Lessons learned from Solar System IR Observations

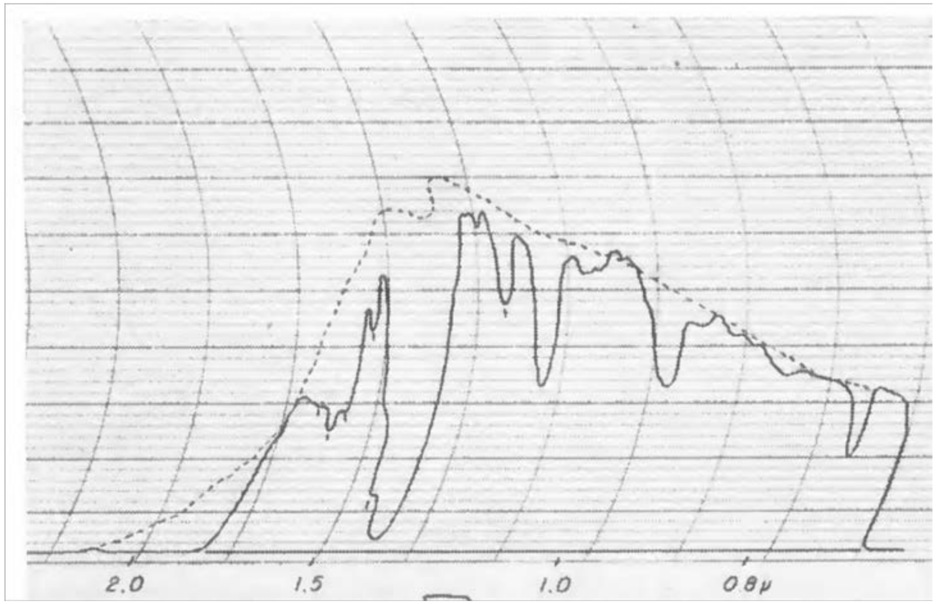
Thierry Fouchet

LESIA – Observatoire de Paris

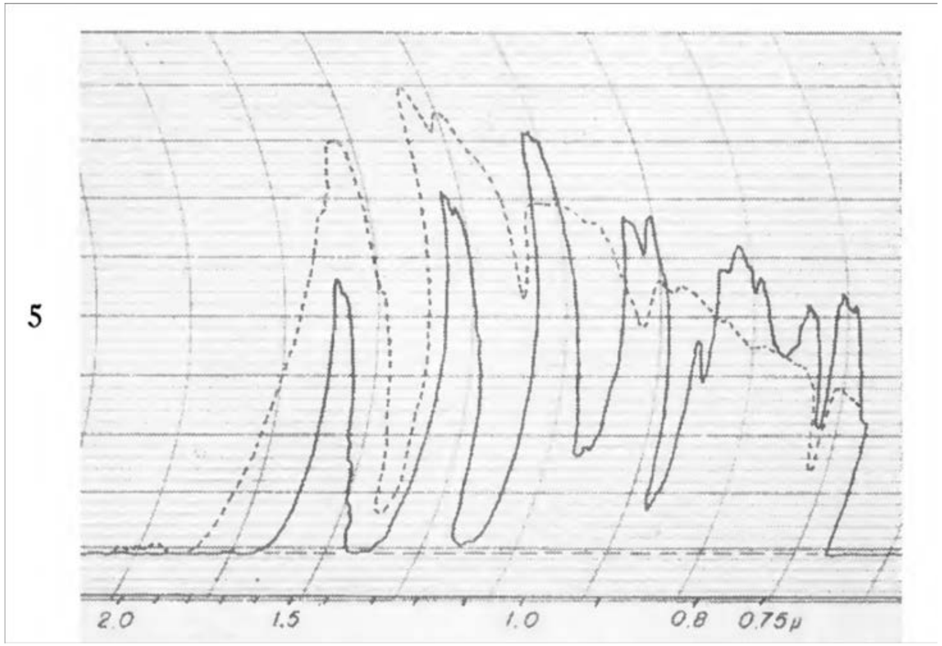
Success of IR spectroscopy in probing Solar System atmospheres

Infrared Spectra of Planets, Gerard P. Kuiper, ApJ, 106, 1947

Venus: CO_2



Jupiter: CH_4 & NH_3



Giant Planets - composition

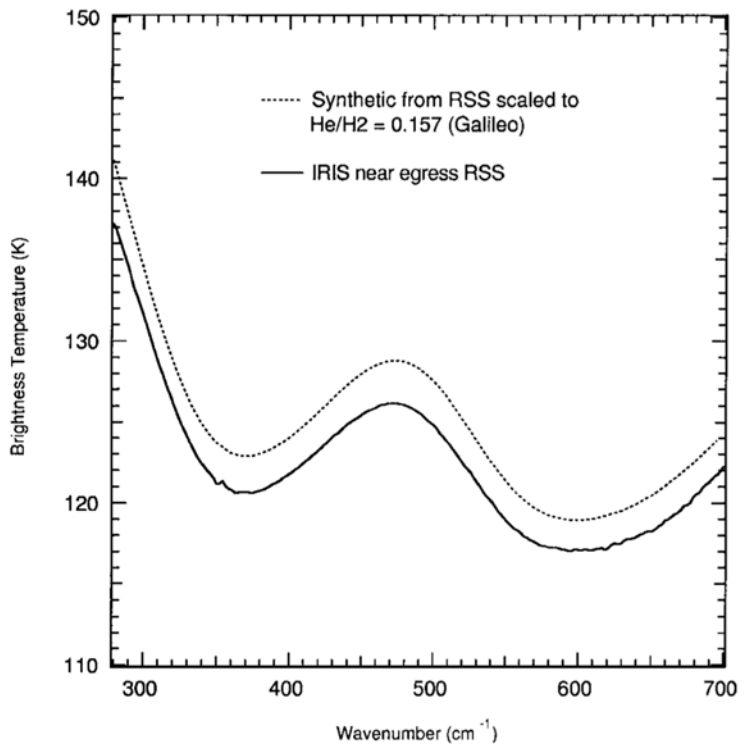
	Jupiter	Saturn	Uranus	Neptune
H_2 He	86,4% 13,4%	94-86% 6-14%	81-86% 12-17%	77-82% 12-17%
Noble gases	Ne, Ar, Xe, Kr			
Thermochemical equilibrium	CH_4: 0.2% NH_3: 6×10^{-4} $H_2O > 10^{-3}$ H_2S: 9×10^{-5}	CH_4: 0.45% NH_3, H_2O, H_2S	CH_4~2%, H_2S	CH_4~2%, H_2S?
Disequilibrium species	PH_3, GeH_4, AsH_3, CO	PH_3, GeH_4, AsH_3, CO		CO
Photochemical products	C_2H_6, C_2H_4, C_2H_2, C_3H_8, CH_3C_2H, C_4H_2, C_6H_6	CH_3, C_2H_6, C_2H_4, C_2H_2, C_3H_8, CH_3C_2H, C_4H_2, C_6H_6	C_2H_2	CH_3, C_2H_6, C_2H_4, C_2H_2
External flux (IDPs, ring systems, impacts)	H_2O, CO, CO_2, CS, HCN	H_2O, CO, CO_2	H_2O, CO	H_2O, CO, CO_2, HCN, CS

Terrestrial Planets - composition

	Venus	**Mars**	**Titan**	**Pluto**
Main gases	CO_2, N_2	CO_2, N_2	N_2, CH_4	N_2
Noble gases	He, Ne, Ar, Kr	Ar, Ne, Kr, Xe	^{40}Ar	
Trace gases	SO_2, H_2O, OCS, HCl, HF	H_2O, CH_4?	H_2O, CO	CH_4, CO
Photochemical products	CO, $H_2SO_{4,}$ SO, ClO, O_2, O_3	CO, NO, O_2, O_3	C_2H_6, $C_2H_{2,}$, C_3H_8, C_2H_4, CH_3C_2H, C_4H_2, $C_3H_{6,}$, H_2 HCN, HNC, CH_3CN, HC_3N, C_2N_2 , C_4N_2 , C_2H_5CN, C_2H_3CN	C_2H_6, C_2H_4, C_2H_2, HCN

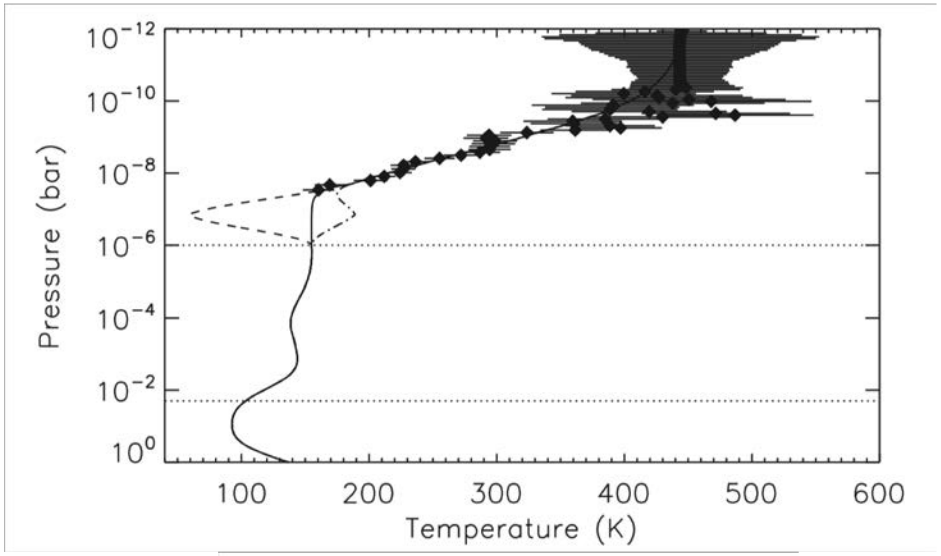
Helium Abundance - In situ needed

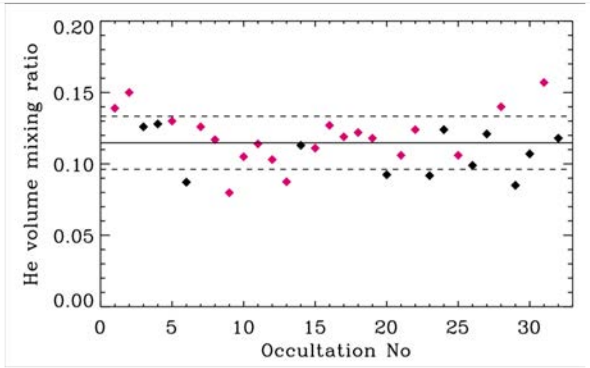
- Determined from H_2-He-CH_4 CIA in 300-700 cm^{-1}
  - Degeneracy between T(p), ortho-to-para ratio, He/H_2, haze opacity
  - Combined radio occultation (RSS) T(p) measurements and IR continuum
- Jupiter:
  - Voyager: He/H_2=0.110±0.032 (Y=0.18, Gautier *et al.* 1981; Conrath *et al.* 1984)
  - Galileo in-situ: He/H_2 = 0.157±0.003 (Y=0.234, von Zahn et al. 1996, 1998)



Saturn Helium Abundance – Still debated

- Voyager
  - RSS+IR Continuum: He/H_2 = 0.034±0.024 (Conrath et al. 1984)
  - IR Continuum only: He/H_2=0.11-0.16 (Conrath & Gautier 2000)
- Cassini
  - RSS+IR Continuum: He/H_2= 0.06-0.085 (Achterberg et al. 2016)
  - Occultation IR / IR Continuum: He/H_2=0.09-0.19 (Banfield et al, 2014)
  - Occultation UV+ Limb IR: He/H_2=0.12±0.02 (Koskinen & Guerlet 2018)





Helium – Uranus & Neptune

- Before Voyager
  - IR Continuum only
  - A claim for a He vmr of 40±20% (Orton et al., Science, 1986)
- Voyager
  - RSS+IR Continuum: He vmr = 0.152±0.033 (Y=0.262±0.048, Conrath et al. 1987).
  - Compatible with Solar abundance

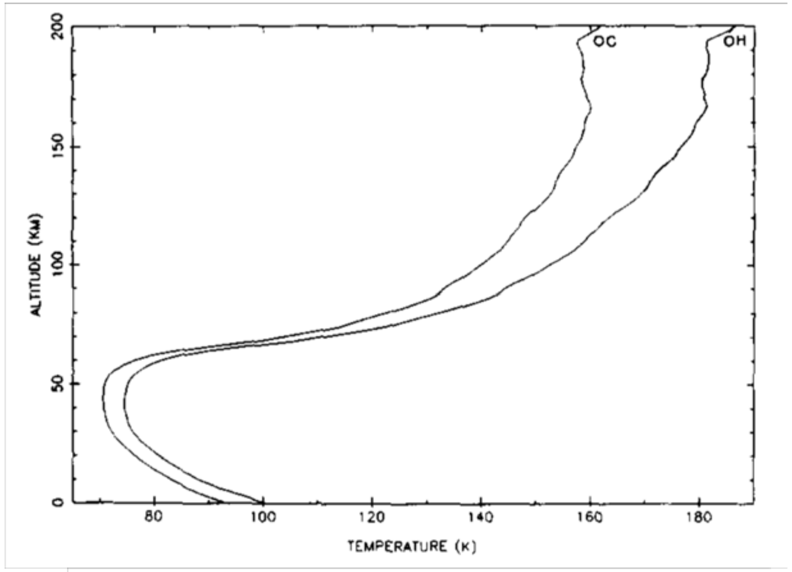
- Voyager
  - RSS + IR Continuum: He vmr= 0.19±0.032 (Y=0.32±0.05, Conrath et al. 1991)

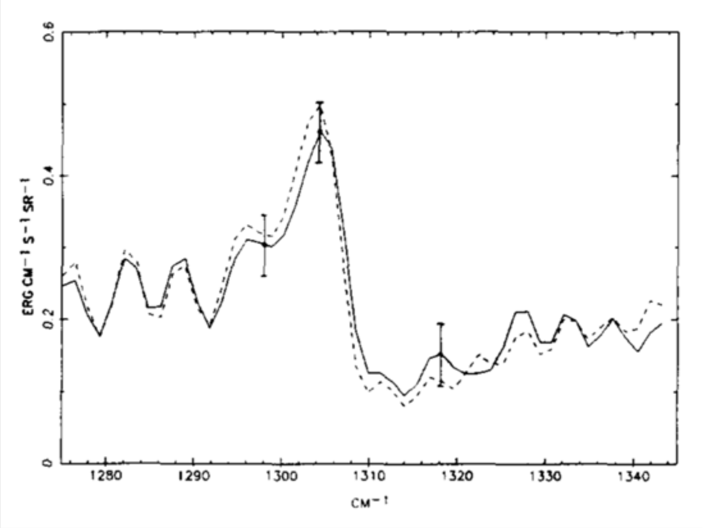
Perspectives

- Helium abundance only known from in-situ measurements
  - Solar System: no precise knowledge for Saturn, Uranus & Neptune
  - Affects evolution models, remote sensing interpretation
- Difficulties
  - He signal is weak
  - Degeneracy: ortho-to-para ratio, T(p), clouds
  - Hot Jupiter: water lines could affect long-wavelength part of the continuum
  - Radio occultation measurements: g not exactly known because of unknown wind speed

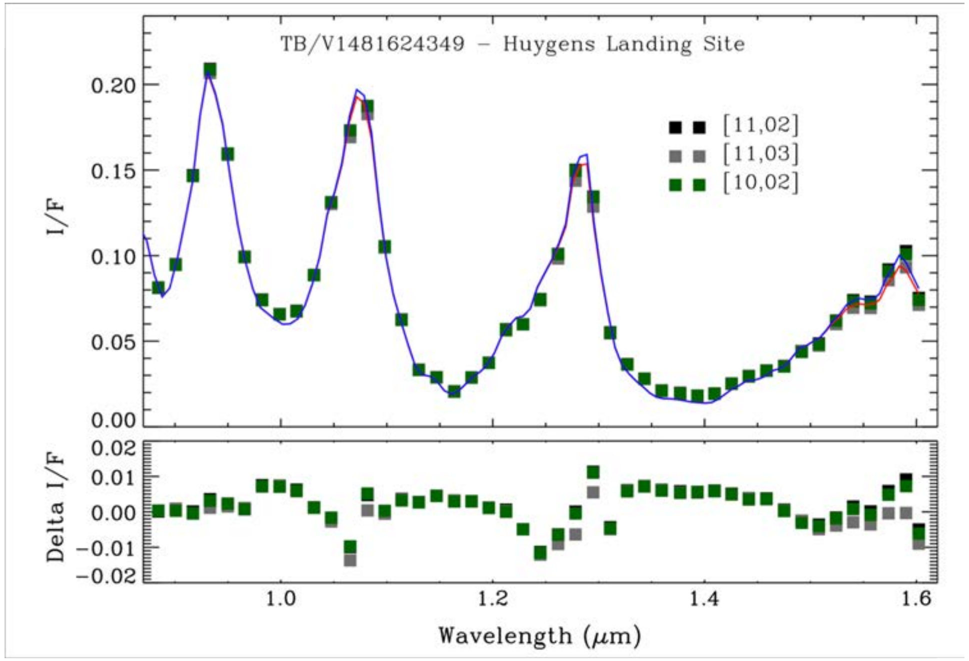
Titan: the debate on tropospheric methane abundance

- Voyager:
  - Radio Occultation (RSS) measures T/m vertical profile
  - CH_4 ν_4 emission measures T and CH_4 vmr
- Analysis
  - N_2, CH_4 and H_2 detected, but what if an abundant gas not detected: Argon
  - $Ar/N_2<27\%$, stratospheric CH_4 vmr = 0.5-3.4%, tropospheric CH_4 vmr as high as 21% (Lellouch et al. 1989)
- Implications:
  - Presence of CH_4-C_2H_6 ocean at the surface (Lunine et al. 1983)
  - Exact composition depended on T_{surf} hence on [Ar]
    - Two poles: pure methane – pure ethane





Titan: the debate on tropospheric methane abundance



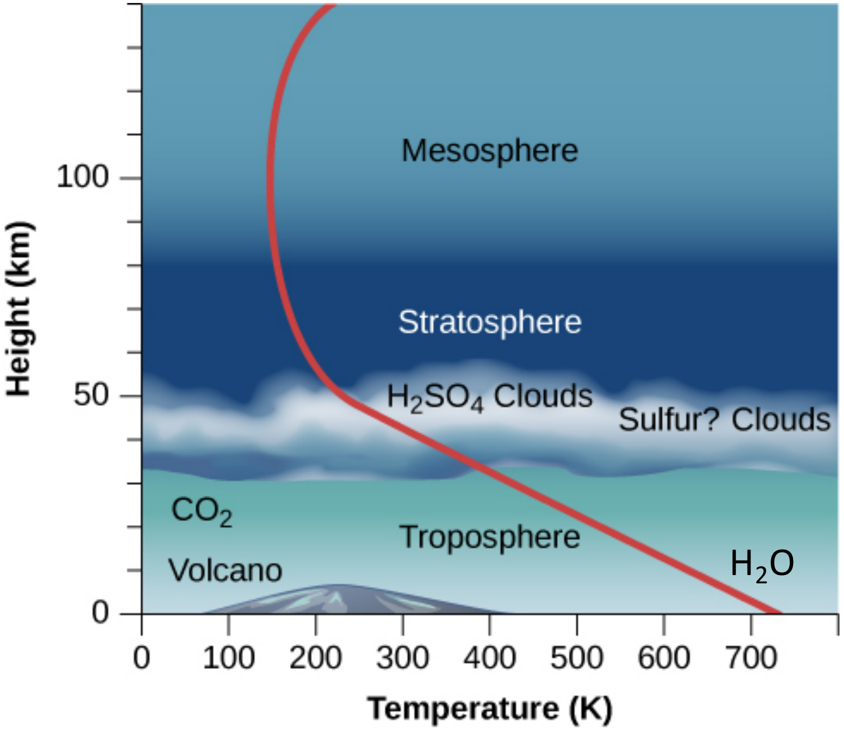
- In principle, near-IR probes the tropospheric CH4 vmr
    - Weak lines only recently measured (Campargue et al. 2010)
    - Clouds, haze parameters weakly constrained
    - CH_4 RH = 25-200% (Courtin et al. 1995; Samuelson et al. 1997)
- Huygens in-situ required
    - CH_4 measured from GCMS and DISR: vmr=5% (Niemann et al. 2005)
    - Aerosols properties from DISR (Tomasko et al. 2008)
    - Possible to reconcile remote sensing and in-situ (Griffith et al. 2012)

Perspectives

- Condensable species: difficult to measure down to the surface
    - Difficulty to measure below the clouds
        - Highly dependent on the cloud scattering properties
        - Very demanding for spectroscopy
        - We still don’t know the H_2O abundance below Jupiter’s cloud deck → C/O ratio?
    - Uncertainties and/or extrapolation on the T(p) profile
        - The relative humidi
- Ocean worlds!

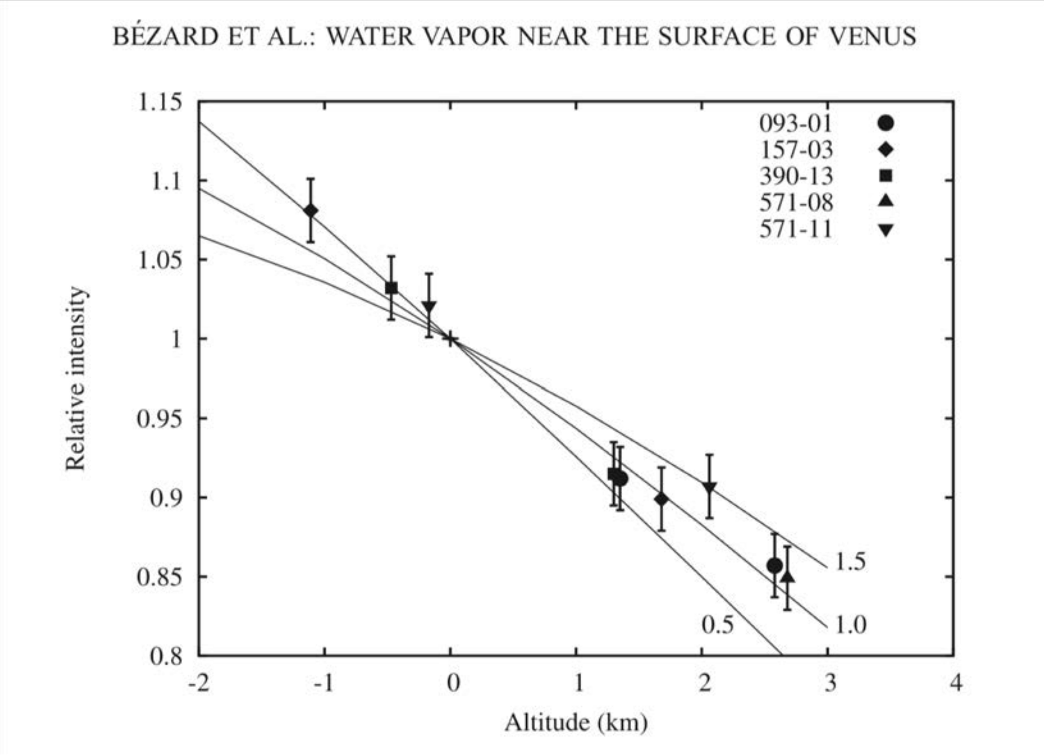
Venus thick atmosphere

- Very long path-length requires knowledge
  - Collisional broadening (CO_2)
  - Sublorentzian lineshape up to several 100 cm^{-1}
  - Additional continuum opacity
    - CO_2 CIA bands
    - Extreme far wings of strong CO_2 bands
- H_2O abundance close to the surface
  - 30±10 ppm (Crisp et al., 1991)
  - 45±10 ppm (Meadows & Crisp 1996)
  - 60±10 ppm (Ignatiev et al. 1997)

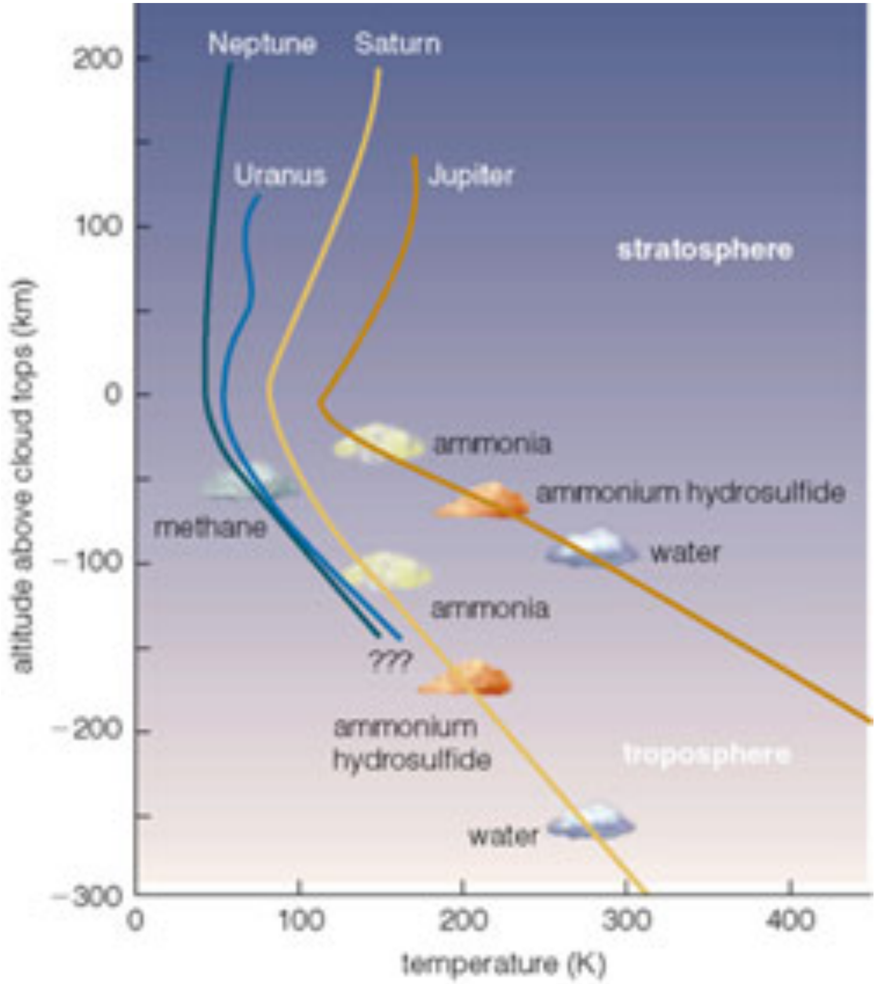


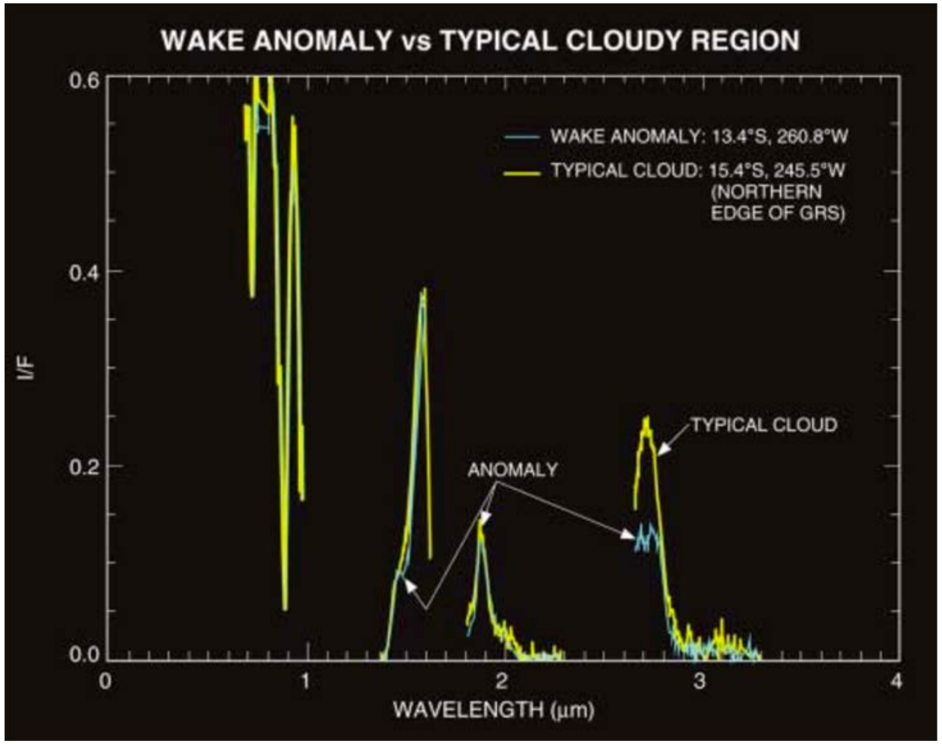
Venus thick atmosphere

- How to independently measure the additional opacity?
  - High spectral resolution of resolved CO_2 lines
  - Relative variations of the intensity at 1.185 µm as a function of surface elevation
  - H_2O abundance of 44 ± 9 ppm (Bézard et al. 2009)



Giant planets cloud chemical composition

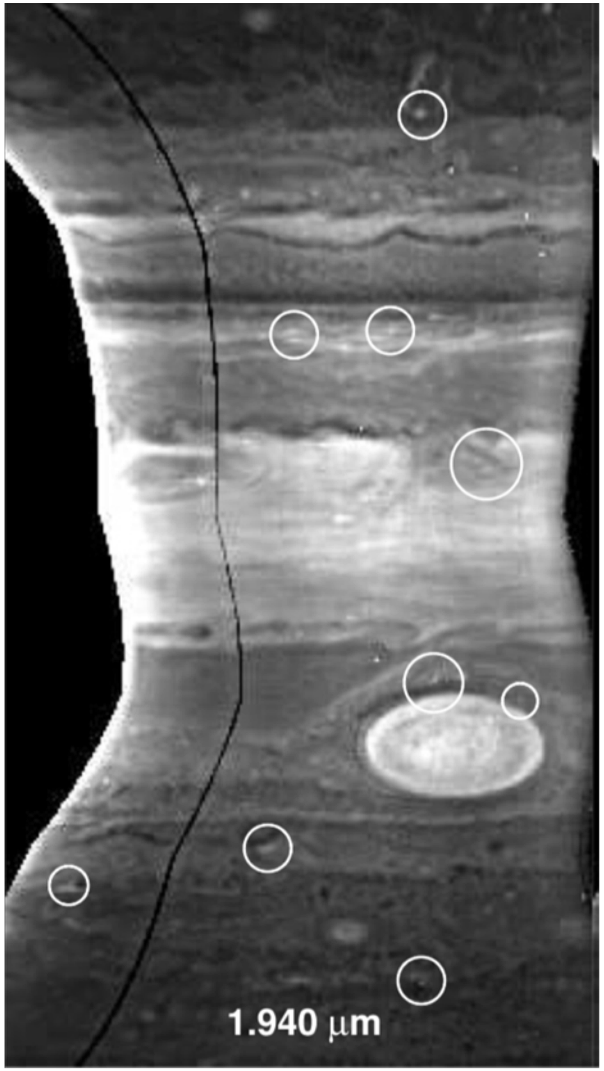




Baines et al. (2002)

Jupiter: only patchy identification of NH_3 clouds

- Color variations remained unexplained: chromophores
  - Need for 2 or 3 chromophores (Simon-Miller et al. 2001)
- Photochemistry :
  - $PH_3 \rightarrow$ red phosphorus (P_4)
  - $NH_3 \rightarrow$ hydrazine (N_2H_4)
  - $NH_3 + C_2H_2 \rightarrow C_{2n}H_{4n-2}N_2$, $C_{2n}H_{4n}N_2$, and $C_{2n}H_{4n+2}N_2$
- Lightening could also play a role
- No definitive spectroscopic identification

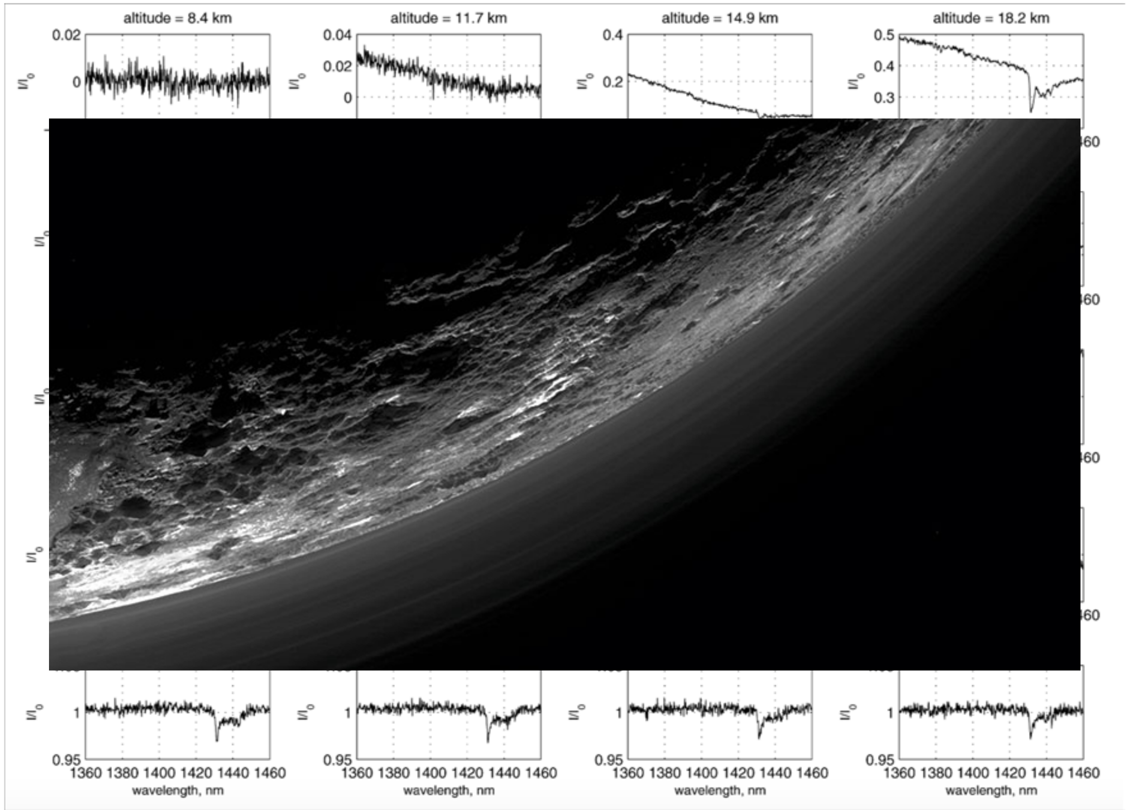


Sromovsky et al. 2018

Perspectives

- The problem of continuum spectroscopy
  - Extremely far wings – Collision induced absorption – spectroscopic parameters
  - Laboratory measurements & Ab initio quantum calculations needed
- Clouds
  - Very difficult to decipher their compositions, spectroscopic parameters, hence opacity

Vertical variations of hazes, clouds & aerosols

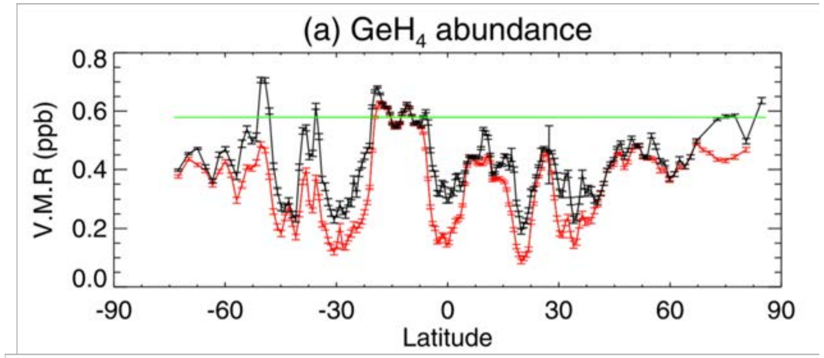


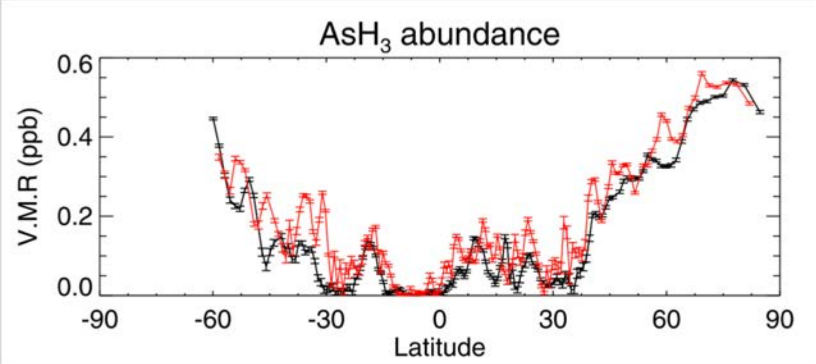
- SPICAM solar occultation on Mars (Fedorova et al. 2009)
  - CO_2 and H_2O gases
  - And several detached layers
    - Small and large particles
    - Detached water ice clouds
    - Caused by sedimentation, convection, waves

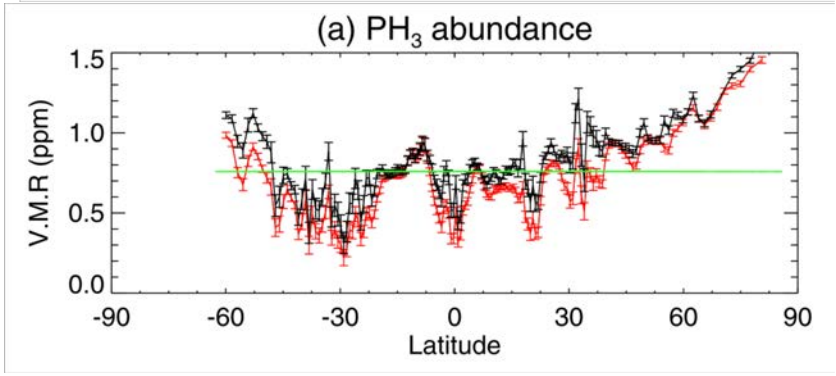
Pluto detached layers seen by New Horizons

Meridional variations of disequilibrium species

- PH_3, GeH_4, AsH_3, CO disequilibrium species
  - At thermochemical equilibrium at p>1000 bars
  - Convection faster than kinetics of destruction → quenched
  - Expected abundances depending on convective heat flux
  - Unexpected and unexplained meridional variations (Giles et al. 2017)

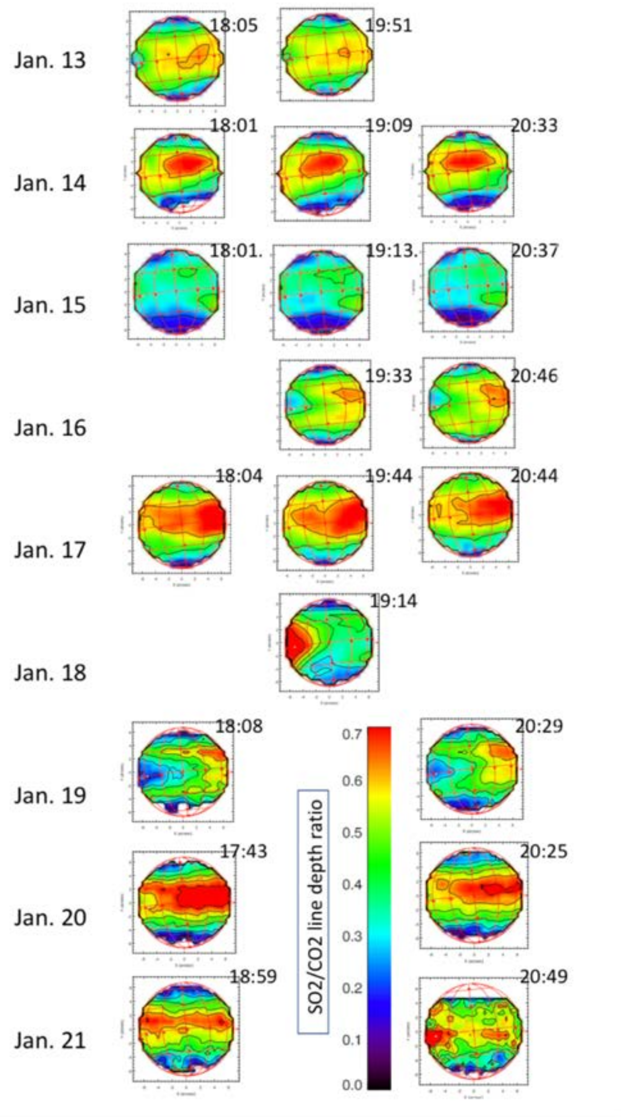






SO_2 Temporal & Spatial Distribution on Venus

- SO_2 abundance above the clouds strongly varying
  - With time, at all scales
  - With latitudes and longitudes
  - TEXES/IRTF (Encrenaz et al. 2019) & UV/SPICAV (Marcq et al. 2016)
- Volcanic eruption?
- Large reservoir of SO_2 within the cloud
  - Puff of SO_2 in upper atmosphere ; convection, planetary waves

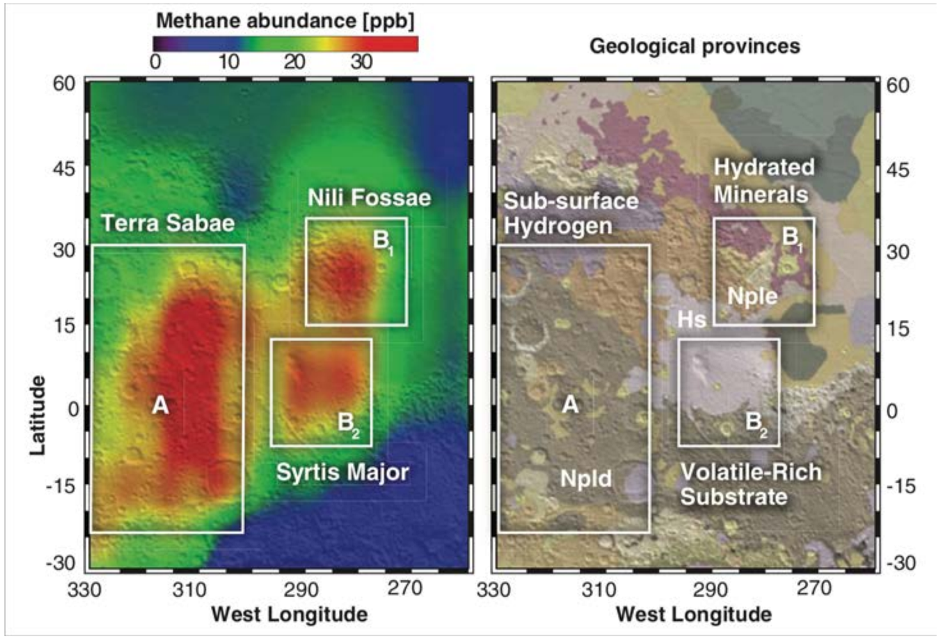


Perspectives

- Take into account the possibility of spatial variability
  - Vertical variations
  - Meridional variations
  - Dusk/dawn variations
- Take into account the possibility of temporal variability
  - When several transits averaged together
- Change the radiative transfer through line saturation

Methane on Mars?

- Three independent detections of methane on Mars
  - 10±3 ppb (CFHT/FTS, Krasnopolsky et al. 2004)
  - Regional variability : 0-30 ppb (MeX/PFS, Formisano et al. 2004)
  - Regional variability: 0-40 ppb (CSHELL/IRTF, Mumma et al. 2009)
- Origin?
  - Cometary impacts?
  - Serpentinization?
  - **Life?**

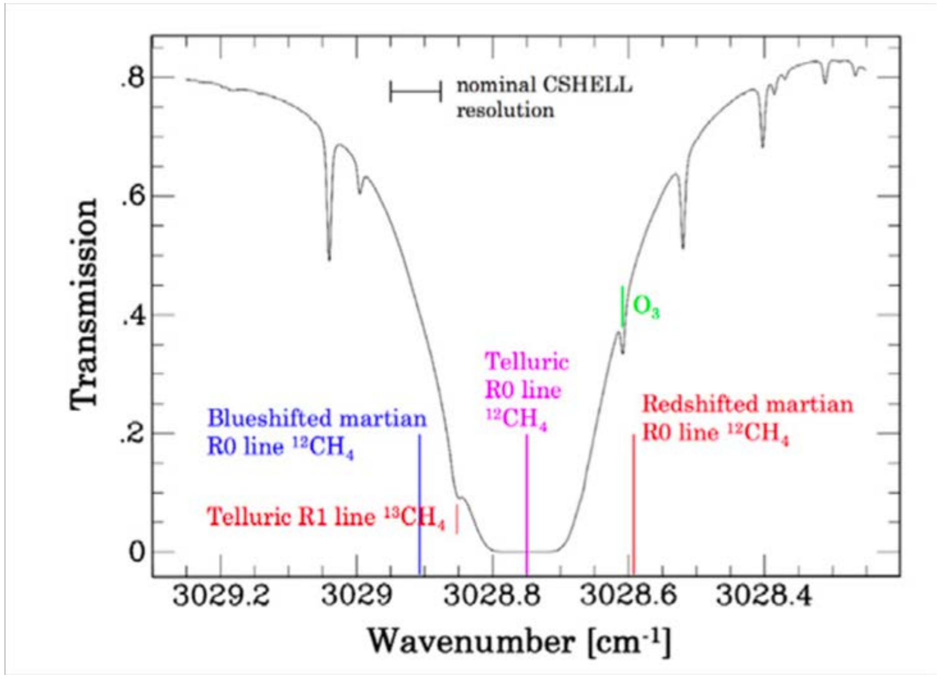


Methane rapidly challenged

Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics

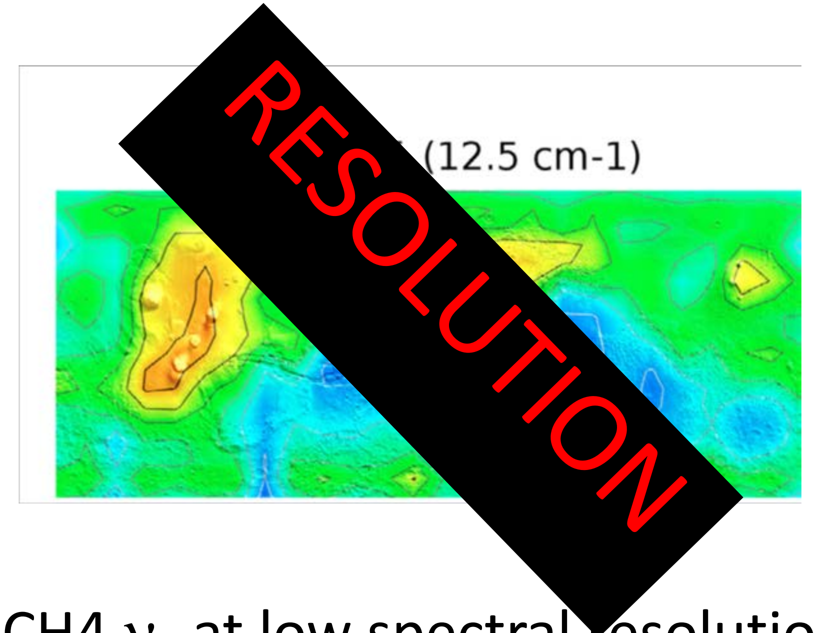
Franck Lefèvre[1] & François Forget[2]

- « Regional, temporal variations imply an unidentified methane loss process that is 600 times faster than predicted by standard photochemistry »
- Oxidation of methane at odds with CO, O_2, O_3 measurements

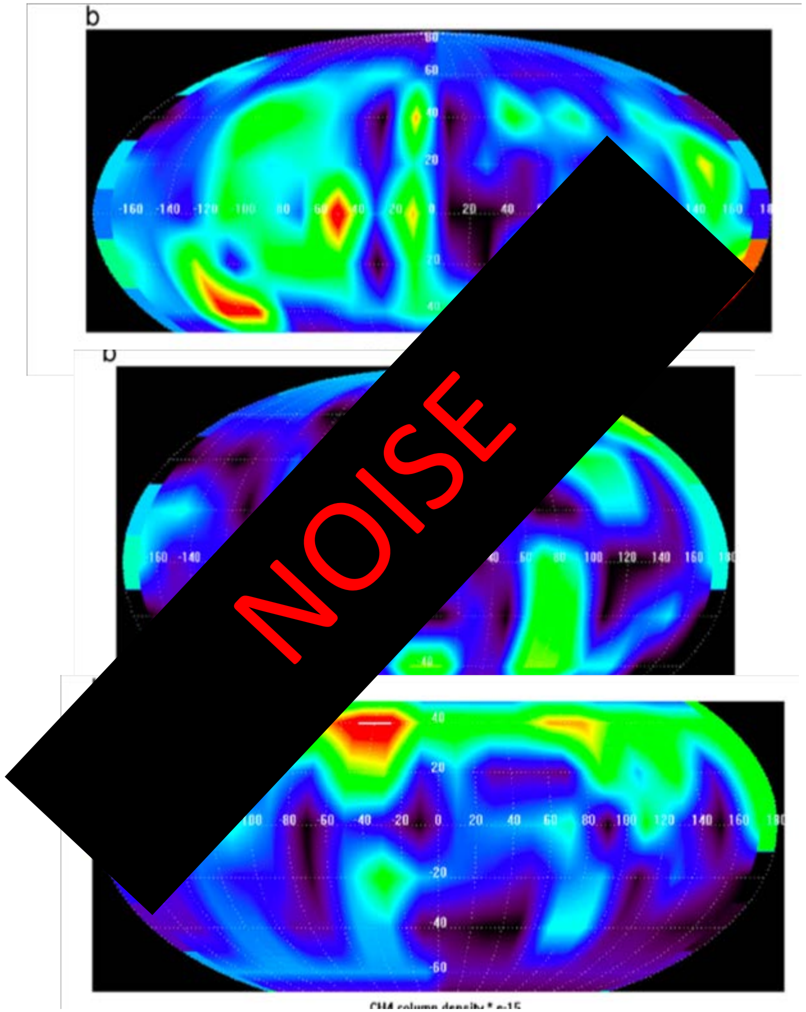


- Zahnle et al 2011: Difficult to correct for terrestrial isotopic lines

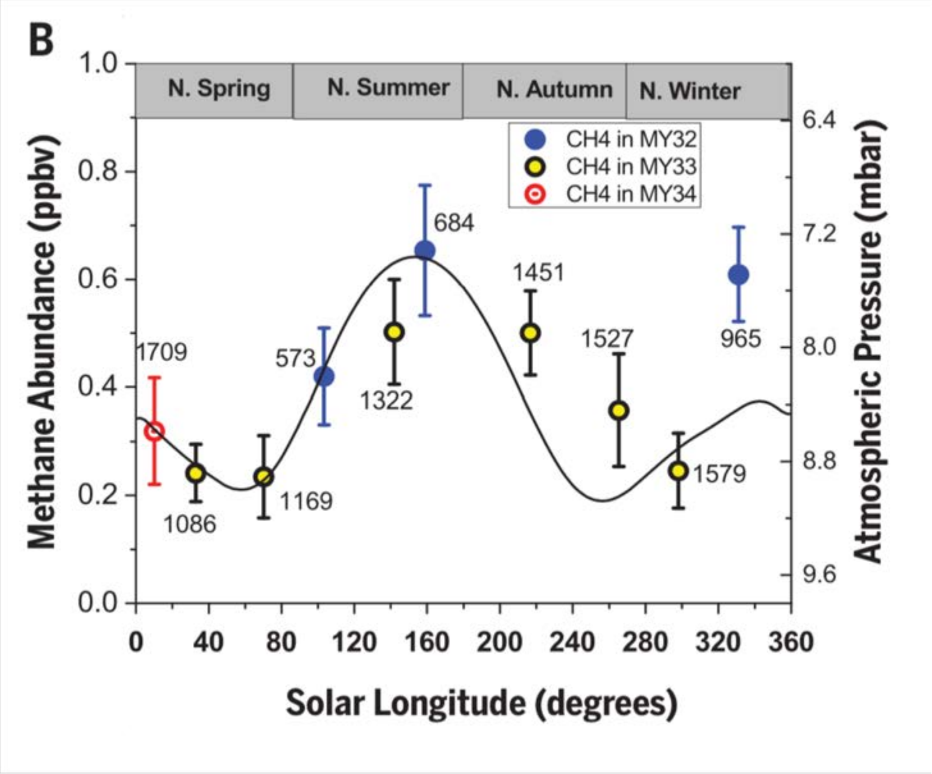
Methane on Mars: from the worst



- CH4 ν_4 at low spectral resolution → a map of water
- Unexplainable seasonal variations



Methane on Mars: to the intriguing



- In situ measurement by a laser diode on MSL (Curiosity rover, Webster et al. 2018)
  - Note the decrease in abundance
  - Correlated with oxygen abundance


PERSPECTIVES

PLANETARY SCIENCE

Play it again, SAM

Lasers shine new light on the drying of Mars while reviving the mystery of methane

By **Kevin Zahnle**

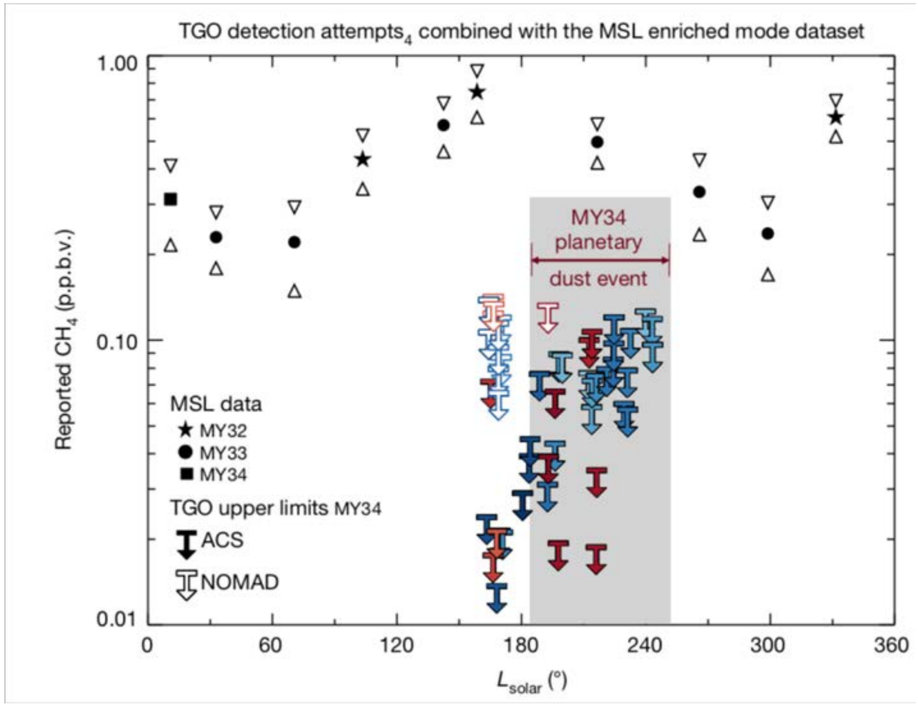
Some discoveries are new, others old. Here, we consider one of each from NASA's Curiosity rover. The new discovery, reported by Mahaffy *et al.* (*1*) on page 412 of this issue, is a remarkable measurement of the deuterium-hydrogen (D/H) ratio in a Gale crater mudstone from 3 billion years ago. On page 415, Webster *et al.* (*2*) report on the latest chapter in the muddy matter of methane on Mars. What links them is that both were made using the tunable laser spectrometer (TLS), part of the SAM (Sample Analysis at Mars) package on the rover.

Martian water is enriched in deuterium (D), hydrogen's heavier isotope, compared with most water in the solar system. The cause of the enrichment is the preferential escape to space of H. The D/H ratio in Mars's air is now about 6 × SMOW (standard mean ocean water; that is, Earth) and

Methane on Mars: and the rebutal

No detection of methane on Mars from early ExoMars Trace Gas Orbiter observations

Oleg Korablev[1]*, Ann Carine Vandaele[2], Franck Montmessin[3], Anna A. Fedorova[1], Alexander Trokhimovskiy[1], François Forget[4],



- Solar occultations in the CH_4 ν_3 band
- Global upper limit = 0.05 ppb
- Is this the end?

Perspectives

- Spectral resolution needed to disentangle species
- Need to investigate possible contaminants
  - G. Villanueva identified several CO_2 weak and isotopic lines in Martian spectra
  - Could it also explain the SAM/Curiosity detection?
- Anonymous referee: « Martian methane was a social construct with social and financial interests »

Conclusions

- IR spectroscopy extremely successful in probing atmospheric chemistry
- But
    - Some species not detectable
    - Very good spectroscopy required to leave ambiguities
    - Spatial & temporal variability
- Carl Sagan: « Extraordinary claim requires extraordinary evidence »