Biomarkers and Detection of Life in our Solar System

Zita Martins
Royal Society University Research Fellow

Dept. Earth Science and Engineering
Imperial College London, UK
One of the most important scientific questions for humanity is “Is there life beyond the Earth?”
Space Missions and Search for Extraterrestrial Life

Missions to Mars

Others places of the Solar System
- Europa
  Moon of Jupiter
  Ice Surface
  Water ocean beneath the surface
  Galileo and EJSM missions (2020 ?)

- Titan
  Moon of Saturn
  Liquid surface; geologically very young
  Lakes of hydrocarbons in the polar regions
  Cassini-Huygens mission(2005)

- Enceladus
  Moon of Saturn
  Voyager (1980s) and Cassini-Huygens missions (2005)
## Mars

| **UV flux** (190-325 nm) | Flux: $\sim 1.4 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$  
(Patel et al. 2002) | Intensity: $\sim 37$ W m$^{-2}$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmospheric composition</strong></td>
<td>95.3% CO$_2$ &amp; 2.7% N$_2$; 1.6% Ar; 0.13% O$_2$; 0.03% H$_2$O</td>
</tr>
</tbody>
</table>
| **Surface temperature** | 140 to 300 K  
*average*: 210 K, diurnal variation |
| **Soil oxidation** | Minerals, radicals  
H$_2$O$_2$, OH$^-$, O$_3$, O$_2^-$ etc |
Photoactivation of nitrates

\[ \text{NO}_3^- \sim \text{hv} \rightarrow \text{NO}_2^- + \text{O}(3P) \rightarrow \text{NO}_2 + \cdot \text{O}^- \]

Absorption of water, oxide radical reacts to form OH⁻

\[ \cdot \text{O}^- + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{OH}^- \]

Metal oxides

\[ \text{MO}_n + \text{H}_2\text{O} \sim \text{hv} \rightarrow \text{MO}_{n-1}\text{OH} + \cdot \text{OH} \]

Photo-Fenton reaction
During the 1976 Viking missions:
Regolith samples - pyrolysed at 500°C for 30 s followed by the analysis of the evolved volatiles using GC-MS

No organic compounds were detected above a threshold level of a few parts per billion in near surface samples at two different landing sites (Biemann et al. 1976)

Amino acids present in several million bacterial cells per gram of soil would not have been detected by the Viking GC-MS (Glavin et al. 2001)

In addition, oxidation reactions involving organic compounds on the Martian surface would likely produce non-volatile products (Benner et al. 2000)
Mars Global Surveyor

Alcove

Apron

Remains of tongue-shaped glaciers

Photo Credit: Malin Space Science Systems/NASA
Search for climatic signal in peri-glacial deposits using MEX HRSC

HRSC 3D color view of the north pole
Follow the Water…

Phyllosilicates and hydrated sulphates aqueous origin MEX

Marwth Vallis
**Science Achievements**

- 3-D high resolution colour images
- Direct measurement of water ice at the South Pole
- Methane detected in atmosphere
- Recent volcanism and periglacial activity
- Frozen sea and tropical glaciers
- Correlation water vapour / ozone destruction
- Phobos high resolution observations
- Relay of Mars images taken by NASA rover
- Methane / water vapour correlation - possible life
- Understanding the Martian water loss process
- Detection of Noachian clays
Opportunity on the Meridiani Planum

“Blueberries”
Sulphate minerals and the search for organic compounds on Mars

Mossbauer Spectrum of El Capitan: Meridiani Planum
Jarosite: \((K, Na, X^+)_3Fe_3(SO_4)(OH)_6\)

Intensity

Velocity

Fe\(^{3+}\) Jarosite
Fe\(^{2+}\) phase
Fe\(^{2+}\) silicate
Magnetic phases

Mars
Gypsum
Calcium sulfate dihydrate

Hydrous sulphate of potassium and iron
Phoenix mission

- Water ice
- Perchlorate (ClO$_4$)
- Carbonates
- Precipitating clouds
MSL and EXOMARS

- ExoMars is scheduled to land on Mars in 2018 (orbiter in 2016). It will search for traces of past and present life on the Red planet.

- MSL will try to detect organic compounds essential to life on Mars.
### Molecules of life

- Essential molecular components of the cell (basic unit of life)

#### Dry composition of E. Coli (unicellular organism)

<table>
<thead>
<tr>
<th>Monomers</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>57</td>
</tr>
<tr>
<td>Amino acids</td>
<td></td>
</tr>
<tr>
<td>RNA</td>
<td></td>
</tr>
<tr>
<td>Nucleobases</td>
<td>24</td>
</tr>
<tr>
<td>DNA</td>
<td></td>
</tr>
<tr>
<td>Lipids</td>
<td>9</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>10</td>
</tr>
</tbody>
</table>

Adapted from Glavin et al. 2004

Parnell et al. 2007
Recognize Life on Mars

How were molecular fossils of Martian life stored and in what form did they remain after different periods of time?

Different degradation rates under Martian conditions

- Proteins
- Amino Acids
- Hydrocarbons

1.1 billion years

>2 billion years

Martins /JA 2011
Potential sources of organic compounds on Mars

The direct synthesis of organic compounds and/or the development of life may have taken place on Mars early in its history …

- Strong UV radiation
- Oxidation processes
- No liquid water
- Toxic atmosphere

Residual organic compounds from either biotic or abiotic sources?
Meteorites contribute with organic matter to Mars
$2.4 \times 10^6 \text{ kg year}^{-1}$ or $\sim 0.1 \text{ nm per year}$ (Zent 1994, Flynn 1996)

Carbonaceous chondrites contain 3-5 wt% organic carbon:

>70% insoluble matter

<30% soluble organic matter
Macromolecular insoluble material consists mainly of aromatic hydrocarbons

(Pendleton & Allamandola 2002)
## Meteorites

Soluble organic compounds present in Murchison

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino Acids</td>
<td>17-60</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
<td>&gt;35</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Hydroxycarboxylic acids</td>
<td>15</td>
</tr>
<tr>
<td>Dicarboxylic acids &amp; Hydroxydicarboxylic acids</td>
<td>14</td>
</tr>
<tr>
<td>Purines &amp; Pyrimidines</td>
<td>1.3</td>
</tr>
<tr>
<td>Basic N-heterocycles</td>
<td>7</td>
</tr>
<tr>
<td>Amines</td>
<td>8</td>
</tr>
<tr>
<td>Amides linear</td>
<td>&gt; 70</td>
</tr>
<tr>
<td>cyclic</td>
<td>&gt; 2</td>
</tr>
<tr>
<td>Alcohols</td>
<td>11</td>
</tr>
<tr>
<td>Aldehydes &amp; Ketones</td>
<td>27</td>
</tr>
<tr>
<td>Sulphonic acids</td>
<td>68</td>
</tr>
<tr>
<td>Phosphonic acids</td>
<td>2</td>
</tr>
</tbody>
</table>

### Typical molecular signatures of life

#### Living organisms
- Nucleobases (AGCTU)
- Hydrocarbons
- L-amino acids

#### Dead organisms
- Nucleobases
- Hydrocarbons
- Mixtures of amino acids (D- and L-, excess of L-)

#### Prebiotic
- Nucleobases
- Hydrocarbons
- Amino acids (>80) (Racemic mixture)

### On Earth:
- Living organisms use L-amino acids
- Over long periods of time amino acids from dead organisms will be converted into equal amounts of L- and D-forms (racemic mixture)

### Non-biological origin:
- Racemic mixtures of amino acids

### On Mars:
- Extremely slow racemisation (due to environmental conditions)
Need to study the processes that altered organic matter

How to distinguish biologic from non-biologic organic matter?

- Mars simulations
- Study meteorites
- Extensive terrestrial field tests
- Site selection – special regions
- In situ instrument development for the identification of biochemical and isotopic biosignatures on Mars
Glycine

D-Alanine

I – Infrared absorption spectrum
II – Amount of material lost after 50 hours of UV irradiation

ten Kate et al. 2005
Meteorites

- Exogenous delivery of organic matter by meteorites could have contributed to the organic inventory of the early Earth and Mars.

$\delta^{13}C$ values (‰) of nucleobases in the Murchison meteorite and soil samples

<table>
<thead>
<tr>
<th>$\delta^{13}C$</th>
<th>Uracil</th>
<th>Xanthine</th>
<th>Thymine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murchison meteorite</td>
<td>+44.5 ± 2.3</td>
<td>+37.7 ± 1.6</td>
<td>n.d.</td>
</tr>
<tr>
<td>Soil</td>
<td>-10.6 ± 1.8</td>
<td>n.d.</td>
<td>-15.9 ± 1.1</td>
</tr>
</tbody>
</table>

Meteorites

Determination of the amino acid content of Antarctic CRs:

Martins et al. MAPS (2007)

Single ion GC-MS traces (m/z 69, 126, 138, 140, 154, 168, 180, 182, 184) of the derivatized (N-TFA, O-isopropyl) EET92042 and GRA95229 meteorites, standard and blank.

1. $\alpha$-AIB
2. Isovaline
3. D-Alanine
4. L-Alanine
5. D-$\alpha$-ABA
6. L-$\alpha$-ABA+D-Valine
7. L-Valine
8. Glycine
9. $\beta$-AIB
10. $\beta$-Alanine
11. D-$\beta$-ABA
12. L-$\beta$-ABA
13. $\gamma$-ABA
14. D-Aspartic acid
15. L-Aspartic acid
16. D-Glutamic acid
17. L-Glutamic acid
Total amino acid abundances (in ppb) present in the CR2s GRA95229 and EET92042 (Martins et al. 2007, this work), the CM2 Y791198 (Shimoyama et al. 1985; Shimoyama and Ogasawara 2002), the CR2 Renazzo (Botta et al. 2002), the CR1 GRO95577 (Martins et al. 2007, this work) and the CM1 LAP02277 (Botta et al. 2007).
Field Test

Atacama, Chile

Mars

Atacama, Chile

Mars

Atacama, Chile

Mars

Atacama, Chile

Mars
Need to have terrestrial soils that are analogues to the soil of Mars.

Field Test Mars Desert Research Station (MDRS)
Field Test Mars Desert Research Station (MDRS)

Martins et al. IJA 2011

Direito et al. IJA 2011
The 10 to 70 min region of the single ion GC-MS traces (m/z 126, 140, 154, 168, 180, 182 and 184) of the derivatized (N-TFA, O-isopropyl) HCl-hydrolysed hot-water extracts of each MDRS desert soil sample.
### Field Test Mars Desert Research Station (MDRS)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogy</th>
<th>Organic Matter</th>
<th>Amino Acids</th>
<th>Post Bacteria</th>
<th>Post Eukarya</th>
<th>Post Archaea</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfates %</td>
<td>Carbonates %</td>
<td>Clays %</td>
<td>ppb&lt;sup&gt;c&lt;/sup&gt;</td>
<td>PS/FDNA</td>
<td>PS/FDNA</td>
</tr>
<tr>
<td>P-1</td>
<td>7</td>
<td>11</td>
<td>15</td>
<td>2</td>
<td>280</td>
<td>+</td>
</tr>
<tr>
<td>P-2</td>
<td>&lt;1</td>
<td>16</td>
<td>1</td>
<td>n.d.</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>P-3</td>
<td>7</td>
<td>3</td>
<td>18</td>
<td>1</td>
<td>730</td>
<td>+</td>
</tr>
<tr>
<td>P-5</td>
<td>2</td>
<td>23</td>
<td>2</td>
<td>n.d.</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>P-6</td>
<td>14</td>
<td>&lt;1</td>
<td>33</td>
<td>2</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>P-7</td>
<td>22</td>
<td>6</td>
<td>2</td>
<td>n.d.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-8</td>
<td>59</td>
<td>8</td>
<td>11</td>
<td>4</td>
<td>4,600</td>
<td>-</td>
</tr>
<tr>
<td>P-10</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>5</td>
<td>2,300</td>
<td>+</td>
</tr>
<tr>
<td>P-13</td>
<td>16</td>
<td>9</td>
<td>2</td>
<td>100,000</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>P-14</td>
<td>73</td>
<td>11</td>
<td>1</td>
<td>3</td>
<td>17,000</td>
<td>-</td>
</tr>
</tbody>
</table>

---

Ehrenfreund et al. *IJA* 2011

Martins et al. *IJA* 2011

Kotler et al. *IJA* 2011
Wish List for Future Instrumentation

- Instruments with higher spatial resolution and fast enough to produce maps of chemistry, mineralogy and organic matter distribution
- Advances in sample handling and preparation
- Develop instruments for *in situ* measurements of the isotopic composition of organic matter, minerals and rocks
- Develop instruments that can combust macromolecular organic matter and detect their fragments
Next Decade — Where to From Here?

**Operational**
- Odyssey
- Mars Express Coop
- MRO

**Launch Year**
- 2009: Mars Science Lab
- 2011: MAVEN
- 2013: ESA/ExoMars Cooperation
- 2016: Lander Mission X
- 2018 & Beyond: The Era of Mars Sample Return?

**Under Review**