsubscript{n}\textsuperscript{+}

28/29/30SiO\textsubscript{3}\textsuperscript{-}

AlSiO\textsubscript{3}\textsuperscript{-}

AlSiO\textsubscript{4}\textsuperscript{-}

Al(SiO\textsubscript{3})\textsubscript{2}\textsuperscript{-}

Al

Si

Na

Jadeite
PDMS Analysis of Meteorites

1. Isna (Egypt, 1970)
   
   **Chondrite:** carbonaceous – CO3

2. Allende (Mexico, 1969)
   
   **Chondrite:** carbonaceous – CV3

   
   **Acondrite:** Shergotito (Martian).
PDMS Analysis of Meteorites

Isna meteorite

Silicon cluster structures

Example:

Positive ion mass spectrum
PDMS analysis of meteorites: Isna, Allende and Zagami

Example: Negative ion mass spectra

184 u: a very stable structure

(Si$_2$O$_8$) (Yu-Hong and Baoxing, 2014)
PDMS analysis of meteorites: Isna, Allende and Zagami

Example:

Negative ion mass spectra

These ion species are actually being “produced” and emitted from interplanetary grains in space:

CR synthesis in **ONE** impact !!!

184 u : a very stable structure
Sputtering of ices

- Analyzed by TOF mass spectrometer
- At cryogenic temperatures
Water -

**Main Series:**

- $(H_2O)_nH^+$
- $(H_2O)_nO^-$, $(H_2O)_nOH^-$

**Most Abundant Emitted Ions:**

- $H^+$, $H_3O^+$
- $H^-$, $O^-$, $OH^-$

**Hydrogen Bridges:**

$H_2O$ ice ejects

- Intense series of ionic clusters
  - $n > 60$

**Main Series:**

- $(H_2O)_nH_2O^+$
- $(H_2O)_nO^-$, $(H_2O)_nOH^-$

*Surface Science, 569 (2004) 149-162*
(H\textsubscript{2}O\textsubscript{n})\textsubscript{H_3O^+} emission decreases as the temperature increases!

\[
Y = Y_0 e^{-k.n}
\]

Lower temperatures: higher yields!
Ammonia - NH₃

most abundant emitted ions:

\( H^+ \), \( NH_4^+ \), \( NH_3^+ \)
\( H^- \), \( NH_2^- \), \( NH^- \)

Hydrogen bridges:

\( H_2O \) e \( NH_3 \) eject

intense series of ionic clusters

main series:

\( (NH_3)_nNH_4^+ \)
\( (NH_3)_nNH_2^- \)
Molecular clusters are ejected into the gas phase → Radio telescopes?
Carbon Monoxide - $\text{C} \equiv \text{O}$

**Dominants:**
- $C_n(CO)_2^+$, $C_n(CO)^+$, $C_n^+$
- $C_n^-$, $O_n^-$

**Abundants:**
- $C^+$, $CO^+$, $O^+$, $CO_2^+$
- $O^-$, $C^-$, $C_2^-$

**Synthesization:**
- $CO_3^-$, $C_2O_3^-$

CR synthesis! **one shot!**

**Graphitization!**

**Carbon Chains**

**Temperatura →**

Carbon Dioxide - O=C=O

dominants:

\[(\text{CO}_2)_n\text{O}_2^+\]

\[(\text{CO}_2)_n\text{CO}_3^-\]

abundants:

\[\text{O}_2^+, \text{CO}_2^+, \text{C}^+, \text{CO}^+\]

\[\text{CO}_3^-, \text{O}^-\]

dominants:

\[(\text{CO}_2)_n\text{O}_2^+\]

\[(\text{CO}_2)_n\text{CO}_3^-\]
Mixture $O_2 + N_2$

**abundants:** $O_2^+, O^+, O_3^+$, $N_2^+, N^+, N_3^+, NO^+$, $O^-, O_2^-$ (no $N^-$)

**Main series:**

$(O_2)_n O_2^+, (O_2)_n O^+, (O_2)_n O_3^+$

$(N_2)_n N_2^+, (N_2)_n N^+$

$O_n^-, O_n N_2^-$

**Synthesis of:**

$NO^+, NO_3^+, O_n NO^+, O_n N_2^+$

$NO^-, N_2O^-$
Figure 5. Comparison between total sputtering \(^8\) and ion yields of water clusters corresponding to bombardment of MeV N ions on water ice at a temperature of 80 K.
**CH₄ Radiolysis: FTIR vs MS**

![Graphs and diagrams related to CH₄ radiolysis, showing absorbance, column density, and fluence impacts.](image)

- **Absorbance**
  - CH₄, C₂H₆, C₂H₄, C₂H₂, CH₃, H₂O peaks are indicated.
  - Comparison before and after radiolysis.

- **Column density**
  - CH₄, C₂H₆, C₂H₄, C₂H₂, CH₃, C₃H₈ are plotted against fluence.
  - Column density (10¹⁸ molecules/cm²) vs fluence (10¹⁴ impacts/cm²).

- **Equations and Wavenumbers**
  - v₃ - 3009 cm⁻¹
  - v₁ + v₄ - 4202 cm⁻¹
  - v₂ + v₄ - 2815 cm⁻¹
  - v₃ + v₄ - 4300 cm⁻¹
  - v₄ - 1300 cm⁻¹

- **Fluence Impact**
  - N₀ ~ 4.09 × 10¹⁸ molecules/cm²

**Astronomy & Astrophysics, A531 (2011) A160**
Formation cross section $\sigma_f$

$$\sigma_f = a S_e^{3/2}$$
Chemistry:

• Hot chemistry ($10^4$ K) in very cold material (10 - 100 K)
  
  \[ RT \rightarrow 1/40 \text{ eV} ; \text{keV} \rightarrow 4000 \text{ K} \]

• Fast chemistry (ps) in solids
  
  No thermodynamical equilibrium

• New pathways for Organic Chemistry:
  
  The bombardment of CO by ions has an interesting and relevant property: the formation of carbon chains

Biochemistry

“Strategical” molecules for the prebiotic synthesis, like HCN and OCN, are easily formed by fast ion impact.
main ion-solid mechanisms

- Sputtering (neutrals and ions)
- Chemical reactions
- Structural modifications (compaction)

Reminder: the 3 relevant mechanisms for synthesis
Final comments: dependence on $S$

From the sputtering and radiolysis experiments:

1- Ion beams interact with matter and transfer energy with a characteristic rate called Stopping Power ($S$).

2- Three main phenomena: dependence on $S$

a) Sputtering (removal of surface material): $Y \sim S^2$

b) Chemical reactions:
   $\sigma_f$ or $\sigma_d \sim S^n$  \hspace{1cm} $2/3 < n < 3/2$

b) Chemical reactions:
   $\sigma_c \sim S^2$

Synthesis / sputtering: $\sigma / Y \sim S^n / S^2 = 1 / S^{2-n}$  \hspace{1cm} $2- n > 0$
Final comments: dependence on $S$

From the sputtering and radiolysis experiments:

1- Ion beams interact with matter and transfer energy with a characteristic rate called **Stopping Power (S)**.

2- Three main phenomena:

   a) **Sputtering** (removal of surface material): $Y \sim S^2$

   b) **Chemical reactions:** 

      $\sigma_f$ or $\sigma_d \sim S^n$

   c) **Compaction** (structural modification): $\sigma_c \sim S^2$

**Conclusion:**

Heavy ions are much more efficient than protons for radiolysis AND sputtering.

**This is:**

- good – large molecules are formed faster by heavy ions
- bad - they destroy the target before processing it enough
Final comments: dependence on $m$ and $T$

$N_2O$ radiolysis (only 2 elements)
**Final comments**: dependence on m and T

- As m increases:
  - low T: synthesis very bad
  - high T: synthesis bad

**N\textsubscript{2}O radiolysis**

**Diagram**:
- Cross section vs. molecular mass (u)
- Temperature levels: 11 K, 60 K, 80 K
- Species: NO, NO\textsubscript{2}, (NO\textsubscript{2}), N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{4}, N\textsubscript{2}O\textsubscript{5}
Final comments: dependence on $m$ and $T$

Amino acids are expected to be “easily” produced in warm regions!

Proteins are not expected to be produced by cosmic rays!

as $m$ increases

(If the $N_2O$ results can be generalized)
CREDITS (lunar rocks & analogues)

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Thanks for the attention!

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SUMMARY

MS has been used to analyze ions coming from the outer space and arriving in Earth, Moon and in orbiting spacecrafts

→ Meteorites, lunar rocks, Mars surface, etc are extensively examined by standard MS techniques

Isotope ratios and isotope dating (e.g. $^{238}\text{U} - ^{206}\text{Pb}$ or $^{14}\text{C}$) give very useful information on the sample origin

→ Cosmic analogue samples have been produced in laboratory and analyzed by MS

Such experiments show in particular what to expect from in situ measurements
a) What Cosmic Rays are?

- **Primary Cosmic Rays** are very energetic ($10^3$ to $10^{22}$ eV) charged particles that traverse outer space.

- Basically, they are:
  - **light ions**: protons + deuterons (87%) and $\alpha$ particles (11%)
  - **heavy 4n ions**: $^{12}$C, $^{16}$O, $^{20}$Ne, $^{24}$Mg, $^{28}$Si, $^{32}$S, $^{40}$Ar, $^{40}$Ca, and $^{56}$Fe (Ni)
  - electrons (~1%)

[unstable ions or neutrals are excluded: neutrons, neutrinos, X-rays, $\gamma$ rays]

- After collision with interstellar matter and atmosphere, **Secondary Cosmic Rays** are formed. They are constituted by:
  - Li, Be, B, neutrons (formed by spallation)
  - pions, kaons, mesons, positrons and $\gamma$ rays
Astronomy:

• To predict mean-lives of molecules in space

CR energy distribution

This means that iron beam (and not protons or alphas) is responsible for chemistry in ISM!

No life without SN?

10 Ga →
Genesis of the Fe-Ni meteorites (6%)
PDMS Analysis of Meteorites

Positive ions

Isna

Counts (a. u.)

Negative ions

m/q

300 310 320 330 340 350 360 370 380 390 400

0,00 0,01 0,02

496 524 553

312 326 340

354 369 382

500 510 520 530 540 550 560 570 580

0,00 0,01 0,02