Microfabricated Organic Analyzer (MOA) for *in situ* Exploration of Mars and other Solar Bodies

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- Prof. Jeff Bada, Scripps Institution of Oceanography, UCSD, amino acid analysis and astrobiology
- Dr. Frank Grunthaner, Jet Propulsion Laboratory, instrument design, operation and flight engineering
Project Goals

- Complete brass-board development of microfabricated capillary electrophoresis (CE) chip and instrument for amino acid analysis
- Integrate the microchip CE system with MOD sampling system to form the Mars Organic Analyzer (MOA)
- Perform field tests of the MOA in Mojave and three Mars-like Atacama sites
- Document maturation, integration and field operation of two MIDP, PIDDP and ASTID-derived instruments
- Enhance TRL of MOA through Mojave and Atacama field testing
- Increase our understanding of limits and constraints of life in extreme environments
- Critically define identity of and sensitivity requirements of potential biomarkers.
Amino Acid Composition and Chirality Analysis

Potential bioorganic signatures:

- Large biomolecules likely degraded by oxidizing surface environment of Mars
- Amino acids have a longer lifetimes in dry, harsh conditions
- Amino acids have been found in meteorites
- Amino acid chirality is indicative of origin:
  - Racemic mixture – abiotic origin
  - Non-racemic mixture – biological origin

Why in situ analysis:

- Significant contamination of Meteorites found on earth by terrestrial sources of life
- Sample return missions are more technologically challenging, costly and time consuming

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Mars Organic Analyzer (MOA) Concept

- Soil samples collected and deposited into Mars Organic Detector (MOD)

- MOD sublimes amino acids onto cold finger coated with fluorescamine\(^1\)

- Fluorescamine-labeled amino acids analyzed for composition and chirality via microchip Capillary Electrophoresis

Composition and Chirality Analysis by CE

• Electroosmotic flow (EOF) sweeps all molecules to the cathode

• CE separates amino acids based on charge/size ratio giving composition information

• Cyclodextrins included in running buffer provide enantiomeric resolution of amino acids

L-aa + CD => L-complex (K_L)
D-aa + CD => D-complex (K_D)

K_L \approx K_D

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Established Separation and Lab-Based Detection System

Analysis of Fluorescein-labeled Amino Acids

Murchison Meteorite Glu and Asp D/L values

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>HPLC</th>
<th>Microchip CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glu</td>
<td>0.3 + 0.3</td>
<td>0.33 + 0.04</td>
</tr>
<tr>
<td>Exterior</td>
<td>0.7 + 0.1</td>
<td>0.65 + 0.07</td>
</tr>
<tr>
<td>Asp</td>
<td>0.3 + 0.1</td>
<td>0.21 + 0.03</td>
</tr>
<tr>
<td>Exterior</td>
<td>0.3 + 0.1</td>
<td>0.30 + 0.06</td>
</tr>
</tbody>
</table>


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Mars Organic Analyzer (MOA)
Advantages of Fluorescamine:

- Fluorogenic reagent
- Reaction time ~1 min
- ~ 50 nM LOD attainable
- Reagent used in MOD

Separation of Mars 7 Standard labeled with Fluorescamine


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Chilean Atacama Desert is one of the driest sites on the planet (<0.5 mm H₂O/year).

The transect from Lat 24° to 28° South at 69.5° West has been extensively studied.

Some areas have unusual surface oxidation chemistry and organic soil concentrations at lab blank levels. Other areas show readily detected microbial and higher life forms.
Analysis of Atacama Soil Extracts

Blank-corrected Concentrations (weight/weight):
- Val = 0.034 ± 0.009 ppm
- Gly = 0.18 ± 0.03 ppm
- Asp = 0.094 ± 0.004 ppm

Blank-corrected Enantiomeric Ratios:
- Mars 7 Standard:
  - D/L Glu = 1.10 ± 0.02
  - D/L Asp = 0.97 ± 0.02
- Atacama Sample # 20
  - D/L Glu = 0.22 ± 0.02
  - D/L Asp = 0.16 ± 0.02

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Mars Organic Analyzer (MOA)
Portable Microchip CE System - Schematic


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Mars Organic Analyzer (MOA)
Portable Microchip CE Instrument

Diode Laser
400 nm 10 mW

Dichroic Beamsplitter

Mirror

Long Pass Filter
T > 450

Confocal Lens

Pin Hole

Hammatsu HC120 PMT

Objective

Channel

Microplate

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Mars Organic Analyzer (MOA)
Portable Microchip CE Instrument

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Mars Organic Analyzer (MOA)
Microfabricated Device

- 4-layer structure, < 4 mm thick
- Diaphragm pumps deliver ~ 1 uL per actuation
- Input/output valves can actuate in under 100 ms
- Flow rates up to 350 nL/s are obtained

- Microfluidic bus has 5 reservoirs for buffer, water, labeling dye, waste, etc., reactor valve and sipper
- Rinsing bus allows device to be used for multiple samples
- 2 separation channels, 21 cm long

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Mars Organic Analyzer (MOA)
Comparison of Lab and MOA Systems

Concentration of each AA = 2.2 μM

Concentration of each AA = 444 nM

• MOA system shows superior sensitivity and comparable separation efficiency

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Mars Organic Analyzer (MOA)
Amino acid concentration in 50 µL collected sample:

Val = 16.2  Ala/Ser = 92.1  Gly = 622.0 µM
Glu = 11.7  Asp = 16.3

Life in Berkeley?

Will’s ALIVE!!!

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Mars Organic Analyzer (MOA)
MOD + CE = MOA

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Mars Organic Analyzer (MOA)
• Amino acid composition and chirality is an ideal means for organic biomarker detection on Mars.

• Microfabricated CE instrument provides a demonstrated means for sensitive amino acid composition and chirality analysis.

• Portable CE instrument has identical separation efficiency and greater sensitivity than standard lab systems.

• Integration of CE with MOD to make MOA will provide sensitive analysis of amino acids in Martian soil.

• Field tests in Mojave and Atacama Deserts are planned as a critical test of technology readiness and analysis capabilities.

• Microchip is a powerful platform for preparation other analytes from other sources for many types of analyses.
Mars Organic Laboratory (MOL): Beyond amino acids

2. E.T. Lagally et al., Lab-on-a-Chip, 1 (2001) 107. Integrated PCR with CE analysis of nucleic acids

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Mars Organic Analyzer (MOA)
Acknowledgements

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