Measuring Methane & its Isotopic Ratios ^{13}C/^{12}C and D/H with the Tunable Laser Spectrometer (TLS) on SAM for the Mars Science Laboratory (MSL) Mission

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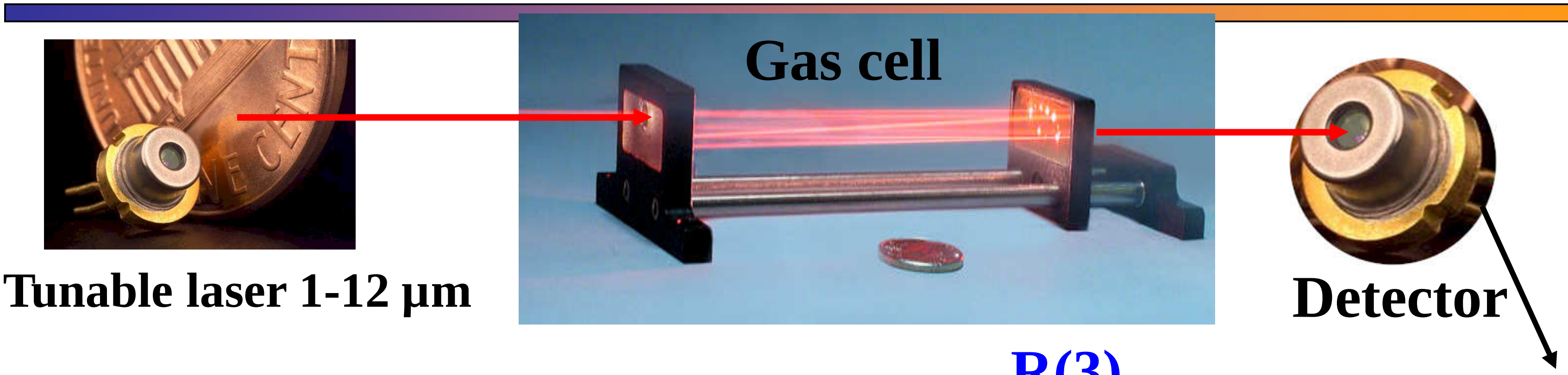
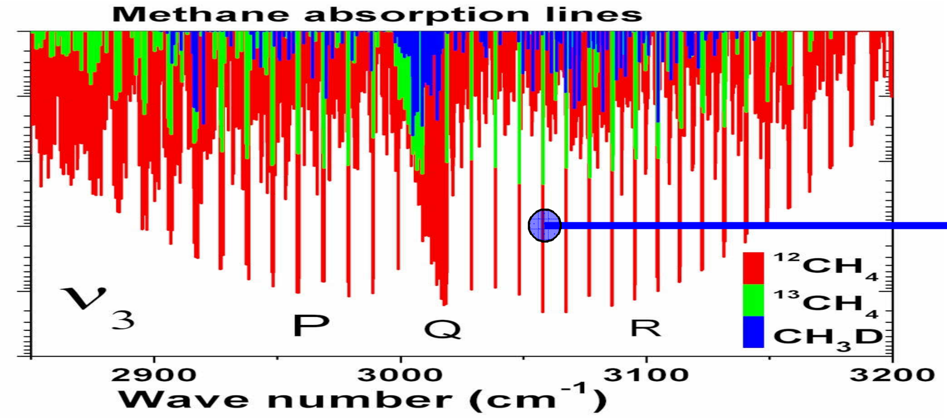
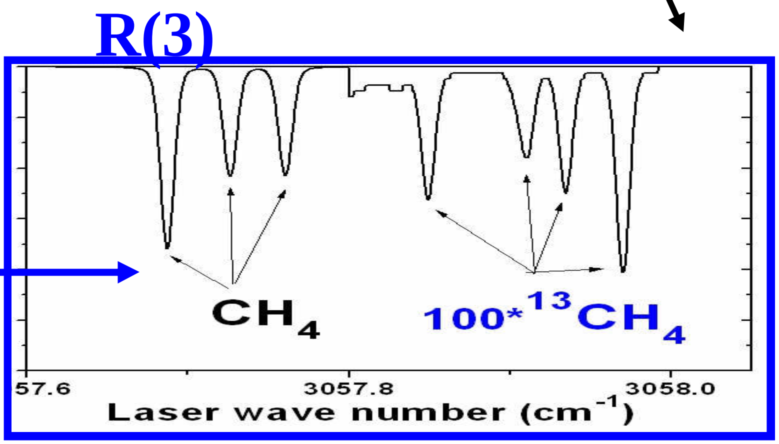
Joint ESA-ASI Workshop on Methane on Mars
ESA/ ESRIN Frascati, Italy
November 25-27th 2009

Jet Propulsion Laboratory
California Institute of Technology

In Situ Laser Absorption Spectroscopy

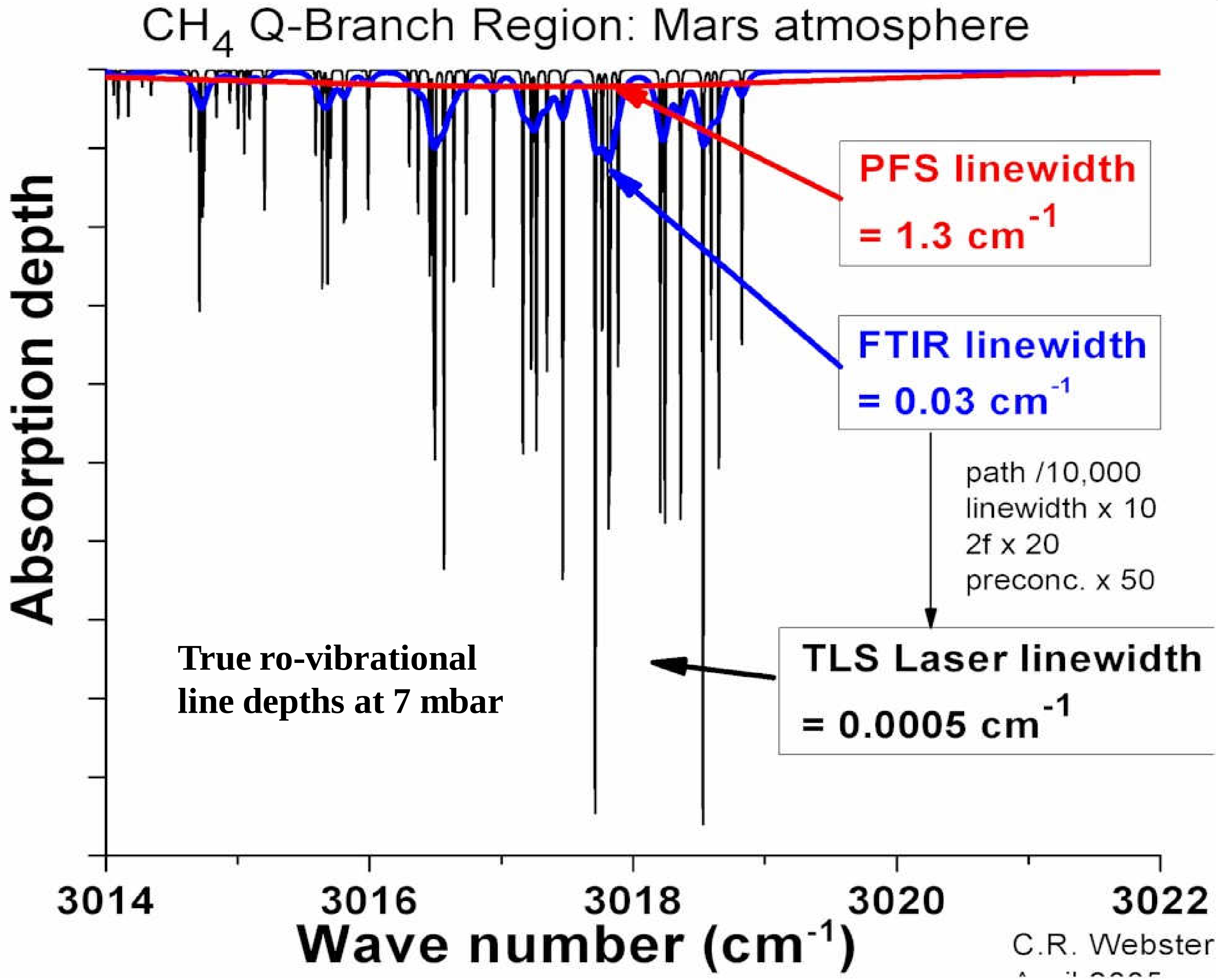






- High sensitivity from ultra-high resolution, intense light sources, and modulation techniques
- Robust optical path with simple interpretation (Beer's law with negligible instrument function) and easy calibration (HITRAN or gas standards)
- Non-invasive

Advantage of ultra-high spectral resolution



PFS linewidth = 1.3 cm^{-1}

FTIR linewidth = 0.03 cm^{-1}

path /10,000
linewidth x 10
2f x 20
preconc. x 50

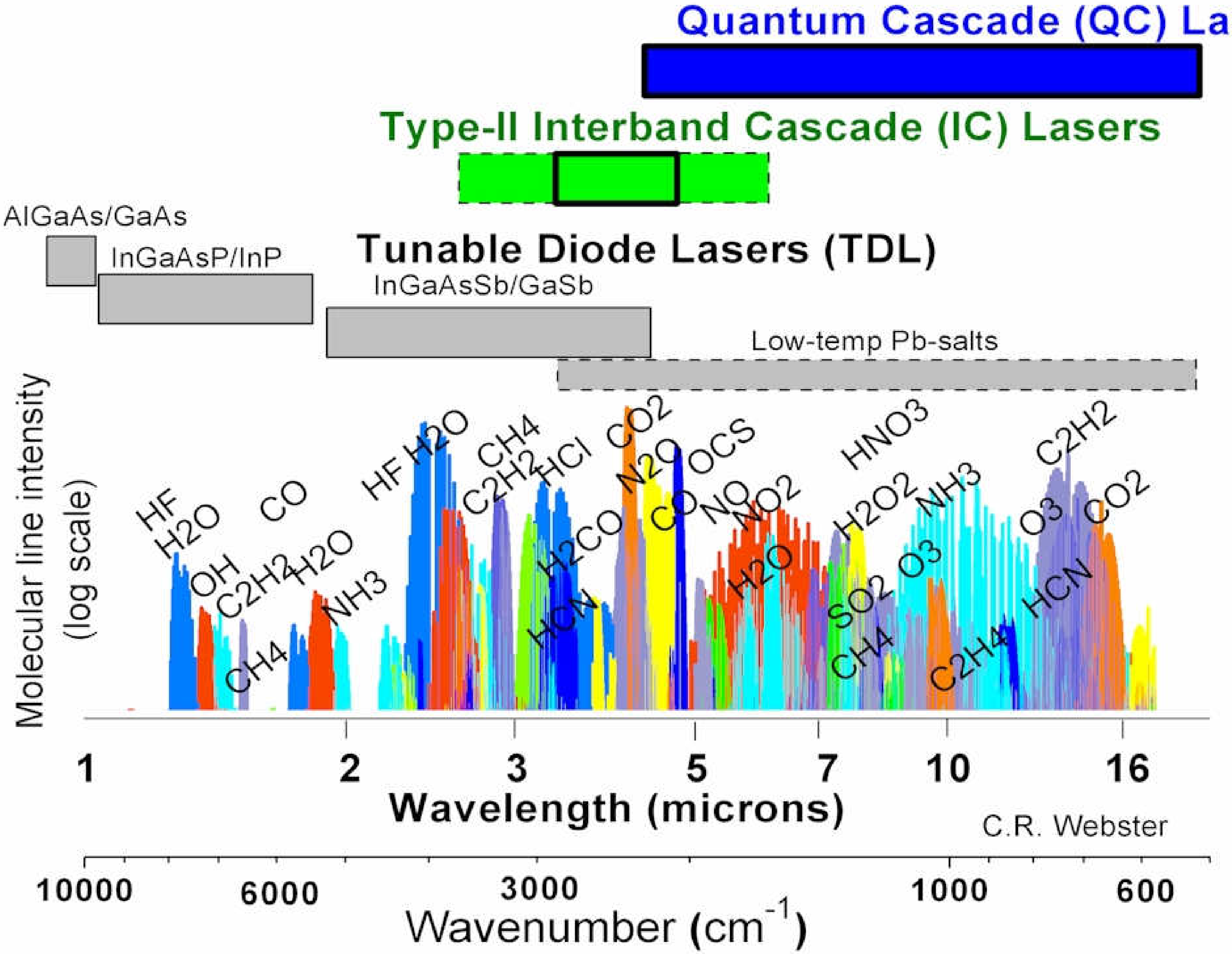
TLS Laser linewidth = 0.0005 cm^{-1}

True ro-vibrational line depths at 7 mbar

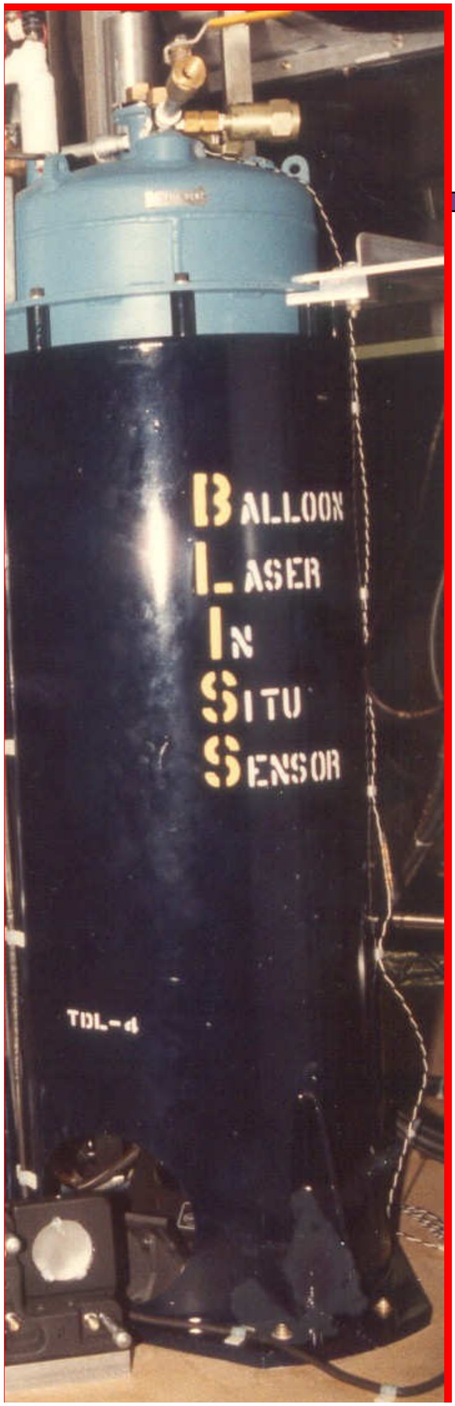
C.R. Webster

Methane detection

Tunable Laser Sources for Gas Measurements



C.R. Webster



cw Tunable Laser Sources

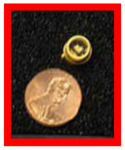
Device	*Mode purity*	*Temp*	*Power*
Pb-salt TDL's	Multi-mode	20 K	0.1 mW
	Fabry-Perot	100 K	0.2 mW
Near-IR TDL's	Single mode	25 ^{o}C	2 mW
Quantum-Cascade QCL's	Single mode	25 ^{o}C	20 mW
Interband-Cascade ICL's	Single mode	-20 ^{o}C	5 mW

1980's

Liq. He

1990's

Liq. N_2



2000's

TEC

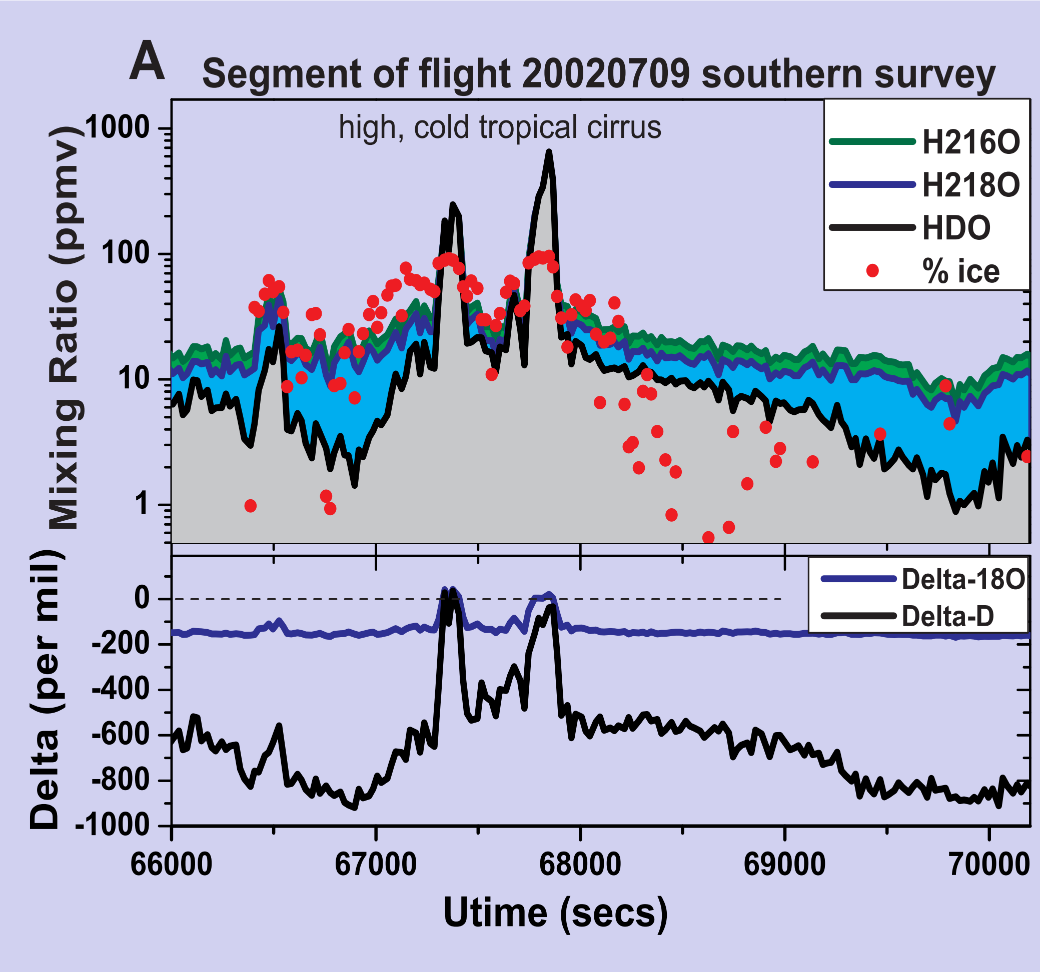
TLS Heritage – Earth Balloon & Aircraft Instruments 1985-present

- 6 instruments: 500+ aircraft flights (Global Hawk, WB-57F, ER-2, DC-8) in 12 major missions; 20 high-altitude balloon flights
- First TLS measurements of O_3, CO, CO_2, CH_4, NO_2, HCl, HNO_3, NO_2, NO/ NO_2, water isotopes

bster

Water isotope ratios D/H, 18O/16O, 17O/16O identify cirrus origin and dehydration pathways

Webster & Heymsfield, *Science*, 302, 1742-1745, 5 Dec 2003.



- •High, cold (~ -72°C) tropical cirrus observed off the east coast of Nicaragua at ~120 mbar (~15 km) near 16°N.
- •Low O_3, high CO, and ER-2 radar suggested that the cloud layers were deep-convectively generated from lower troposphere .

Cirrus ice particles have <u>isotopic signatures of water from low altitudes,</u> therefore *lofted from below*

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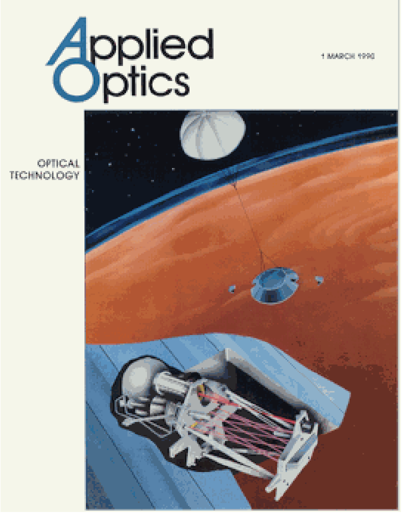
TLS Heritage – Planetary Instruments

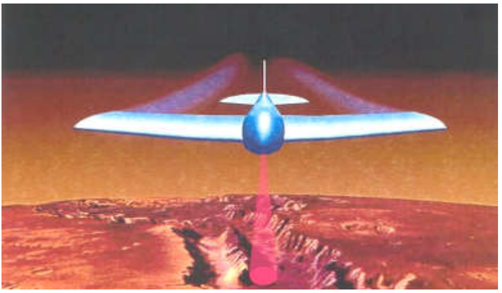

Applied Optics

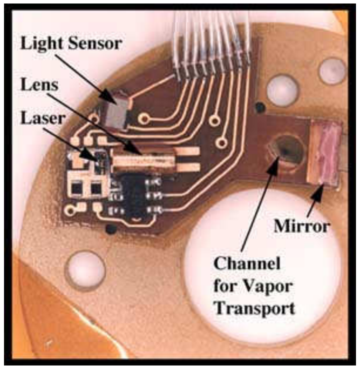
1 MARCH 1990

OPTICAL TECHNOLOGY

Cassini Huygens Probe PIRLS development – Webster et al. 1985

Mars Scout instrument developments – MBLISS, CHILL, Pascal, MOD, Ares, Chronos, etc.





DS-2 TDL water probe


MVACS Mars Polar Lander TDLS

Mars Laser Hygrometer– Webster et al. 1995

MARS SCIENCE LABORATORY

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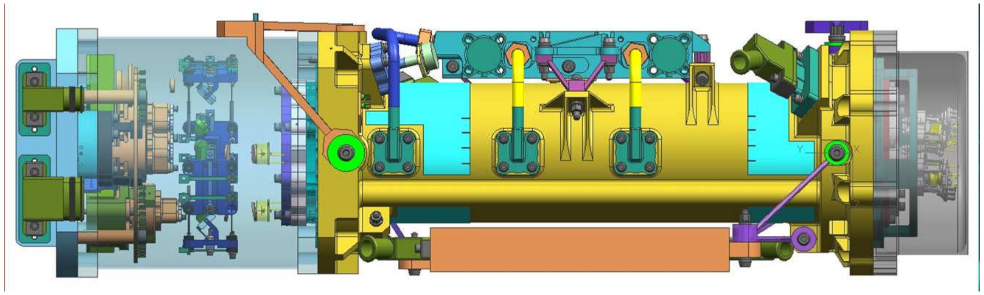
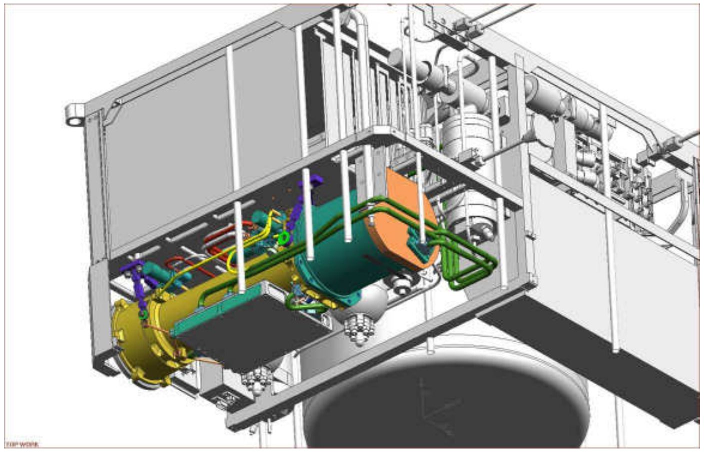
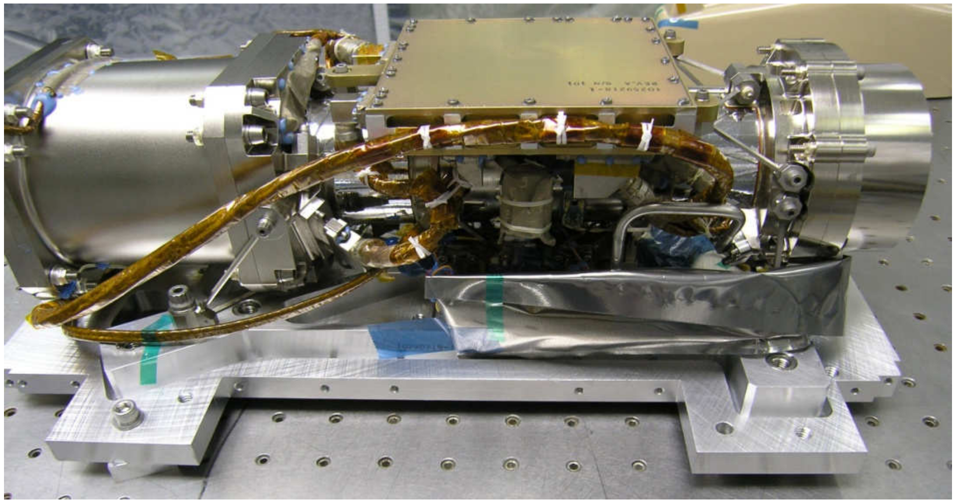
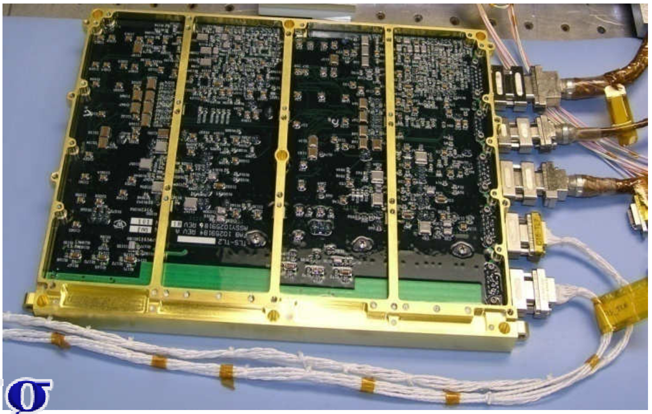
Tunable Laser Spectrometer (TLS) for Sample Analysis at Mars (SAM) on the 2009 MSL Mission

The Tunable Laser Spectrometer (TLS, JPL instrument PI Chris Webster) is one of three instruments (QMS, GC, TLS) that make up the Sample Analysis at Mars (SAM) analytical chemistry lab (Suite PI Paul Mahaffy, GSFC) on NASA’s 2009 Mars Science Laboratory (MSL).









TLS total mass =3.7 kg

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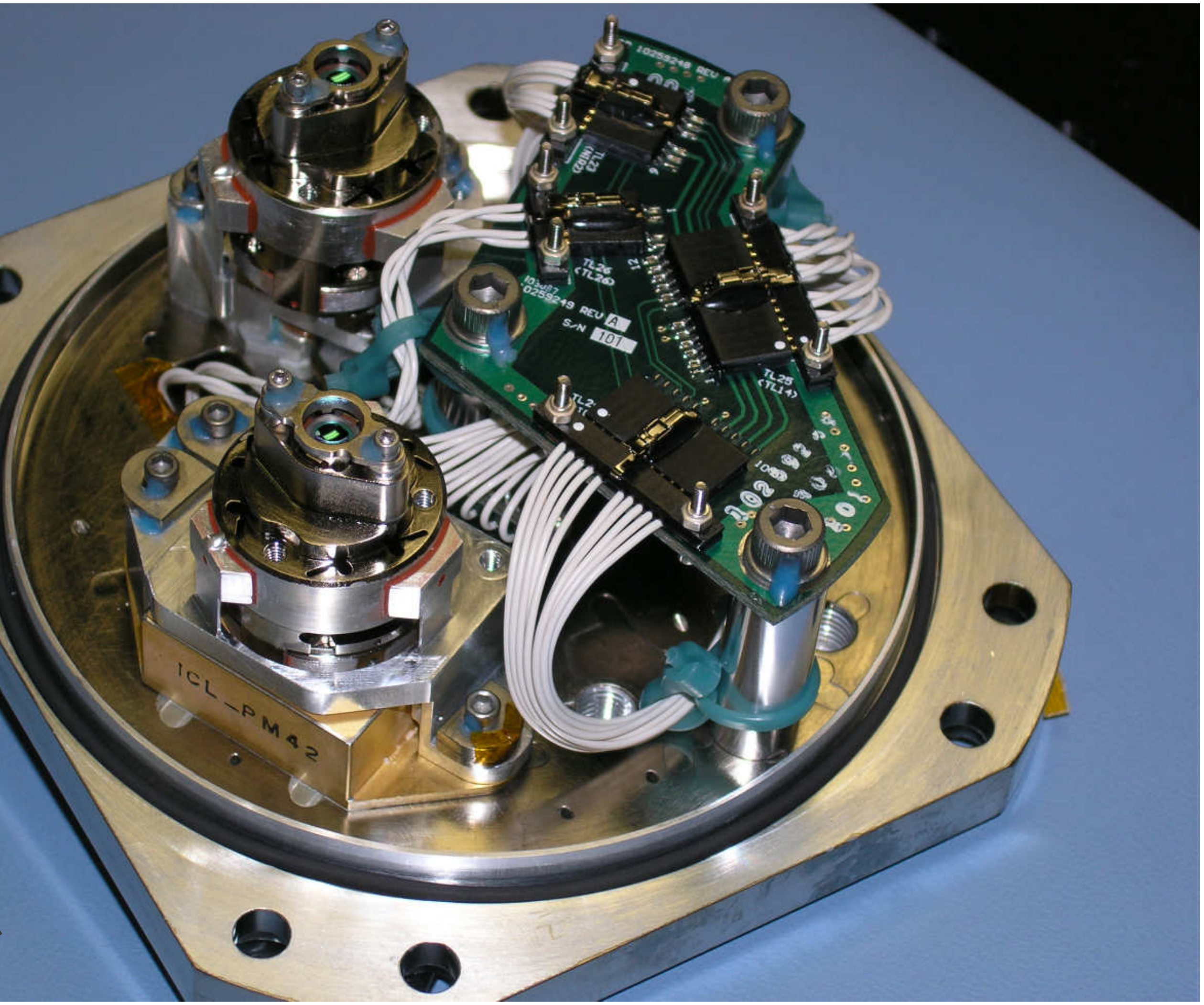
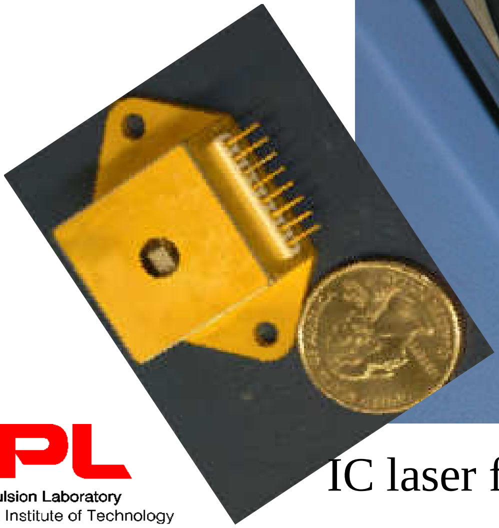
TLS Tunable IR Laser Sources

NIR TDL from Nanoplus, Germany





IC laser from JPL

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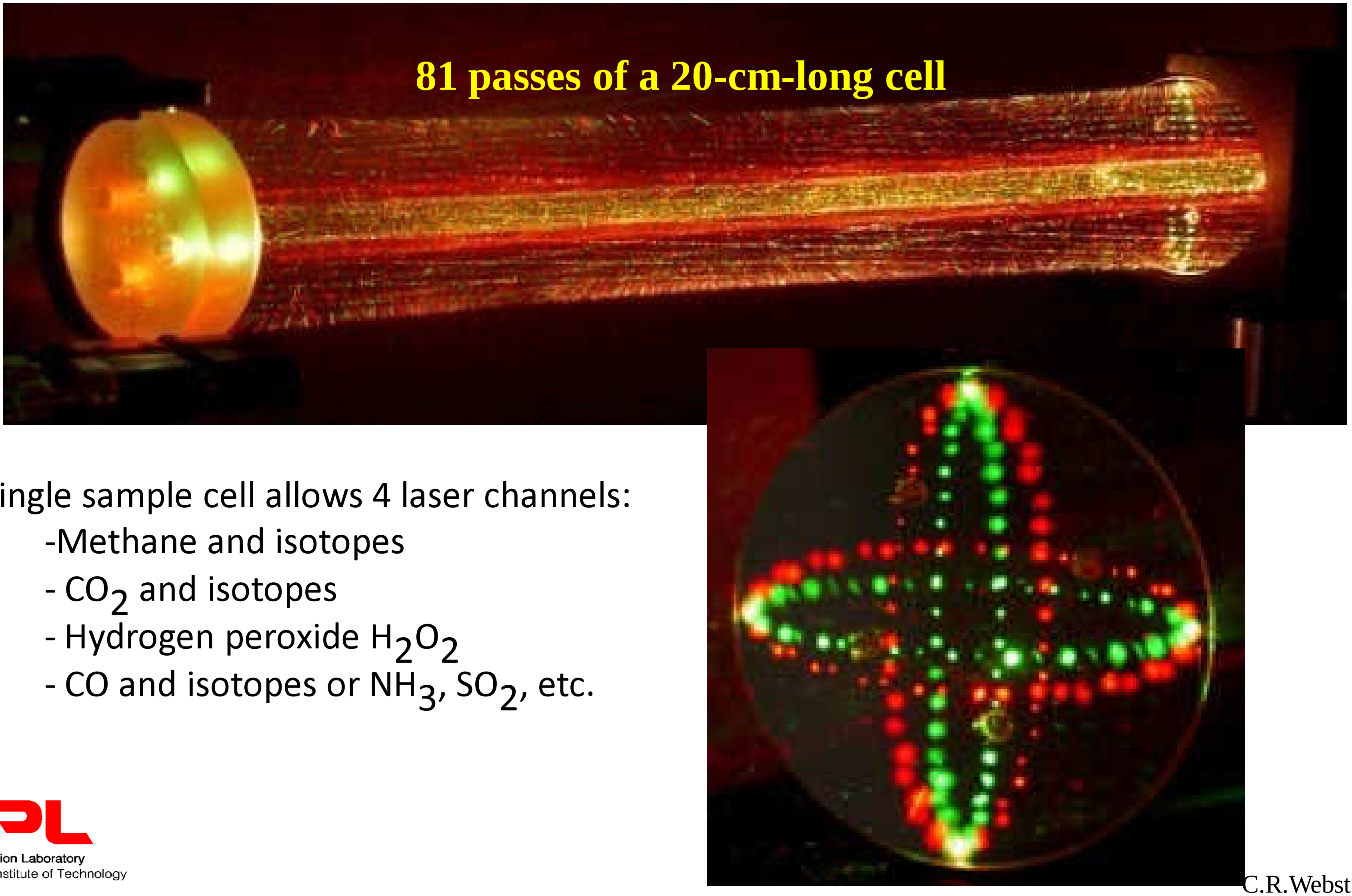
TLS is a 4-channel spectrometer



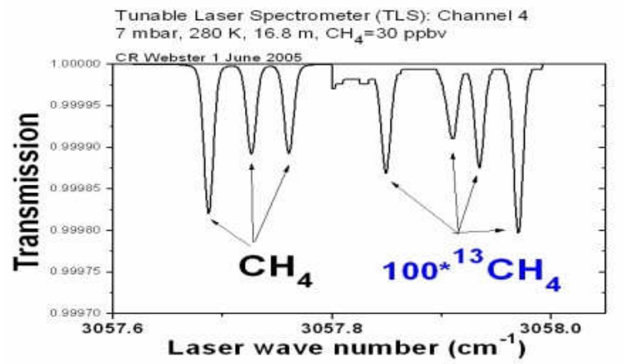
- Single sample cell allows 4 laser channels:
  - -Methane and isotopes
  - - CO_2 and isotopes
  - - Hydrogen peroxide H_2O_2
  - - CO and isotopes or NH_3, SO_2, etc.

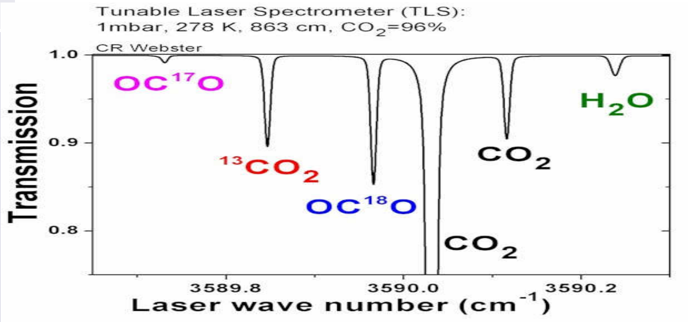
C.R.Webster

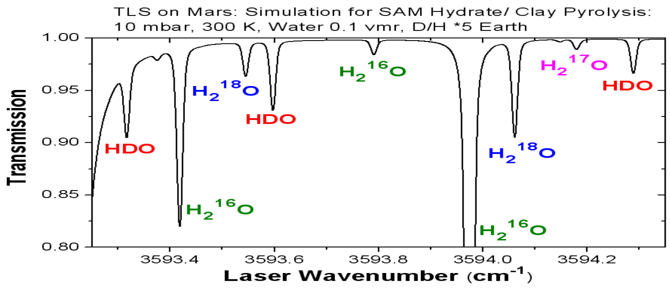
TLS Measurement Capability

TLS Expected Measurement Capability in SAM

Channel	Wave-length	Channel name	Expected Capability with SAM
1 - IC laser	3.3 µm	Methane	CH_4 to 0.1 ppbv (1 pptv in SAM) Delta-^{13}C to 2 per mil
2 - Near-IR	2.785 µm	CO_2	CO_2 to 1ppmv H_2O to 1 ppmv Delta-^{13}C to 2 per mil Delta-^{18}O to 3 per mil Delta-^{17}O to 5 per mil
	2.783 µm	H_2O	H_2O to 0.1 ppmv Delta-D to 2 per mil Delta-^{18}O to 3 per mil Delta-^{17}O to 5 per mil


Tunable Laser Spectrometer (TLS): Channel 4
7 mbar, 280 K, 16.8 m, CH_4=30 ppbv
CR Webster 1 June 2005


Tunable Laser Spectrometer (TLS):
1mbar, 278 K, 863 cm, CO_2=96%
CR Webster


TLS on Mars: Simulation for SAM Hydrate/ Clay Pyrolysis:
10 mbar, 300 K, Water 0.1 vmr, D/H *5 Earth

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TLS Gas Detection Capability

TLS Achieved Stand-alone Sensitivities during Therm-Vac Testing *without* SAM pre-concentration

TLS Target Gas	Required Limit of Detection (LOD) -10 °C to 20 °C	Limit of Detection (LOD) achieved in 100 secs.				
		42 °C	26 °C	10 °C	6 °C	-25 °C
Carbon Dioxide	1 part per million (1 ppm)	0.3	0.6	0.2	0.1	0.3
Methane	2 parts per billion (2 ppb)	0.4	1.3	0.4	0.7	1.2

- TLS has been built, delivered and installed into SAM. Following successful room temperature and environmental testing (therm-vac and vibration) at JPL, TLS will continue SAM suite-level testing and calibrations;
- For CO_2, TLS achieves an LOD of 0.5 ppm in 100 seconds, and 0.2 ppm in 500 seconds. ***This capability translates to an LOD of ~10^{-8} weight% carbon in soil;***
- For CH_4, TLS alone achieves an average LOD of 0.8 ppb in 100 seconds, and 0.3 ppb in 900 seconds. ***This latter capability translates to an LOD of ~0.001 ppb (1 part per trillion) methane with SAM enrichment;***
- For H_2O, TLS achieves an LOD of 0.5 ppm in 100 seconds, and 0.2 ppm in 500 seconds. ***This capability translates to ~5 x 10^{-10} weight% of water in Martian soil.***

Isotope Ratios Characterize Atmospheric Loss, Exchange with Volatiles, Biological Processes

- Martian atmosphere is characteristic of significant early loss
  - D/H double that of mantle, and ~5 times that of Earth (*Owen, 1988*) – implies Mars once had ocean several times size of ice reservoir today (500 m)- several Earth oceans
  - $^{15}N/^{14}N$ nearly 60% higher than Earth
  - $^{13}C/^{12}C$ enrichment in atmosphere

Isotope Ratios as Biomarkers

Life's catalysts (enzymes) preferentially use <u>lighter isotopes</u> during metabolism (easier, faster): N, C, S, and O biogeochemical cycles

- $^{13}C/^{12}C$ of organic C matter is 2-4% lower than that of inorganic C (carbonates) because organisms preferentially fix ^{12}C during organic biosynthesis.
- Earth bacteria can produce CH_4 with $\delta^{13}C$ *depleted by as much as 11%*

Measurement of isotope ratios can provide an <u>independent</u> signature to confirm biogenic origin of disequilibrium gases

Stable Isotope Ratios in H, C, O

Hydrogen:

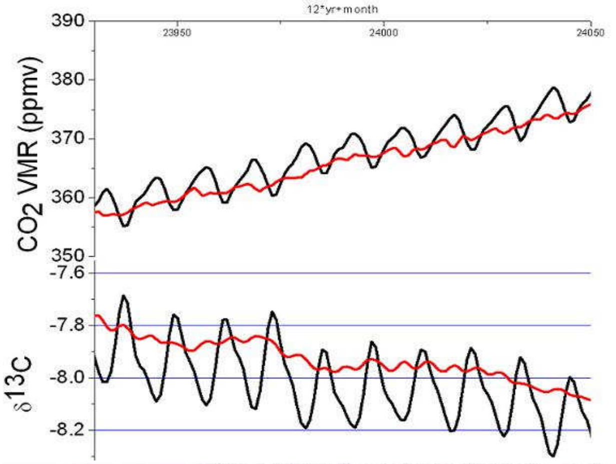
- D/H identifies planetary origin, evolution (atmospheric escape), and original water content
- Geological evolution with $^{18}O/^{16}O$

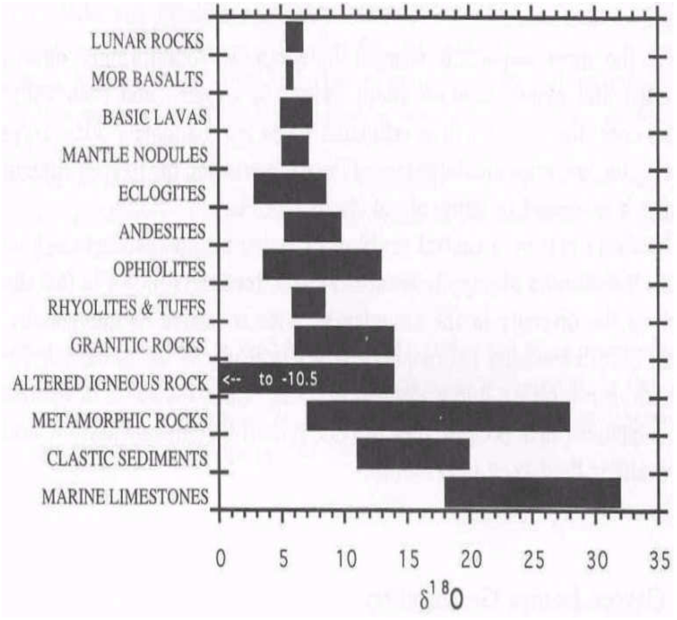
Carbon:

- Identify sources and sinks for atmospheric CO_2, since $^{13}C/^{12}C$ changed by plant photosynthesis, but not by air-sea exchange
- Monitor $^{13}C/^{12}C$ emitted in CO_2 from volcanoes to warn of activity (differs from air)
- Biological activity (e.g. rise of atmospheric oxygen) as seen in $^{13}C/^{12}C$ of CO_2 or CH_4

Oxygen:

- Precipitation maps of global rainfall
- Paleothermometry using (i) $H_2{}^{18}O$ in ice core sampling details the climate record and (ii) using ^{18}O in fossil shell carbonate identifies early ocean temperatures
- Marine limestones formed under evaporative conditions
- Oxygen isotope geochemistry of magmatic rocks – e.g. fractionation between silicate melts and coexisting fluids at high temps (Eiler group)
- Meteorite classification



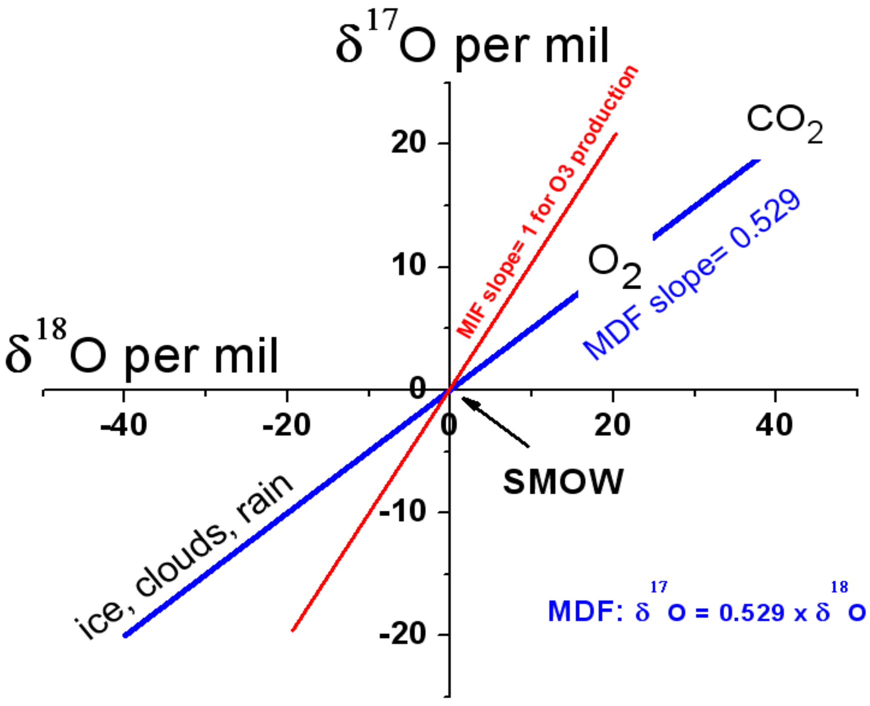


Mass-dependent fractionation (MDF)

- Most chemical reactions & physical processes depend on mass
    - Fractionation of ^{16}O, ^{17}O ^{18}O in lunar samples from Apollo Missions on mass-dependent line (like Earth) consistent with Giant Impact model

- Three-isotope plots provide data on atmospheric source-sink processes, e.g.
    - Studies of ^{16}O, ^{17}O ^{18}O in CO_2 reveal photochemical coupling to O_3
    - Studies of ^{16}O, ^{17}O ^{18}O in N_2O not fully explained – Yung, Eiler groups

- Mass-independent fractionation (MIF) exists
    - Usually in gas phase in non-thermodynamic equilibrium - related to symmetry (Thiemens, Yung)
    - Hyperfine interactions (S-O coupling in isotopes with odd mass no., like ^{33}S and ^{17}O)



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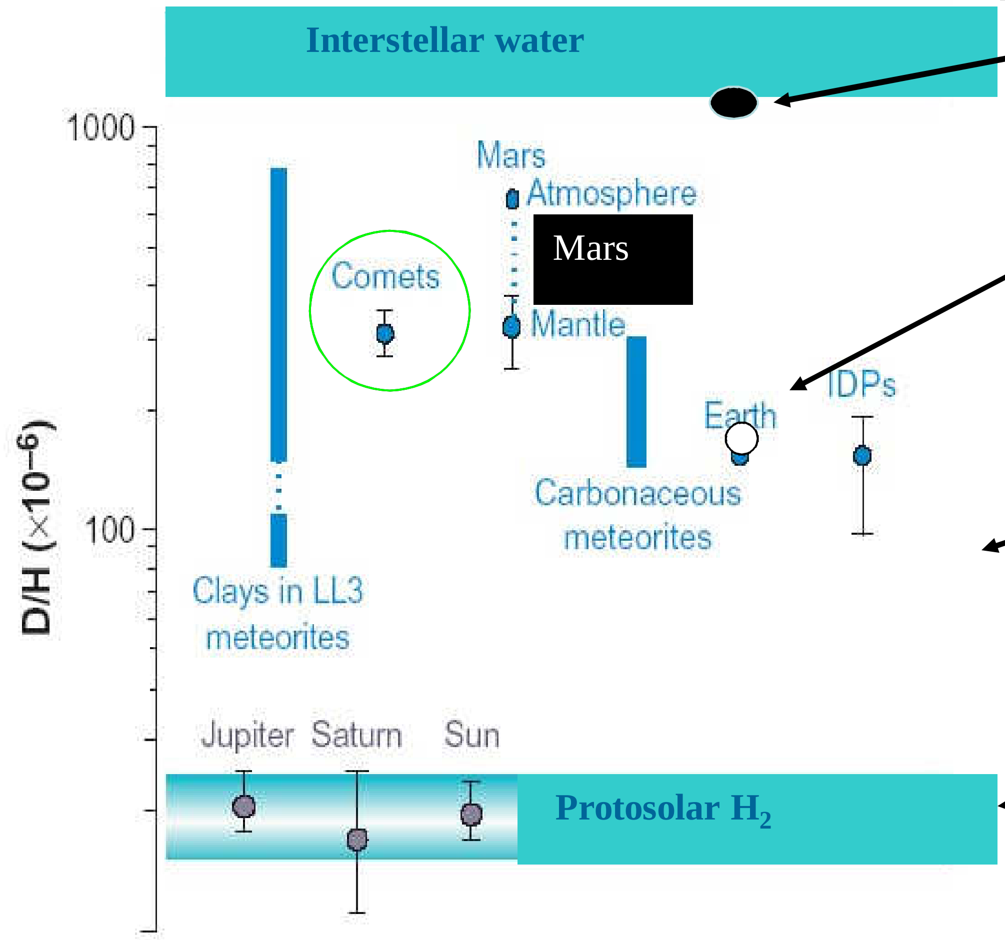
Absolute D/H ratio and the Origin of Planetary Water….



An isotopic enigma. Distribution of the hydrogen isotopic composition in solar system bodies. Blue, water; purple, molecular hydrogen.

Francois Robert, *Science*, 293, 1056-1058, 2001

Very high D/H of **Venus** since no magnetic field to shield solar wind stripping away atmosphere

High D/H of **Earth** (150 x 10^{-6}) demonstrates clear connection between the solar system and interstellar water

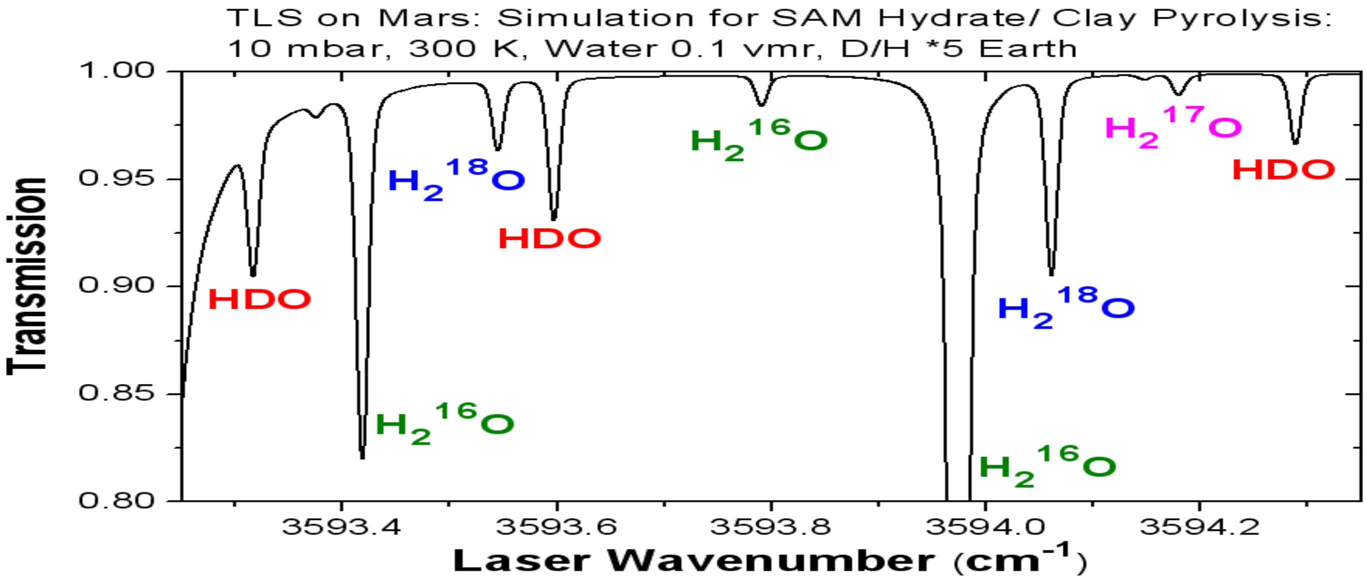
D/H for water condensed at Earth's distance should be ~80 x 10^{-6}, close to protosolar values

Sun & planets formed 4.5 billion years ago from protosolar nebula of mainly H and He

TLS will measure D/H, 18O/17O/16O in Water

- SAM will interrogate atmosphere and hydrated soils and clays
- What is D/H and O-isotope ratios of the Mars atmosphere compared to interior?

  -While delta-D Viking, impact glass ~440% terrestrial, ALH 84001 and interior SNC's are 78%, 90%



This region is not *ideal* for water isotopes in the atmosphere due to CO_2 interferences, but is excellent for the high water abundances expected from the SAM pyrolysis (CO_2 scrubbing also available)

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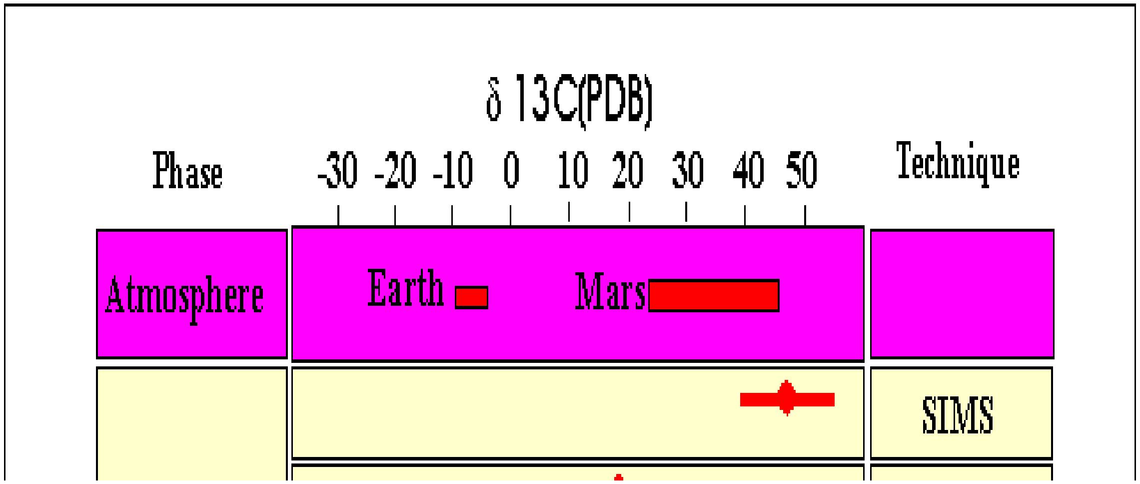
Expectations for delta-13C

Stable Isotope Evidence for Low Temperature Carbonate Concretions in the

Martian Meteorite ALH84001.

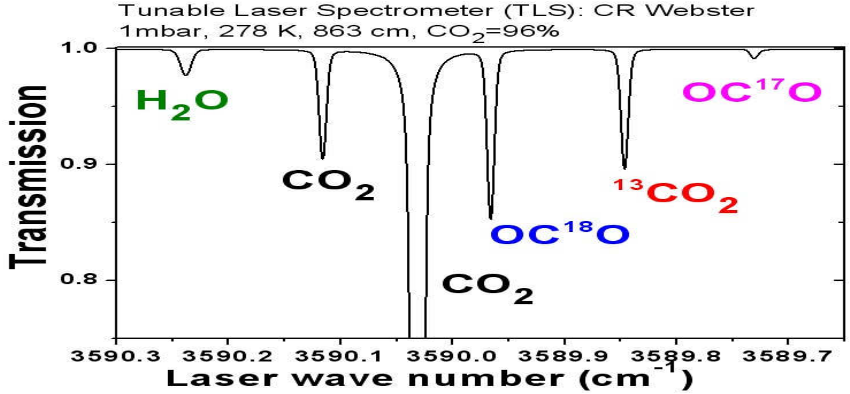
J.W Valley , J.M. Eiler, C.M. Graham



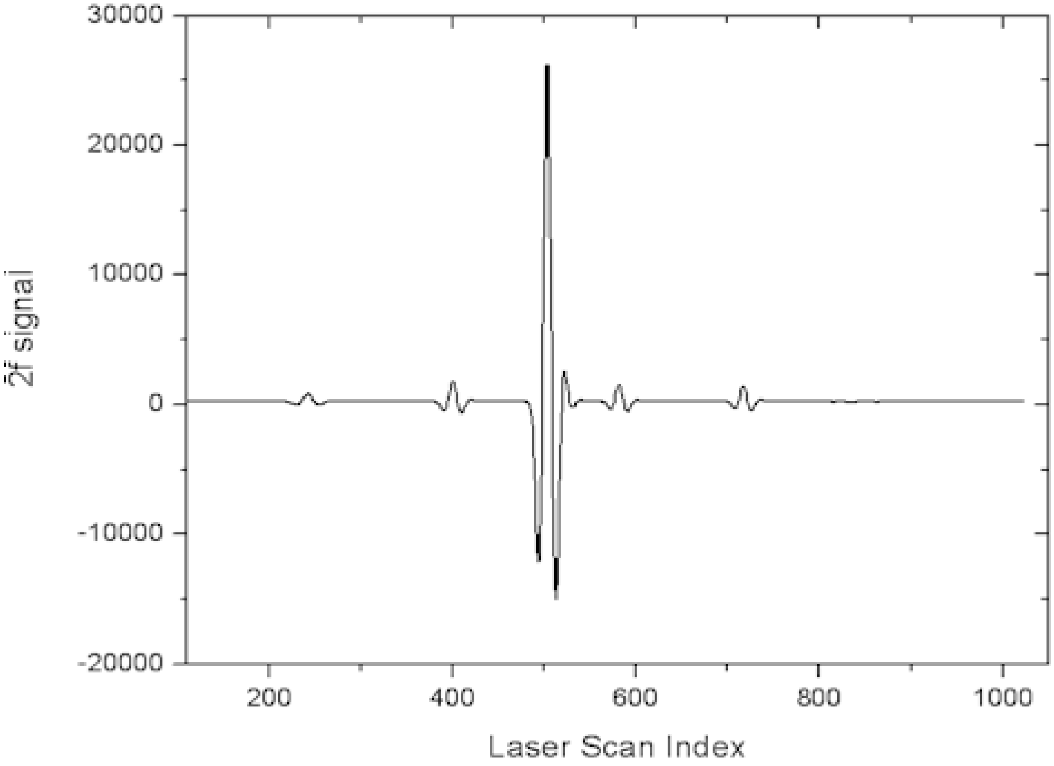
$\delta^{13}C$= 46±8‰ for the core of one carbonate concretion is :

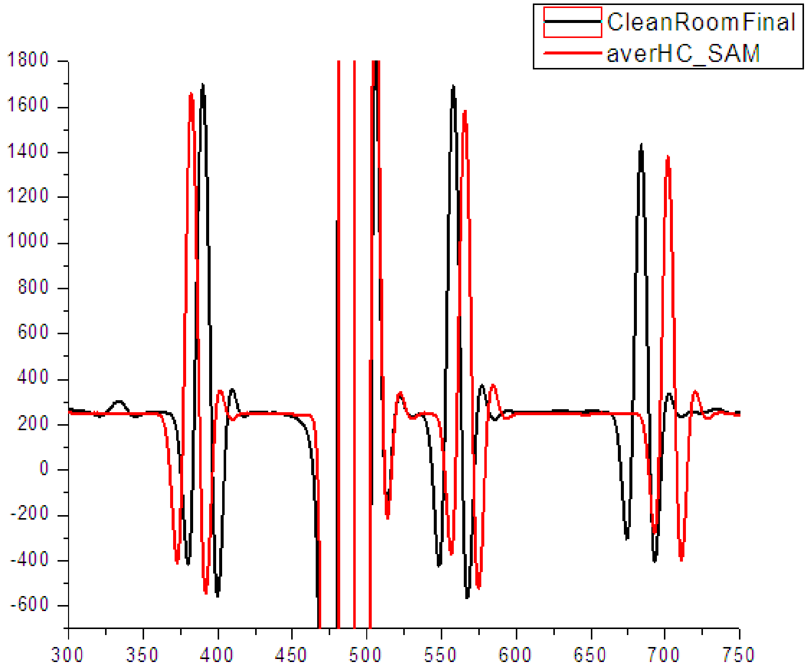
- 40-50‰ higher than typical terrestrial values and
- consistent with equilibration with a reservoir of similar $\delta^{13}C$ to the Mars atmosphere.

TLS- CO_2 Isotope Spectra



TLS spectra for CO_2 show SNR's of ~40,000+ for main line

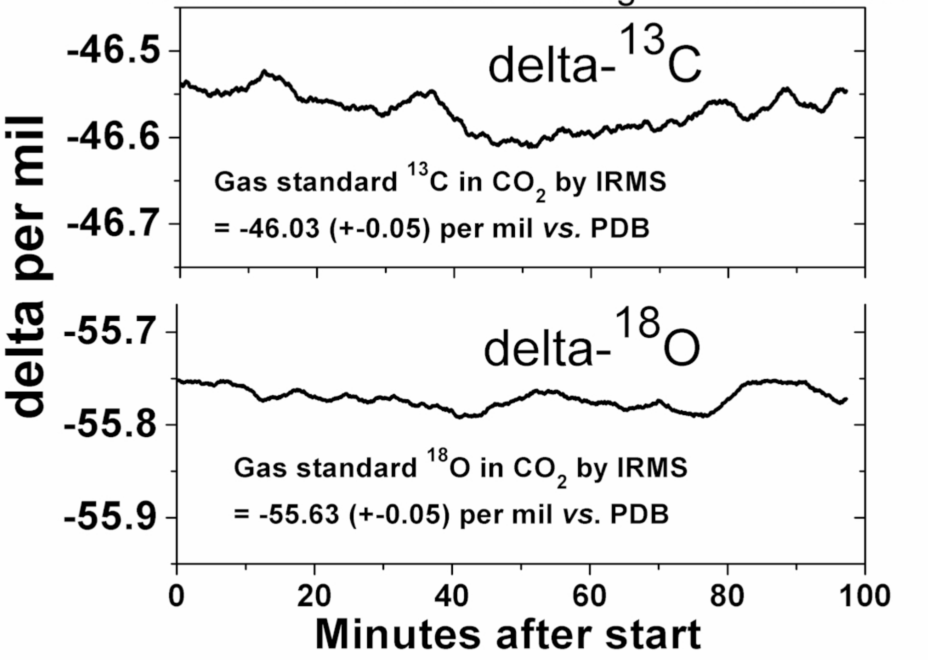




TLS will measure $^{13}C/^{12}C$ and 18O/17O/16O in Carbon Dioxide *(atmospheric and evolved)*

- What is 13C/12C of atmosphere compared to interior?
  - Delta-13C of atmosphere is poorly measured (0+- 50 per mil), but AL84001 is ~46 per mil and interior SNC's are -30 to 41 per mil
- What is 18O/16O of atmosphere compared to interior?
  - Delta-18O of atmosphere is also poorly known (0 +- 50 per mil), ratios of 18O/17O/16O in Martian meteorites silicates and water differ slightly and from Earth values (see plot).

Actual lab measurements using TDL at 2303 cm^{-1}



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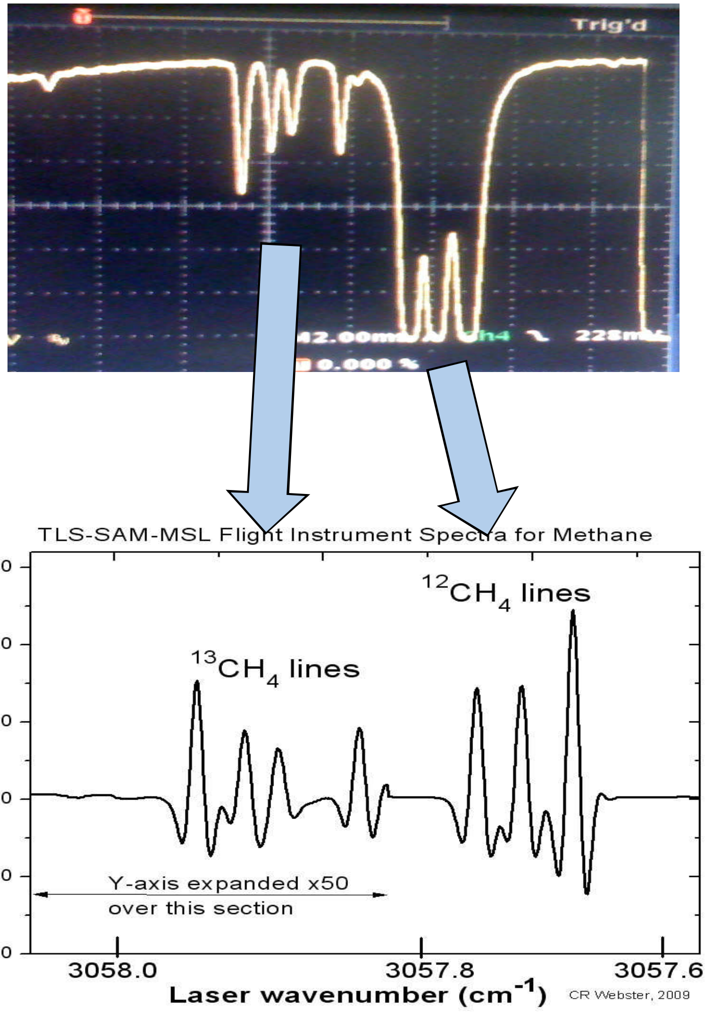
Tunable Laser Spectrometer (TLS) – Sensitivity for Methane

- **From -25 to 42 °C (therm-vac), TLS alone achieves an average LOD of 0.8 ppb in 100 seconds, and ~0.3 ppb in 900 seconds.**
- **SAM preconcentration will range from 50-100, possibly more.**
- **An overall pre-concentration of ~100 translates to an LOD of 0.003 ppb (3 parts per trillion) methane with SAM enrichment.**
- **With higher pressure or longer integration time, TLS *has capability at 1 part-per-trillion* (!)**

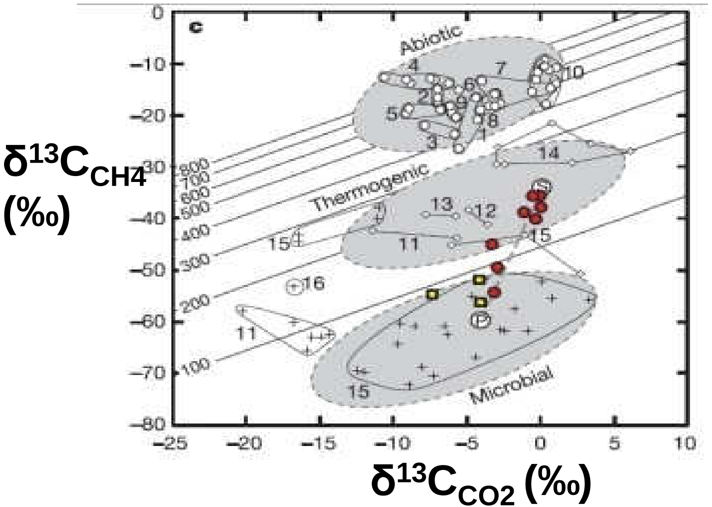


TLS limit of detection for CH4 in Mars atmosphere

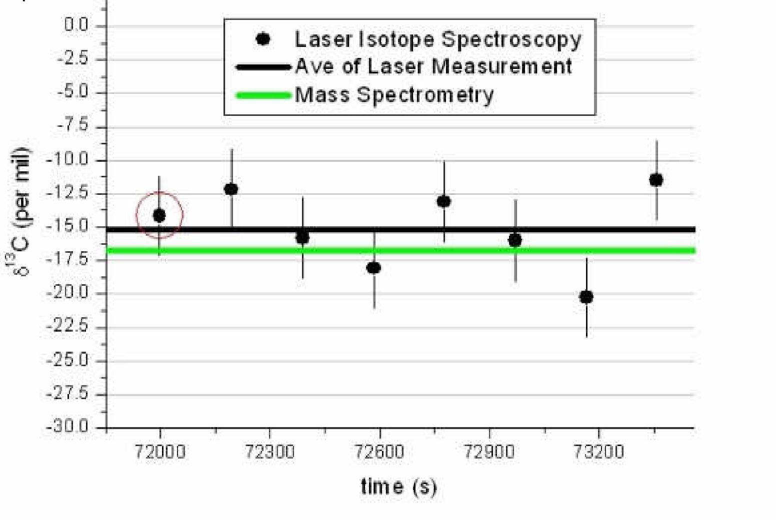
Total enhancement		LOD 100 secs	LOD 4 hours
1	Failure of enrichment	0.8 ppbv	70 parts-per-trillion
50	Minimal expected	16 parts-per-trillion	2 parts-per-trillion
100	Expected	8 parts-per-trillion	1 parts-per-trillion

Tunable Laser Spectrometer (TLS) – Sensitivity for $^{13}C/^{12}C$ in methane

- TLS-SAM-MSL will measure isotope ratios *in context* with other isotope ratios
  - 13C/12C in CH4 *compared with* 13C/12C in CO2
- Need to determine isotope ratio to 10 per mil (1%)
- If Mars has 24 ppbv methane, TLS will need:
  ~1 hour with SAM enrichment of only 50.



Ueno et al. Nature, March 2006 analys sions in the early Archaean era before 2.5 Gyr ago showing requirements for 13C/12C; Bottom: actual measurements from TLS prototype showing capability for measuring isotope ratio to better than the 10 per mil requirement.



CH4 at 24 ppbv in Mars atmosphere

SAM enrichment factor		Integration time needed for 13C/12C to 10 per mil
1	Failure of enrichment	130 days
50	Minimal expected	1 hour
100	Nominal expected	20 minutes

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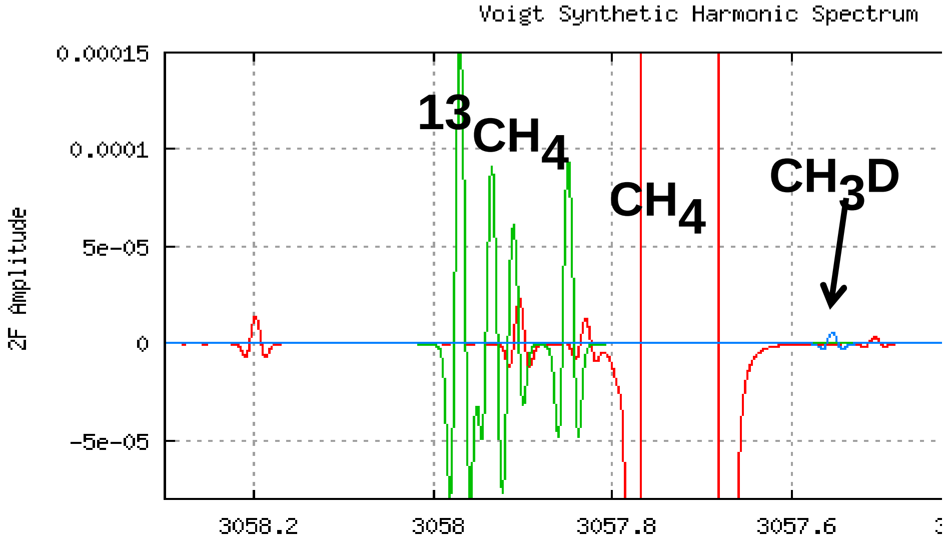
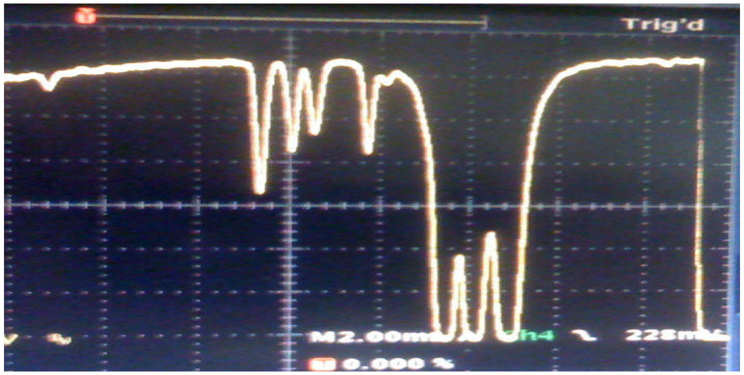
Tunable Laser Spectrometer (TLS) – Sensitivity for D/H in methane

- TLS-SAM-MSL will measure isotope ratios *in context* with other isotope ratios
  - D/H in CH_4 *compared with* D/H in H_2O
- Need to measure D/H to 100 per mil (10%)





CH_4 at 24 ppbv in Mars atmosphere

SAM enrichment factor		Integration time needed for D/H to 100 per mil
1	Failure of enrichment	Never
50	Minimal expected	30 hours
100	Nominal expected	8 hours

Next Generation TLS for Mars, Venus, Titan, Moon, comets

Next- Generation TLS:

- Will incorporate digital spectrometer to reduce mass & power, allow several simultaneous channels, and tailor signal processing;
- May be a combination of gas processing (enrichment, pressure) and enhanced cavity techniques – IF THE PLANETARY MEASUREMENT REQUIREMENTS WARRANT THE INCREASE IN COMPLEXITY!

TLS on SAM on MSL:

- TLS alone has sub-parts-per-billion sensitivity for CH_4, CO_2, SO_2, H_2O_2, NH_3, etc. and other gases
- As part of the SAM suite, TLS gains sensitivity of 50-100 in enrichment and up to 10 in pressure to expect sensitivity to ~ 1 part-per-trillion methane
- TLS is low mass (3.7 kg), low volume, low power and high TRL (8)
- With a simple change of modular laser source packages, TLS can accommodate 4 laser channels covering a variety of wavelengths (1-12 µm)- all in a single gas cell with the same optics!
- In providing both 2f and direct absorption measurements for a fixed known path, TLS is easily calibrated through HITRAN and through gas standards
- The TLS optical cell is robust to misalignment, loss of power, launch vibration.

Deliverance…