Laser Induced Breakdown Spectroscopy for Lunar Surface & Volatile Exploration

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Outline

- What is LIBS?
- Does it work on the Moon?
  - LIBS in vacuum
  - Detection limits
  - Volatile observations
- What is ChemCam / SuperCam?
  - Powerful combination of elemental compositions plus active and passive mineralogy measurements (+ imaging)

Much of this presentation comes from:
Laser-Induced Breakdown Spectroscopy (LIBS)

Sirven et al., JAAS
LIBS

- Uses a focused, pulsed laser to ablate a small amount of the target material in the form of a luminous plasma.
  - Laser energy density > 10 MW/mm$^2$
- Optical emission lines are observed representing the elements present in the target.
- Intensities are calibrated to produce quantitative compositions.
- Repetitive laser pulses remove dust and profile into the rock or soil.
  - Depths to ~1 mm in rock and 1 cm in soil allow compositional gradients to be determined.
LIBS at Different Ambient Pressures
LIBS Lunar Analog Spectra

- Lunar soil simulant JSC-1
- In ‘lunar vacuum’
- Distance = 1.5 m
- Laser energy 17 mJ
- Shows all major elements and some trace elements
- Non-optimized
Accuracies of Major Elements

- Relative error of prediction (in %)
- Root mean square error product (in wt. %)
- Based on calibration model of 12 standards
  - Compared to > 400 standards used for ChemCam on Mars

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>FeO</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>K (ppm)</th>
<th>Ni (ppm)</th>
<th>Mg #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Med REP (%)</td>
<td>1.55</td>
<td>10.3</td>
<td>6.97</td>
<td>8.83</td>
<td>13.61</td>
<td>13.16</td>
<td>20.77</td>
<td>21.84</td>
<td>113.04</td>
<td>76.84</td>
<td>10.21</td>
</tr>
<tr>
<td>RMSEP (wt %)</td>
<td>0.78</td>
<td>1.18</td>
<td>1.03</td>
<td>0.02</td>
<td>0.9</td>
<td>1.15</td>
<td>0.61</td>
<td>0.43</td>
<td>1705</td>
<td>39.7</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Limits of Detection Compared to Lunar Abundances

Al & Fe cover very large ranges on the Moon

Limits of detection. Some low-K soils and breccias would pose a challenge for this set of commercial spectrometers.
Water Ice Observations

- Partial spectrum of lunar soil simulant JSC-1 mixed with ~25% H₂O ice under vacuum, interrogated with 50 mJ laser pulse at a distance of 3 m. A very strong hydrogen peak is seen.
What is ChemCam?

- ChemCam is a combined remote LIBS + hi-res imager operating on Mars since 2012
- >350,000 spectra of ~12,000 observation points
- > 10,000 images
- Laser & telescope on rover mast, spectrometers in rover body
- Joint French-US instrument
- Mass = 10 kg
What is SuperCam?

- = ChemCam plus remote Raman and VISIR spectroscopy
- Being built for Mars 2020, mass = 10 kg
- Elemental composition + mineralogy is powerful combination
- Raman + VISIR highly complementary
  - Different types of minerals are observed by the two
    - E.g., Raman sees feldspar, invisible to IR
Raman and Infrared Spectroscopy

- **Raman Active Modes:** change in induced dipole moment of molecule

  Induced dipole moment (P): \( P = \alpha E \)

  Polarizability (\( \alpha \)): Charges in a molecule separated under the influence of an external field (E)

- **IR Active Modes:** Change in the permanent dipole moment of the molecule \( M = \mu E \)

![Diagram](image)

**Symmetric Stretch**
- **Raman Active**
- **IR Inactive**

**Asymmetric Stretch**
- **Raman Inactive**
- **IR Active**

**Bend**
- **Raman Inactive**
- **IR Active**
A SuperCam-like instrument would revolutionize lunar exploration by providing rapid comprehensive elemental and molecular (mineralogical) compositions of the lunar surface.
Backup
Fundamental Raman Scattering

Virtual State
- a quasi-excited, intermediate state that arises from the polarization of the molecule in an external electric field
  - not a real energy level
  - scattering occurs on the time scale of a nuclear motion, $\sim 10^{-13}$ sec

Raman Scattering
- The molecular electric field oscillates at the frequency of the passing wave
- Molecular polarizability can induce dipole.
  - if polarizability is constant, scattering is elastic (Rayleigh) scattering
  - if polarizability is not constant, inelastic (Raman) scattering is allowed
- Raman signal lifetime $\sim$ laser pulse width
LIBS Timeline

For target @ 7 m
Laser Fires
Light Travel Time (2 way)
Raman Signal Rec’d
End of Raman Exposure

For target @ 7 m

Raman / Time-Resolved Fluorescence Timeline

Intensifier delay as long as 500 µs