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# Miniature Tunable Laser Spectrometers for Quantifying Atmospheric Trace Gases, Water Resources, Earth Back-Contamination, and In Situ Resource Utilization

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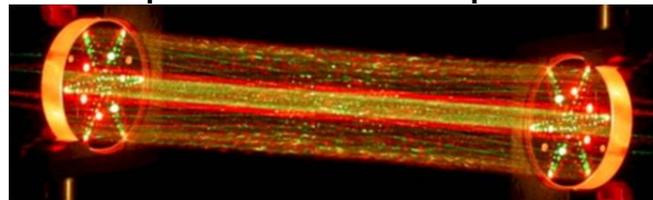
Concepts and Approaches for Mars Exploration  
Lunar & Planetary Institute, Houston, Texas  
June 12-14<sup>th</sup> 2012

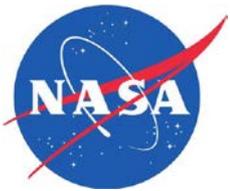


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# Tunable laser spectrometers

- The TLS technique has seen wide applicability in gas measurement and analysis for atmospheric analysis, industrial, commercial and health monitoring and space applications;
- In Earth science using balloons and aircraft over 2 decades, several groups (JPL, NASA Langley & Ames, NOAA, Harvard U., etc) have demonstrated the technique for ozone hole studies, lab kinetics measurements, cloud physics and transport, climate change in the ice record;
- The recent availability of high-power (mW) room temperature lasers (TDL, IC, QC) has enabled miniaturized, high-sensitivity spectrometers for industry and space
  - Mars, Titan, Venus, Saturn, Moon
  - Commercial isotope ratio spectrometers (e.g. Picarro) are replacing bulkier, complex isotope ratio mass spectrometer (IRMS)

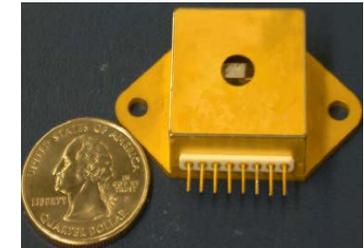
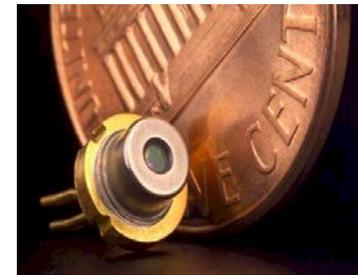
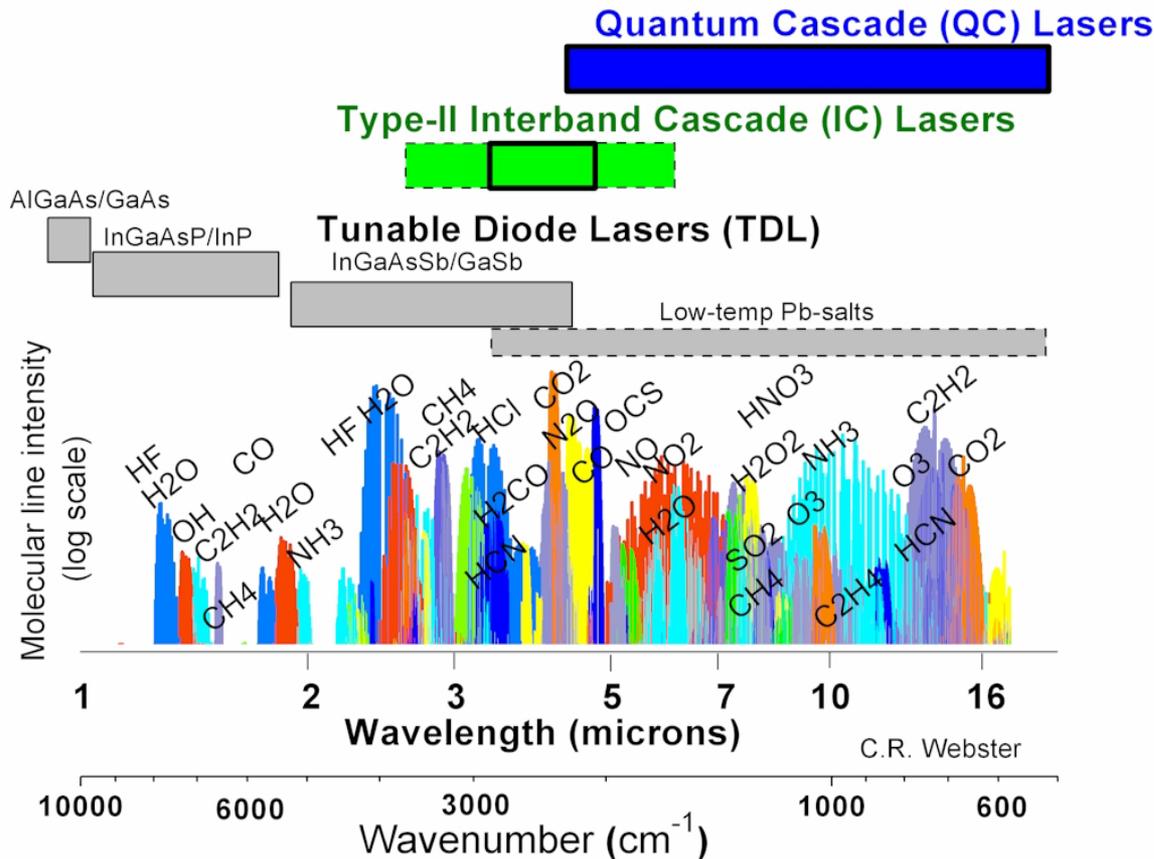




# Lasers and Detectors for a TLS

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Solid-state miniature devices available at room temperature (TEC stabilized)

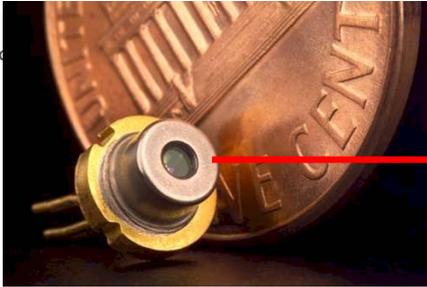


TLS laser –  
100 g

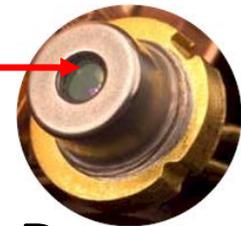
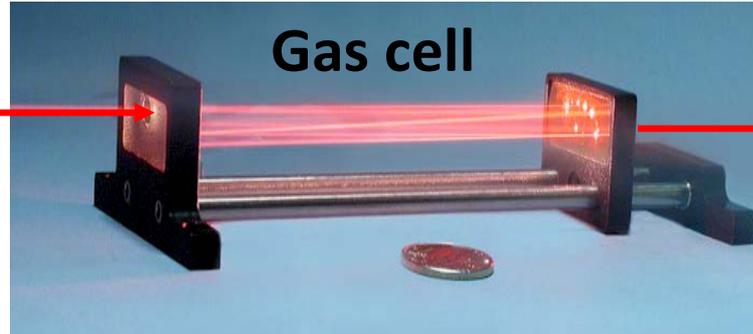


# Tunable Laser Absorption Spectroscopy

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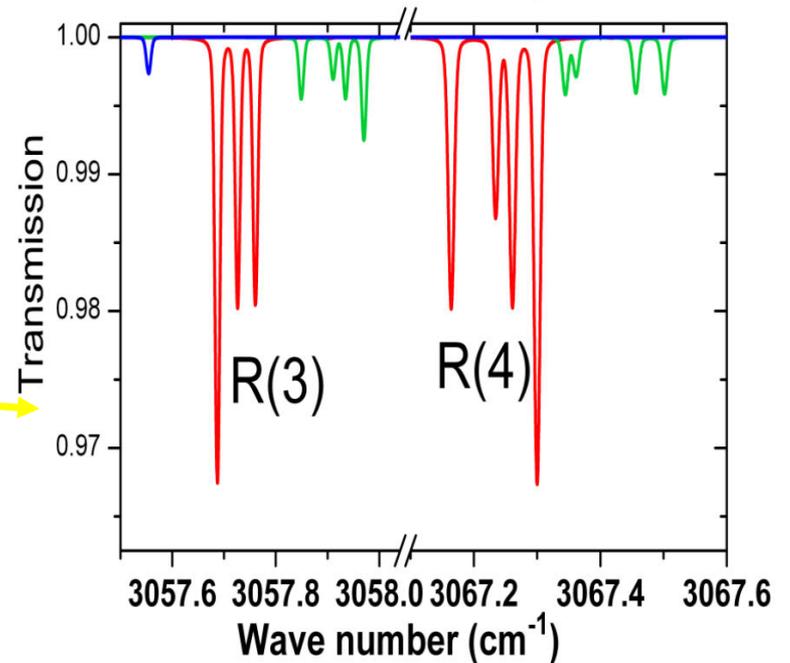
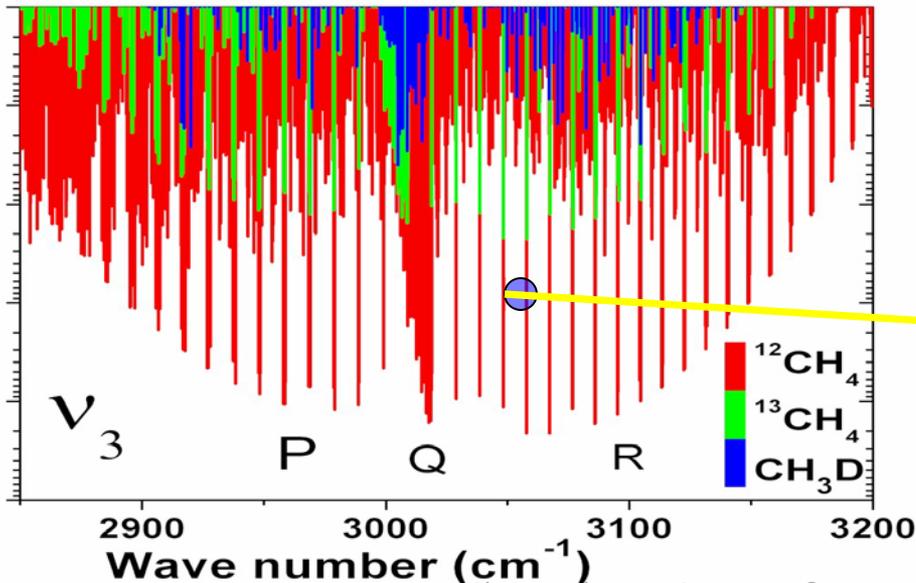
**Tunable laser**  
1-12  $\mu\text{m}$



**Detector**



**Methane absorption lines**



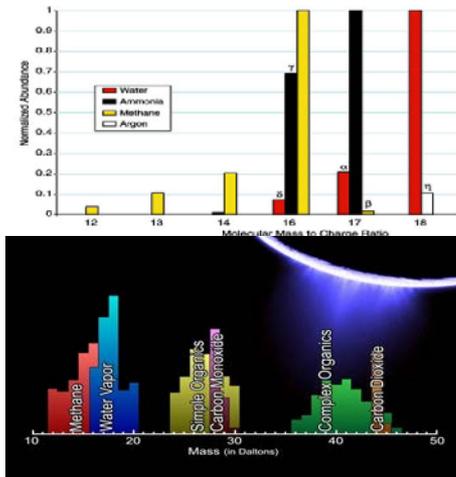


# Comparing the Mass Spec. and TLS

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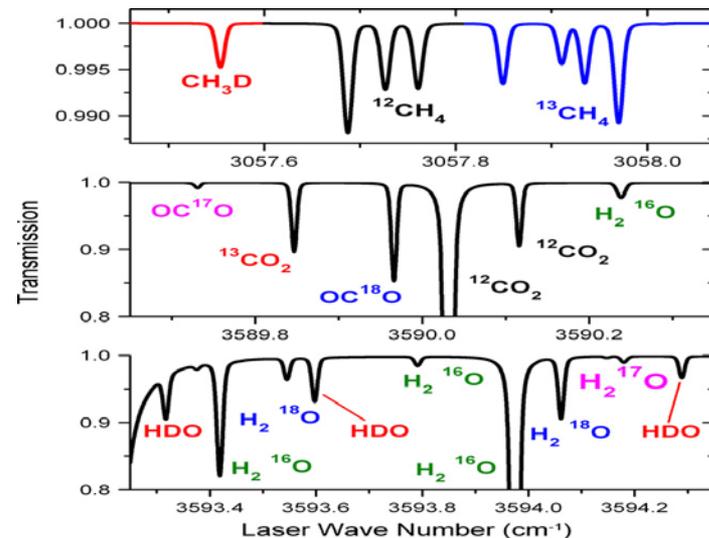
## Mass Spectrometer:

- Surveys all gases;
- Essential for noble gases & complex organics;
- High vacuum instrument needing pumps, bakeout
- Mass interferences in D/H, CO/N<sub>2</sub>, <sup>13</sup>CO<sub>2</sub> (Phoenix), methane, ammonia and water.



## Tunable Laser Spectrometer:

- Targets specific gases- no interference;
- Direct, non-invasive, with high sensitivity to water, methane, other gases;
- Carbonates, hydrates to 10<sup>-9</sup> wt%
- High precision ~0.1% CHNOS isotope ratios without interferences
- “High” pressure (0.1-100 mbar) instrument
- All solid-state with no moving parts.

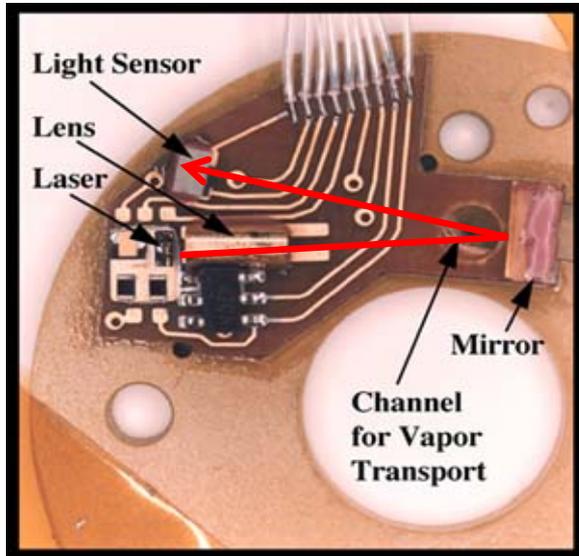




# Cell configurations for TLS

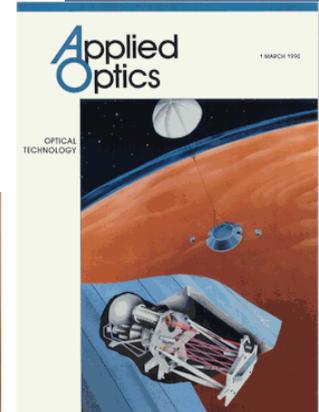
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- Open path Herriott cell or to reflector
  - DS-2 penetrator, Cassini Huygens, Mars 98 MVACS, atmospheric probes, Mars balloon



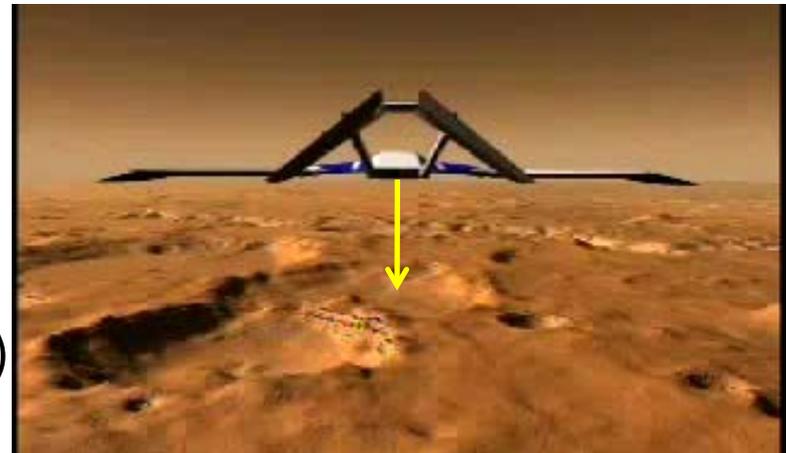
DS-2 penetrator TLS for H<sub>2</sub>O- 3cm path

Mars Probe Hygrometer

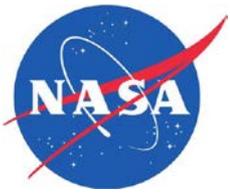


Earth balloon TLS

- Open path to surface (topographic)  
Mars airplane (Joel Levine, Wendy Calvin)



NASA Ames ARES



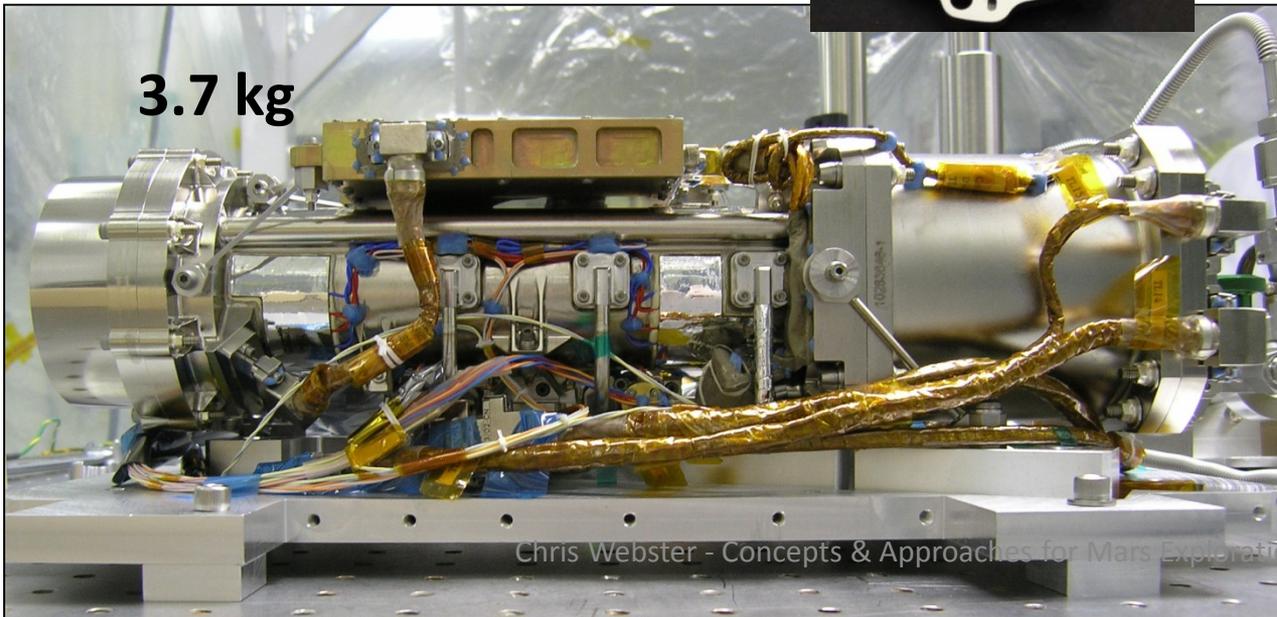
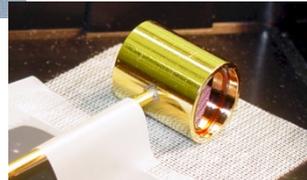
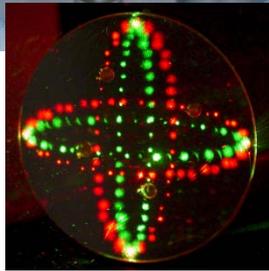
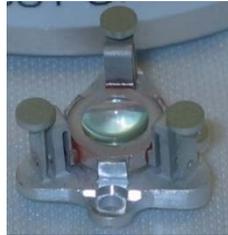
# Surface Landers & Rovers

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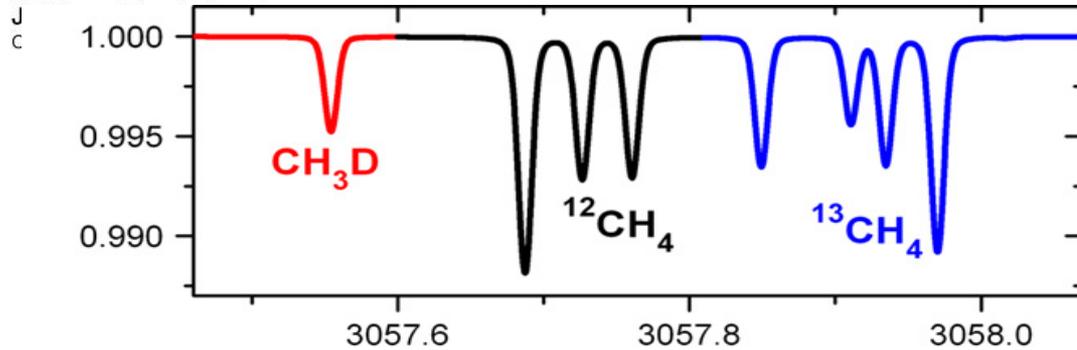




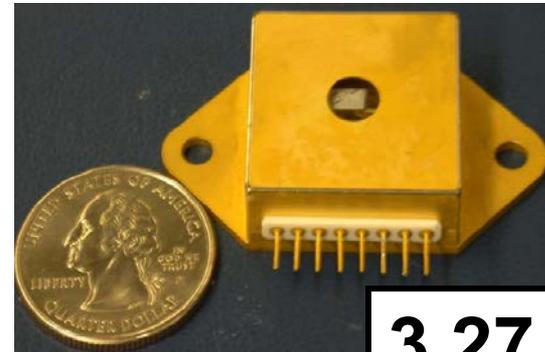
# TLS flight hardware



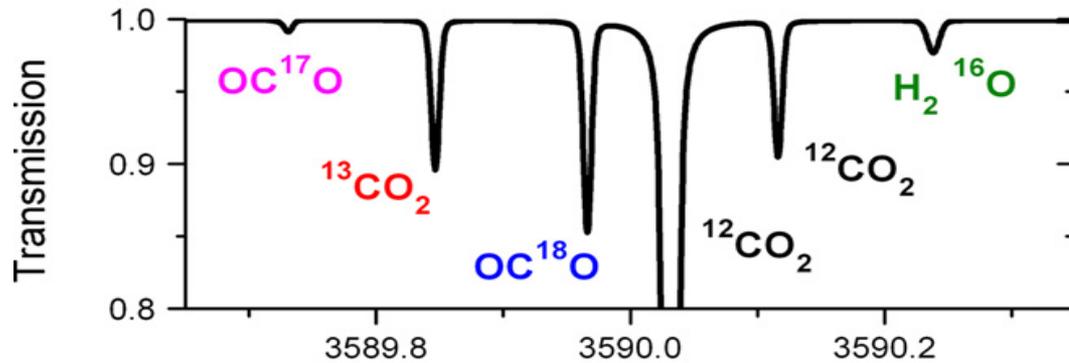
# TLS target spectral regions



JPL IC laser



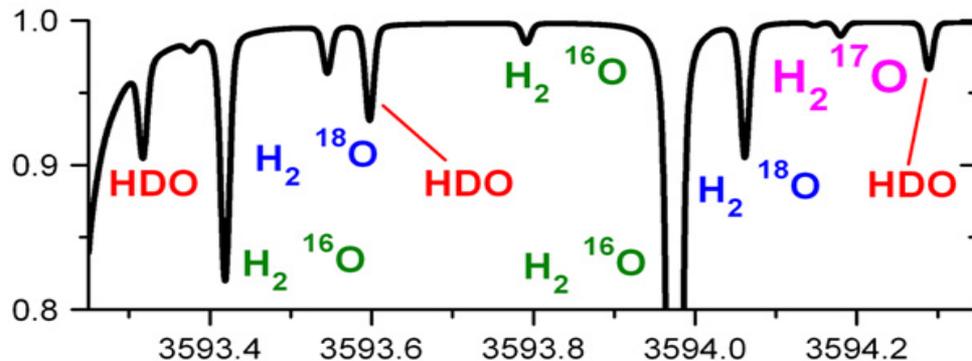
**3.27 μm**



Nanoplus TDL



**2.78 μm**





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# Gas abundances

- High spectral resolution provides high sensitivities (ppb or less) for numerous gases:
  - HCl, HF, NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, O<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>
- Rocks, solids, liquids are made to produce gases through pyrolysis, laser ablation, combustion, reaction;

# Stable isotope ratios

- Carbon <sup>13</sup>C/<sup>12</sup>C identifies biological & chemical processing:
  - Plants deplete <sup>13</sup>C by 2-4% and bacteria can produce 12% depletion;
  - C isotopes in carbonates reveal formation temperatures
- Oxygen-18 identifies rock and meteorite types, and is an indicator of solar system origin and evolution
- D/H reveals planetary origin and outgassing (escape)
- S and N isotopes detail biological and dynamical processing



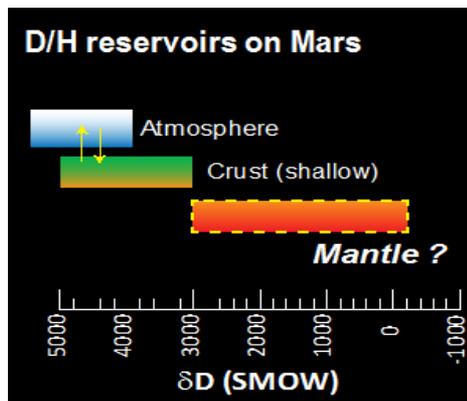
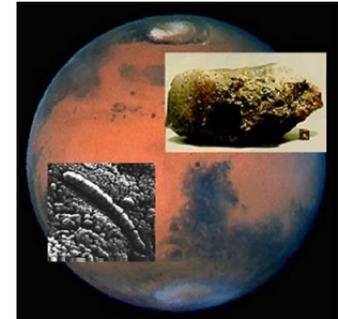
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# High Science Return Isotope Ratio Measurements for Mars

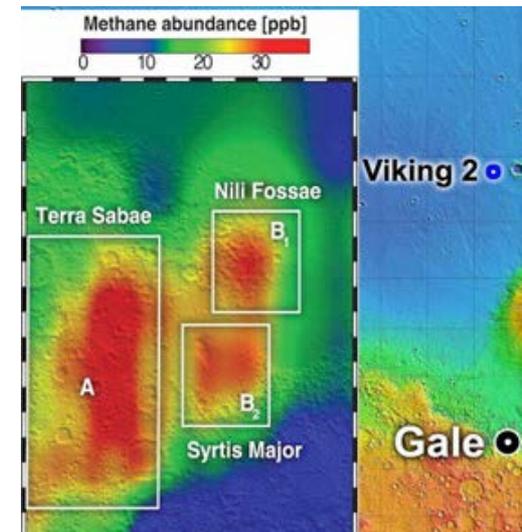
**Carbonates in the Martian meteorite Allan Hills 84001 formed at  $18 \pm 4$  °C in a near-surface aqueous environment**

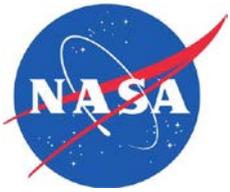
- Itay Halevy, Woodward Fischer, John Eiler, 2011

- K-Ar dating says meteorite is 4 billion years old;
- Isotope ratios in  $^3\text{He}$ ,  $^{21}\text{Ne}$  and  $^{38}\text{Ar}$  say it was in space (cosmic ray exposure) for 10-20 million years!
- $^{14}\text{C}$  dating says that it sat in Antarctica for 13,000 years;



- **What will MSL-SAM reveal about Mars?**
- **Is Mars  $\text{CH}_4$  biogenic?**





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# ISRU resources

- ISRU for Mars- use of resources found or manufactured for habitation- building materials, water, oxygen for breathing, fuel, energy sources, shielding materials;
  - The availability and detection of water is critical for exploration
    - Frozen surface ice, subsurface water within a meter
  - A miniature TLS can be extremely sensitive to water and other volatile gases evolved from clays, hydrates, carbonates
    - TLS detection limit for evolved H<sub>2</sub>O, CO<sub>2</sub> is 10<sup>-9</sup> weight% carbonate, hydrates in rocks
    - For CH<sub>4</sub> fuel production through Sabatier process, TLS can monitor both reactants (CO, CO<sub>2</sub>) and product (CH<sub>4</sub>, H<sub>2</sub>O)
- CO<sub>2</sub> + 4H<sub>2</sub> → CH<sub>4</sub> + 2H<sub>2</sub>O or the reaction CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O



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# Space station, on-surface cabins, astronaut health diagnostics

- Laser beam around top perimeter of cabins and on-surface structures monitor
  - Respiratory and waste gases  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  (humidity)  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ;
  - Contaminants like  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2\text{H}_2$  (hydrazine);
- Earth back-contamination
  - Across-capsule monitor of ppb  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  for microbial activity during sample return back to Earth;
- Astronaut health
  - In-suit or in-helmet monitor of respiratory gases  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and of key isotope ratios for breath analysis
  - e.g.  $^{13}\text{CO}_2/^{12}\text{CO}_2$  for human breath diagnosis of vital organs, stomach ulcers

