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APPLIED PHYSICS LABORATORY

Applying Isotopic Fractionation to the Origin and Evolution of volatiles

Case studies for Titan with applications to Io

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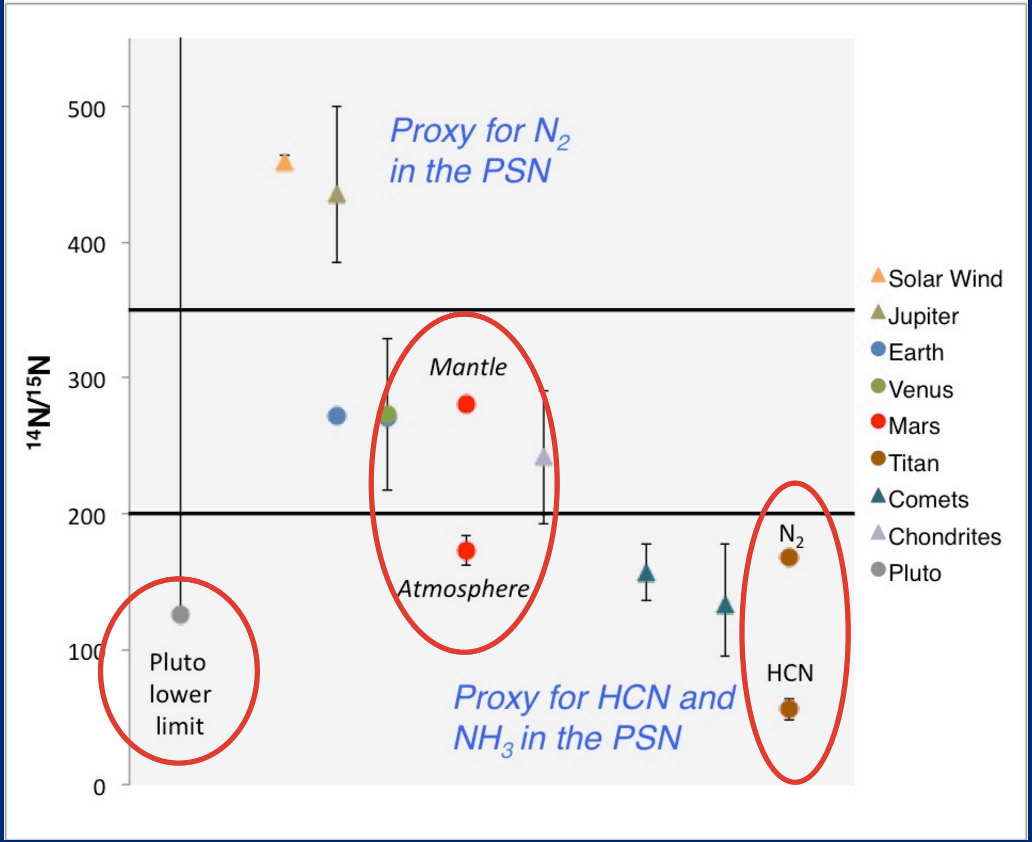
Titan, Pluto, and Mars: What is the origin of nitrogen and how has it evolved?



Adapted from Mandt et al. (2017)

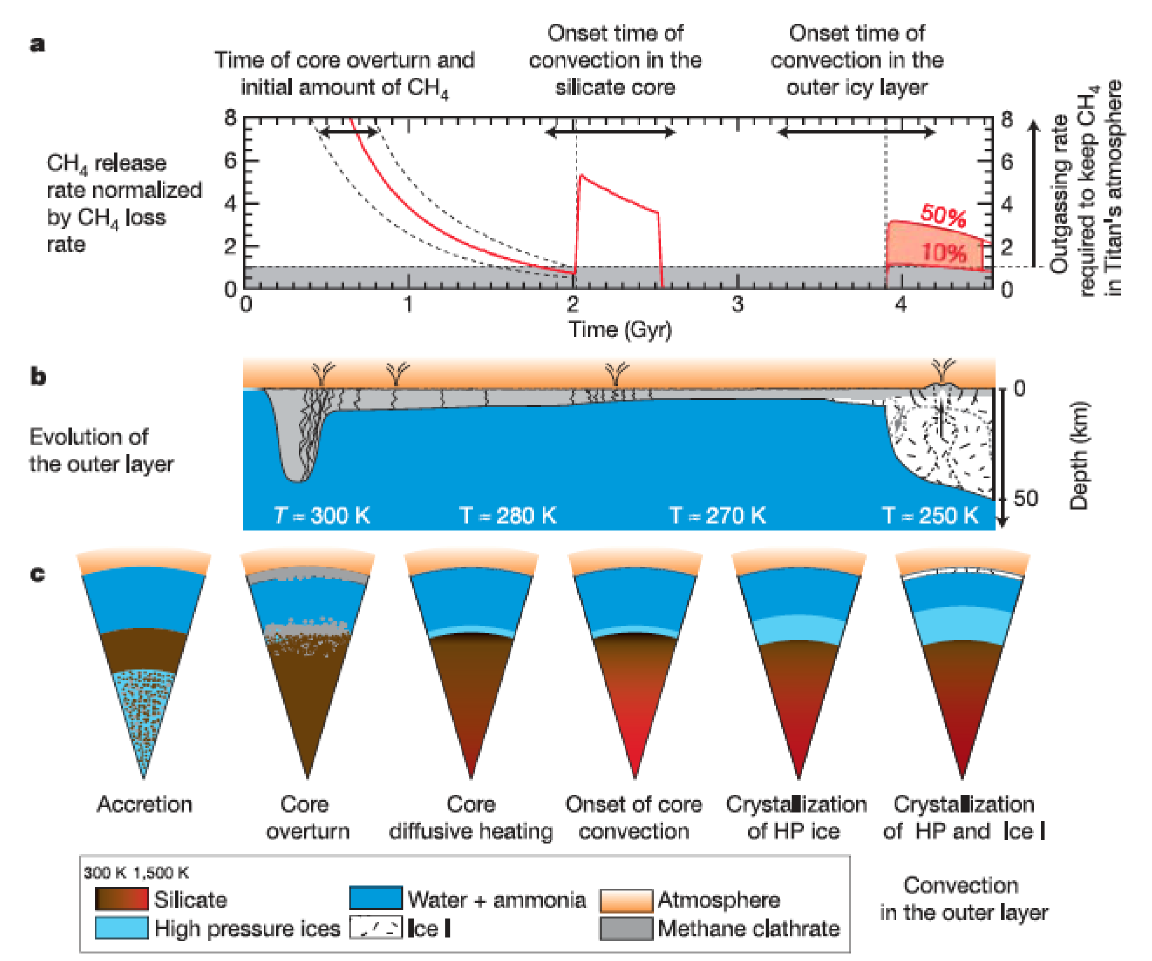
- Primordial (triangles) ratios represent values preserved from the Protosolar Nebula (PSN)
  - Jupiter
  - Solar Wind
  - Comets
  - Meteorites
- Evolved (circles) ratios have changed over time
  - Terrestrial planets and Titan
- Objectives
  - Determine origin of Titan's nitrogen
  - Compare how Titan evolves with Mars
  - Can the lower limit for Pluto be used to determine the origin of its nitrogen

We have looked at how the nitrogen ratio changes over time to study the formation conditions of Titan and Pluto

Titan: How long has methane been present in the atmosphere?

Tobie et al. (2006)

- Photochemistry rapidly destroys methane
- Titan's interior has evolved over time
- Outgassing rates of methane may not have been constant
- Primordial $^{12}C/^{13}C$ is limited to a narrow range
- Objectives
  - Determine how long the current inventory of methane has been present in the atmosphere
  - Determine limits for the primordial D/H in methane
  - Determine the total production of organics



The Carbon ratio in methane is a useful tool for understanding the history of outgassing activity at Titan

Modeling the evolution of an atmosphere

$$\frac{dn}{dt} = P - L$$

- The inventory of a constituent varies over time based on production and loss processes
- Fractionation occurs when there is a difference in the relative production or loss rates of constituents and their isotopes
  - e.g. Escape – The lighter isotope escapes more easily than the heavier, resulting in a lighter ratio over time
- Fractionation changes the measured ratio in an atmosphere over geologic time scales

$$f = \text{fractionation factor}$$

Modeling how an atmosphere evolves requires understanding production and loss processes and how they differ between isotopes

Outputs of modeling the evolution of the isotopic ratios

Time scale

- The time scale can be derived by integrating the production and loss equation over time for both the light and heavy isotopes

$$dn/dt = P - L$$

Total Inventory

- The fractionation factor defines the total amount of a species fractionated using the Rayleigh distillation relationship

$$\frac{n_1^0}{n_1} = \left(\frac{R}{R_0}\right)^{(1/(1-f))}$$

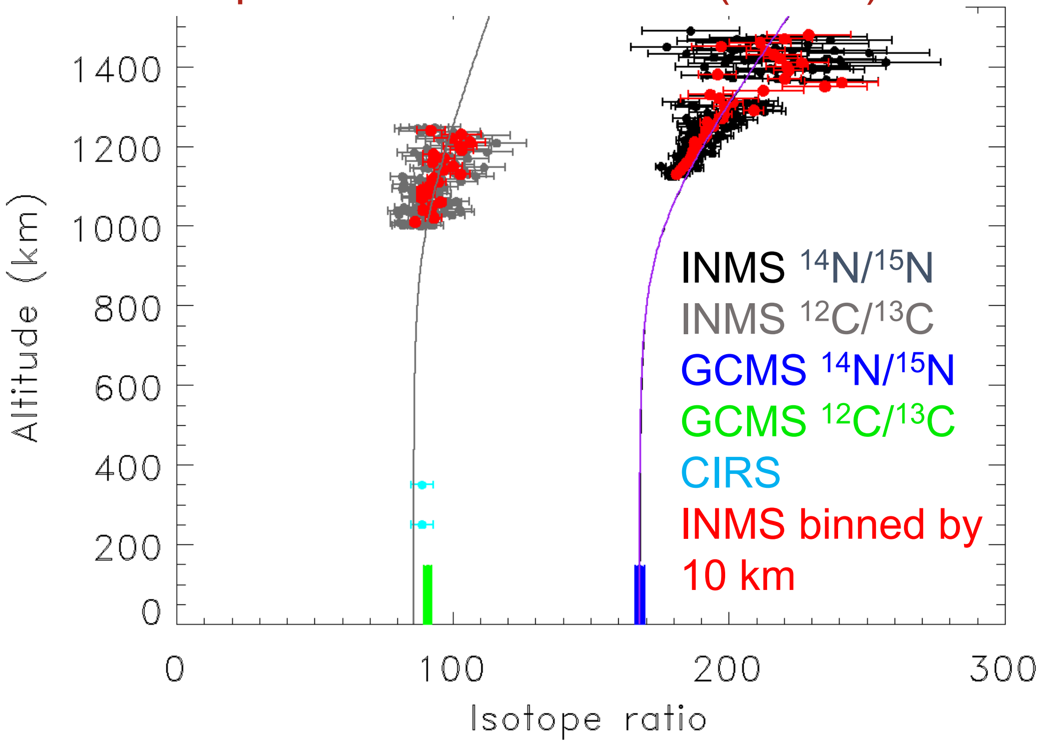
Initial Ratio

- If the initial ratio is not known, but the processes are well-understood, upper and/or lower boundaries can be determined
- Determining an initial ratio has implications for the formation of Titan

Different inputs are required depending on the outputs sought from the model

Determining the fractionation factor using observations: Atmospheric Escape

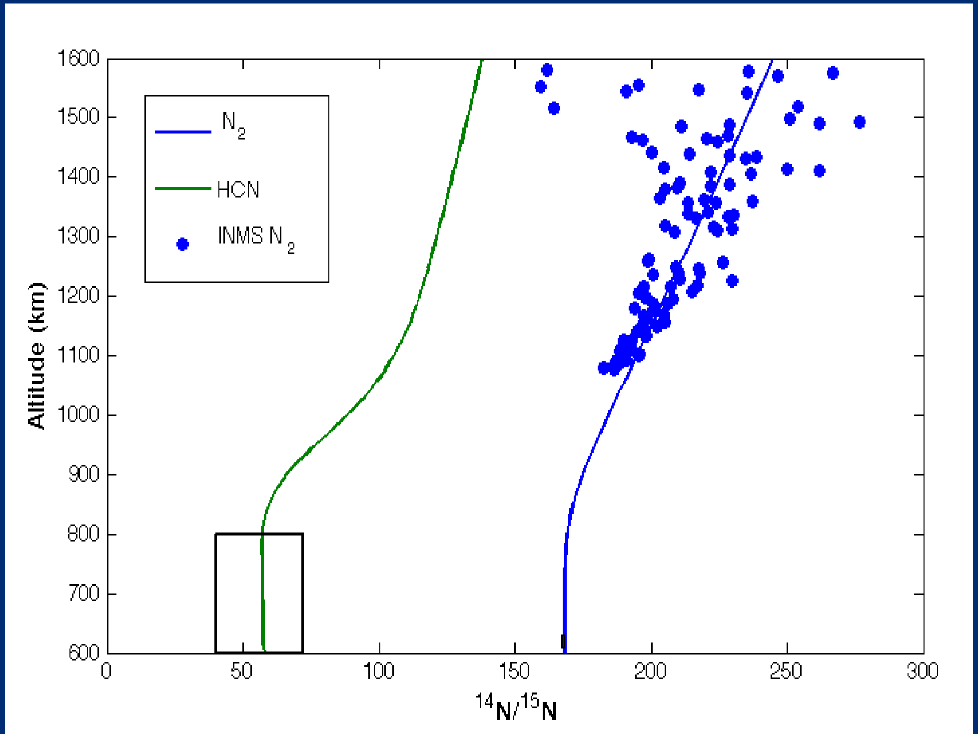
Adapted from Mandt et al. (2012a)



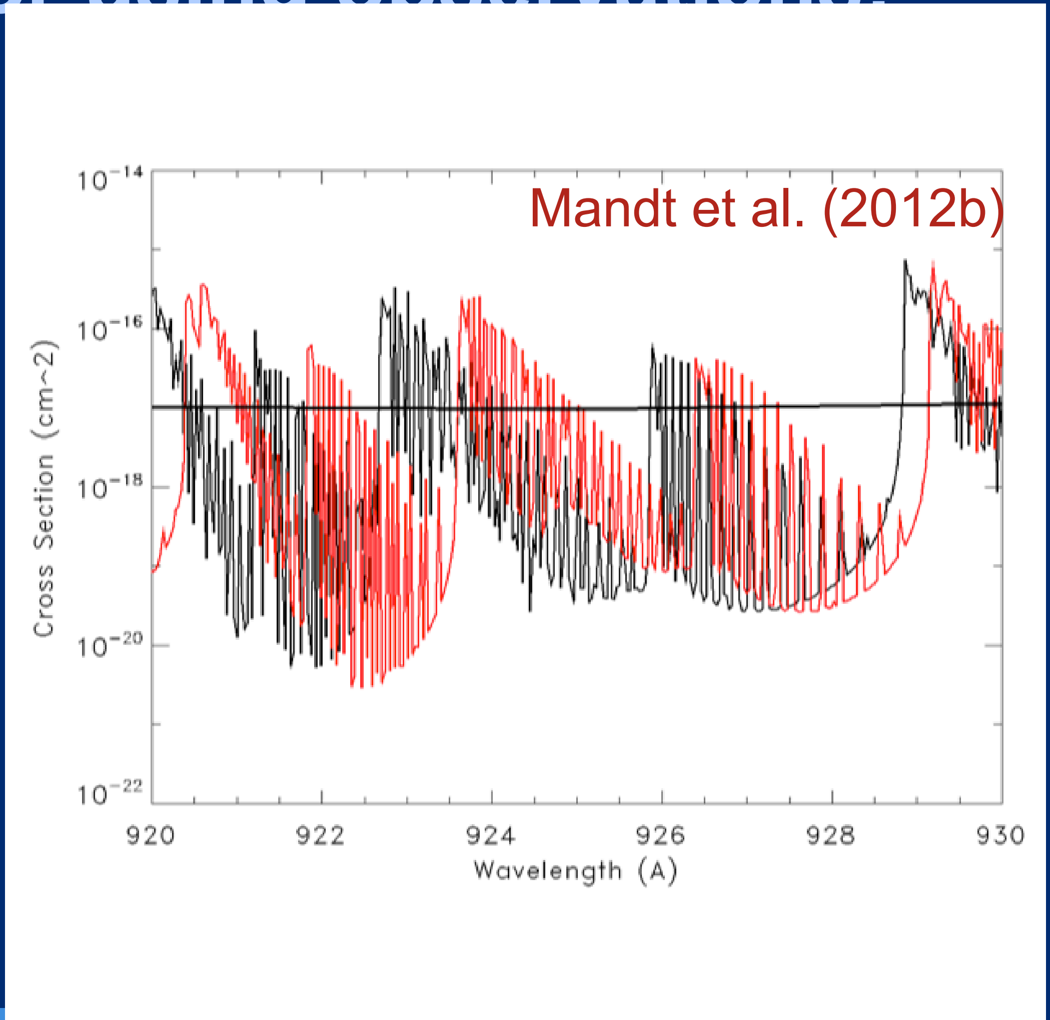
- Can determine *f* with isotope ratios at different altitude
- At Titan used observations from multiple instruments compared with model
  - Cassini Ion Neutral Mass Spectrometer (INMS) above 1000 km
  - Cassini Composite Infrared Spectrometer (CIRS) between 200 and 400 km
  - Huygens Gas Chromatograph Mass Spectrometer (GCMS) at the surface
- Only observation for Pluto is a lower limit on the amount of $HC^{15}N$ present – Pluto is currently unconstrained

The Cassini-Huygens mission provided direct observations of diffusive fractionation

Determining the fractionation factor using observations: Photochemistry



- Offset in wavelength of nitrogen photoabsorption cross sections
- Self shielding fractionation
- Creates large difference between N_2 and HCN



Self shielding in the photodissociation of N_2 leads to a much lower $^{14}N/^{15}N$ in HCN

Two methods available for determining photochemical fractionation

- Model the loss of $^{14}N_2$ and $^{14}N^{15}N$ with validation

$$f = {L_2}/{L_1} \cdot {1}/{R}$$

- Observations of $^{14}N/^{15}N$ in N_2 and a photochemical product

$$f = \frac{R_{\text{reactant}}}{R_{\text{product}}}$$

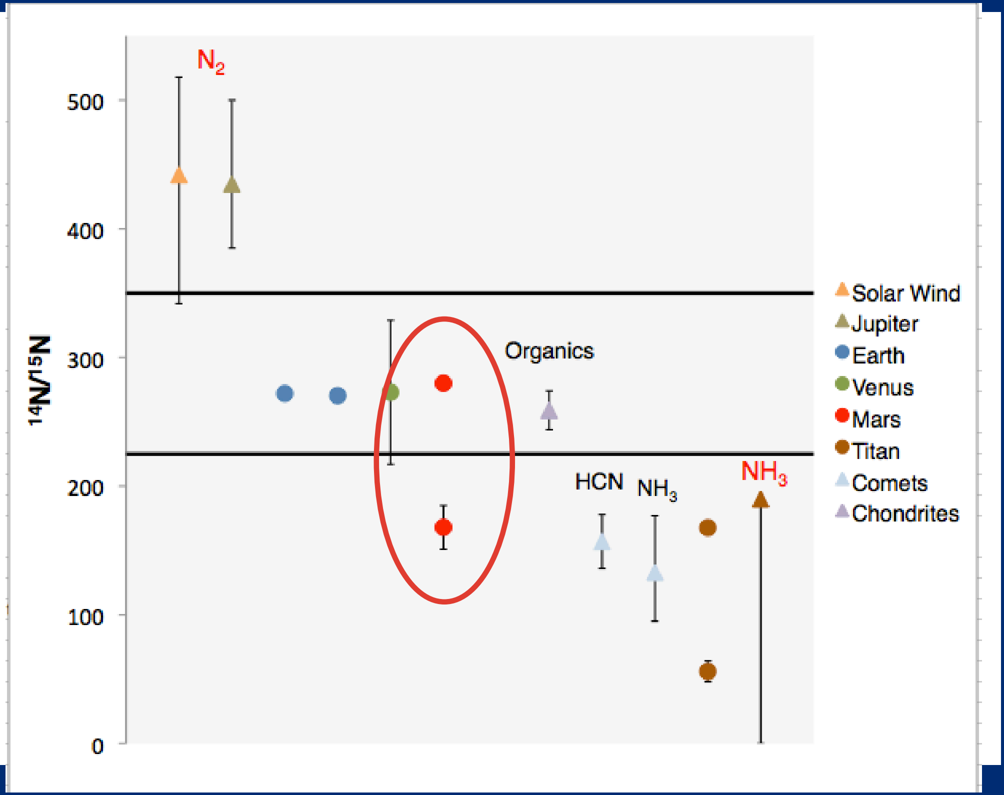
- Both methods have limitations

Table 1: Input parameters needed to calculate photochemical fractionation
$^{14}N_2$ Production ($cm^{-3}\ s^{-1}$)
$^{14}N_2$ Loss ($cm^{-3}\ s^{-1}$)
$^{14}N^{15}N$ Production ($cm^{-3}\ s^{-1}$)
$^{14}N^{15}N$ Loss ($cm^{-3}\ s^{-1}$)
$^{14}N/^{15}N$ in column density of N_2
$^{14}N/^{15}N$ in column density of HCN
$^{14}N/^{15}N$ observed in HCN
f based on HCN
f based on loss rates

Using models to determine fractionation is complicated, while observations can capture processes that may be missing from models.

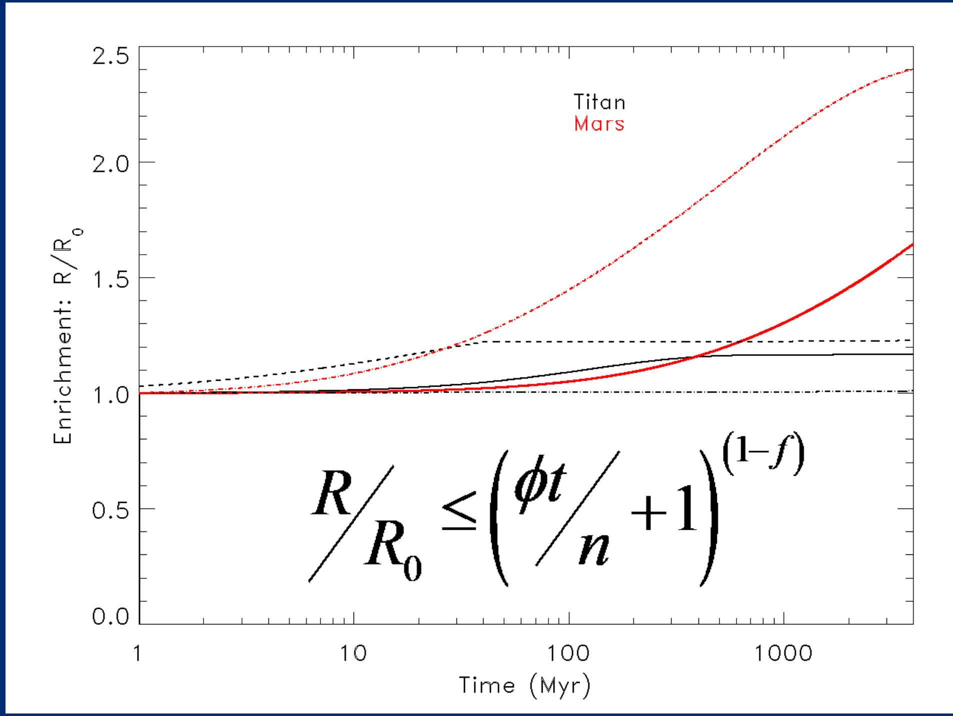
Titan: Can the primordial value be terrestrial?

Mandt et al. (2014)



- Titan
  - Origin of nitrogen is based on the primordial ratio
  - Look for upper limit – only evaluate escape
  - Upper limit is within comet range for NH_3
- Mars
  - Titan can't evolve much, but Mars did
  - Loss rate relative to column density is much larger than Titan's

Mandt et al. (2015a)

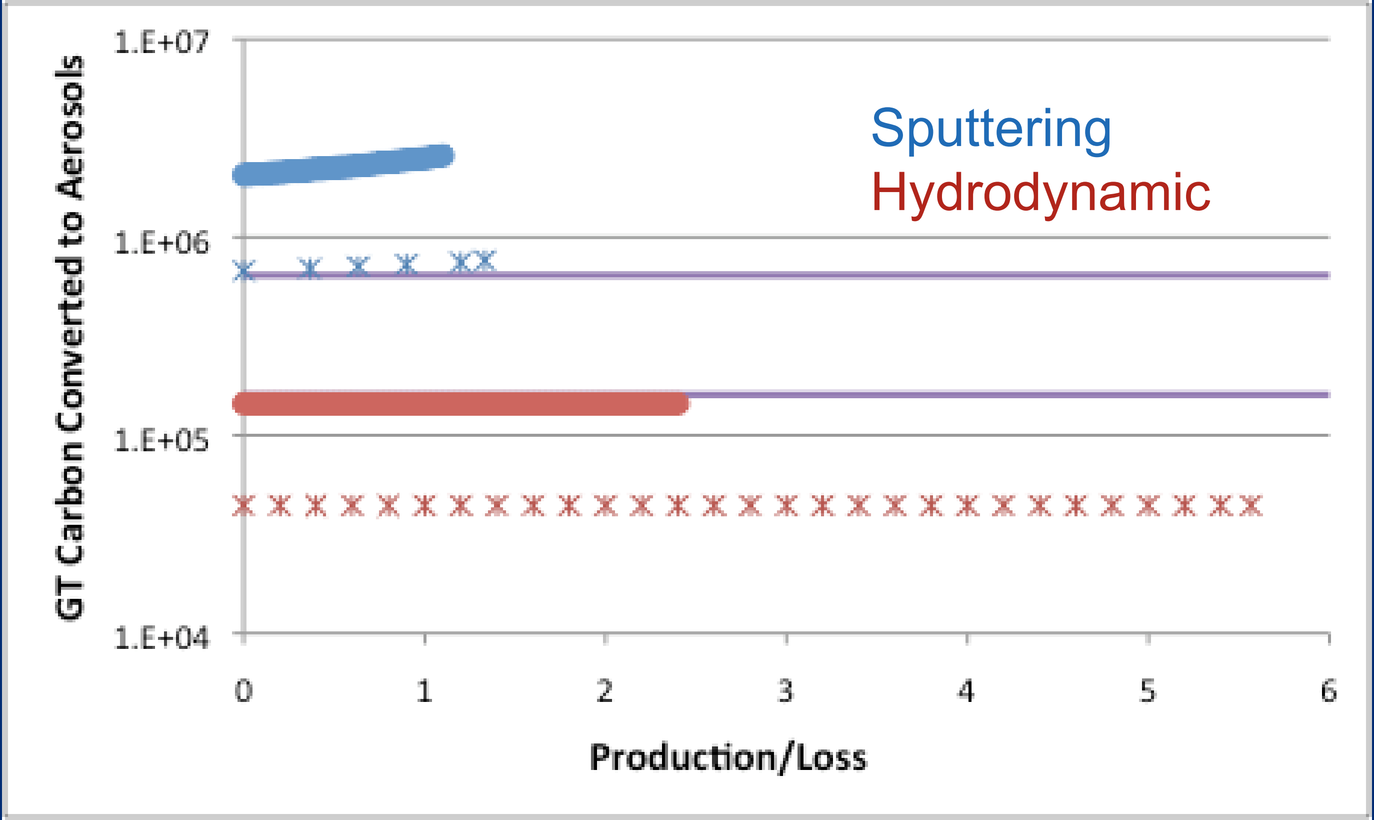


Upper limits for escape fractionation limit evolution of nitrogen at Titan but allow evolution of nitrogen at Mars

Titan: How long has methane been present in the atmosphere?

- Results depend on the relative loss rate compared to production (cryovolcanism)
- Two possible current $^{12}C/^{13}C$ based on INMS (stars) and GCMS (circles)
- Timescales
  - Upper limit based on ratios is less than 500 Myr
  - Steady state upper limit is 1 Byr based on amount of methane currently present
- Primordial D/H higher than protosolar value (purple line) but lower than Enceladus (green line)
- Amount of carbon converted to aerosols compared to estimates of surface inventories (Lorenz et al. 2008)

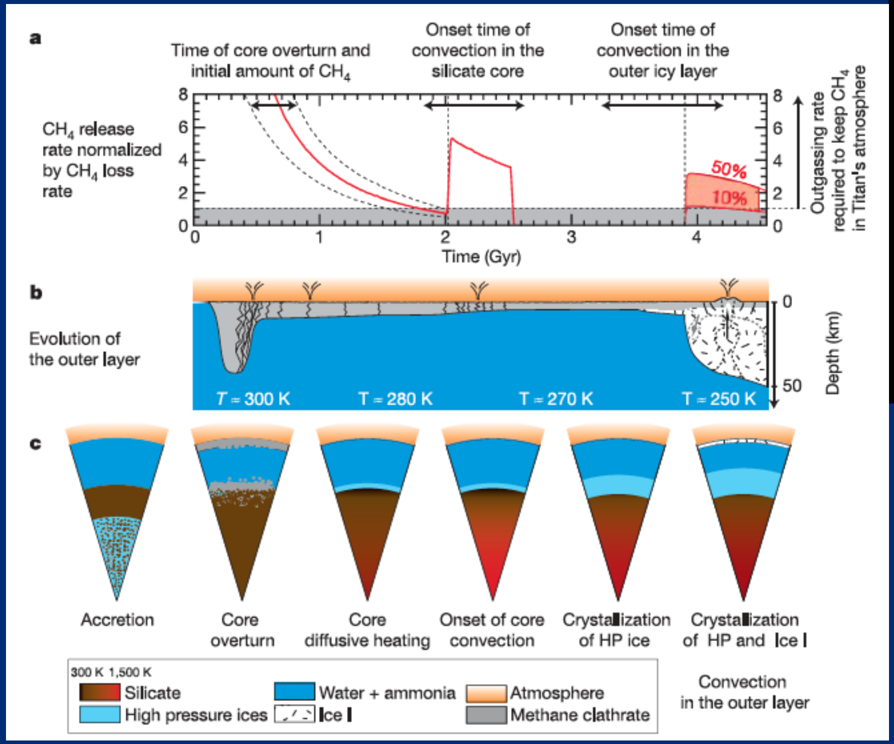
Mandt et al. (2012a)

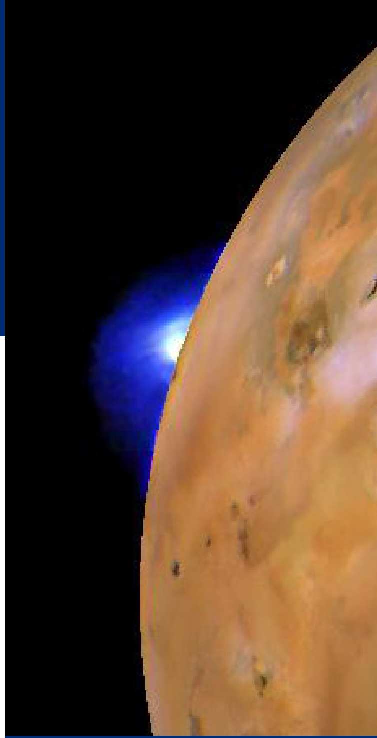


If methane is outgassed at a large enough rate to create a steady state in the isotope ratio, the amount of methane in the atmosphere must increase over time

Applying this methodology to understanding the history of Io

- Tidal heating of Galilean moons
  - Decreasing with distance from Jupiter
  - Extensive volcanism on Io
  - Europa, Ganymede and Callisto have retained substantial amounts of water ice
- Burning questions
  - Did Io form as a mostly rocky moon, or did it form with large amounts of ice like other giant planet moons?
  - How much water and other volatiles were lost from Io due to tidal heating?
  - What volatiles remain in trace quantities?



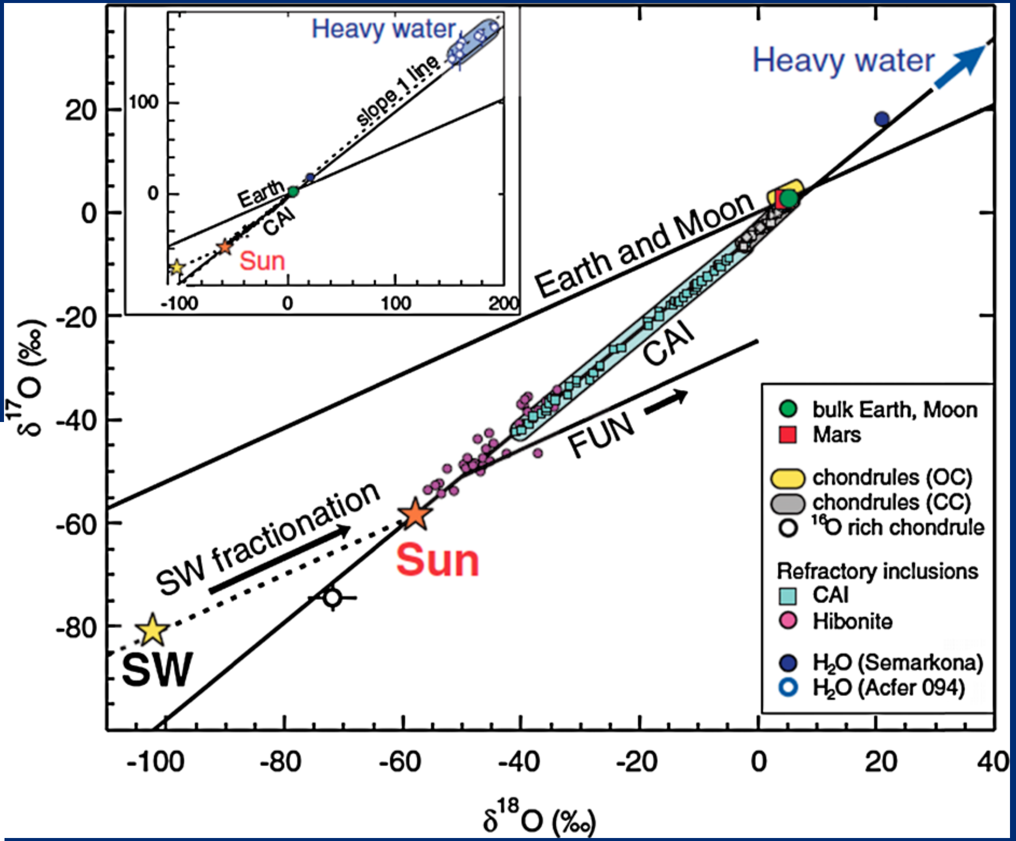


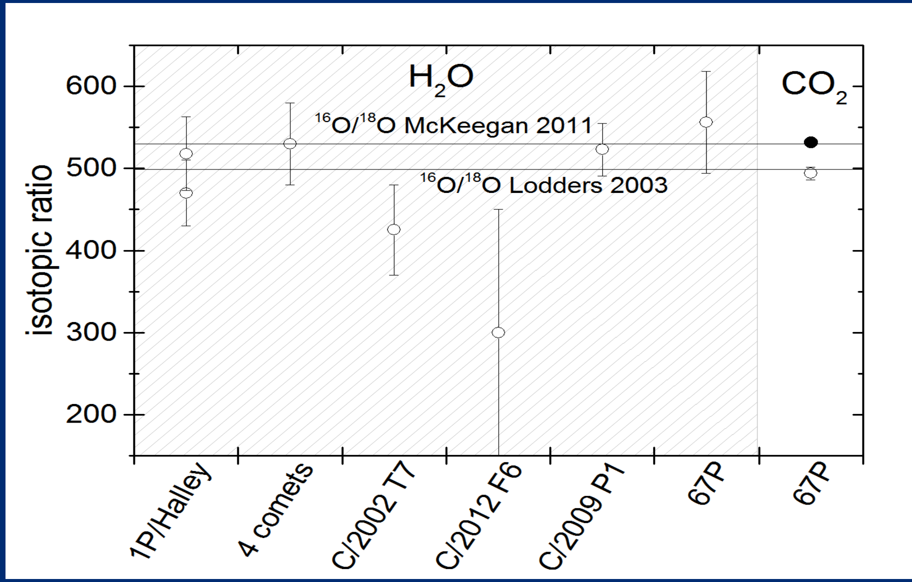
We have used isotopes to constrain how the interior of Titan has evolved over time. Can we do the same with the interior of Io?

Observable isotopes at Io: Oxygen

- Sublimated atmosphere:
  - Isotopes will have evolved by chemistry, escape, condensation and sublimation since first outgassed
  - Known: SO_2, S_2, O_2
  - Are there any noble gases, carbon- or nitrogen-bearing constituents?
- Volcanic plumes:
  - Primordial or evolved?
  - Expected: SO_2, S_2, O_2, KCl, NaCl
  - Same question
- Isotopes to target
  - $^{17}O/^{16}O$ and $^{18}O/^{16}O$
  - ^{32}S, ^{33}S, ^{34}S, ^{36}S
  - Na, Cl and K isotopologues
  - Others?

Inventory of pre-Rosetta Oxygen isotopes from Mandt et al. (2015b)



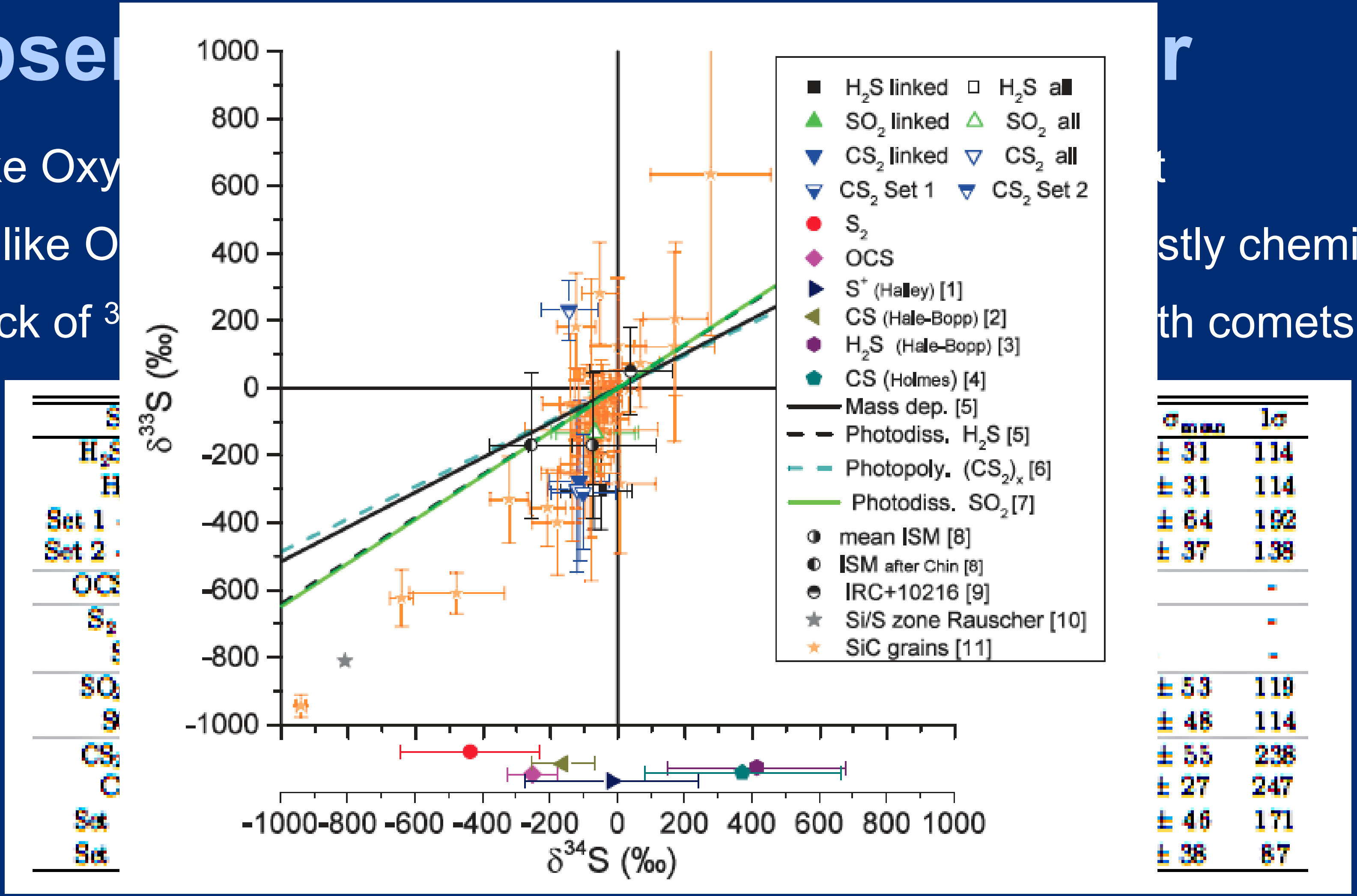


Rosetta determinations so far from Haessig et al. (2017)

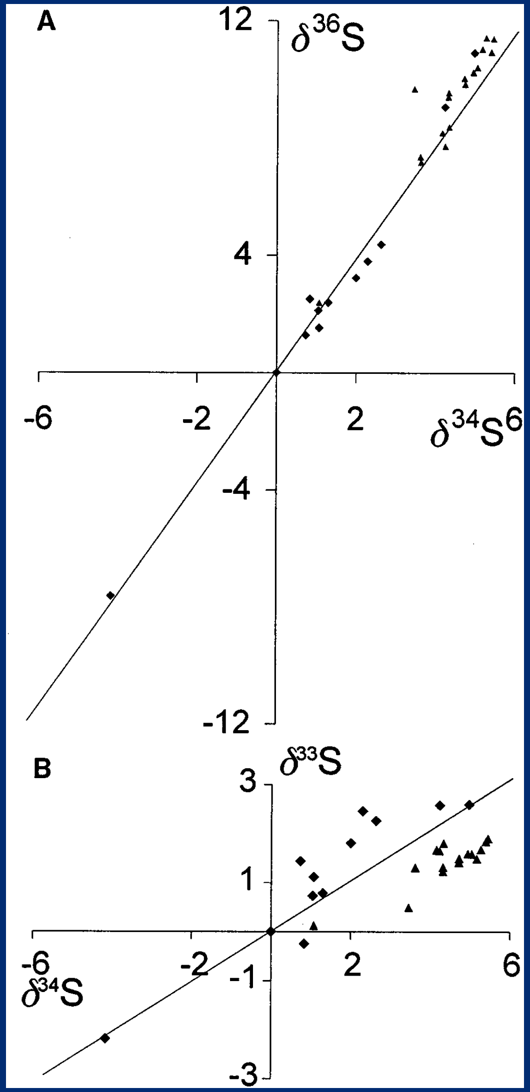
Oxygen isotopic state is very process dependent. Comet observations suffer from large uncertainties and lack of ^{17}O.

Obse r

- Like Oxy t
- Unlike O stly chemical
- Lack of 3 th comets



Rosetta Sulfur isotopes from Calmonte PhD thesis (2017)

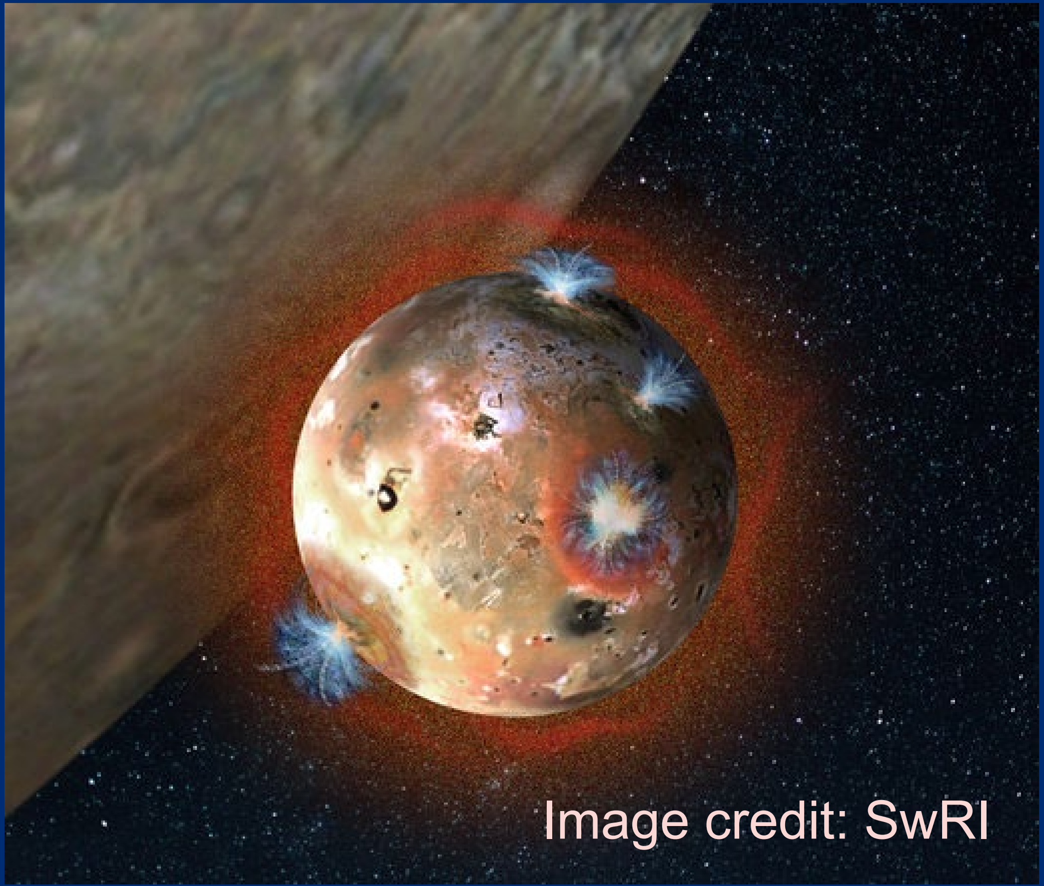


Inventory of pre-Rosetta Sulfur isotopes from Mandt et al. (2015b)

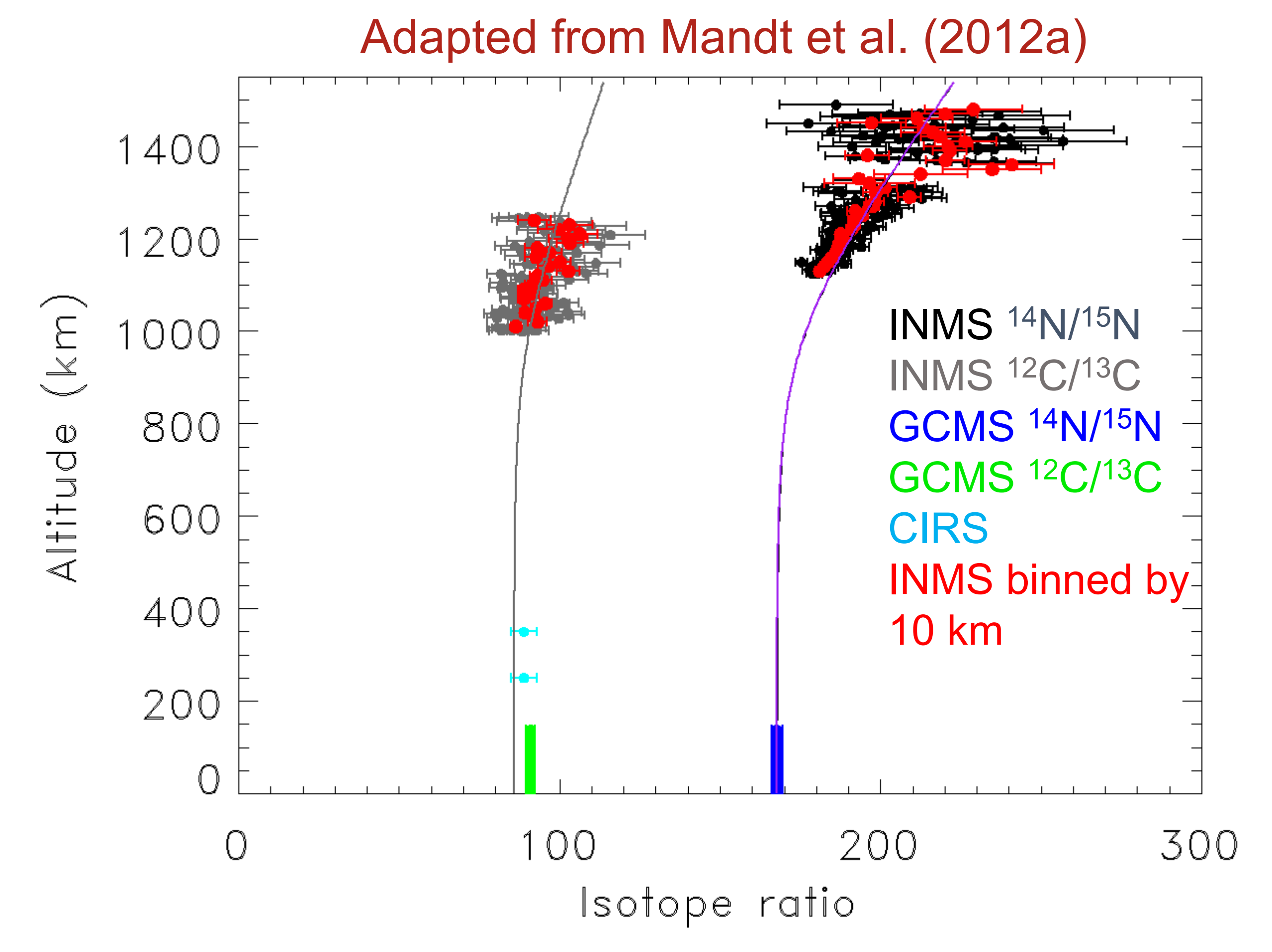
Observations with Rosetta suggest relationship to SiC grains, but unclear if this is coincidence or related to formation of comets.

Measurement strategy for Io

Plumes vs. Sublimated atmosphere



Escape fractionation



Comparing plume composition with sublimated atmosphere can trace the interior composition. Altitude profiles of isotopes can directly measure effects of escape on the isotopes.

Conclusions

- We have learned many things from the isotope ratios measured at Titan
  - Titan's methane has been present in the atmosphere for less than 1 billion years
  - Titan has too much nitrogen for the ratio to evolve over time
  - Titan's nitrogen originated as ammonia in the protosolar nebula
- Pluto is unconstrained – NFDAP funded to explore with modeling
- Burning questions for Io
  - Did Io form as a mostly rocky moon, or did it form with large amounts of ice like other giant planet moons?
  - How much water and other volatiles were lost from Io due to tidal heating?
  - What volatiles remain in trace quantities?
- Proposed approach
  - Measure composition of sublimated atmosphere and volcanic plumes
  - Measure altitude dependence of isotope ratios
  - Search for trace species

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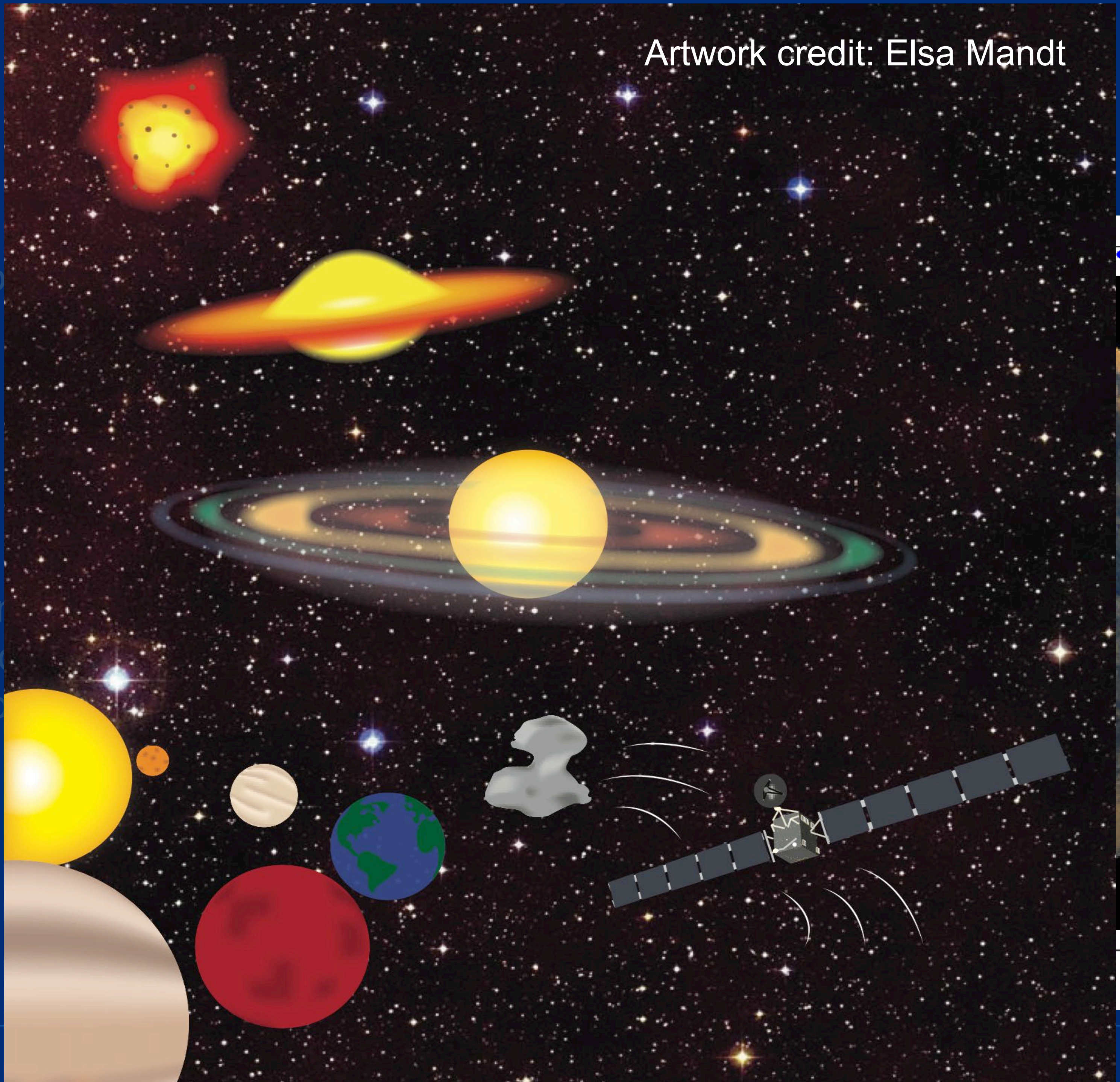
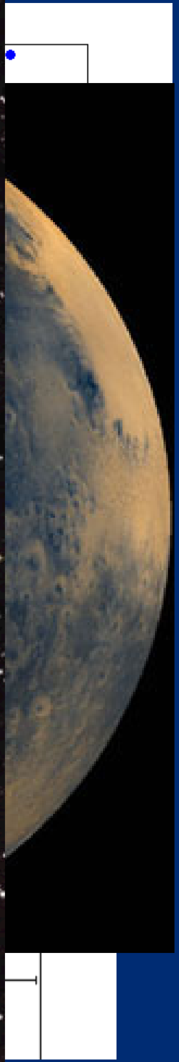
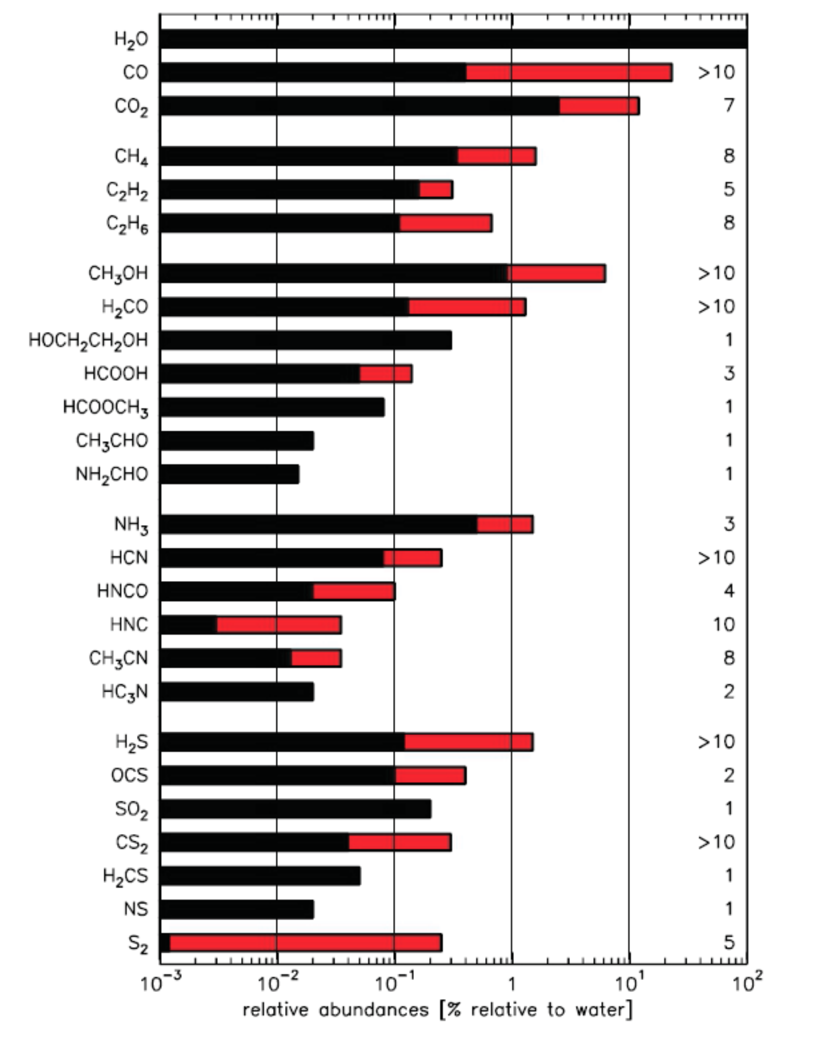




Bockelee-Morvan 2011

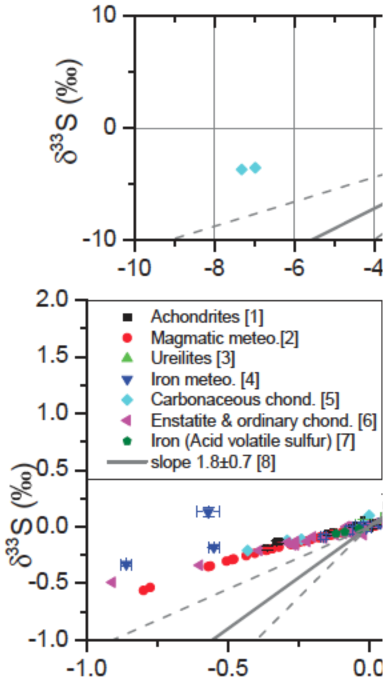


Calmonte thesis

Table 1.6.2: Isotope fractionation for sulfur bearing volatiles due to photodissociation using UV.

Species	Slope in $\delta^{34}S,\delta^{33}S$ space	Reference
H_2S	0.64 - 0.7	(Chakraborty et al., 2013)
CS_2	0.485 ± 0.005	(Zmolek et al., 1999)
SO_2	0.649 ± 0.006	(Farquhar et al., 2000)
		(Masterson et al., 2011) *
		(Masterson et al., 2011) †
		(Lin et al., 2011)

erent pressures



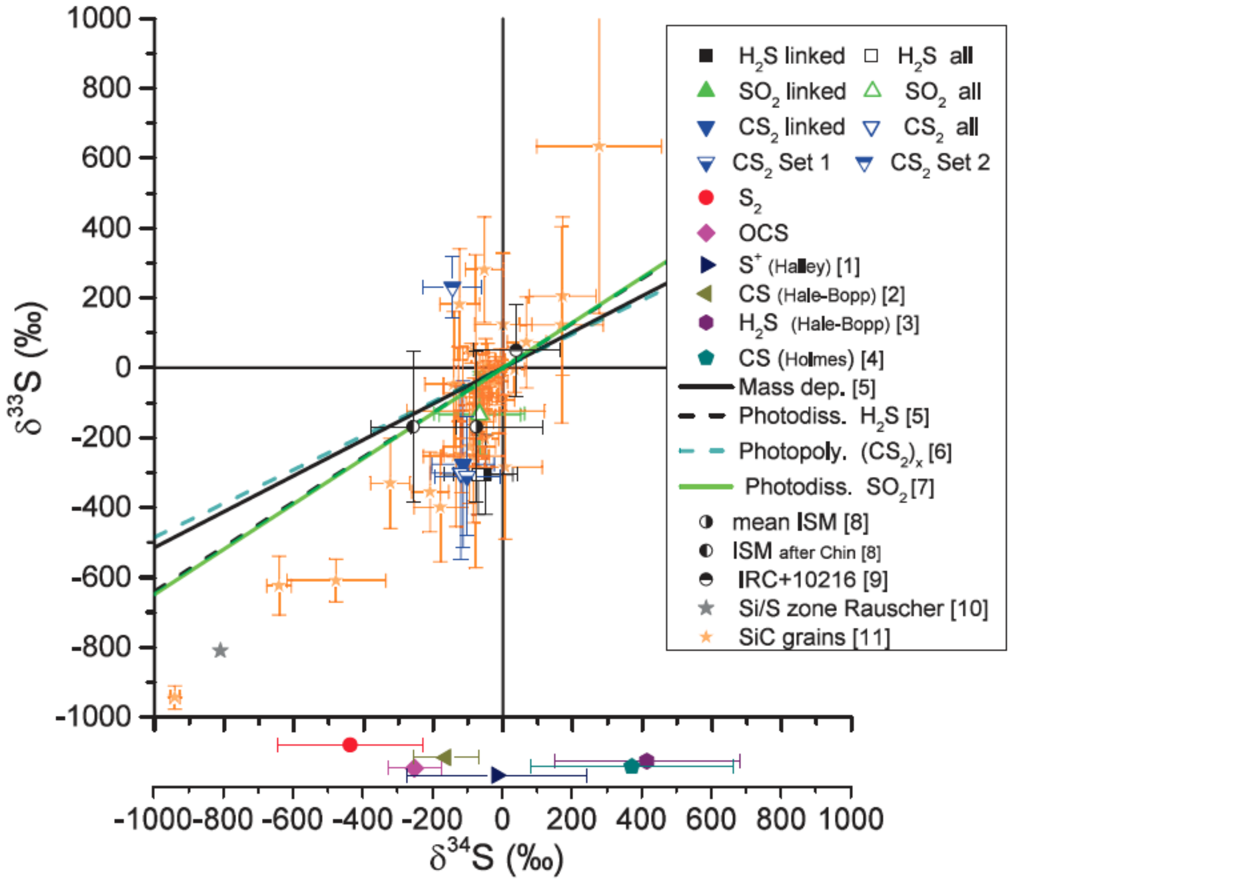


Fig. 1.6.1: Sulfur three isotope plot
are from [1] (Rai et al., 2005), [2] (A
and Thiemens, 1991), [5] (Gao and T
(Franz et al., 2010). The slope [8] bas
section 1.6.5)

ic ratio in comets.

	Species	Reference
	$^{34}S^+$	(Altwegg, 1996)
pp †	$C^{34}S$	(Jewitt et al., 1997)
pp ‡	$H_2{}^{34}S$	(Crovisier et al., 2004)
	$C^{34}S$	(Biver et al., 2008)

etry (JCMT), ‡ radio spectrometry (30m

Stable Isotopes key to Io's Past?

- Has Io been as active as today for billions of years?
- Io recycles itself rapidly, leaving no macroscopic record of its distant past.
- Given an assumed fractionation process, isotopic fractionation tells us fraction of mass lost
- Lower molecular mass generally results in more fractionation for a given mass fraction lost
- We can measure present-day mass loss with INMS and PIMS
- We can measure several useful isotopes with INMS
- This integrates study of mass loss with tidal heating theme

- How does volcanic outgassing influence the isotopes and would volcanic plumes be primordial?