Measurement of nitrogen fractionation in Solar System objects

Philippe Rousselot

Institut UTINAM, Besançon, France.

Earth

→ Atmospheric N_2 used as the standard value for nitrogen isotopic ratio.
Nier, 1950:

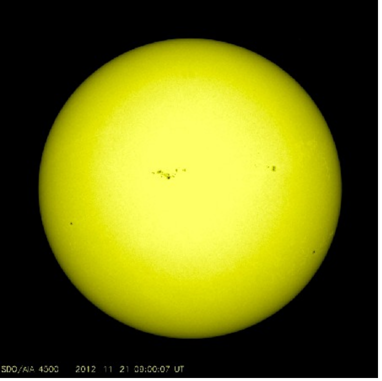
$$^{14}N/^{15}N=272$$

$$^{15}N/^{14}N=3.676\times10^{-3}$$

→ All variations computed with respect to this standard value :

$$\delta^{15}N = ((^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard}-1) \times 1{,}000$$

→ Most variations on Earth are on the order of 10‰ (Cartigny & Marty, 2013)



Measuring the $^{14}N/^{15}N$ presolar from the Sun

→ First attempts based on the analysis of solar ions implanted in lunar soils (Becker & Clayton, 1975 ; Kerridge, 1975).

→ Problem: both ^{15}N-rich and ^{15}N-poor components were found.

→ Variations first thought to represent a secular change of the nitrogen isotopic composition of the Solar Wind, but no known solar process could be invoked to produce these variations

→ Variations later explained by mixing between solar and planetary N (J. Geiss, P. Bochsler, 1982 ; Wieler et al., 1999).

→ Variations with depth (a few tens of nm) in lunar regolith grains measured by ion microprobe analysis: ^{15}N depleted by at least 24 % relative to Earth (Hashizume et al., 2000), or lower limit $^{14}N/^{15}N=357$.

→ Analysis of lunar regolith collected by Apollo 17 near the Shorty crater, below 50 cm depth, and dated to 3.7 Gy, provided $^{14}N/^{15}N$ similar to terrestrial value in the mantle (Kerridge et al., 1991)

→ Solar Wind directly analyzed by Genesis (Marty et al., 2011):

Genesis : NASA sample-return probe that collected a sample of solar wind particles and returned them to Earth for analysis. Genesis was launched on August 8, 2001, and crash-landed in Utah on September 8, 2004.

→ Ion-probe analysis of Genesis Concentrator silicon carbide target done with secondary ion mass Spectrometry at the CRPG (Nancy, France).

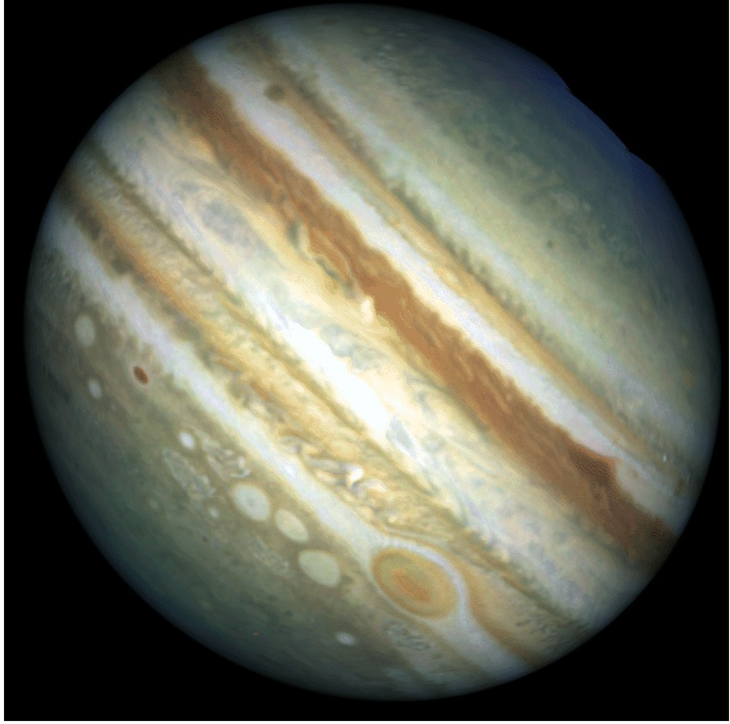
→ These measurements yield a $^{14}N/^{15}N$ ratio for the Solar Wind of **459** (95% confidence level), or $^{15}N/^{14}N=(2.178\pm0.024)\times10^{-3}$.

→ Sun's bulk $^{15}N/^{14}N$ ratio obtained after correction for isotopic fractionation taking place during acceleration of Solar Wind from the photosphere and, possibly, in the convective zone of the Sun:

$$\mathbf{^{14}N/^{15}N = 441\pm5}$$
$$\mathbf{^{15}N/^{14}N = (2.268\pm0.028) \times 10^{-3}}$$

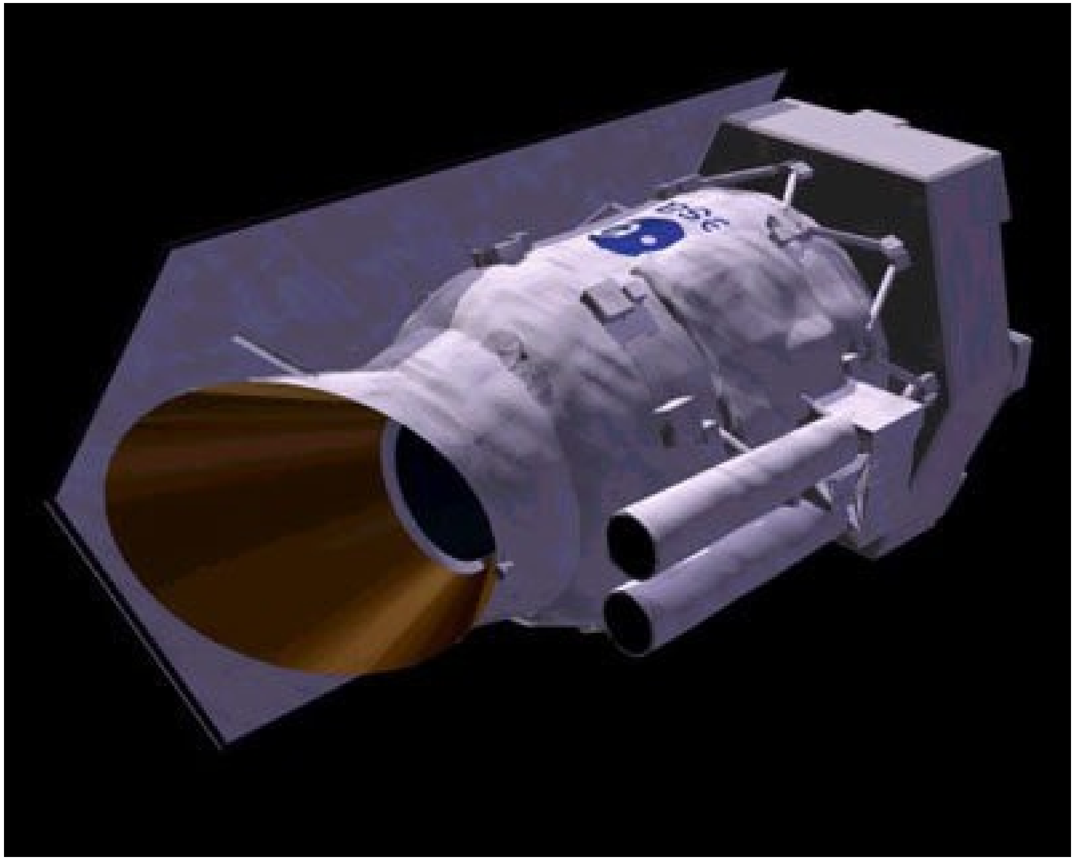
→ Very strong depletion in ^{15}N relative to terrestrial:
$\delta^{15}N = -383\pm8‰$

Jupiter

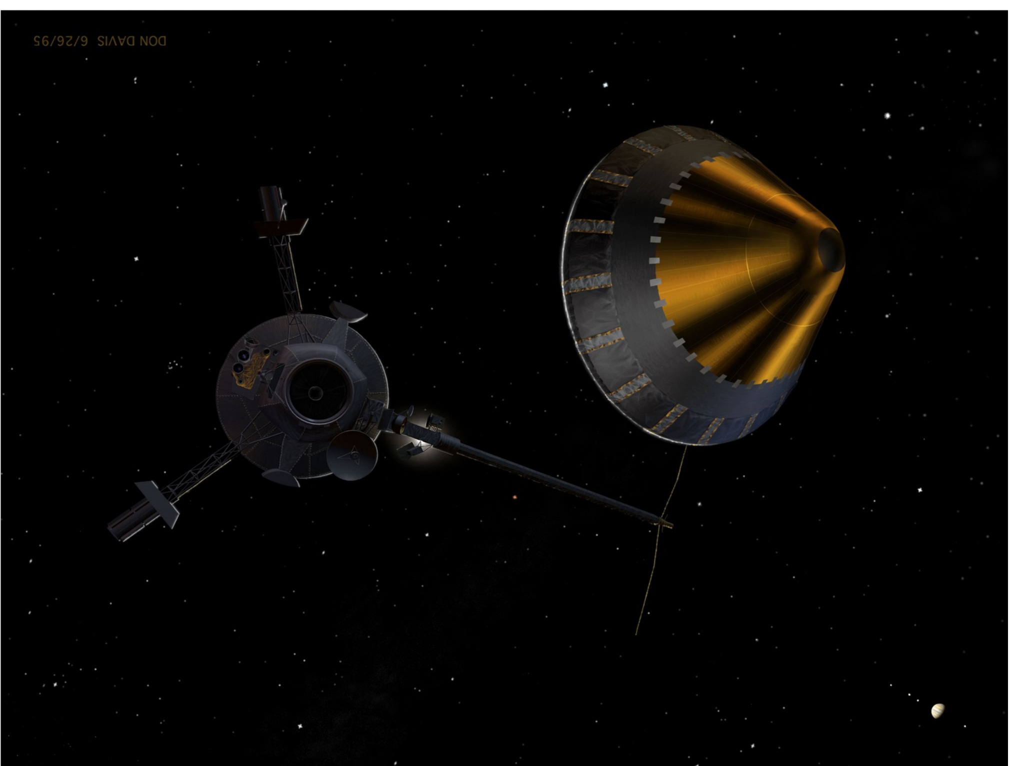


→ First measurements of $^{14}N/^{15}N$ ratio in Jupiter (Encrenaz et al., 1978 ; Tokunaga et al., 1980) based on IR ground-based spectra of $^{15}NH_3$ but not conclusive: uncertainty with a factor of two possibly consistent with the terrestrial atmosphere.

→ Spectra obtained with the Infrared Space Observatory (ISO) + Short Wave Spectrometer (SWS) at 10 μm provided a low $^{14}N/^{15}N$ ratio of 526 ($^{15}N/^{14}N=1.9^{+0.9}_{-1.0}x10^{-3}$) for the ammonia (Fouchet et al., 2000). Measurement done at P=0.5 bars above the ammonia condensation level (possible isotopic fractionation induced by ammonia condensation).

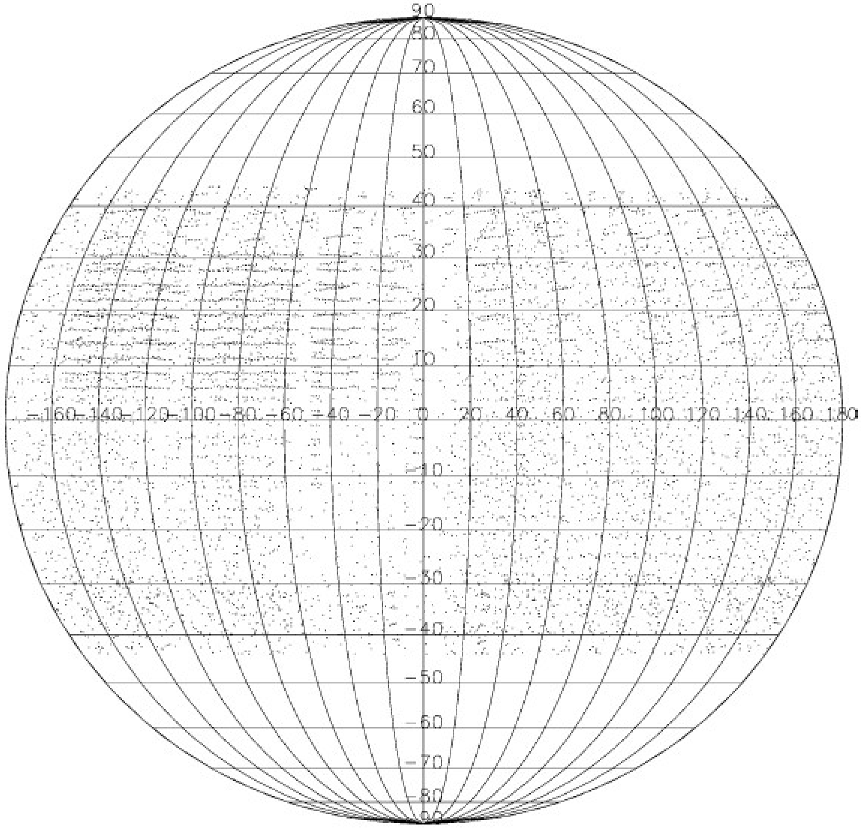


→ Galileo Mass Probe Mass Spectrometer in situ measurements in Dec. 1995 provided **$^{14}N/^{15}N=435\pm57$** ($^{15}N/^{14}N=(2.3\pm0.3)\times10^{-3}$) also for ammonia (Owen et al., 2001). Measurement done between 0.9-2.9 bars of pressure below the NH_3 cloud base (no fractionation effect but Galileo probe entered Jupiter in a region highly depleted in condensibles).



→ Measurements performed with Cassini spacecraft + Composite Infrared Spectrometer (CIRS) during a fly by. These measurements were performed at different latitudes to test for possible spatial variations (Fouchet et al., 2004).

→ Complex data processing / modeling because ammonia mixing ratio decreases very rapidly with altitude because it condenses and it is photolyzed by the UV solar flux (i.e. it is not obvious to measure $^{14}NH_3$ and $^{15}NH_3$ at the same altitude).

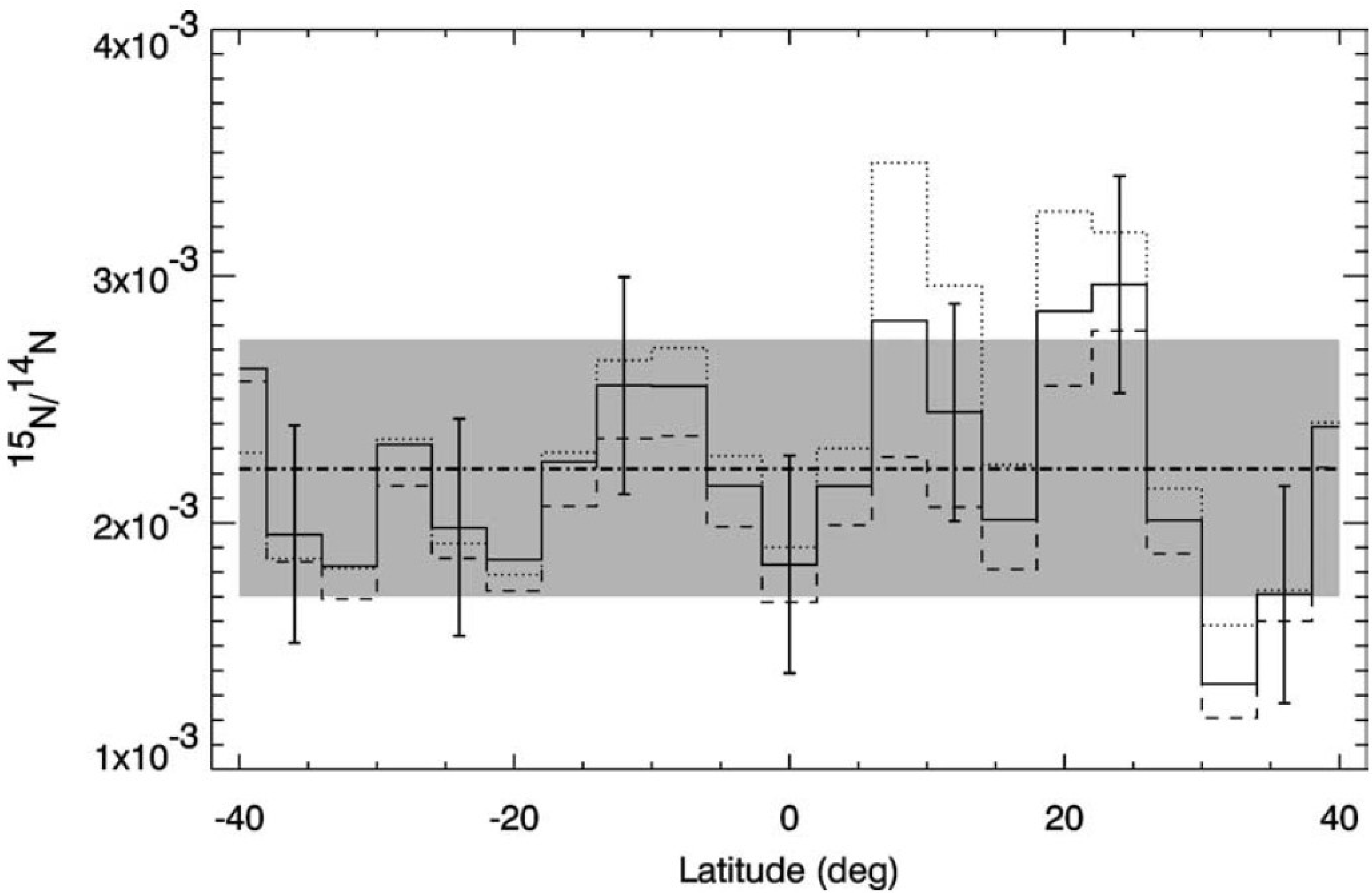


Distribution of CIRS/FP3 beam locations on Jupiter.

→ Conclusion: no significant variations of $^{15}N/^{14}N$ ratio observed in Jupiter atmosphere with the latitude.

$^{14}N/^{15}N = 450 \pm 30$

$^{15}N/^{14}N = (2.22 \pm 0.15) \times 10^{-3}$



Discussion :

→ $^{14}N/^{15}N$ ratio measured in Jupiter's atmosphere in NH_3 molecules agrees with the solar bulk value.

→ Jupiter exhibits the same relative abundance of N, C, Ar, Kr and Xe as the Sun (Owen et al., 1999 ; Mahaffy et al., 2000) and its hydrogen and helium define solar nebula isotopic ratio.

→ Both are considered as representative of the protosolar nebula

→ Nitrogen was probably delivered on Jupiter as N_2, supposed to be the dominant form of nitrogen in the outer solar nebula and in the interstellar cloud that preceded it.

Comets

→ Nitrogen is present in comets mainly as NH_3 (about 0.7 % relative to H_2O) and HCN (about 0.25%). Also HNC (about 0.04%), CH_3CN (about 0.02%), HC_3N (about 0.02%), HNCO (about 0.1%), NH_2CHO (about 0.015%), as well as N_2, recently identified by Rosetta.

→ $^{14}N/^{15}N$ measured only on NH_3 and HCN, so far.

$^{14}N/^{15}N$ measured with HCN (first measurements):

→ HCN is photodissociated in CN and this ratio was measured in both species (bright CN lines in the optical range), even if all CN does not come from HCN (other sources of CN but less important).

→ First measurement in comet C/1995 O1 (Hale-Bopp) with HCN (Jewitt et al., 1997) in the sub-millimeter range. $^{14}N/^{15}N=323 \pm 46$. Ziurys et al. (1999) found 330 ± 98.

→ Same ratio derived from CN (optical high resolution spectroscopy): $^{14}N/^{15}N=140 \pm 35$ (Arpigny et al., 2003)…

→ Comet 17P/Holmes outburst (October 24th, 2007 ; V=17→ 2.5) permitted also to measure simultaneously $^{14}N/^{15}N$ with HCN and CN (Bockelée-Morvan et al., 2008). $^{14}N/^{15}N=139 \pm 26$ in HCN and 165 ± 40 in CN.

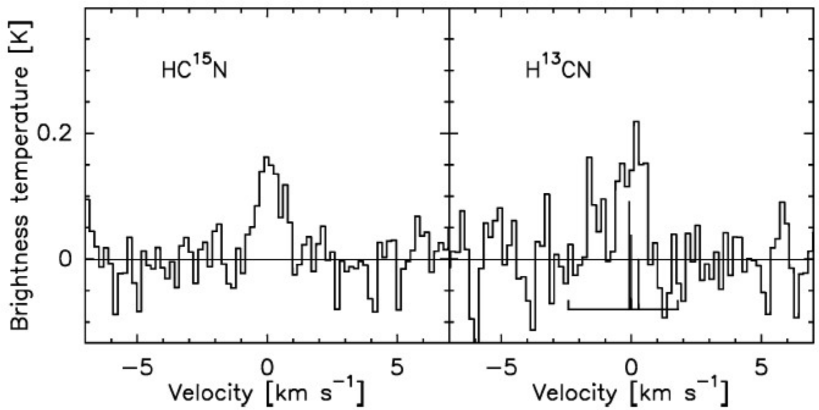
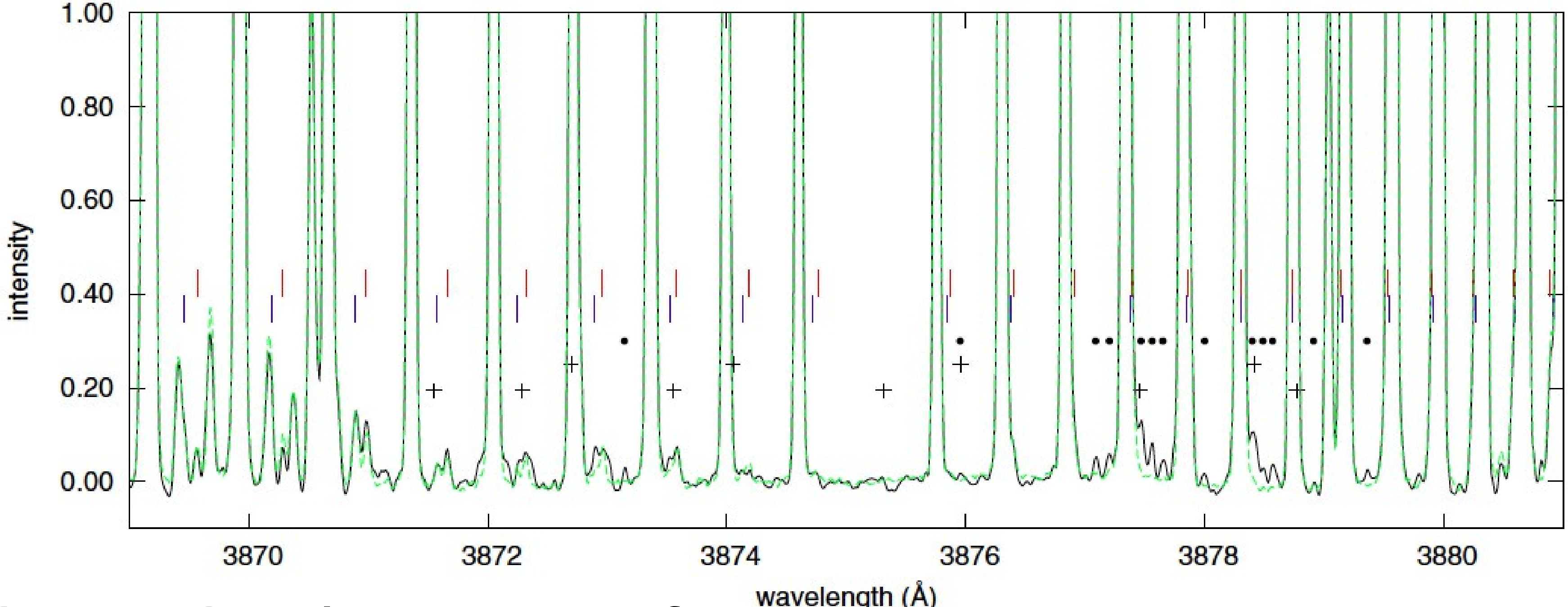


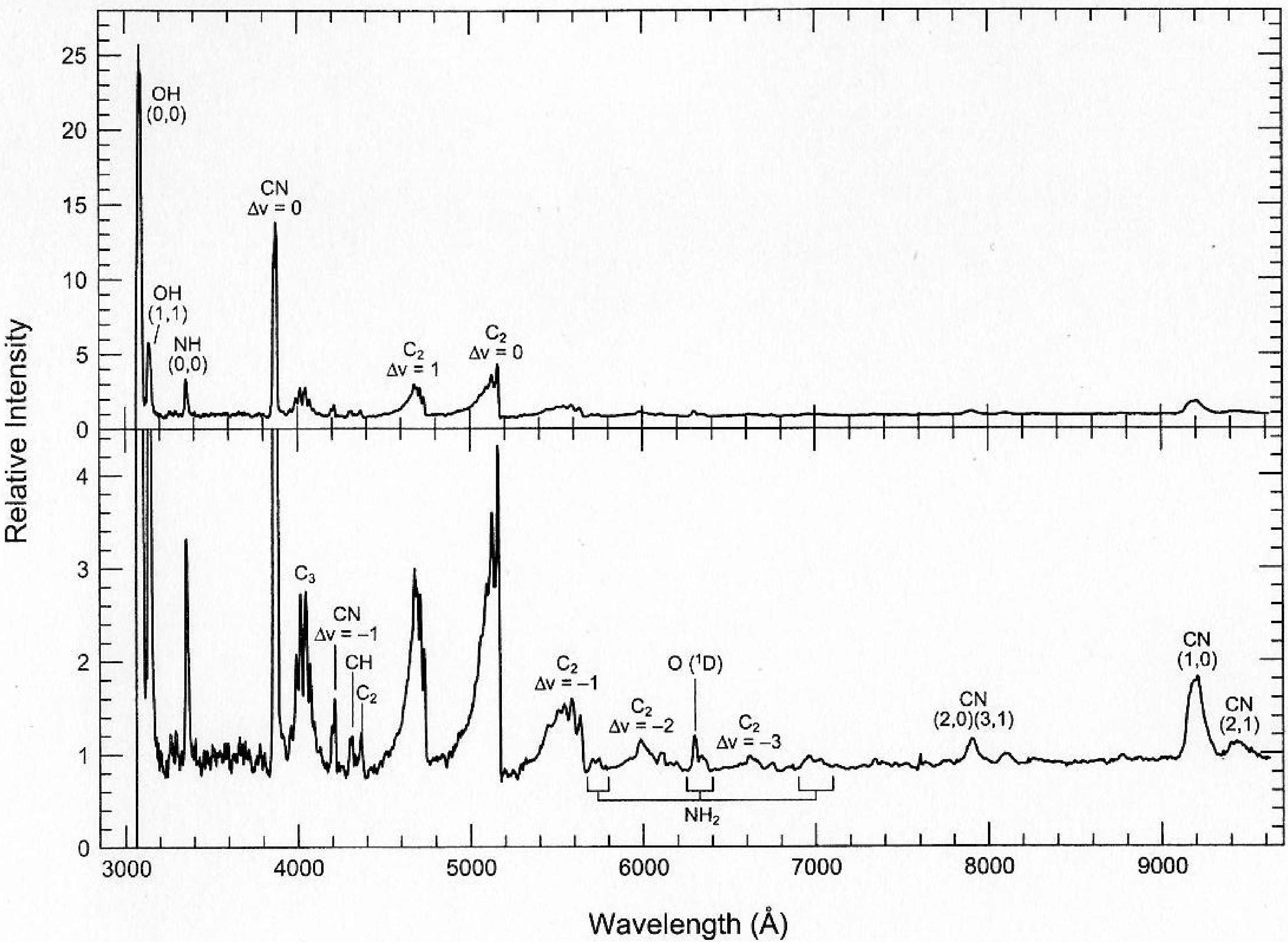
FIG. 1.—Spectra of the J = 3–2 lines of $HC^{15}N$ and $H^{13}CN$ in comet 17P/Holmes on 2007 October 27–28. The velocity frame is with respect to the comet rest velocity. The positions and relative intensities of the hyperfine components of $H^{13}CN$ J = 3–2 are shown.

→ Reanalysis of Hale-Bopp sub-millimeter data conducted by Bockelée-Morvan et al. (2008): $^{14}N/^{15}N=205\pm70$ (Jewitt et al., data) and 152 ± 30 (Ziurys et al. Data).

→ $^{14}N/^{15}N$ measured with CN emission lines at 388 nm (VLT+UVES high-resolution spectrometer). Relatively easy to do with a fluorescence model.

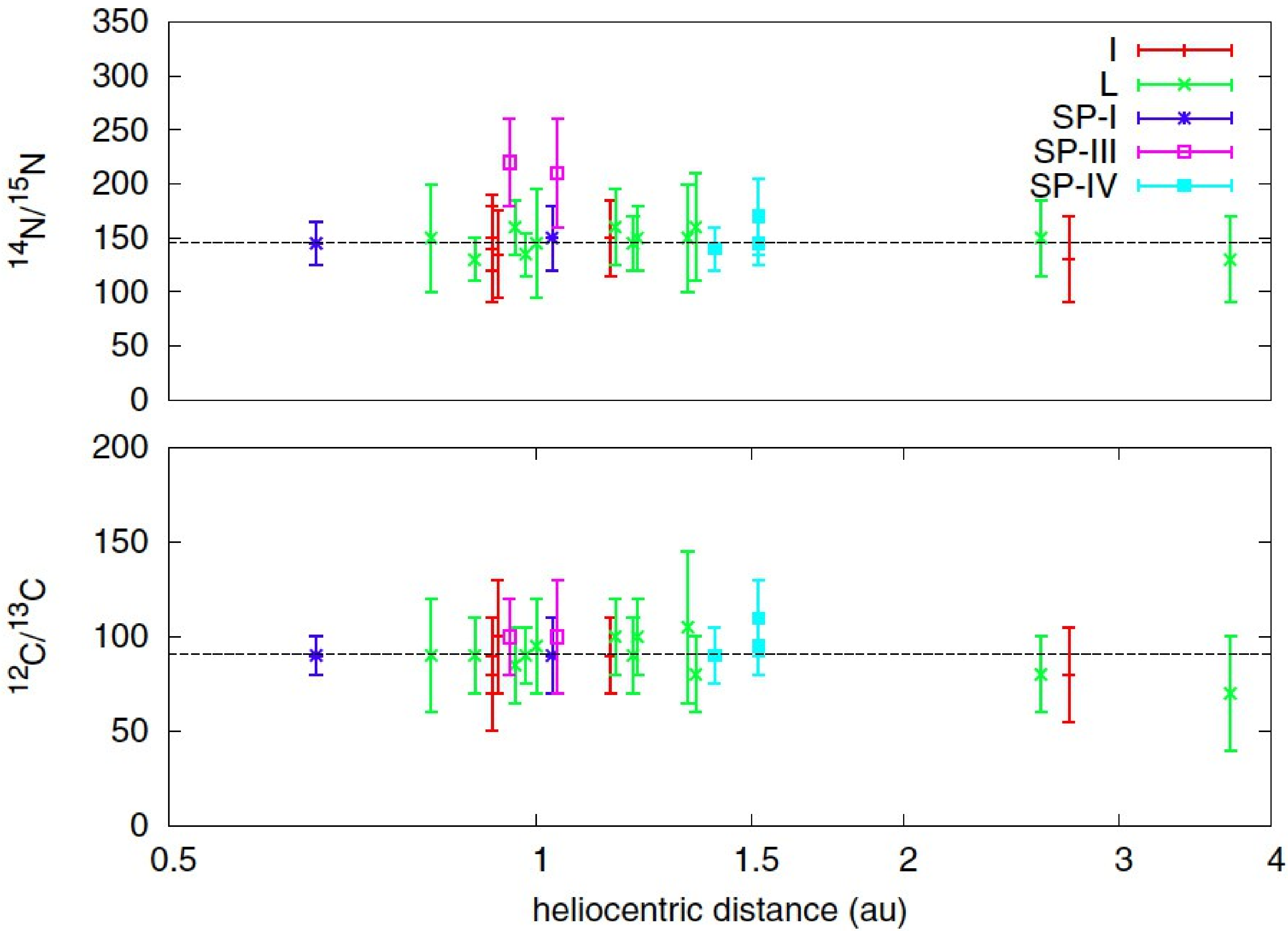


Observational spectrum of C/2001 Q4 (NEAT) obtained by VLT+UVES (black: nucleus, green: 50 000 km). Red ticks : $^{13}C^{14}N$ lines. Blue ticks : $^{12}C^{15}N$ lines (Manfroid et al., 2009)



Cometary optical spectrum.

→ Average of 18 comets observed with VLT+UVES provided a mean **$^{14}N/^{15}N=147.8 \pm 5.7$**
($^{15}N/^{14}N=(6.8\pm0.2)\times10^{-3}$) (Manfroid et al., 2009). Similar values found for subsequent observations.



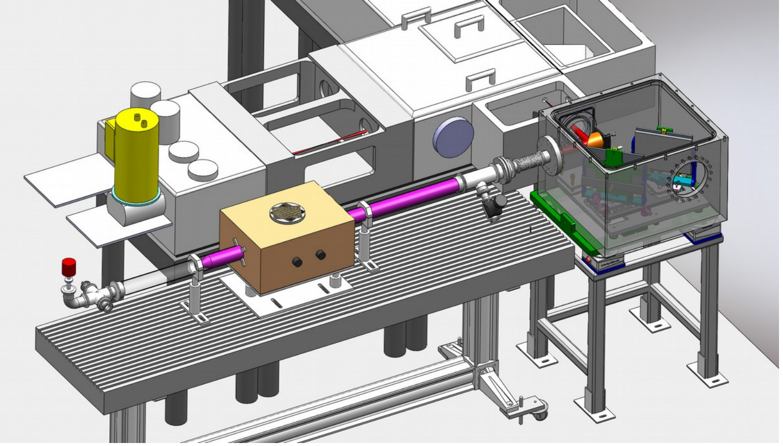
$^{14}N/^{15}N$ measurements for NH_3:

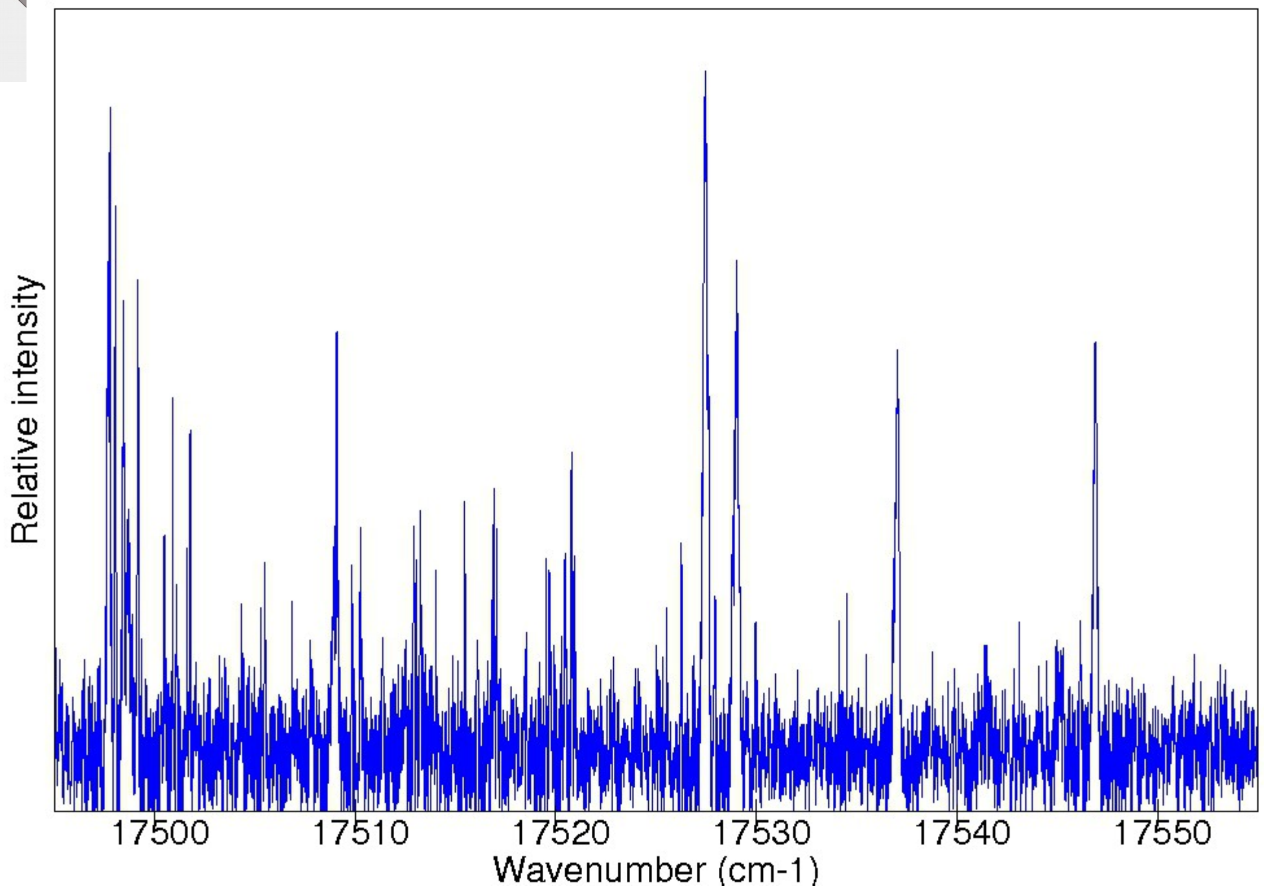
→ Direct measurement through inversion (radio), rotational (submillimeter), or vibrational (near-IR) difficult because $^{15}NH_3$ lines too weak.

→ NH_3 photodissociated in NH_2 (95 % of efficiency) and NH_2 has bright emission lines in the optical range.

→ Problem : $^{15}NH_2$ lines are weak and accurate wavelengths are required.

→ Accurate measurement of these wavelengths performed in laboratory at the Advanced Infrared Line Exploited for Spectroscopy (AILES) of synchrotron SOLEIL.



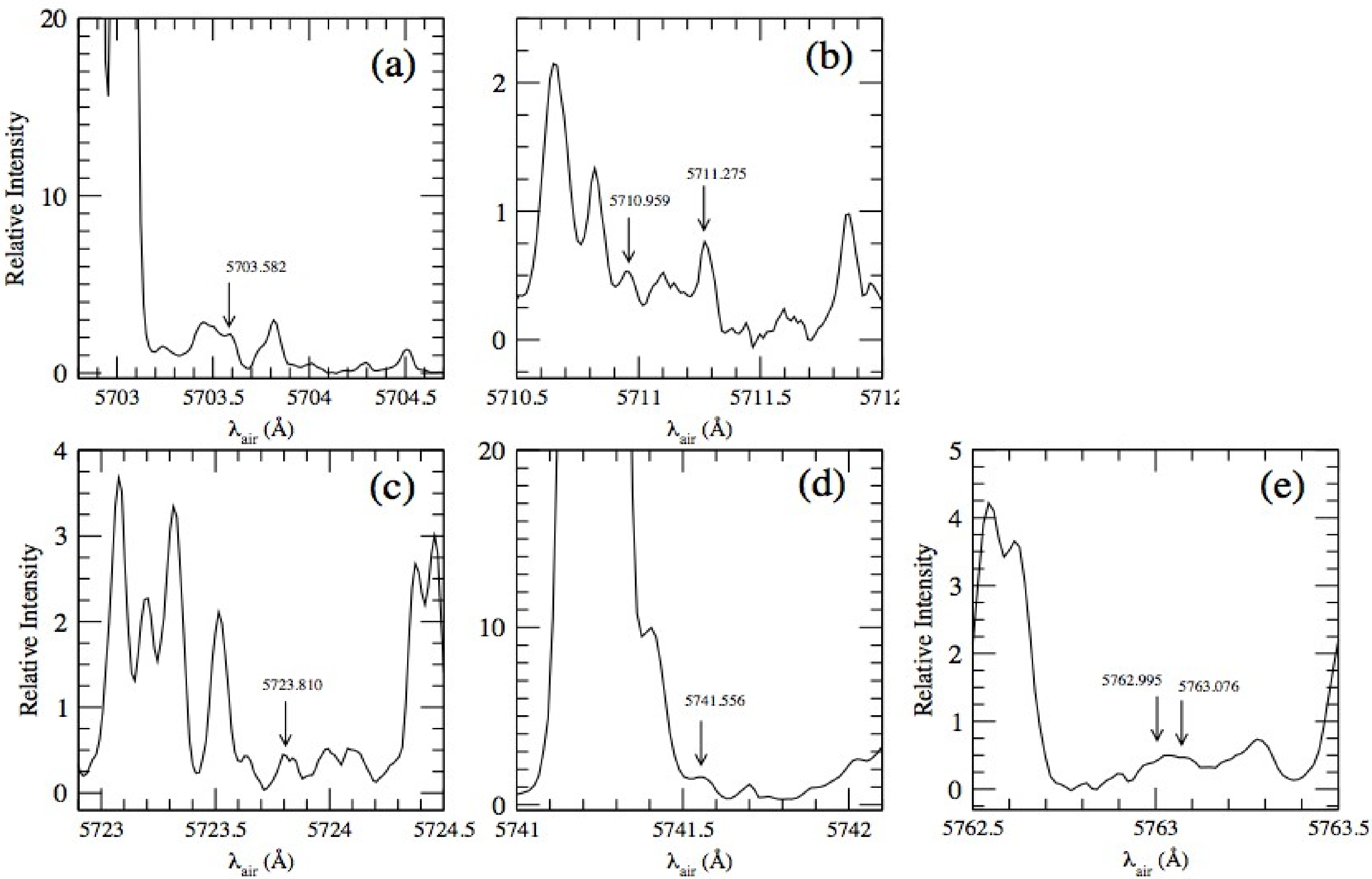


Fourier Transform (FT) Spectroscopy in the range 5550-6250 Å ($16000-18000\ cm^{-1}$) of different products obtained by the dissociation / reactions of $^{15}NH_3$: $^{15}NH_2$, $^{15}N_2$, H_2 and ^{15}NH.

→ observational data: 39 spectra obtained on 12 different comets between 2002 and 2011 with UVES at VLT. R≈80,000

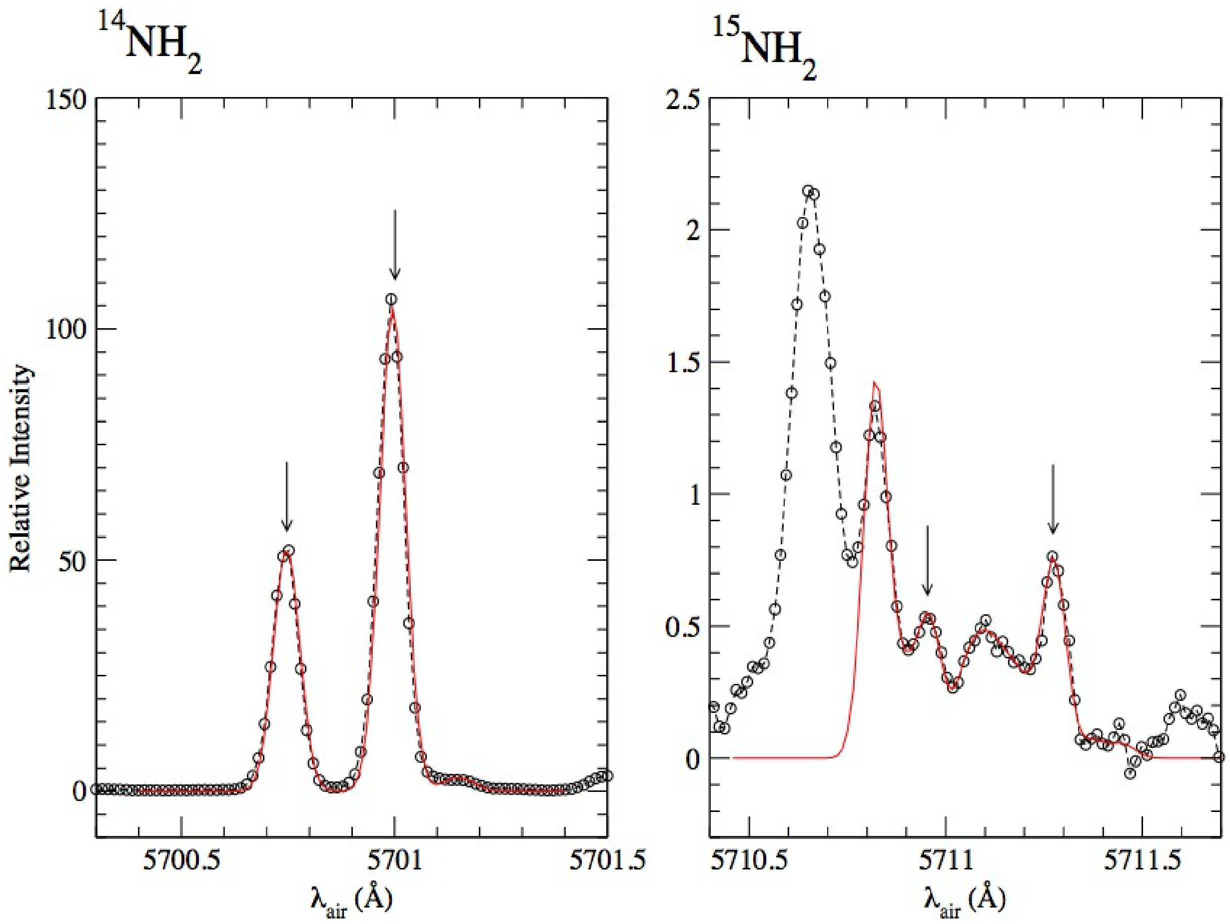
→ all spectra co-added to obtain a very high S/N ratio average spectrum in spectral range studied.

→ positive detection of 7 $^{15}NH_2$ lines



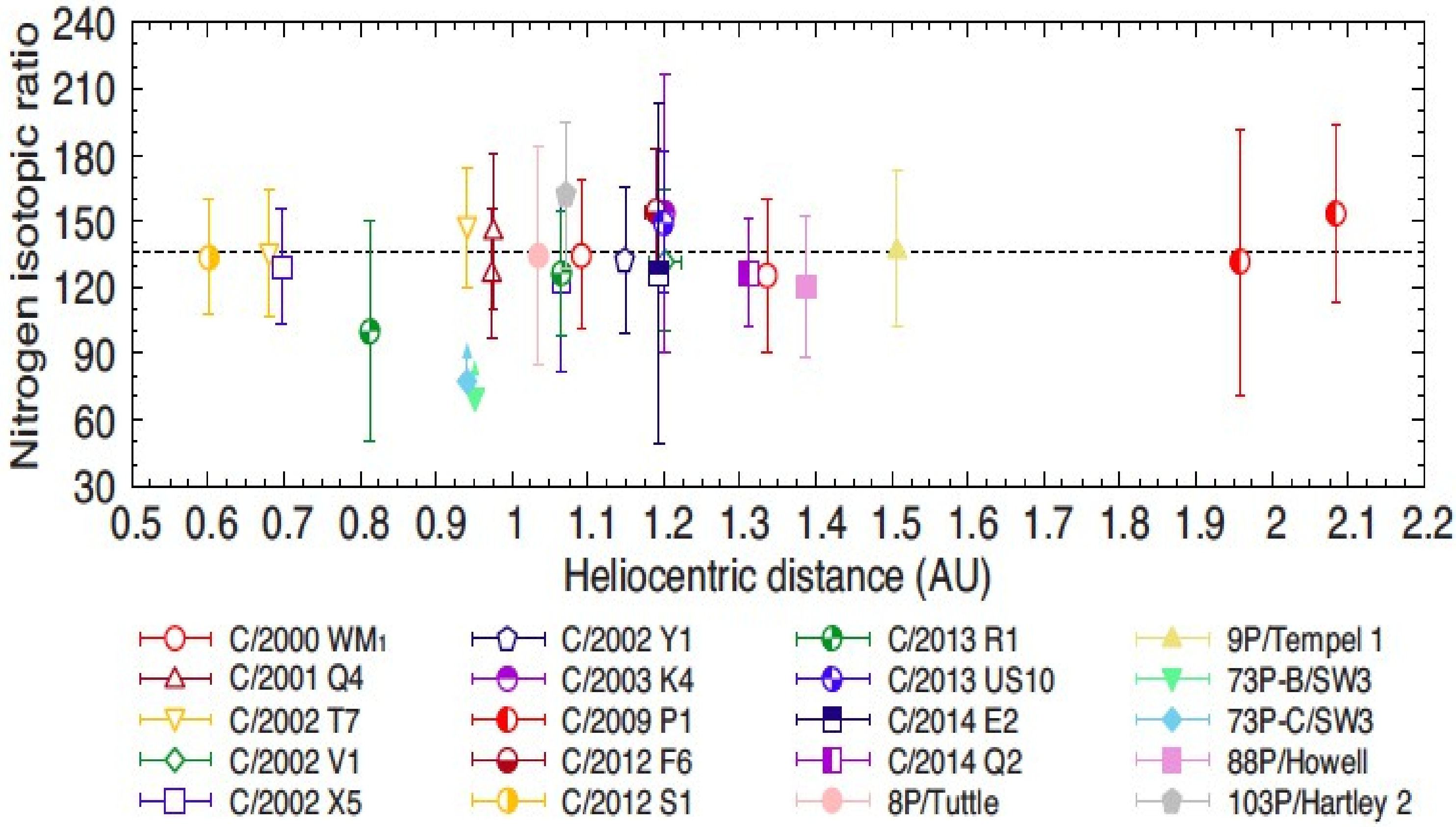
→ **Average $^{14}NH_2/^{15}NH_2$ = 127 ± 32** (Rousselot et al., 2014)

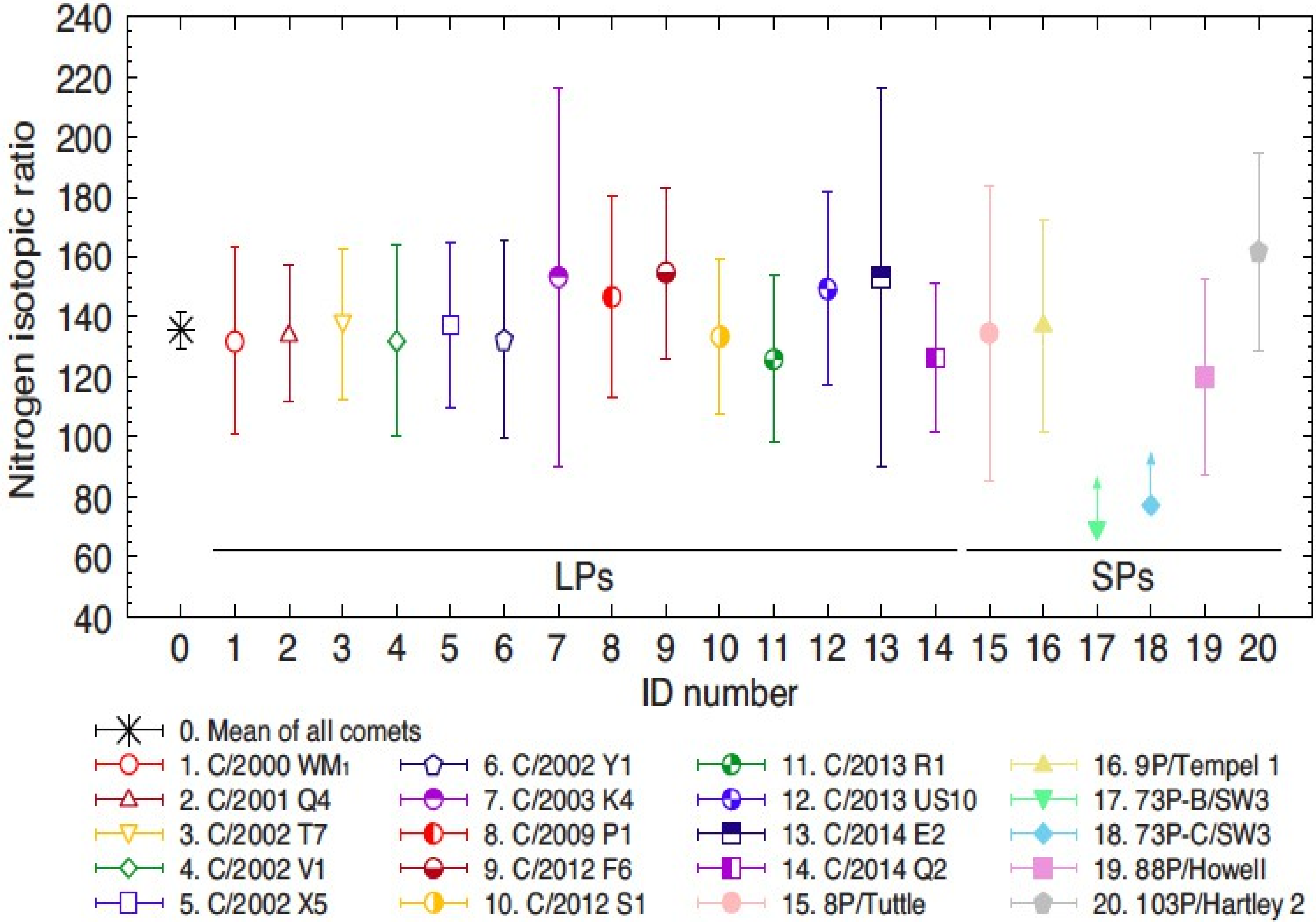
→ Work done without a fluorescence model of $^{14}NH_2$ and $^{15}NH_2$ (complex issue) but realistic because of the numerous comets involved (i.e. range of heliocentric velocities) and lines.

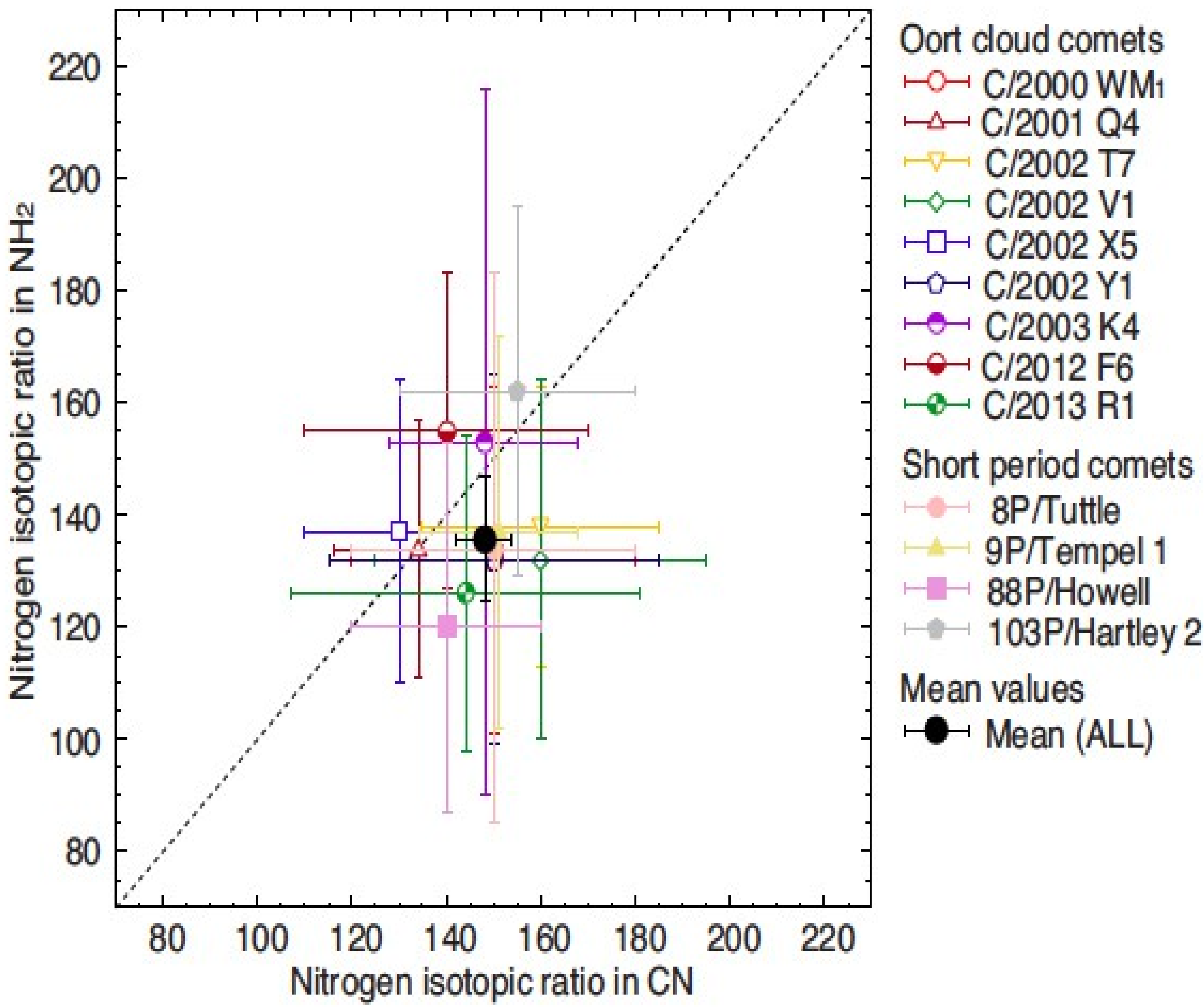


→ Ratio $^{14}N/^{15}N$=139±38 in comet C/2012 S1 (ISON) (Shinnaka et al., 2014) and 126±25 in comet C/2014 Q2 (Lovejoy) (Shinnaka and Kawakita, 2016). Based on the same $^{15}NH_2$ lines, without fluorescence model.

→ Study of individual comets (but still without any fluorescence modeling): Shinnaka et al., 2016. Average mean $^{14}N/^{15}N$=135.7 (18 comets). No variation detected vs comet type or heliocentric distance.




Nitrogen isotopic ratio
240
220
200
180
160
140
120
100
80
60
40
LPs
SPs
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
ID number
0. Mean of all comets
1. C/2000 WM1
2. C/2001 Q4
3. C/2002 T7
4. C/2002 V1
5. C/2002 X5
6. C/2002 Y1
7. C/2003 K4
8. C/2009 P1
9. C/2012 F6
10. C/2012 S1
11. C/2013 R1
12. C/2013 US10
13. C/2014 E2
14. C/2014 Q2
15. 8P/Tuttle
16. 9P/Tempel 1
17. 73P-B/SW3
18. 73P-C/SW3
19. 88P/Howell
20. 103P/Hartley 2



Oort cloud comets
C/2000 WM1
C/2001 Q4
C/2002 T7
C/2002 V1
C/2002 X5
C/2002 Y1
C/2003 K4
C/2012 F6
C/2013 R1
Short period comets
8P/Tuttle
9P/Tempel 1
88P/Howell
103P/Hartley 2
Mean values
Mean (ALL)
Nitrogen isotopic ratio in NH2
Nitrogen isotopic ratio in CN
80
100
120
140
160
180
200
220

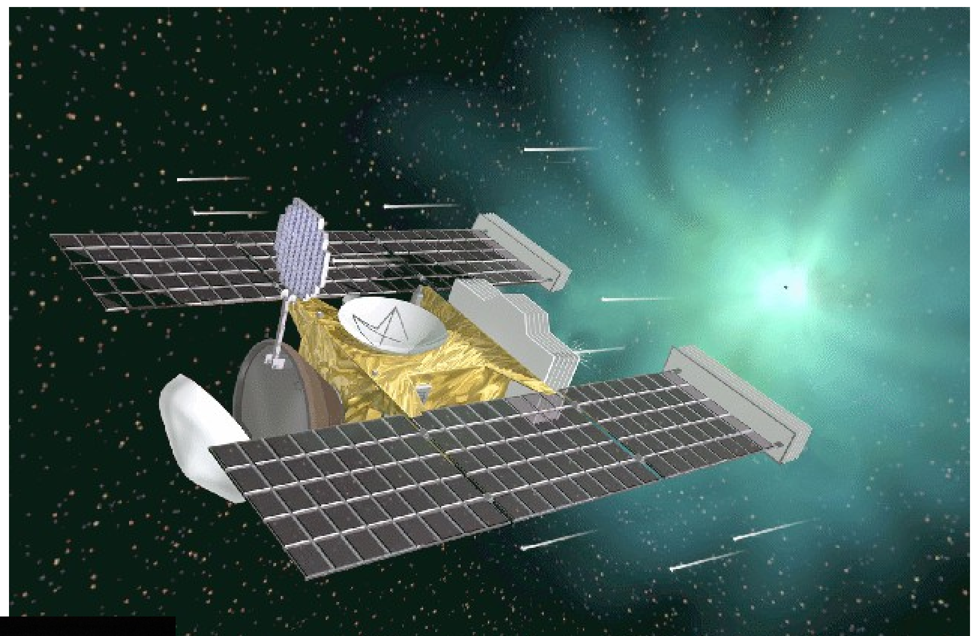
→ Measurement from Rosetta (ROSINA mass spectrometer): $^{14}NH_3/^{15}NH_3 = 118 \pm 27$ (see talk of Suzanne Wampfler this morning).

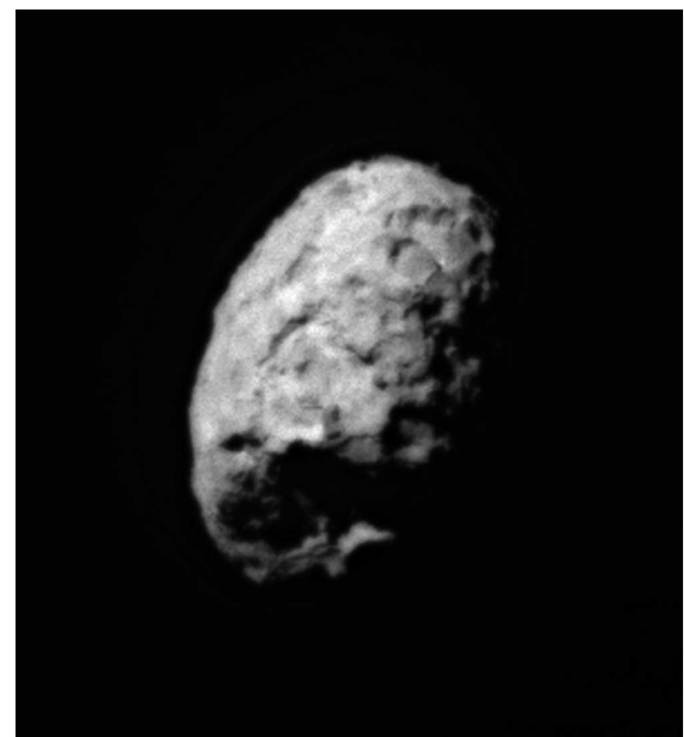
→ Difficult measurement because m/z=18.01 for H_2O and 18.023 for $^{15}NH_3$.

Stardust:

→ NASA spacecraft that flew by comet 81P/Wild 2 on January 2^{nd}, 2004 and collected dust grains.

→ Dust grains landed on Earth on January 15th, 2006.





→ Ice lost, only silicate and metal grains survived.

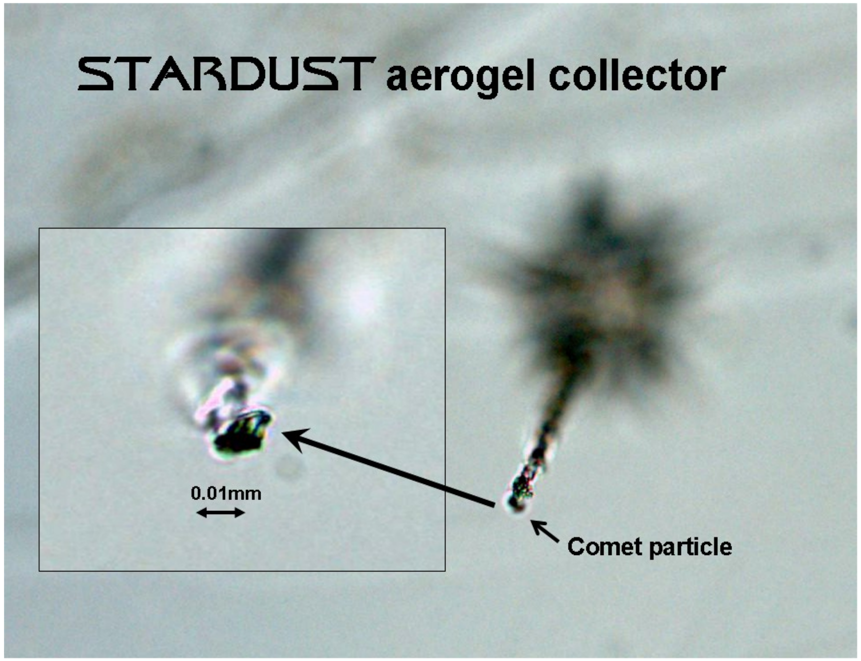
→ Grain composition very heterogeneous.

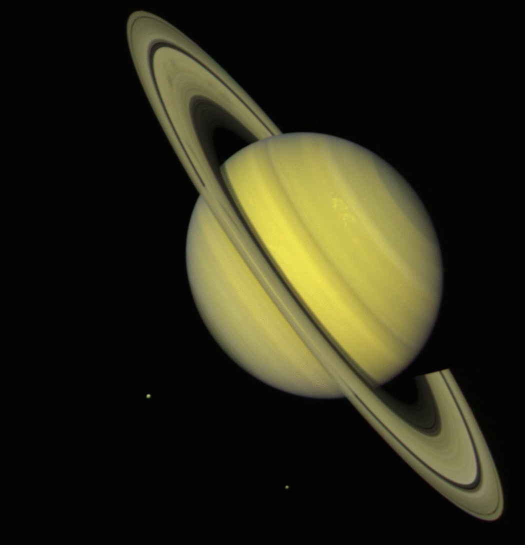
→ Olivine, formed at high temperature (1300 K).

→ Organic materials very volatil that can survive only above 5 au from the Sun.

→ Similarities with meteorites.

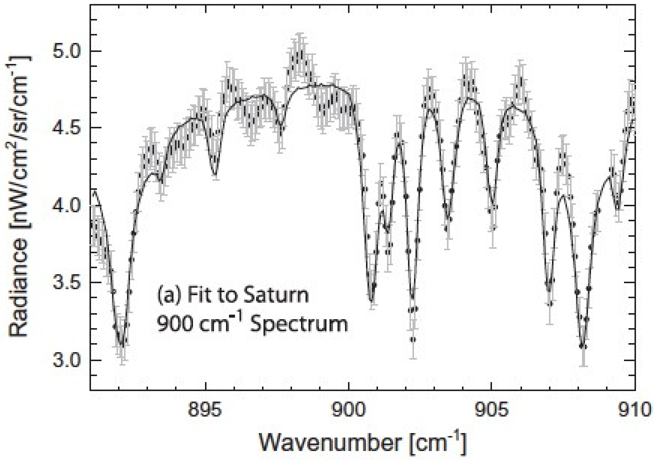
→ Large variation of ^{15}N fraction ($^{14}N/^{15}N$=118-270) including « hotspots » highly enriched in ^{15}N.





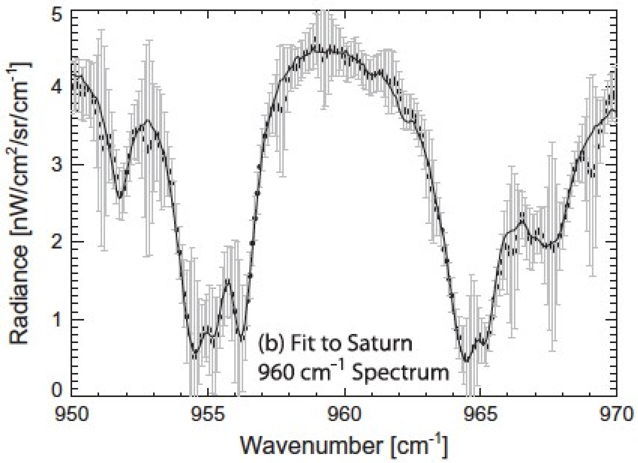
Saturne

→ Only ground-based observations with IR NASA's Infrared Telescope Facility (IRTF) + Texas Echelon cross Echelle Spectrograph (TEXES) for NH_3 (Fletcher et al., 2014):



$^{14}N/^{15}N>500$

$^{15}N/^{14}N<2x10^{-3}$

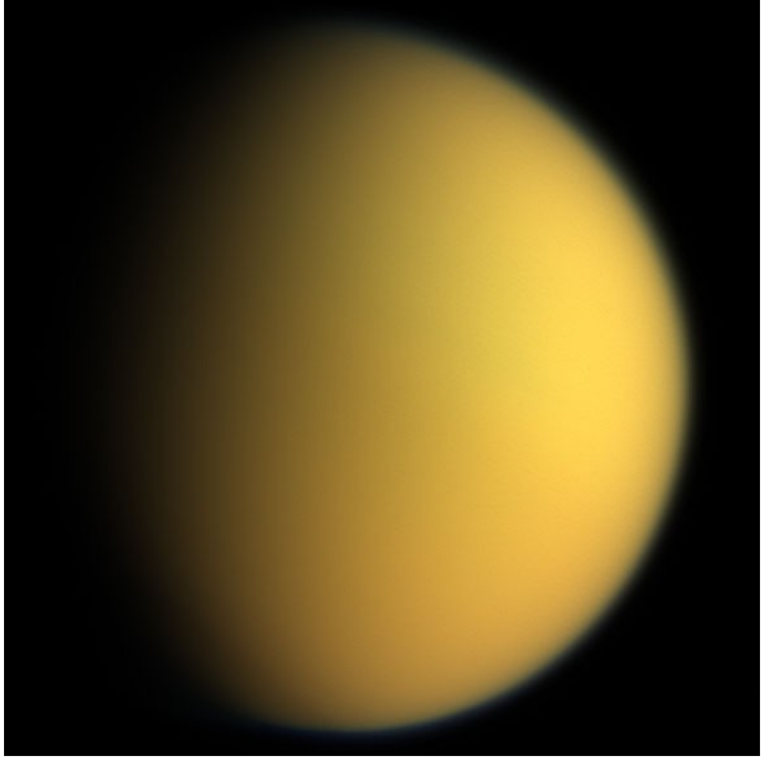


→ Low ^{15}N enrichment favoured accretion of primordial N_2, rather than condensed nitrogen molecules (NH_3, HCN, CN, etc.) with high ^{15}N enrichment.

→ C/N solar for Jupiter but supersolar for Saturn (i.e., Saturn's nitrogen enrichment is lower than its carbon enrichment), implying that the source reservoirs for both planets are not necessarily the same.

→ If both planets formed from a reservoir of cold-trapped N_2 in amorphous ices, we might expect a solar balance of enrichments on Saturn too, which does not appear to be the case.

Titan



→ Nitrogen is abundant in Titan's atmosphere (pressure at ground=1.5 bars):

N_2 = 98.4 %

CH_4 = 1.4 %

H_2 = 0.1-0.2 %

+ trace amounts of ethane, diacetylene, methylacetylene, acetylene, propane, hydrogen cyanide HCN.

→ Voyager remote sensing instruments identified major and minor species constituents in the stratosphere but did not manage to measure isotopic ratios or noble gas concentration.

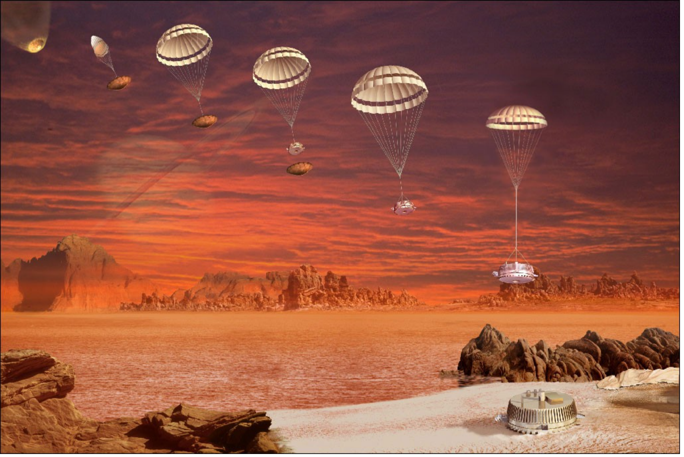
$^{14}N/^{15}N$ from HCN

→ First measurements for $^{14}N/^{15}N$

→ Marten et al., 2002 : $HC^{14}N/HC^{15}N$=60-70 from IRAM submm 30m-telescope (temperature profile based on Voyager observations from Coustenis and Bezard, 1995)

→ Gurwell (2004) : $HC^{14}N/HC^{15}N$=94±13 (with T profile from Coustenis & Bezard) and 72±9 (from T profile based on Voyager radio occultation).

→ Cassini/CIRS limb observations : **$HC^{14}N/HC^{15}N$=56±8** (Vinatier et al., 2007) (T profile from simultaneous CH_4 observations)



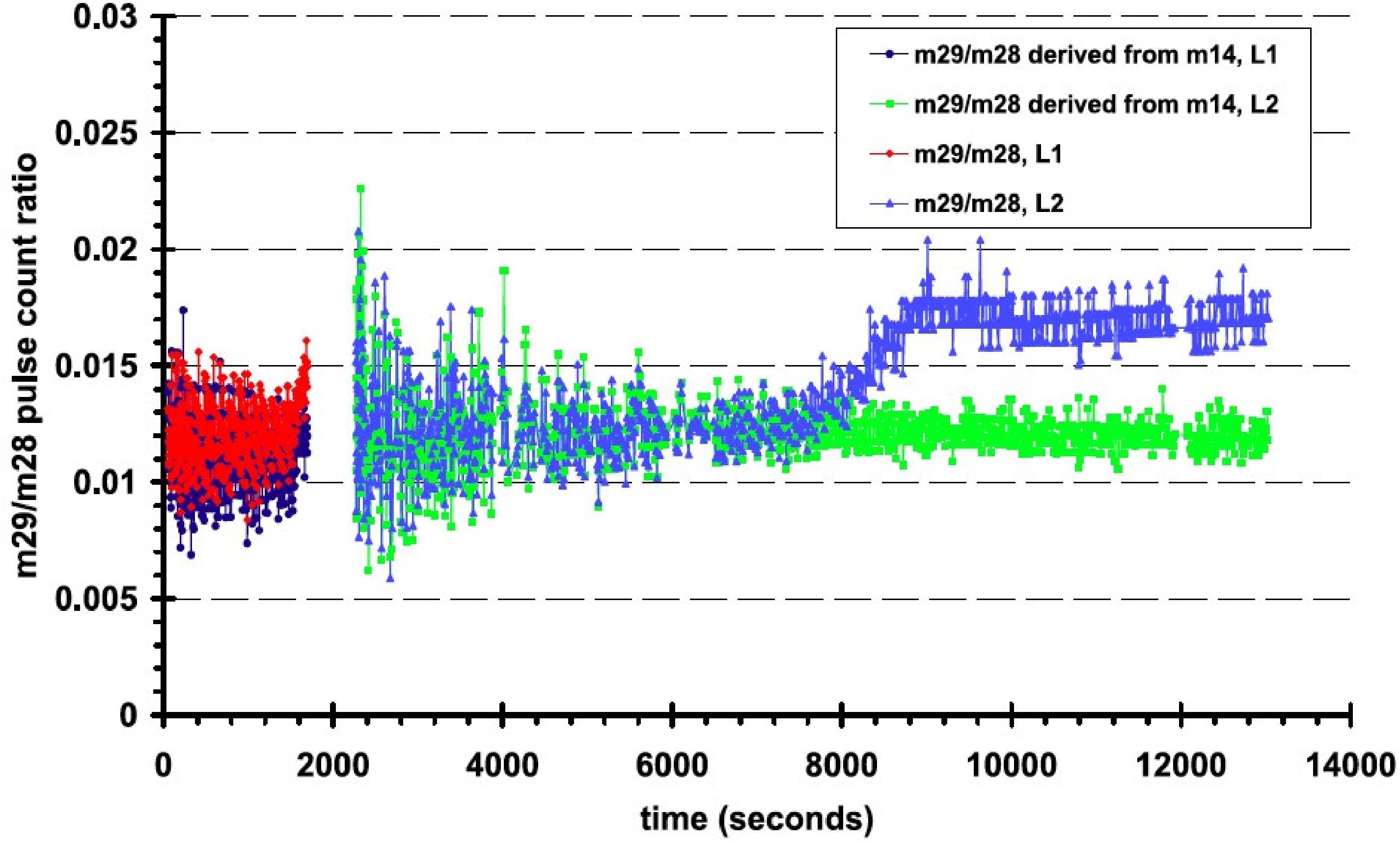
$^{14}N/^{15}N$ from N_2

→ In situ measurement of $^{15}N/^{14}N$ performed during the descent of the Huygens probe sent by Cassini on Titan on January 14th, 2005.

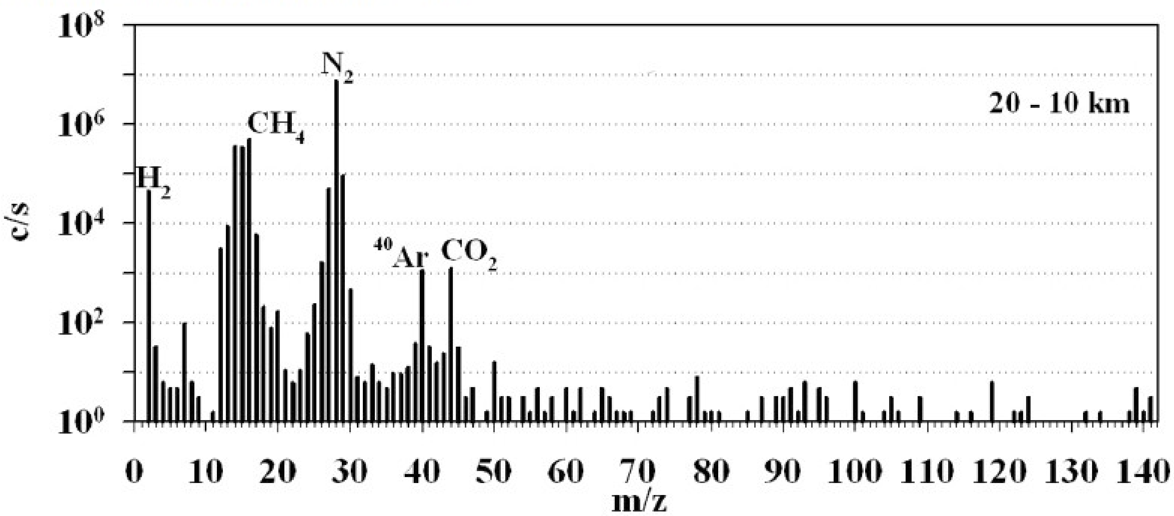
→ Gas Chromatograph Mass Spectrometer (GCMS) on-board Huygens was designed to measure the composition of the ambient atmosphere.

→ Data acquired during 148mn (146 km down to the surface) with additional 72 mn after impact on the ground.

→ $^{14}N/^{15}N$ measured with $^{14}N^{14}N$ and $^{14}N^{15}N$ (and D/H with HD H_2 and $^{12}C^{13}C$ from $^{12}CH_4$ $^{13}CH_4$)



Pulse count ratios of m/z = 29 ($^{15}N^{14}N^{+}$) to m/z = 28 ($^{14}N_2^{+}$) (red and blue) and m/z = 29 to m/z = 14 proxy (black and red) versus time from sequence initiation shown for the leak L1 and leak L2 regions. The increase in the m/z = 29 to m/z = 28 count ratios at ~1500 and 7000 s results from counter saturation at high count rates for m/z = 28.

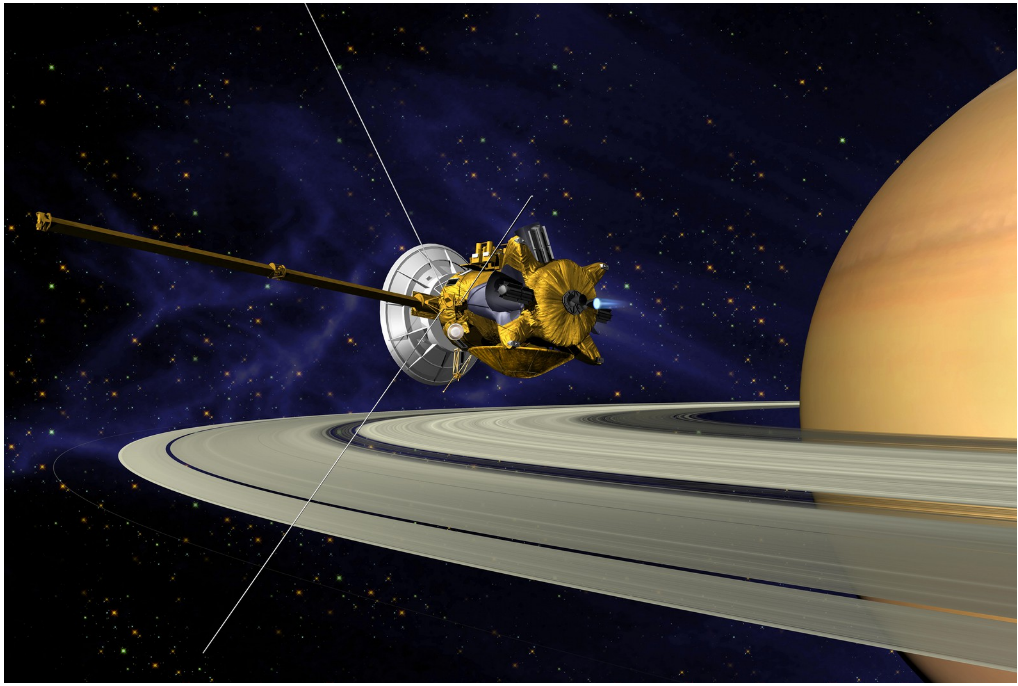


→ Result (average of all data):

$^{14}N/^{15}N = 167.7 \pm 0.6$

$^{15}N/^{14}N = (5.96 \pm 0.02) \times 10^{-3}$

→ Mandt et al. (2009), from data acquired by Cassini Ion and Neutral Mass Spectrometer (INMS) computed a value of $^{14}N/^{15}N=143$ ($^{15}N/^{14}N=7\times10^{-3}$) for the lower, mixed atmosphere.



→ Discrepancy with GCMS results probably due to the model dependant extrapolation of the INMS data from the region of measurements above 1000 km to the homosphere.

→ Mandt et al. (2009) calculated the N isotope fractionation induced by sputtering, thermal and hydrodynamic escape of N: primordial $^{14}N/^{15}N<190$ to fit above value. The initial $^{14}N/^{15}N$ ratio cannot have significantly changed since the formation of Titan.

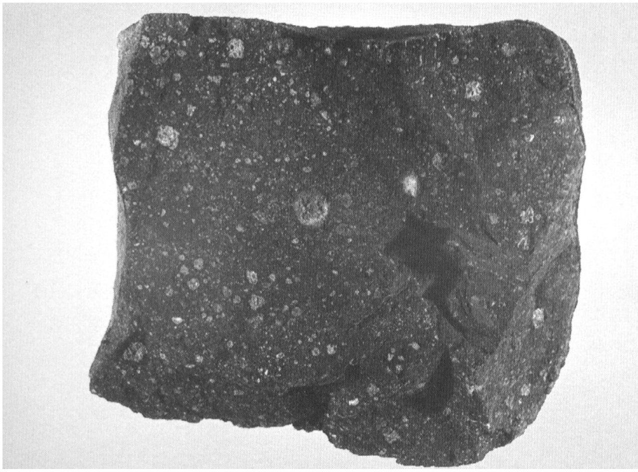
→ Krasnopolsky (2016) computed initial $^{14}N/^{15}N=129$ (in agreement with NH_3 in comets). He also computed present ratio in nitriles, from N isotope fractionation, to be 57, in agreement with HCN.

→ It is generally assumed that N_2 is of secondary origin in this atmosphere and was delivered in a less volatile form, probably NH_3. NH_3 could be converted to N_2 by heating and fireballs during the accretion, thermolysis in the interior and photolysis in the atmosphere.

Meteorites

→ Nitrogen mostly hosted in organics, mainly in insoluble organic matter (IOM) and nitrides, in primitive meteorites.

→ Carbonaceous chondrites :
bulk N isotope composition similar to terrestrial value (within 5%) (except CR carbonaceous chondrite, richer in ^{15}N by up to 25%).



→ A few meteorites (CB-CH group) with bulk ^{15}N enrichements up to 150 %.

→ Isheyevo meteorite: ^{15}N hotspot with the most extreme enrichments found in the solar system ($^{14}N/^{15}N$ as low as 50).

→ ^{15}N hotspots typically found in IOM of primitive meteorites and Interplanetary Dust Particules (<50μm volatile-rich grains snowing onto Earth's surface, some of them probably coming from comets)

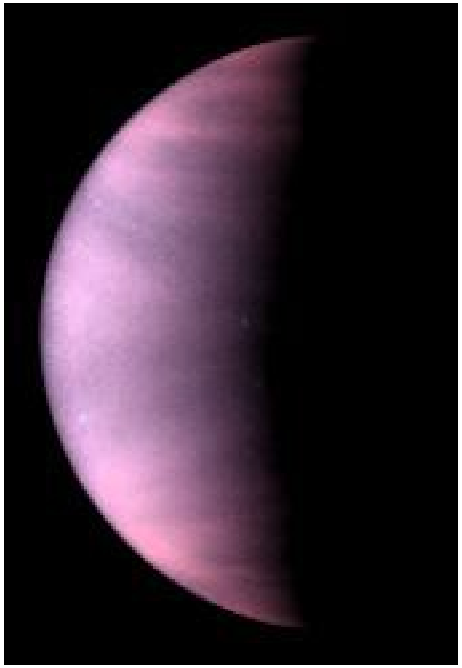
→ $^{14}N/^{15}N=424$ measured in a carbon-bearing titanium-nitride (osbornite) in a calcium-aluminum-rich inclusion (CAI) from the carbonaceous chondrite Isheyevo : formed by gas-solid condensation in a high-temperature (≈2000 K) region of the solar nebula. Because isotopic fractionation at high temperature is small, isotopic compositions of the Isheyevo osbornite are representative of the solar nebula and, hence, of the Sun (Meibom et al., 2016).

Venus

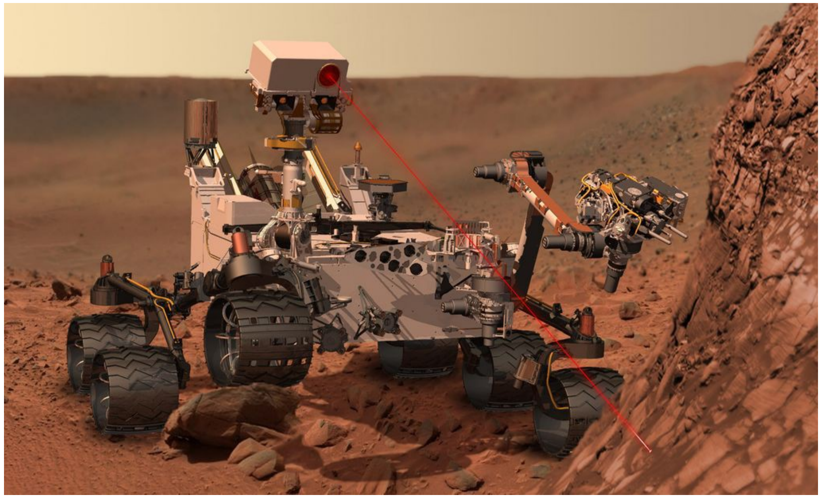
→ Atmospheric measurement done in situ by Pioneer Venus sounder probe with N_2 (Hoffman et al., 1979). $^{14}N/^{15}N$ similar to terrestrial atmosphere, but large uncertainty :

$$^{14}N/^{15}N=272\pm54$$

$$^{15}N/^{14}N=(3.7\pm0.7)\times10^{-3}$$



Mars



→ Measurements done in situ by Mars Science Laboratory (instrument Sample Analysis at Mars, SAM) with N_2 (1.89 % of the atmosphere): $^{14}N/^{15}N=173\pm11$ (Wong et al., 2013).

→ Value in agreement with previous measurement done by Viking : independent measurements of $^{14}N/^{15}N$ were conducted by mass spectrometers on Viking Lander 2 (Owen et al. , 1977; Owen , 1992) and the two Viking lander aeroshells (Nier and McElroy , 1977). The surface and descent measurements found $^{14}N/^{15}N=170\pm15$ and 168 ± 17, respectively.

ALH84001

→ Martian meteorite of 1.93 kg found in 1984 (Antarctica)

→ Formed about 4 Gy before now, in Mars

→ Ejected from Mars 15 millions years ago

→ Fall on Earth 13000 years ago

→ Ancient (4 Gy) Mars atmosphere analyzed from ALH84001 : $\delta^{15}N=7‰$ (Mathew & Marti, 2001)

→ Both ALH84001 and Chassigny (another martian meteorite) show a primitive $\delta^{15}N=-30‰$, probably representative of Mars interior.

→ The enrichment of ^{15}N is due to preferential escape of ^{14}N from the Martian atmosphere (e.g., McElroy et al., 1976; Fox and Dalgarno , 1983; Fox and Ha´c , 1997; Chassefière and Leblanc , 2004).

→ Some models of sputtering and photochemical escape of nitrogen to space suggest that exchange with surface/interior reservoirs is needed to buffer the nitrogen against excessive fractionation due to escape (Jakosky et al., 1994; Zent et al., 1994), leading to a loss of 90% of atmospheric nitrogen over time (Jakosky and Phillips, 2001).

Pluto

→ Only one **lower limit** obtained by ALMA observations of HCN (no detection of $HC^{15}N$) by Lellouch et al., 2017: **$HC^{14}N/HC^{15}N>125$**

→ Translating the result into the bulk $^{14}N/^{15}N$ ratio in Pluto's atmosphere, and ultimately into the $^{14}N/^{15}N$ ratio in the building blocks that formed Pluto, is however a complex problem...

→ This lower ratio excludes, nevertheless a ration similar to Titan in HCN (56).

Conclusion

→ At least 3 isotopic reservoirs in the solar system:

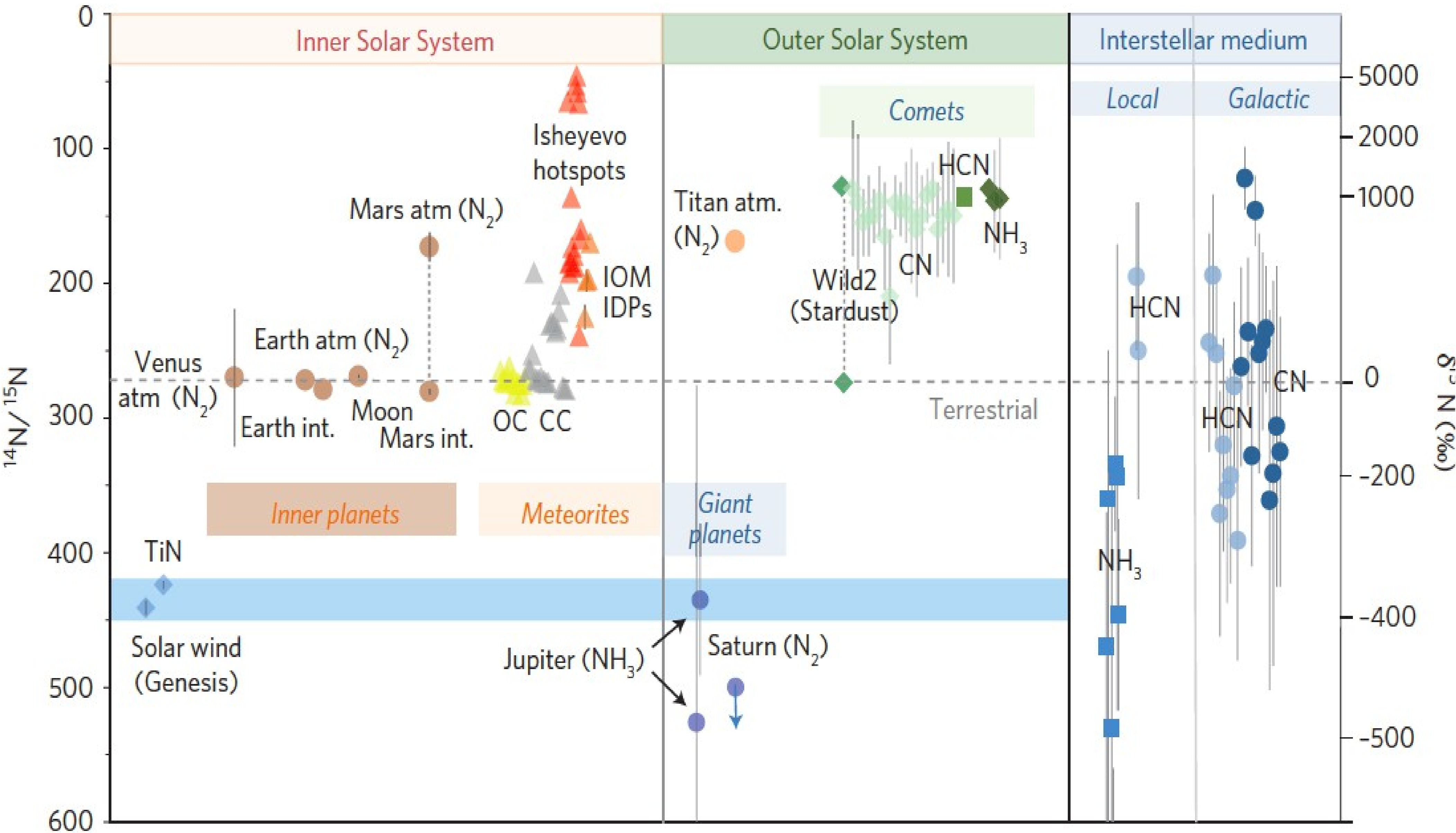
→ PSN poor in ^{15}N ($^{14}N/^{15}N$=441)

→ inner solar system (planets + bulk meteorites) enriched by a factor of 1.6 / PSN ($^{14}N/^{15}N$=272)

→ cometary ices enriched by a factor of 3 / PSN ($^{14}N/^{15}N$=147)

→ ratios ≈ consistent with an increase of ^{15}N with heliocentric distance (qualitative agreement with D/H)

→ Initial homogeneous ^{15}N poor solar system (?)



(Furi et al., 2015)