Measuring Isotope Ratios across the Solar System

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International Workshop on Planetary Science Instruments 2012
NASA GSFC, Greenbelt, Maryland
October 16-20, 2012

Stable Isotopic Abundances

Atomic No.	Symbol	Mass No.	Isotopic % composition
1	H	1 2	**99.9885** **0.0115**
2	He	3 4	**0.000137** **99.999863**
6	C	12 13	**98.93** **1.07**
7	N	14 15	**99.632** **0.368**
8	O	16 17 18	**99.757** **0.038** **0.205**
16	S	32 33 34 36	**94.93** **0.76** **4.29** **0.02**
17	Cl	35 37	**75.78** **24.22**

Reference Standards:

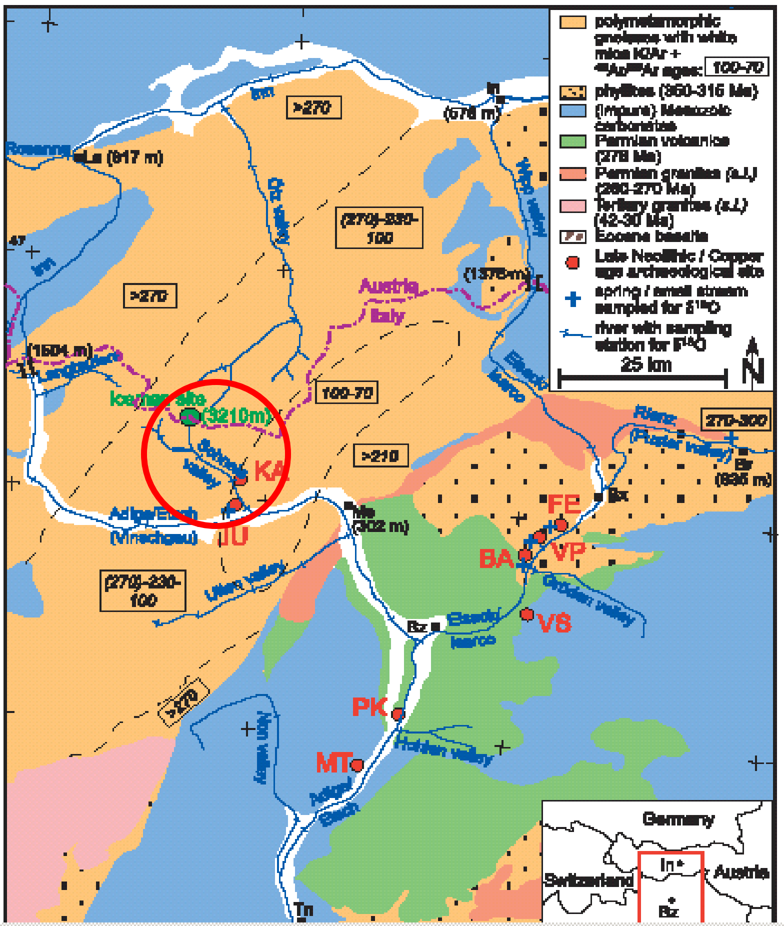
Hydrogen isotopes	Standard Mean Ocean Water (SMOW) from Potomac river distributed by NBS Vienna-SMOW
Carbon isotopes	PeeDee Belemnite (PDB) limestone in S. Carolina, derived from marine fossils
Nitrogen isotopes	Atmospheric nitrogen
Oxygen isotopes	Atmospheric oxygen, PDB, SMOW
	Canyon Diablo meteoric troilite (CDT), a sample of troilite (FeS) from Meteor Crater in Arizona

Origin and migration of Alpine “Iceman”

1991- remains of 5,200-year old “Iceman” found in Alpine glacier 3 km above sea level – Wolfgang Muller et al. *Science*, 302, 862-866 (2003)

- Struck by an arrow, and bludgeoned to death!

“Iceman” isotopic analysis compared with local geology and hydrology



- Measured $^{87}Sr/^{86}Sr$ *vs.* $^{206}Pb/^{204}Pb$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in Iceman’s teeth & bones, and $^{40}Ar/^{39}Ar$ in Iceman’s intestine - compared with local geology and hydrology

- Inferred habitat and range from childhood to adulthood as within 60 km SE of site

- Showed Alpine valleys were permanently inhabited during terminal Neolithic.

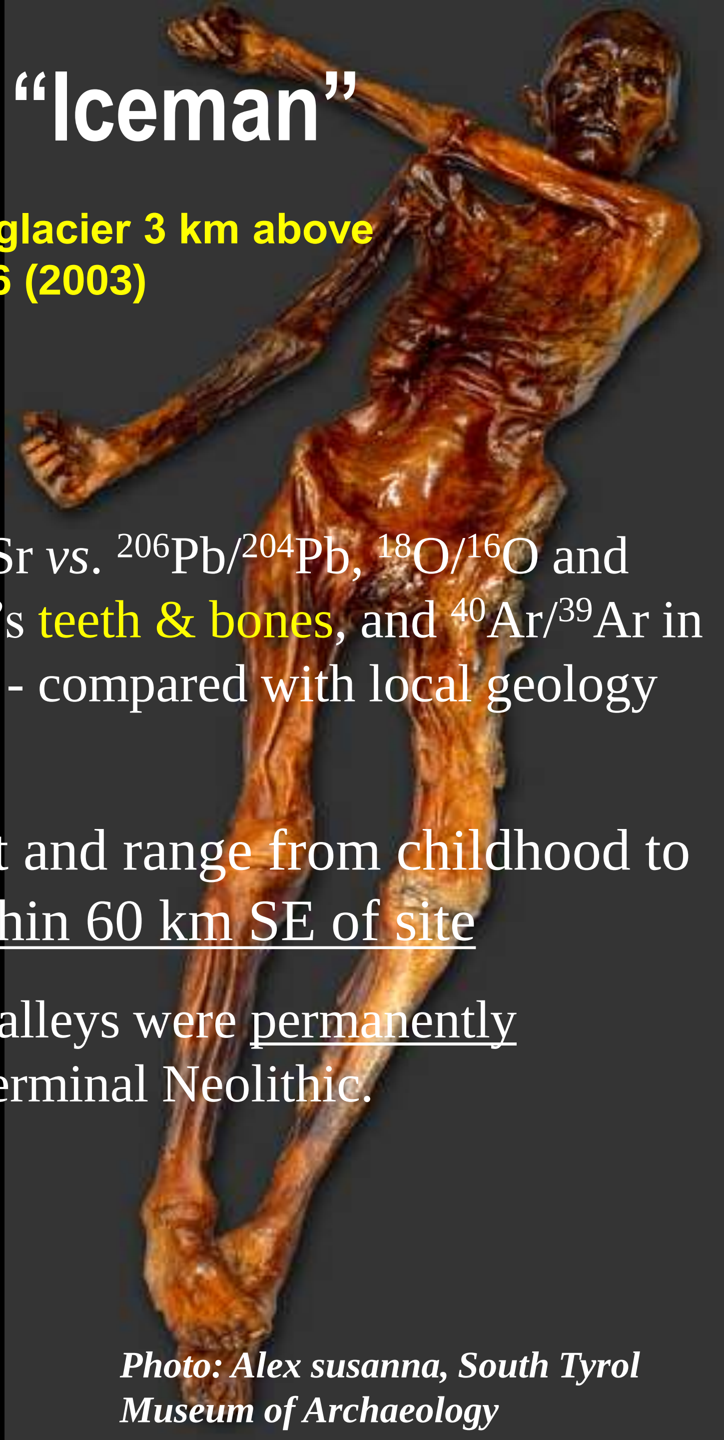
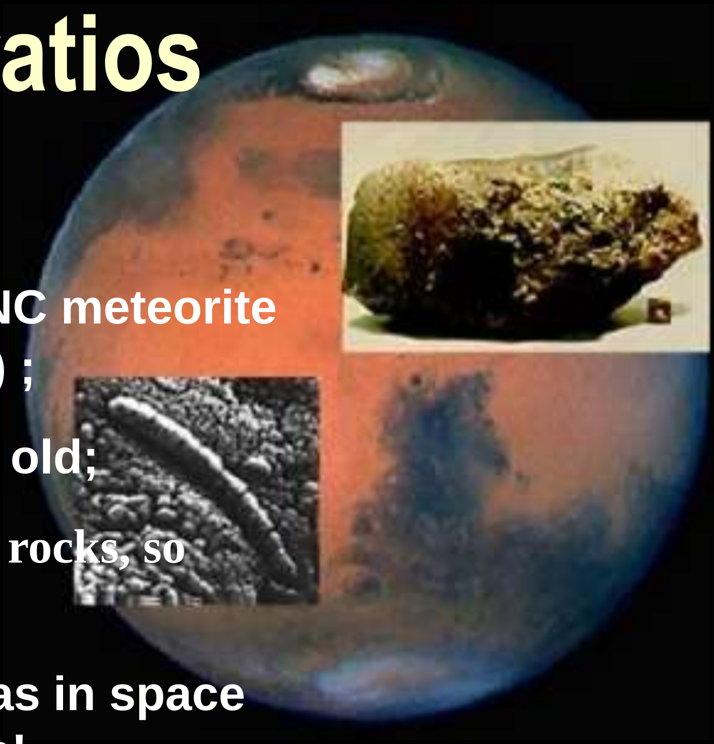


Photo: Alex susanna, South Tyrol Museum of Archaeology

Isotope ratios provide evidence of:

- Planetary origin and evolution
- Atmospheric escape
- Volatile recycling and transportation
- Solid-liquid-gas interactions: hydrological, carbon, nitrogen, sulfur cycles
- Climate records, atmospheric transport, cloud microphysics
- Photochemical processes
- Geophysical processes
- Radiation exposure
- Biological origin and interactions

The power of isotope ratios



Alan Hills ALH 84001 Meteorite:

- $^{18}O/^{17}O/^{16}O$ and $^{15}N/^{14}N$ identifies it as an SNC meteorite from Mars (shergottite, nakhlite, chassignite) ;

- K-Ar dating says meteorite is 4 billion years old;
  - ^{40}K decays to ^{40}Ar that only leaks out of hot rocks, so *specifies the last time the rock cooled to solid;*

- Isotope ratios in ^{3}He, ^{21}Ne and ^{38}Ar say it was in space (cosmic ray exposure) for 10-20 million years!

- ^{14}C dating says that it sat in Antarctica for 13,000 years;

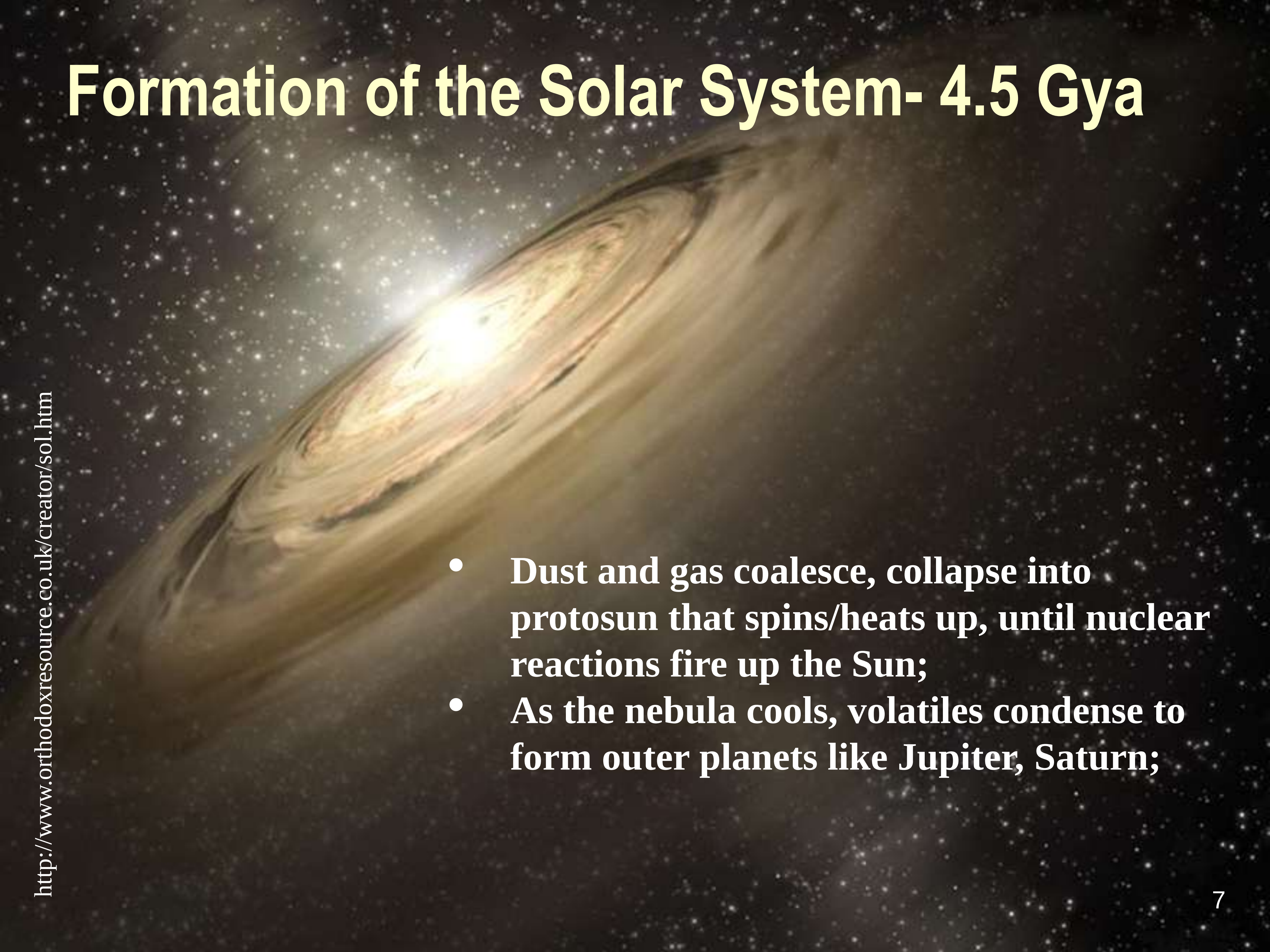
- $^{13}C/^{12}C$ and $^{18}O/^{16}O$ enrichment in its' carbonate identifies secondary alteration with isotopically-heavy water in the atmosphere;

- $^{18}O^{13}CO/CO_2$ establishes that the carbonate precipitated at 18 ± 4 ^{o}C from gradually evaporating water.

Origin of the Elements

- Big Bang conditions **only synthesized H, D, ^{3}He, ^{4}He and ^{7}Li** *(Cyburt et al. 2002)-* primordial compositions of galaxies and stars- and shut off at expansion period;
- Elements were formed by nuclear reactions (nucleosynthesis) in stars *(Burbidge et al., 1957)* that began 3 mins after the Big Bang and is ongoing today;
- Stars and supernovae that synthesize elements can return heavy-element-enriched matter to interstellar gas for new stars *(see Truran "Meteorites, comets, and Planets", Treatise on Geochem., Elsevier, 2003);*
- **H-burning** powers stars for ~90% of lifetime, producing He, while **He-burning** produces large amounts of ^{12}C and ^{16}O, and some Ne; subsequent processes produce all elements;
- In a planet-forming nebula, global abundance of water determined by O: C ratio that varies across Galactic disk- In our galaxy, should search closer to center of Milky Way, not edge (Gaidos, 2000).

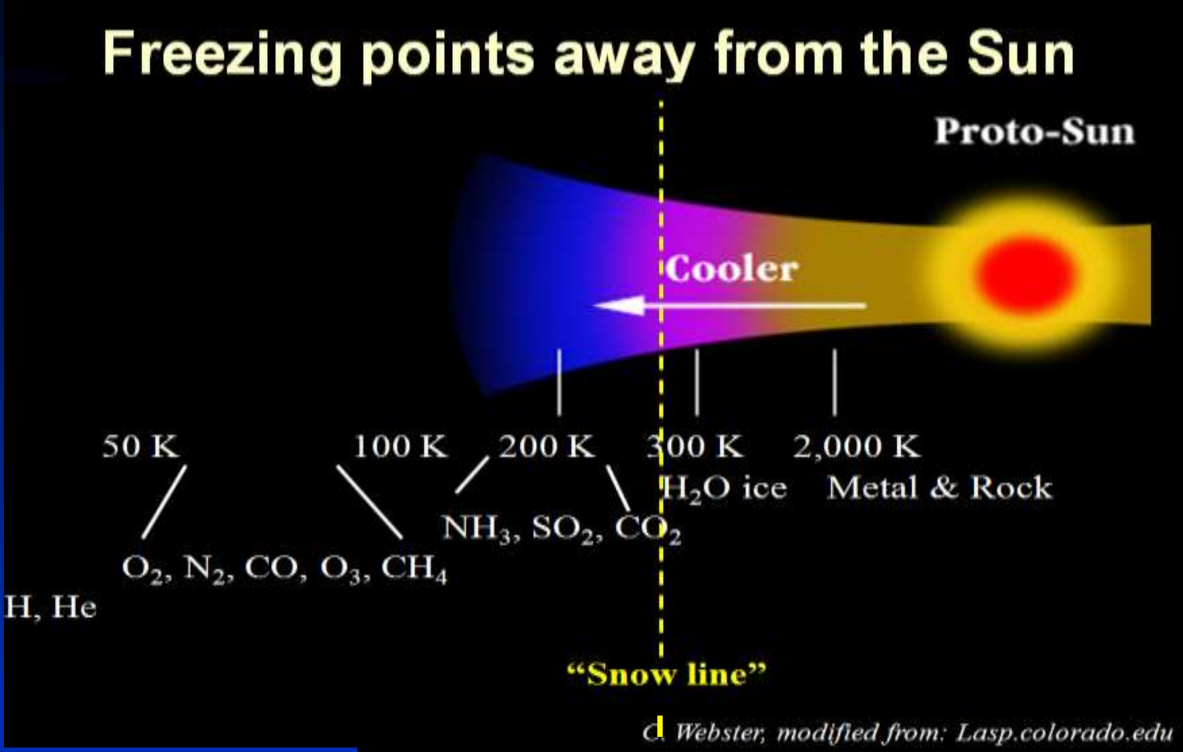
Formation of the Solar System- 4.5 Gya



http://www.orthodoxresource.co.uk/creator/sol.htm

- Dust and gas coalesce, collapse into protosun that spins/heats up, until nuclear reactions fire up the Sun;
- As the nebula cools, volatiles condense to form outer planets like Jupiter, Saturn;

Transport across the solar system



C. Webster, modified from: Lasp.colorado.edu

H_2 and N_2 gas | H_2 and N_2 gas

H_2O water ice ----sublimes--→ H_2O (g) + H_2 (g) - H, D isotope exchange

NH_3 ice ----sublimes--→ NH_3vap + N_2 vap -no N isotope exchange

Isotopic fractionation

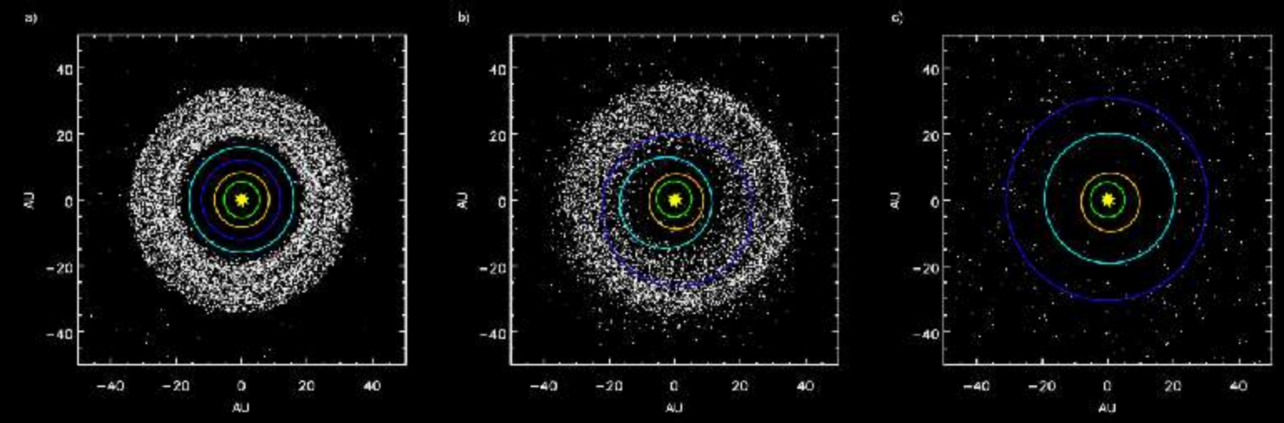
Atomic mass affects *bond-strengths, velocities, diffusion rates*

- **Equilibrium fractionation** – mass dependent
  - Substitution of heavy isotopes reduces zero point vibrational energies
  - Strongest at low temperatures with lighter elements
  - Water vapor above liquid or ice
- **Kinetic (chemical) fractionation** – mass dependent, directional
  - Usually good for first-order reactions
  - During evaporation, condensation - Rayleigh
- **Mass-independent fractionation (MIF)**
  - Seen in atmospheric photochemistry of oxygen and sulfur
  - Also seen in O isotopes of CAI in meteorites like Allende

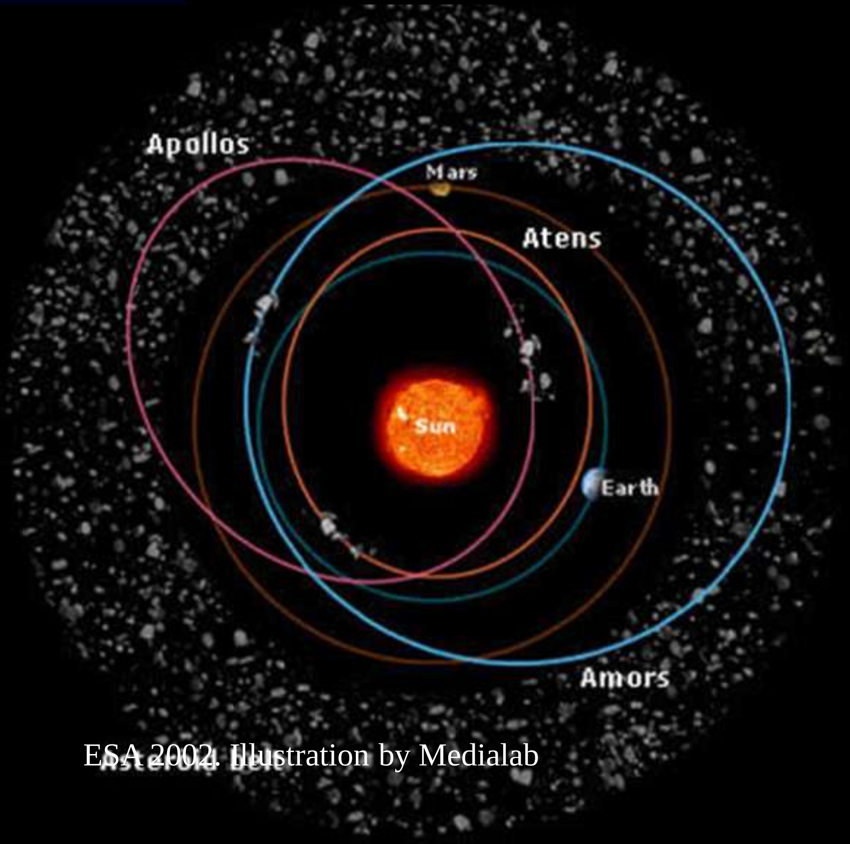
Generally expect large differences in D/H, moderate differences in d^{18}O, significant differences in d^{13}C, d^{15}N and d^{17}O, and small differences in d^{33}S

The Nice Model- *oui, c’est ca!*

- After dissipation of gas/dust, 4 giant planets are in compact circular orbits, surrounded by large disk of planetesimals/comets (~35 Earth masses) out to 35 AU;
- Jupiter migrates inward to 1.5 AU truncating inner disk of planetesimals at 1 AU, then slowly migrates out with pull of Saturn as inner planets form;
- Saturn migrates out until in 1:2 orbital resonance with Jupiter that completely destabilizes SS bodies;
- Orbital resonances between Jupiter and Saturn sweep up planetesimals (~100) and shift Neptune and Uranus into elliptical orbits, scattering comet/asteroid bodies toward and away from Sun;
- Solar system undergoes a **100 million year Late Heavy Bombardment period.**

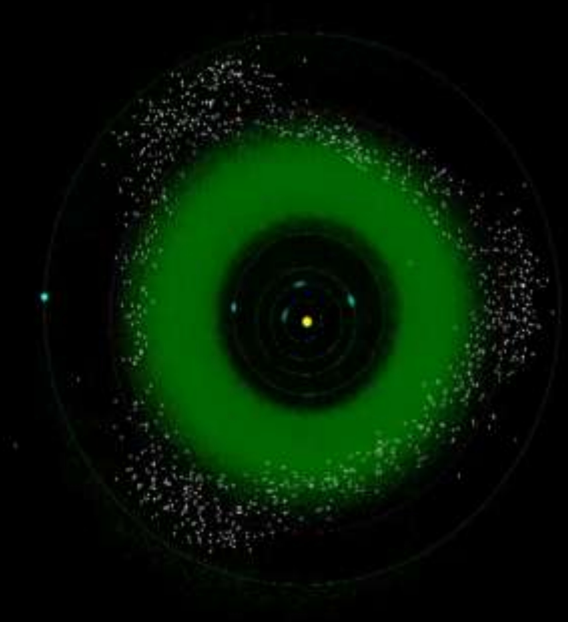


Families of Asteroids



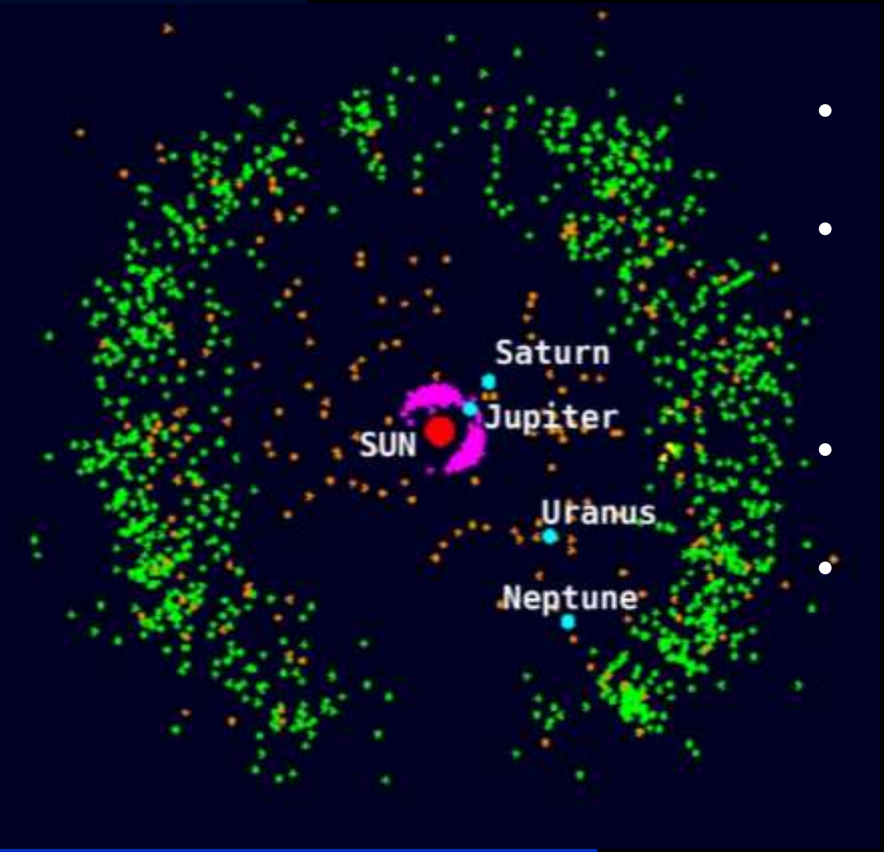
ESA 2002. Illustration by Medialab

L4 Trojans



L5 Trojans

From Jupiter’s Trojans to the Kuiper Belt

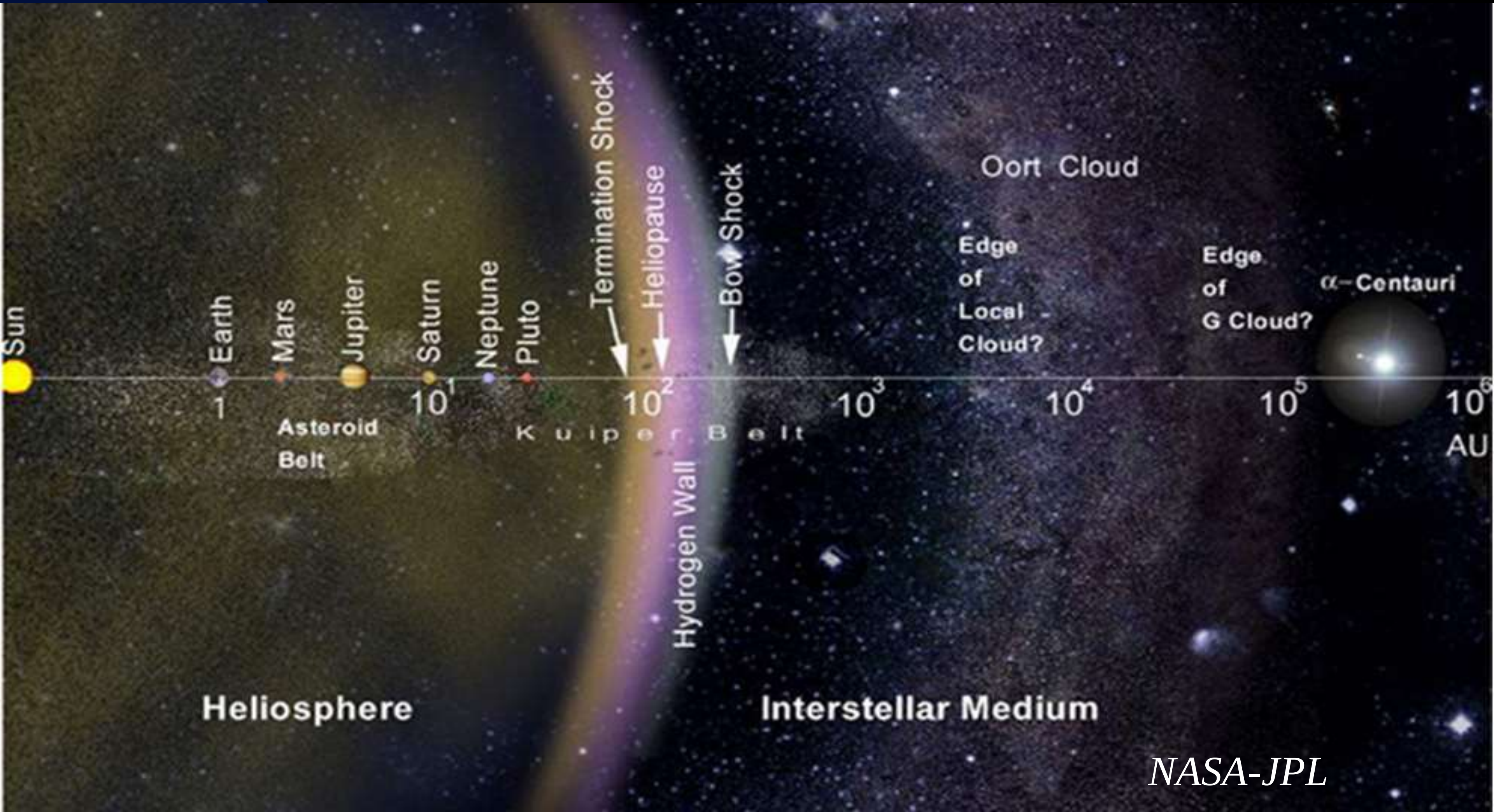


- Jupiter’s **Trojan asteroids** (magenta) librate around Lagrange points L4 and L5.
- **Centaurs** (orange) orbit between Jupiter and Neptune- escaped Kuiper belt and now experience numerous interactions with giant planets- will burn up at Sun or be ejected to interstellar medium;
- **Kuiper belt KBO’s** (green) discovered 1992; outside Neptune (30 AU) and between 40-47 AU
- “Plutinos” at 39.4 AU, orbit Sun exactly twice for every 3 Neptune orbits (as does Pluto). Some in 2:1 resonance called “Twotinos”

http://www.lpl.arizona.edu/undergrad/classes/spring2011/Hubbard_206/Lectures4/Apr12.htm

Oort Cloud

From comet trajectories, Oort hypothesized (1950) a spherical shell of comets (H_2O-, NH_3-, CH_4- ice) around Sun at 50,000 AU. The two main comet reservoirs are the Kuiper Belt and Oort Cloud (>1 trillion!)



NASA-JPL

Isotopic Ratios in the Solar System

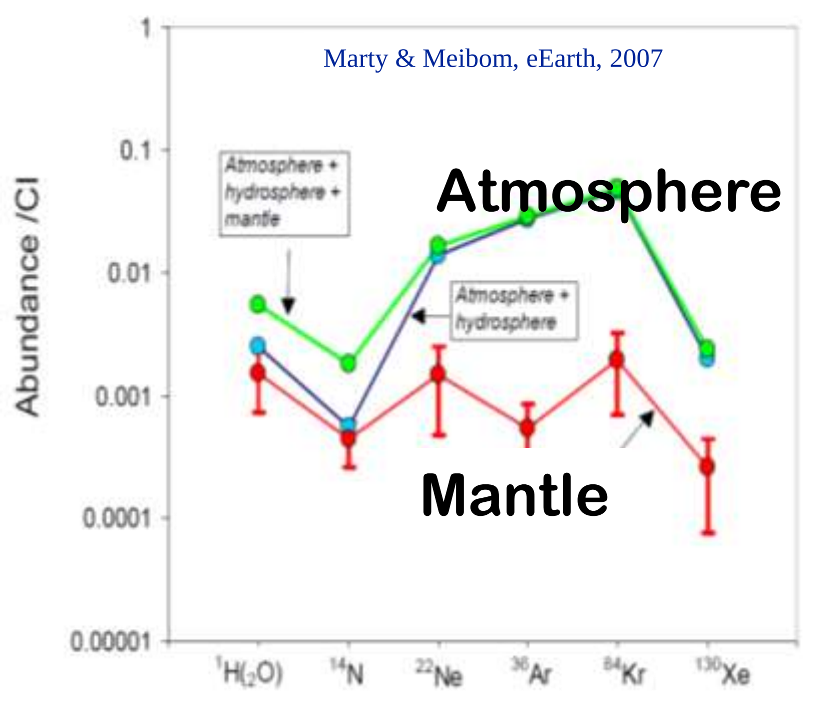
- Isotopic ratios depend on the *specific* stellar source. And stars inject new elements into the ISM enriching the galaxy as a whole; isotope ratios homogenized in a hot solar nebula….. BUT…..

- Presolar material (grains) discovered to have survived in primitive meteorites (e.g. “stardust” in Murchison Meteorite) that show very different Xe, Ne and O isotope ratios [1960’s and 1970’s];
  - Reflect the stellar atmosphere in which the grain condensed
  - Values range *2-4 orders of magnitude difference (!) from solar* for $^{14}N/^{15}N$, $^{12}C/^{13}C$ and $^{16}O/^{18}O$;
  - The carriers for the anomalous noble gas ratios were SiC, diamond, and graphite that were also anomalous in ALL their isotope ratios*

**E. K. Zinner, Presolar Grains, MCP, Ed. A. Davis, Elsevier 2003*

Noble gas evidence for C- and H_2O-transport during Late Heavy Bombardment

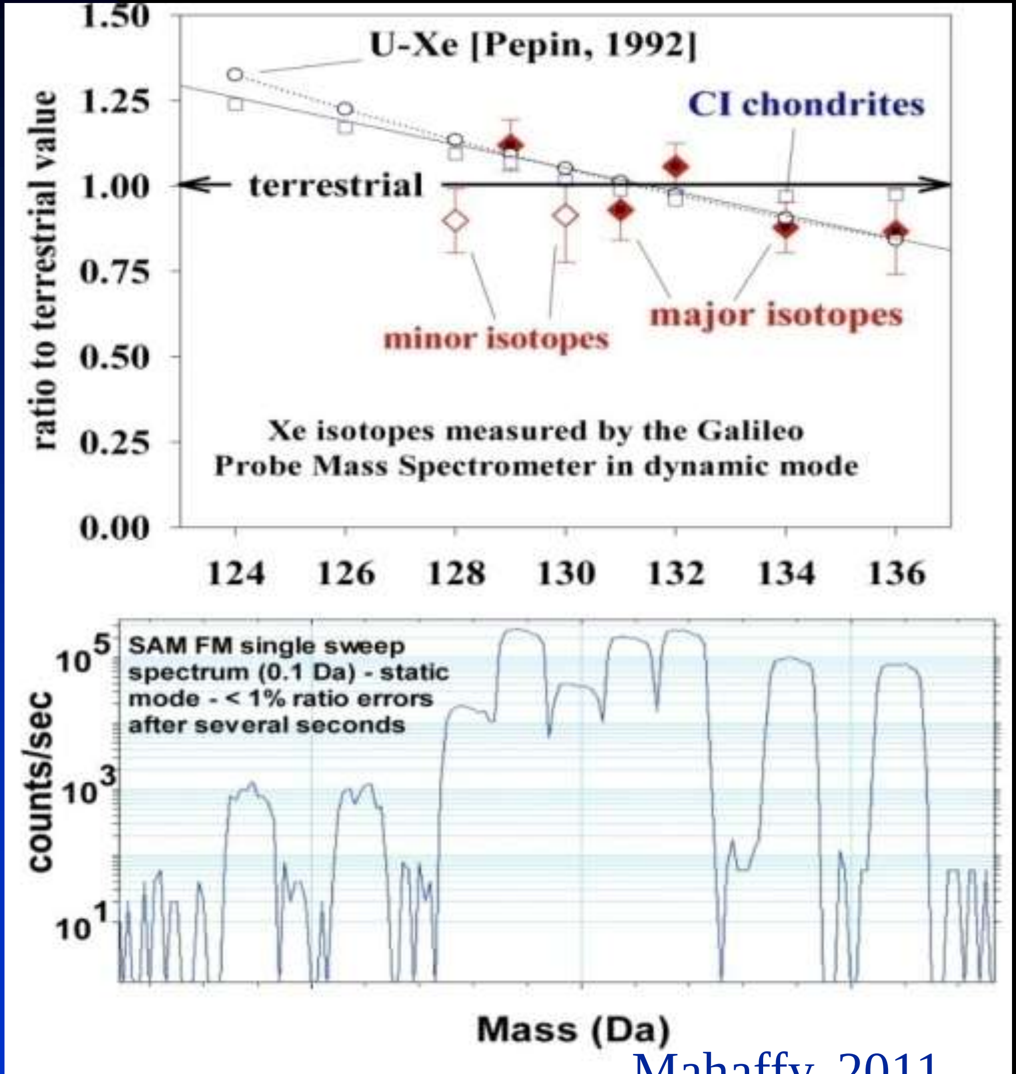
- Thermo dynamical conditions in SS produced PHASE SEPARATION of solids from gases- Earth and inner planets formed by collecting solids, not gases. So, noble gases also rare!
- So what causes noble gas excess on Earth??



- Mantle strongly degassed by 10^2-10^3
- Atmospheric excess by factor of 10 cannot be from mantle (since H_2O & N not high)
- Noble gases believed trapped in icy planetesimals originating >15 AU where very low temps favor trapping;
- **Implies 1-5 x 10^{16} kg of organic C added to Earth during LHB (comparable to mass of present day biosphere)- *Marty & Meibom, 2007***

see F.A. Podosek, "Noble Gases", MCP 2003

The Xe isotope anomaly



Mahaffy, 2011

- Solar noble gas ratios are the same as those in the original solar nebula;
- Fractionation results from subsequent atmospheric and planetary volatile evolution;
- Earth atmosphere Xe shows severe mass-dependent fractionation (4% per amu) and has 7% too much ^{129}Xe;
- Anomaly threatens our fundamental understanding of solar system formation;
- Is the Sun enriched in heavy Xe and why?

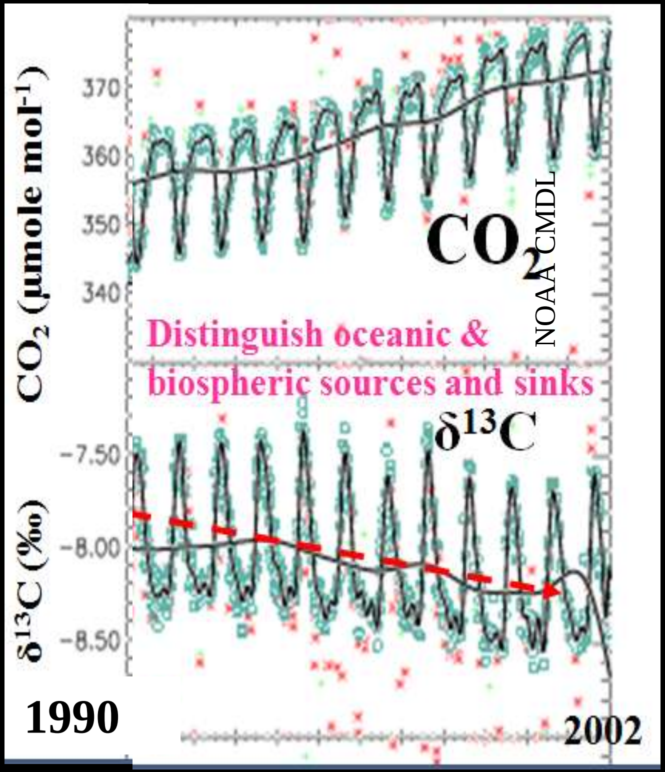
Terrestrial Carbon and $^{13}C/^{12}C$ Ratio

Life's catalysts (enzymes) preferentially use lighter isotopes during metabolism (easier and faster)

By physical processes (evaporation, diffusion through leaf stomata) and enzymatic reactions, plants take up ^{12}C over ^{13}C:

-2.7% for C_3 plants (wheat, rice, soybean, sugar beet, most plants, fossil fuels- use *Calvin-Benson* photosynthetic pathway)

-1.3% for C_4 plants (salt marshes, tropical grasses, sugar cane- use *Hatch-Slack* photosynthetic pathway)



The terrestrial CO_2 challenge:
1 ppm in 400 and 0.1 per mil d^{13}C

Breath Analysis

- looking for Helicobacter Pylori bacteria that cause gastritis, stomach and duodenal ulcers, and are linked to stomach cancer


www.cellsalive.com

1982: Australian doctors link ulcers to Helicobacter Pylori - spiral-shaped bacterium that lives in stomach and duodenum

- Adapts to extreme environment of deadly bath of stomach acids & enzymes by living in mucus of stomach lining and creating neutralizing, protective bases
- Immune system white cells and T-cells cannot reach lining

Urea hydrolysis:

$C{=}O(NH_2)_2^- + H^+ + 2H_2O \xrightarrow[\text{urease}]{} HCO_3^- + 2NH_4^+$

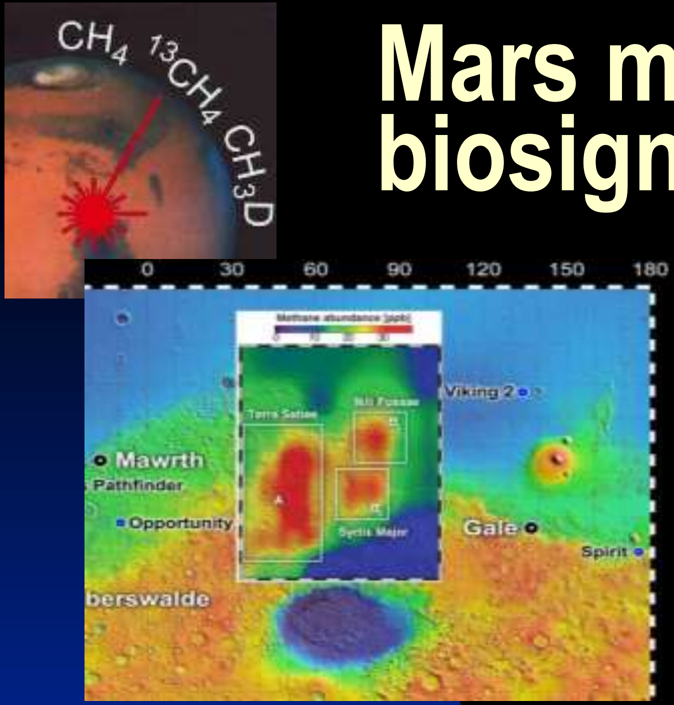
Urea urease bases ($CO_2 + NH_3$)

- •Take baseline breath CO_2 sample after fasting
- •Eat high calorie meal and drink ^{13}C urea in water
- •Record $^{13}C/^{12}C$ ratio in CO_2 as function of time
- •H. Pylori present if ^{13}C enhanced

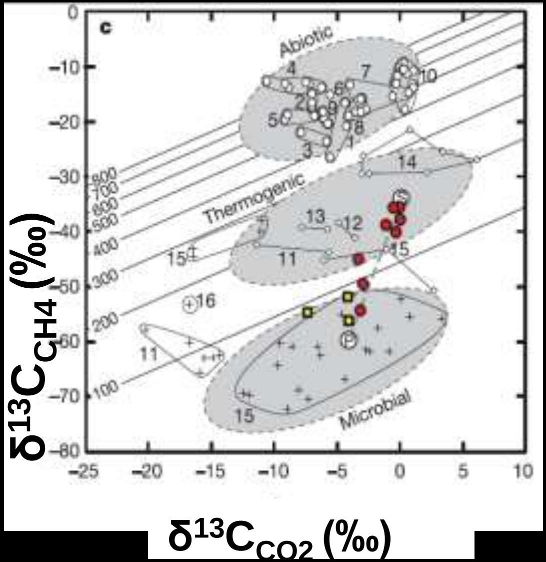
…the old method of breath analysis

www.bizarrenews.com

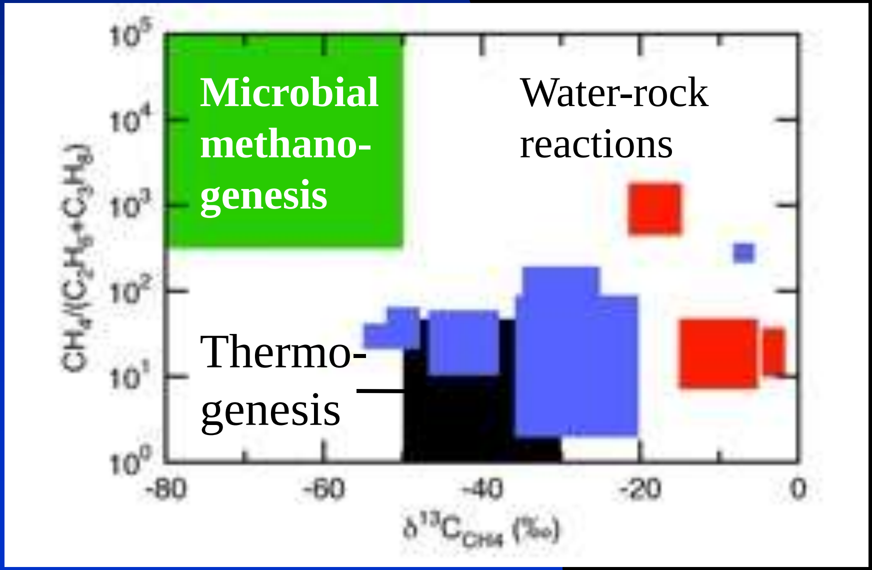
Mars methane as a possible biosignature?



Observation	Method	Gale Crater
Mars Express PFS	Mars orbit	10-15 ppbv
Mumma- IRTF	Earth telescope	20-30 ppbv
SAM-TLS	Mars in situ	TBA ± 2 ppbv



Ueno et al. Nature, Mar 2006 analysis of methane-bearing fluid inclusions in the early Archaean era before 2.5 Gyr ago



Mark Allen et al, Eos Trans, 2006

Amanda Tamaz/ Brad Bebout – isotopic and hydrocarbon ratios not a conclusive biogenic indicator *in hypersaline environments*

Oxygen isotope geochemistry

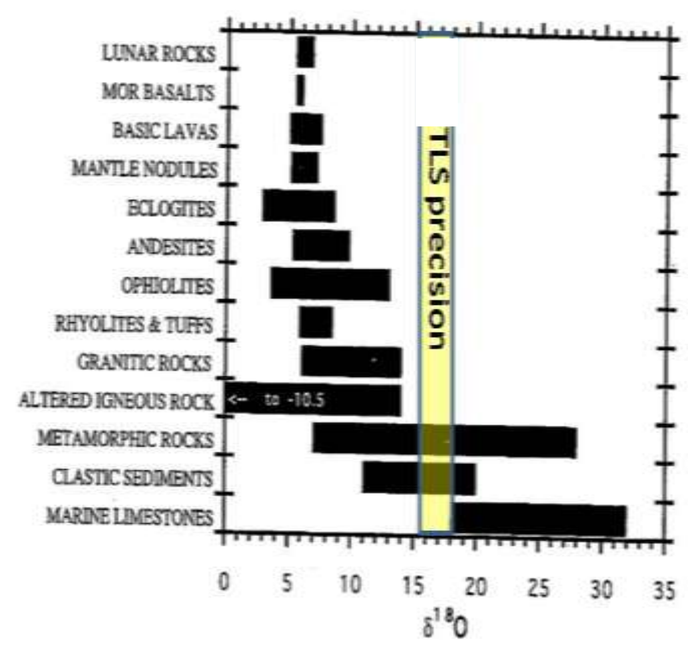
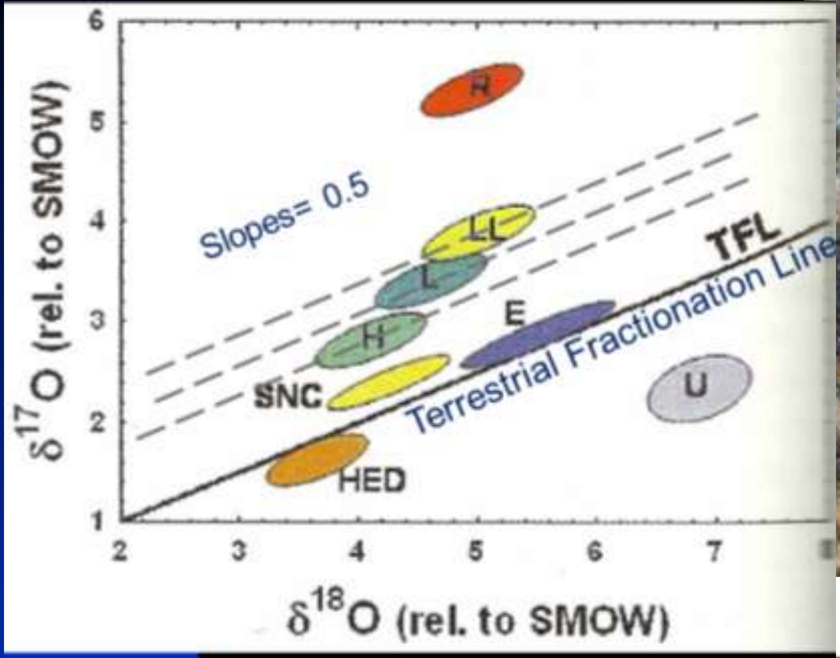


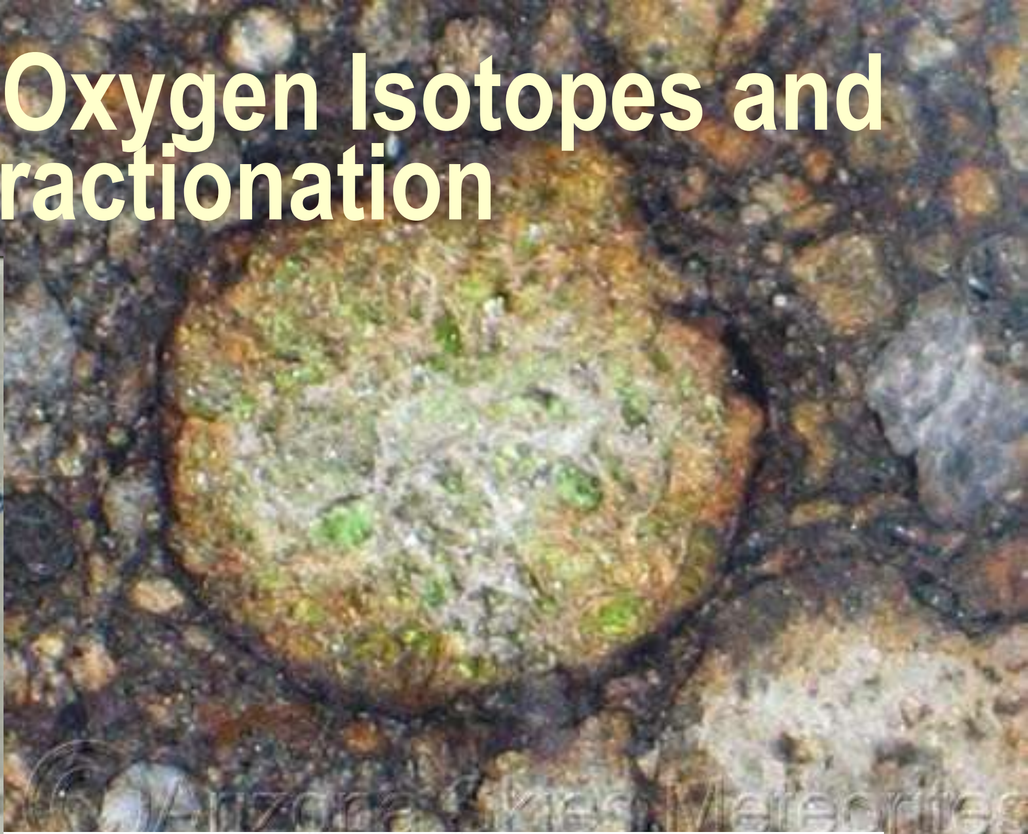
Figure and text after *Criss*, *1999*

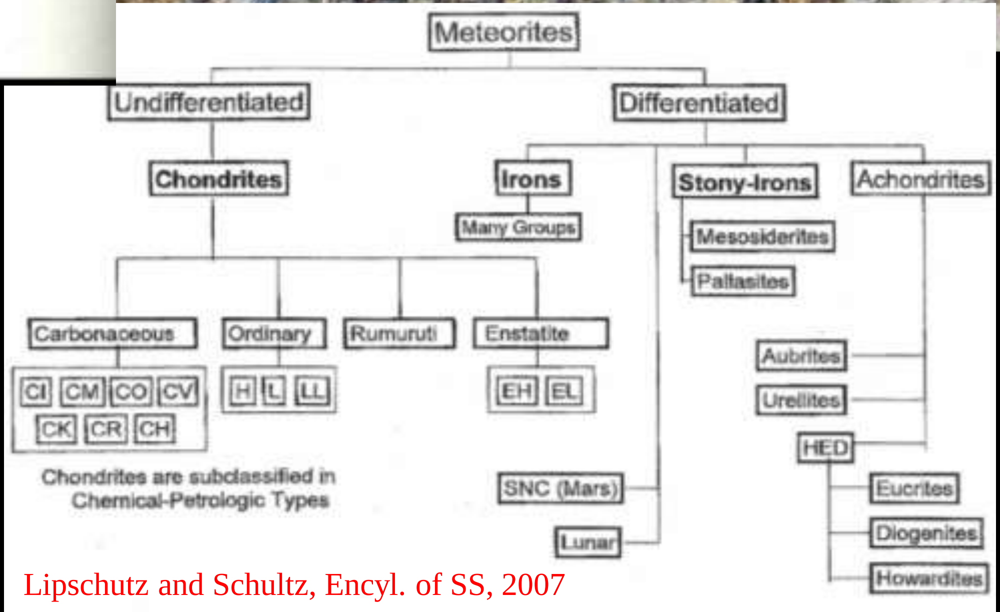
Emerald trade routes

- Bulk Earth is 30% oxygen, and Earth’s crust & mantle contain 44 wt% oxygen;
- Diversity in d^{18}O due to interactions of rocks with terrestrial hydrosphere (89 wt% oxygen);
- Mantle reservoir is 6‰
- Igneous rocks show wide range (-10 to 16‰) due to alteration processes: fluid-rock interactions, hydrothermal alteration.
- Sedimentary rock formation occurs in surficial environments intimately in contact with hydrosphere, with large (low temp) fractionations (10-20‰).
- High salinity seawater already has high d^{18}O, and then marine limestones precipitate with 30‰ higher d^{18}O than surrounding water due to large calcite-water and quartz-water fractionations at the low temps of Earths surface;

Meteorite classes, Oxygen Isotopes and Mass Dependent Fractionation





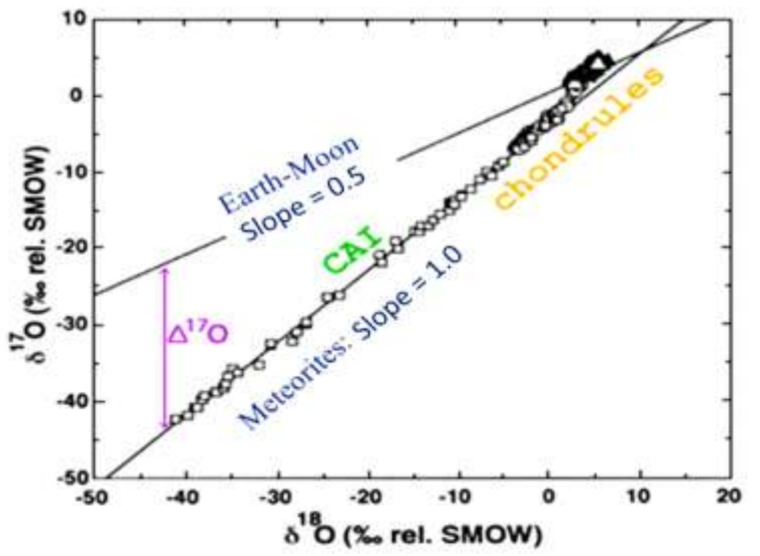


Lipschutz and Schultz, Encyl. of SS, 2007

Oxygen Isotopes and the Formation of the Moon

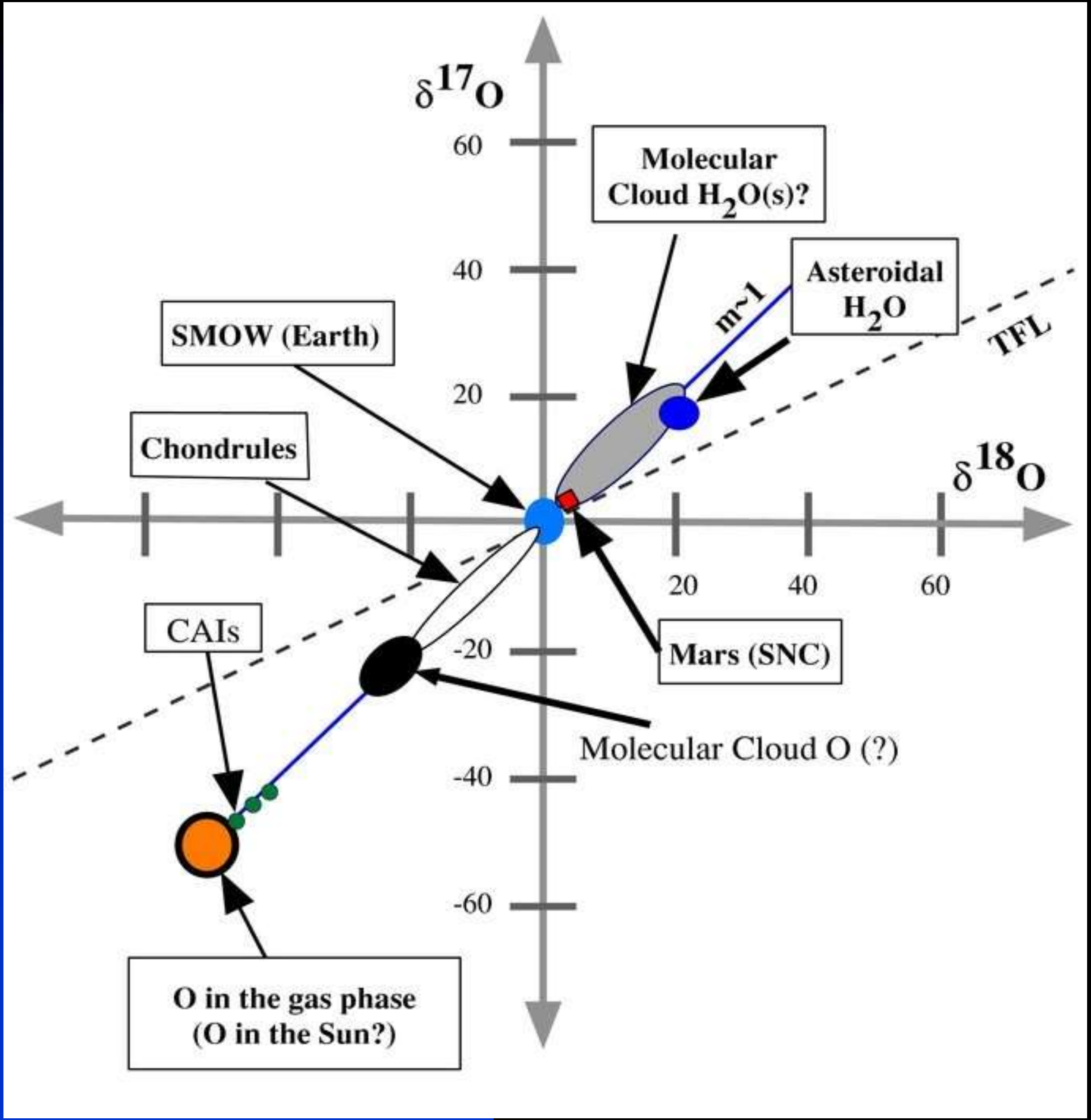
- During final stages of terrestrial planet accretion 4.5 Gya, Theia (size of Mars, already differentiated into silicate mantle and metal core) collided with Earth;
- Theia's mantle was torn into orbit to become metal-poor Moon, while metal core fell to Earth;
- Oxygen isotope ratios show Earth and Theia originated from the same region of nebula

Universetoday.com

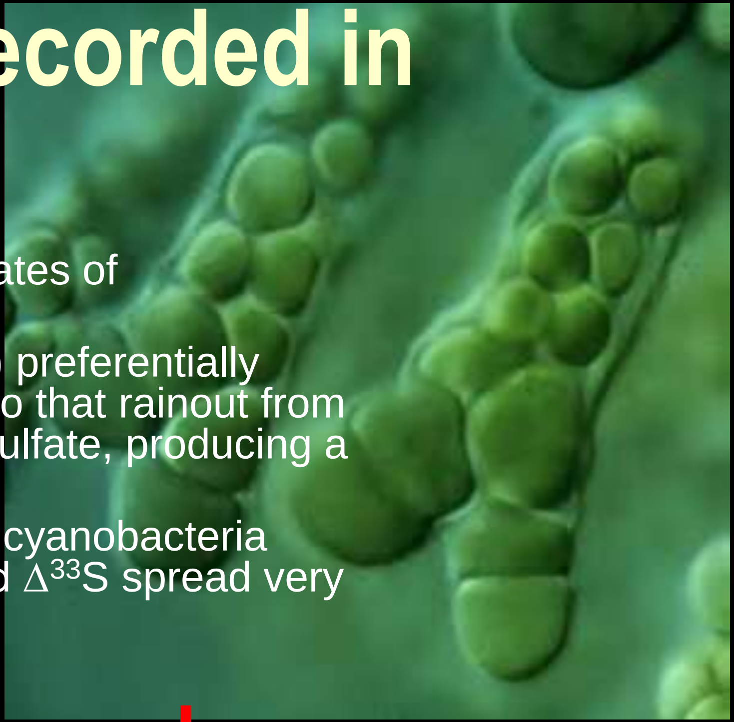


(From Clayton, R., 1993, Oxygen Isotopes in Meteorites. *Annu. Rev. Earth Planet. Sci.*, v.21, p. 123.)

Figure 2 from A Heterogeneous Chemical Origin for the 16O-enriched and 16O-depleted Reservoirs of the Early Solar System
Gerardo Dominguez 2010 ApJ 713 L59 doi:10.1088/2041-8205/713/1/L59

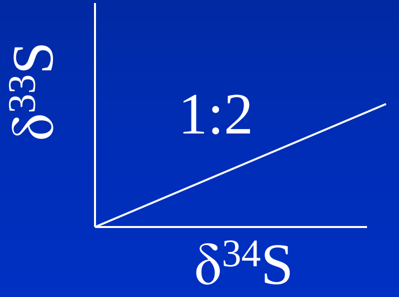


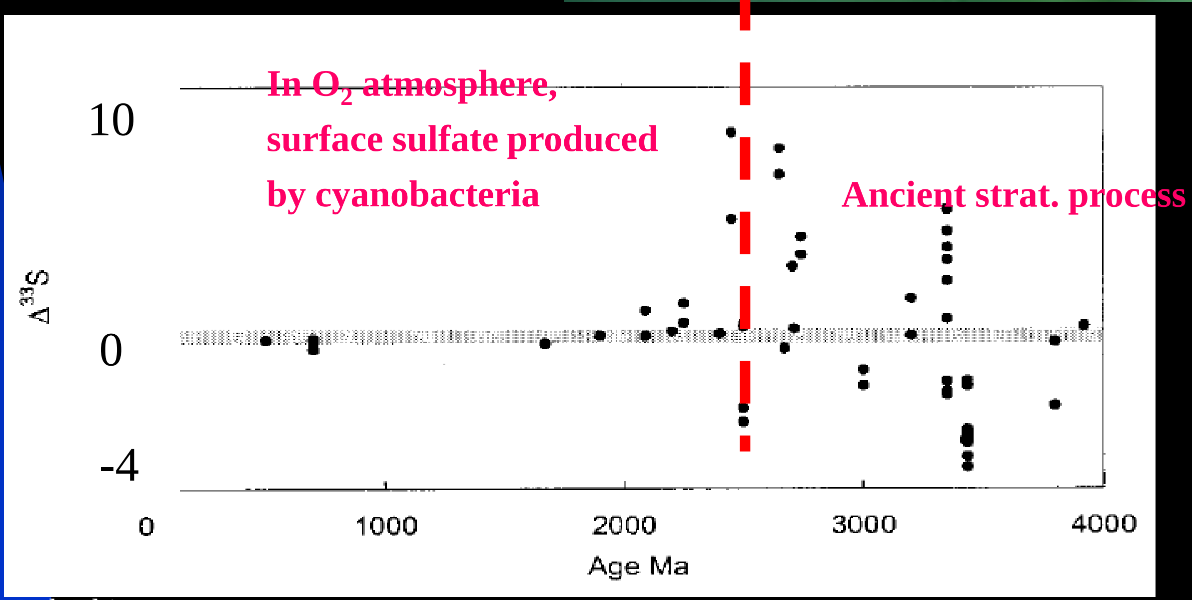
The emergence of life recorded in sulfur isotopes



Mass-independent fractionation (MIF) in S seen in sulfates of Precambrian sedimentary rocks

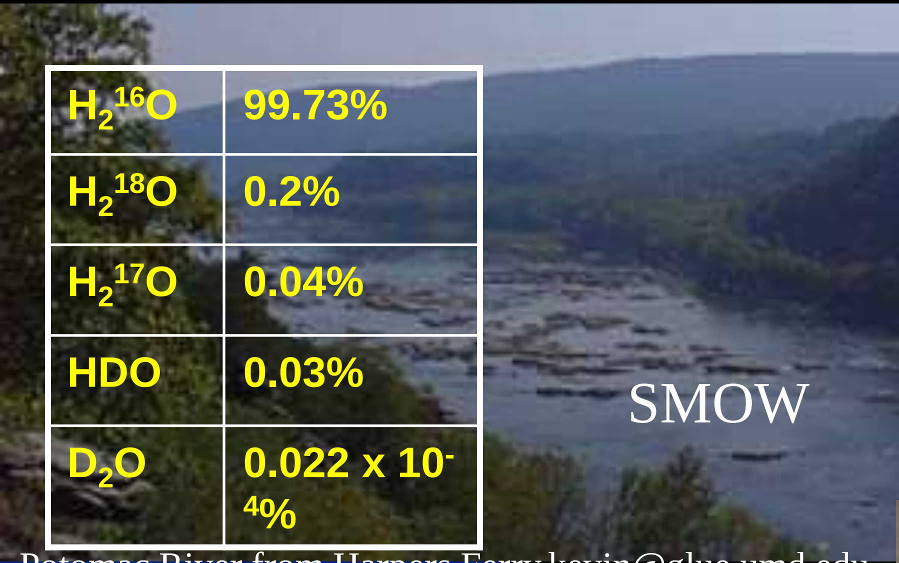
- UV radiation in absence of O_2 (O_3) (*λ<200 nm*) preferentially changes ^{33}S to ^{32}S and ^{34}S in SO_2 photolysis so that rainout from stratosphere was the main source of surface sulfate, producing a large $\Delta^{33}S$ spread
- But ~ 2.2 Gy ago, with O_2 (O_3) in atmosphere, cyanobacteria became the main source of surface sulfate and $\Delta^{33}S$ spread very narrow





James Farquhar, Huiming Bao and Mark Thiemens
Science, 289 p756-759 (2000)

Water Isotope Ratios

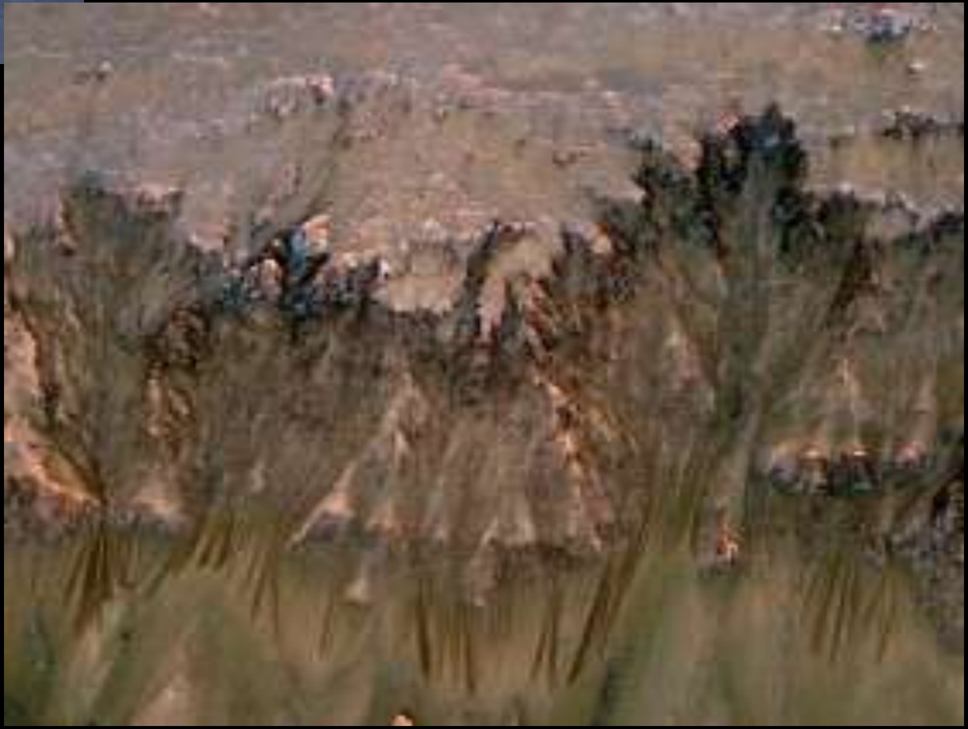


$H_2{}^{16}O$	99.73%
$H_2{}^{18}O$	0.2%
$H_2{}^{17}O$	0.04%
HDO	0.03%
D_2O	0.022×10^{-4}%

SMOW

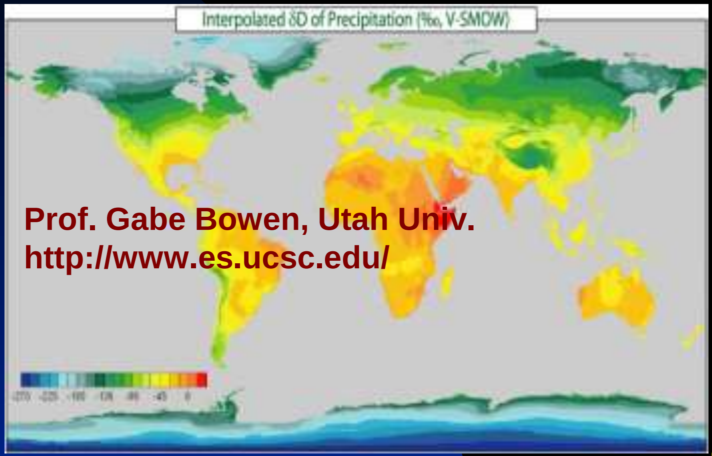
Potomac River from Harpers Ferry,kevin@glue.umd.edu

Terrestrial- Huge reservoirs connected through the hydrosphere



Martian- Isolated briny flows of partial melt

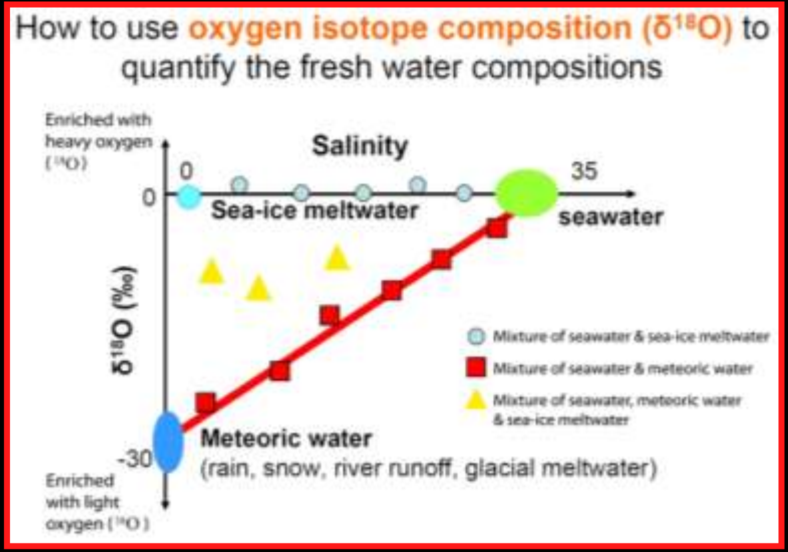
Terrestrial Rainfall, Ocean Salinity & Circulation, and the Climate Record



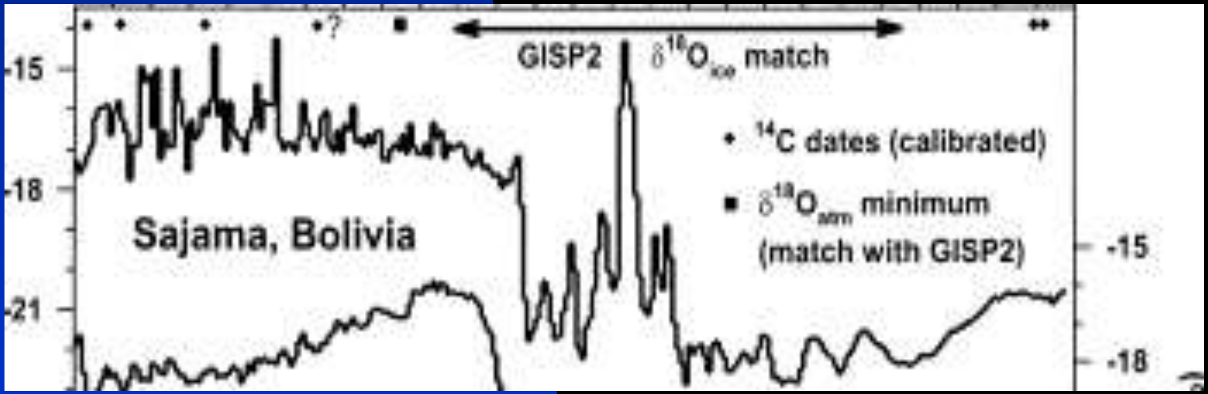
Prof. Gabe Bowen, Utah Univ.
http://www.es.ucsc.edu/

δD

$\delta^{18}O$



lgmacweb.env.uea.ac.uk



Ice core samples from Himalayas suggest 1990's warmest decade for 1,000 years – Lonnie Thompson

Today ago

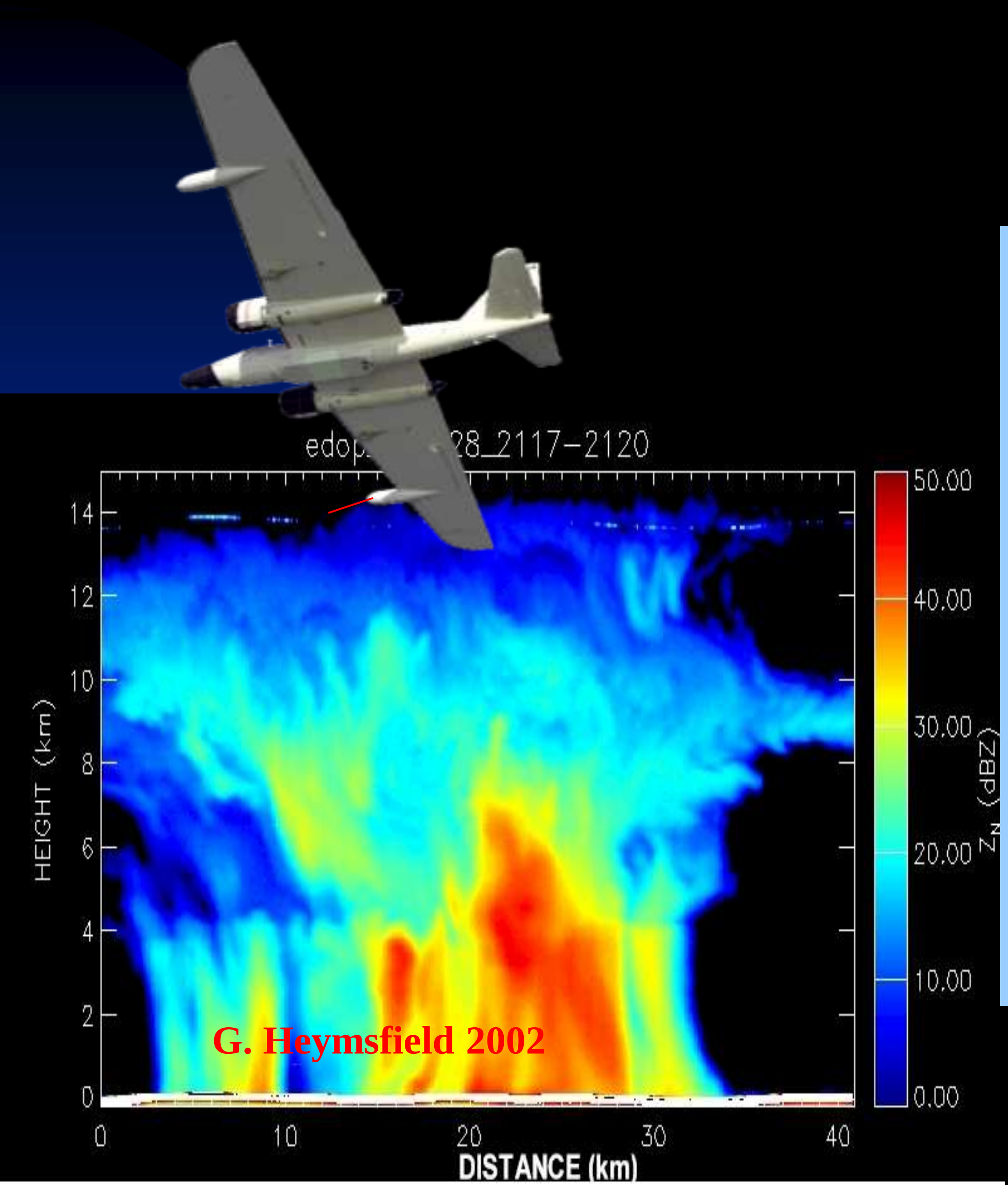
10,000 years ago

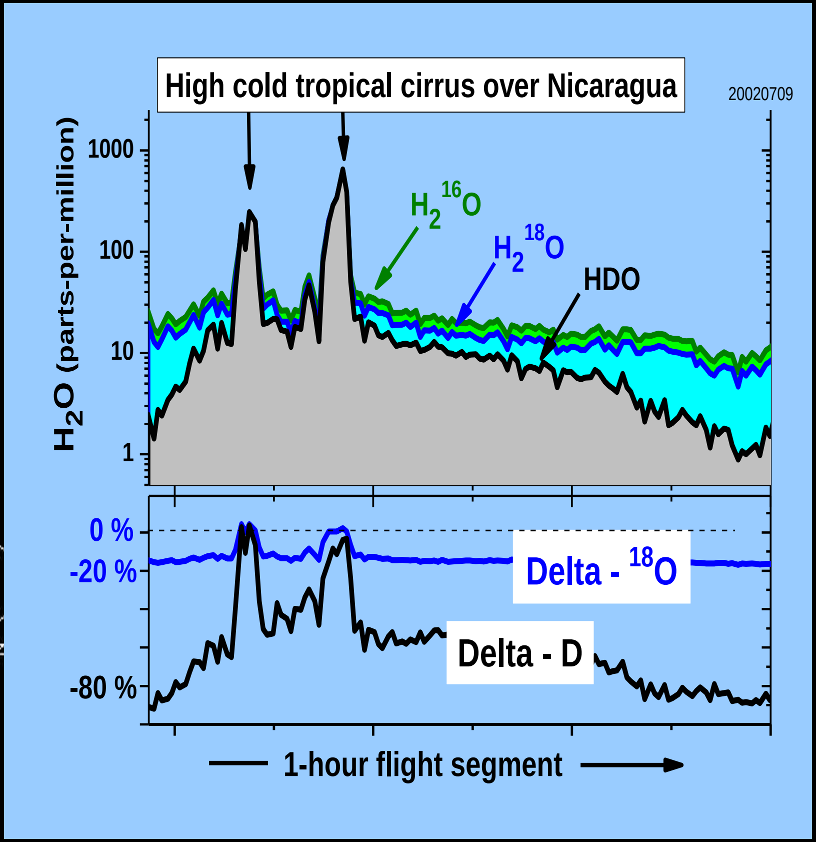
25,000 years

Vostok ice core is ~2 km long collected 1970-83

Investigating cirrus: lofted ice particles

•High, cold (~ -72ºC) tropical cirrus over Nicaragua

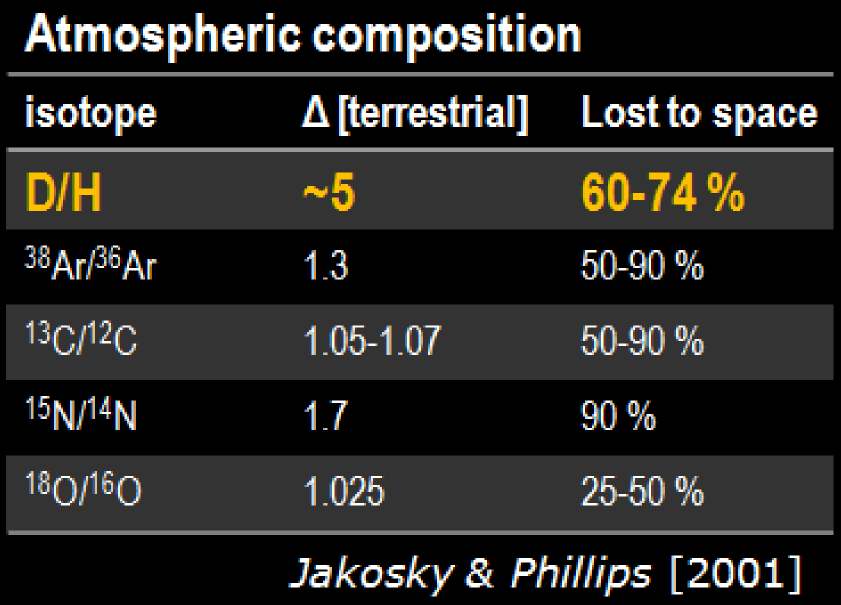




C.R. Webster and A.J. Heymsfield, *Science*, 302, 1742-1745 (2002)

The Martian atmosphere shows significant early loss

- ~ 99% of the original volatile inventory was lost 3.8 Billion years ago
- D/H is ~5 x Earth (Owen, 1988) – implies Mars once had an ocean several times the size of its ice reservoir today (500 m)- several Earth oceans!
- Viking - atmospheric $^{15}N/^{14}N$ nearly 60% higher than Earth- led to understanding that SNC meteorites were from Mars.

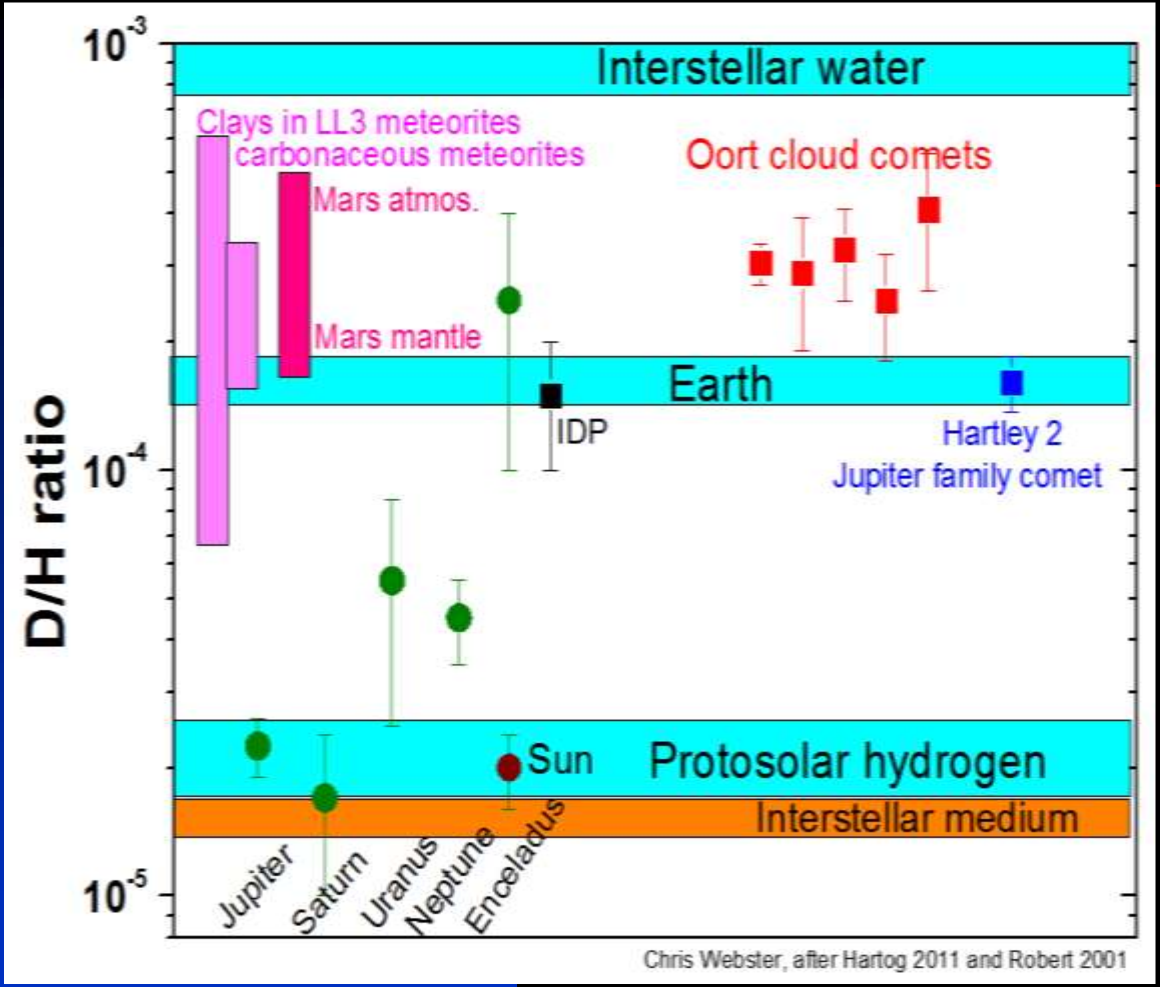


Atmospheric composition

isotope	Δ [terrestrial]	Lost to space
D/H	~5	60-74 %
$^{38}Ar/^{36}Ar$	1.3	50-90 %
$^{13}C/^{12}C$	1.05-1.07	50-90 %
$^{15}N/^{14}N$	1.7	90 %
$^{18}O/^{16}O$	1.025	25-50 %

Jakosky & Phillips [2001]

D/H ratio and the Origin of Earth's water….



Chris Webster, after Hartog 2011 and Robert 2001

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

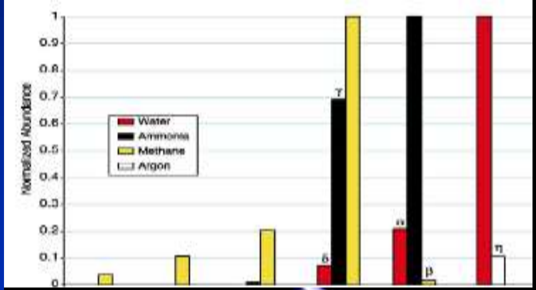
Sun & planets formed 4.5 Gya from protosolar nebula of mainly H, He

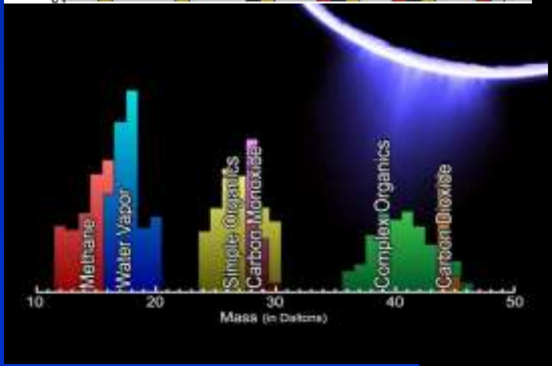
Were ices stable enough near habitable zone? OR was water delivered by stable hydrated silicates?

The Emergence of Tunable Laser Spectrometers

Mass Spectrometer:

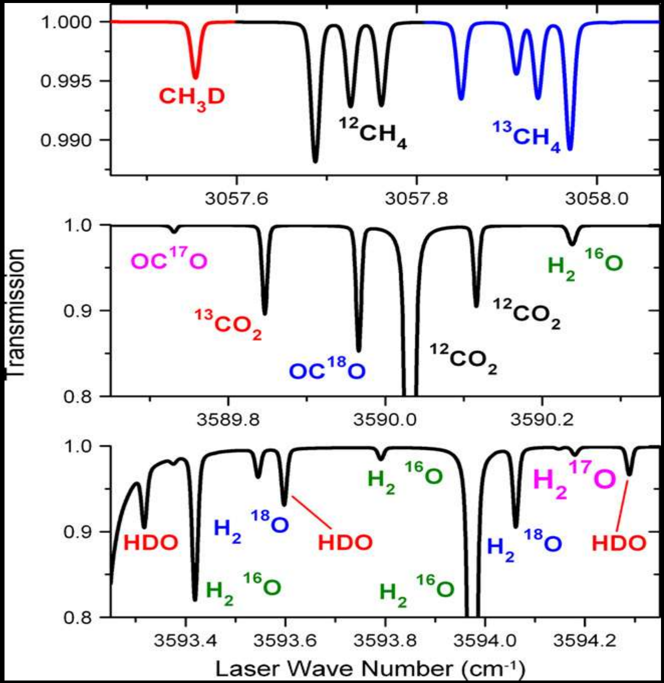
- Surveys all gases;
- Essential for noble gases & complex organics;
- Mass interferences in D/H, CO/N2, 13CO2, methane, ammonia and water.



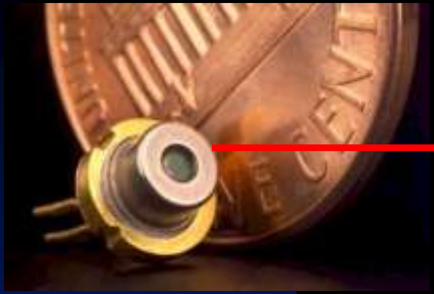


Tunable Laser Spectrometer:

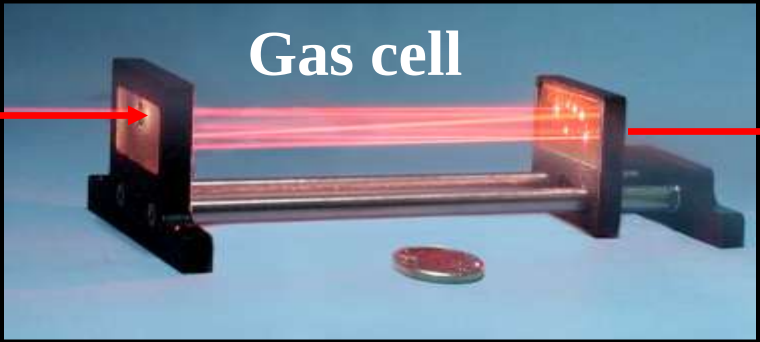
- Targets specific gases- no interference;
- Direct, non-invasive, high sensitivity to water, methane, other gases;
- Carbonates, hydrates to 10^{-9} wt%
- High precision ~0.1% CHNOS isotope ratios



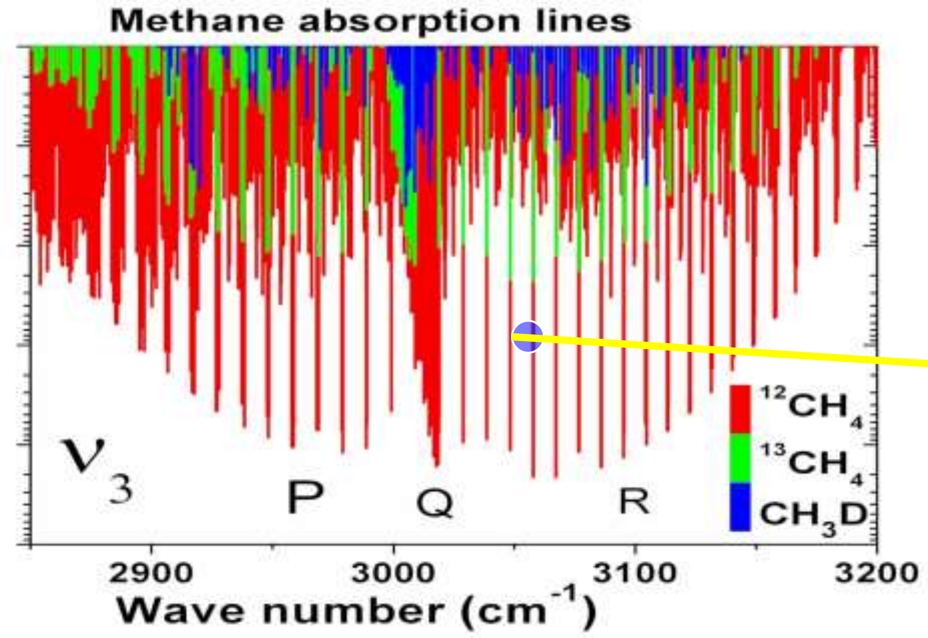
Laser Absorption Spectroscopy

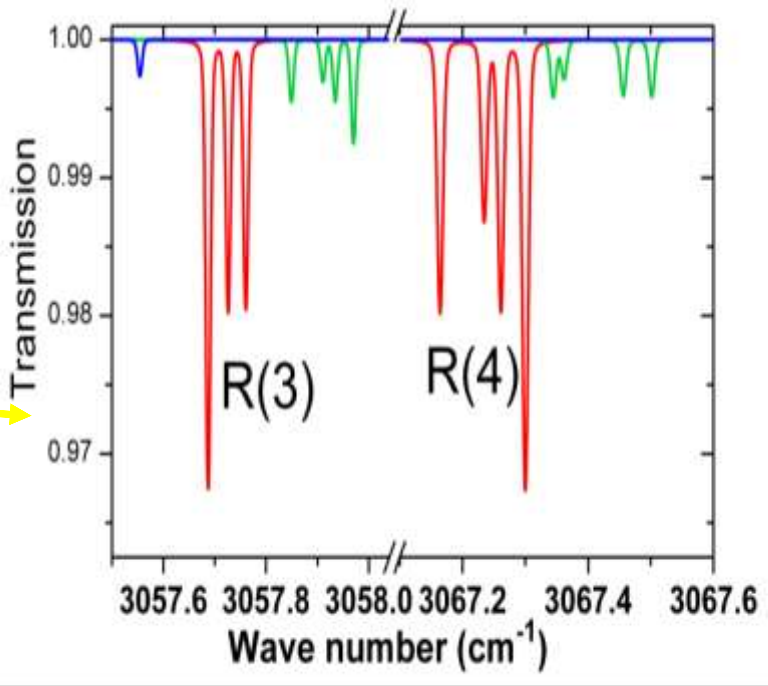


Tunable laser
1-12 µm

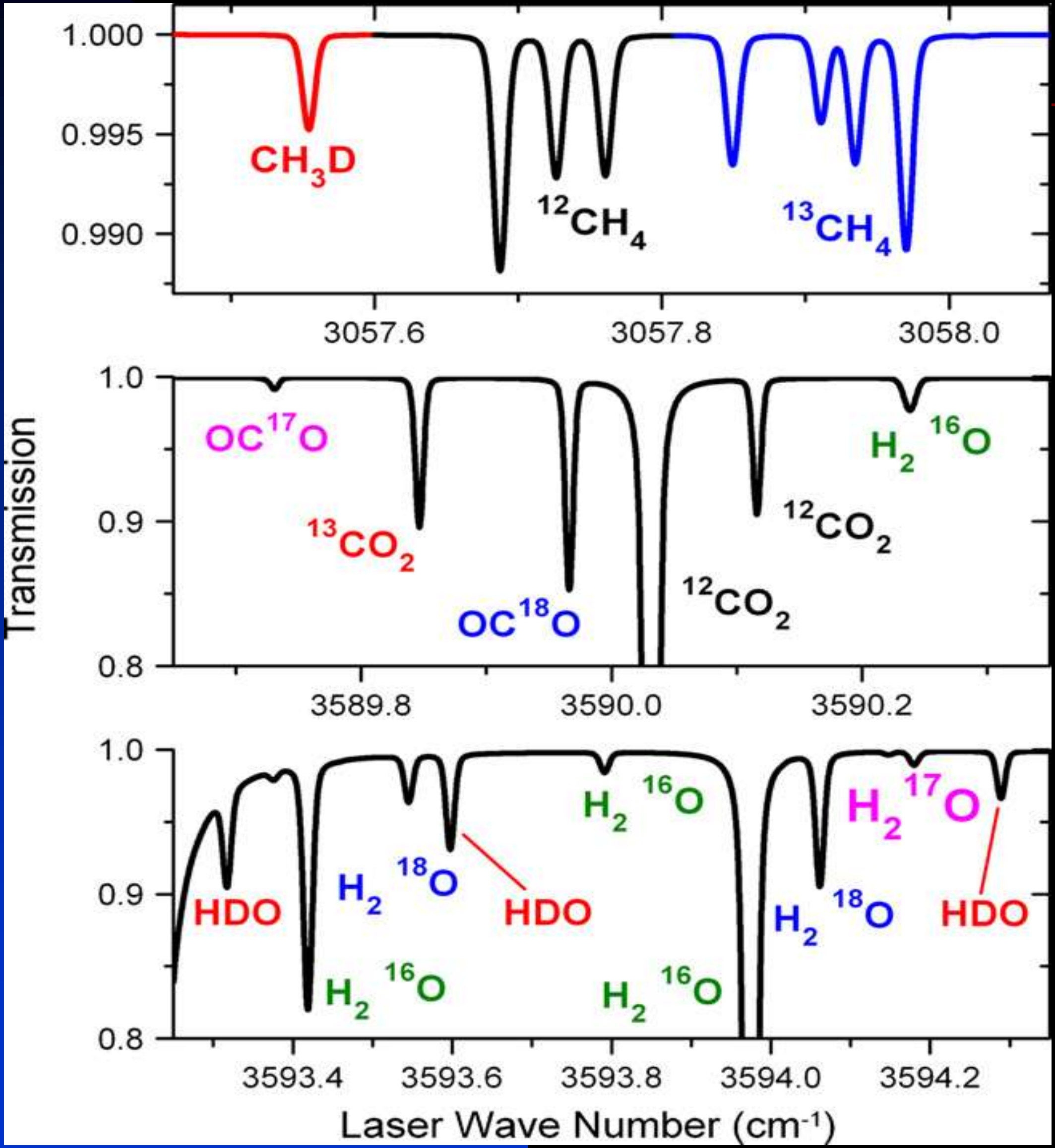


Detector

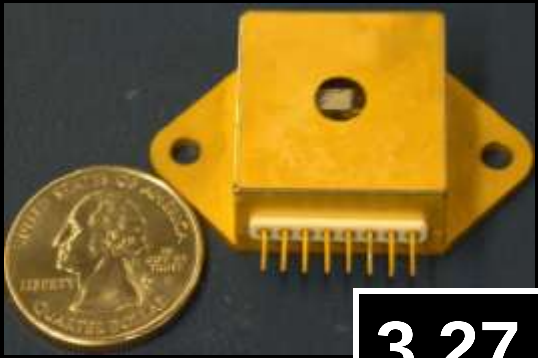




TLS target spectral regions- chosen wisely!



JPL IC laser

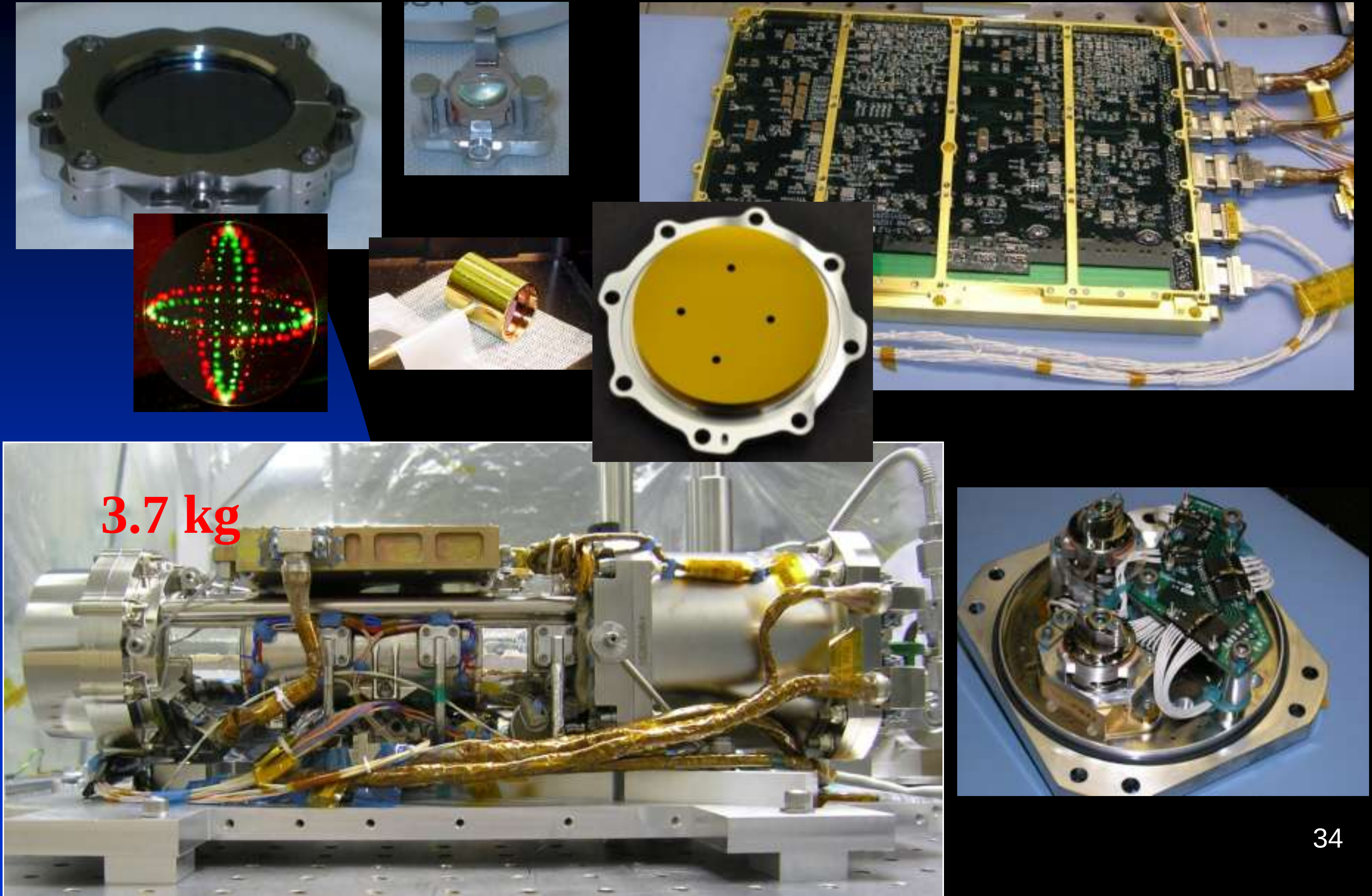


3.27 µm

Nanoplus TDL

2.78 µm

TLS flight hardware



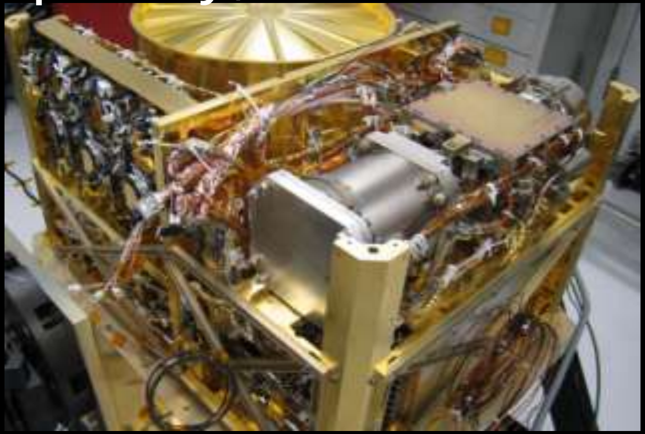
SAM is the most sophisticated planetary instrument suite ever flown

- Quadrupole Mass Spectrometer
- Tunable Laser Spectrometer
- 6 GC columns
- Sample Manipulation System
- 2 pyrolysis cells
- 16 Gas Processing manifolds
- 2 high conductance valves
- 52 microvalves
- 51 gas line heaters
- Combustion & cal gases
- 2 scrubbers and 2 getters
- hydrocarbon trap
- 2 turbomolecular pumps
- 2 He tanks at 2400 psi
- 4 heat pipes
- Electronics stack
- ~ 600 m of harness wire
- Solid Sample Inlet Tubes
- Thermal shields

SAM PI is **Paul Mahaffy**, NASA GSFC
GC lead is **Michel Cabane**, Univ. Paris
TLS lead is **Chris Webster**, JPL

TLS enhanced in SAM

- The SAM suite **enables TLS operation** in providing power, valving, plumbing, evacuation, cal gas, etc.
- SAM **enables EGA and combustion production** for TLS analysis of evolved gases from solid samples;
- SAM **enables TLS methane $^{13}C/^{12}C$ isotope measurement and ultra-low methane detection** (~50 times) through methane enrichment capability;
- SAM **enables atmospheric water isotope measurements** by water enrichment that enhances TLS detection by ~50 times;



SAM-TLS will measure CH_4, H_2O, CO_2 and their isotope ratios

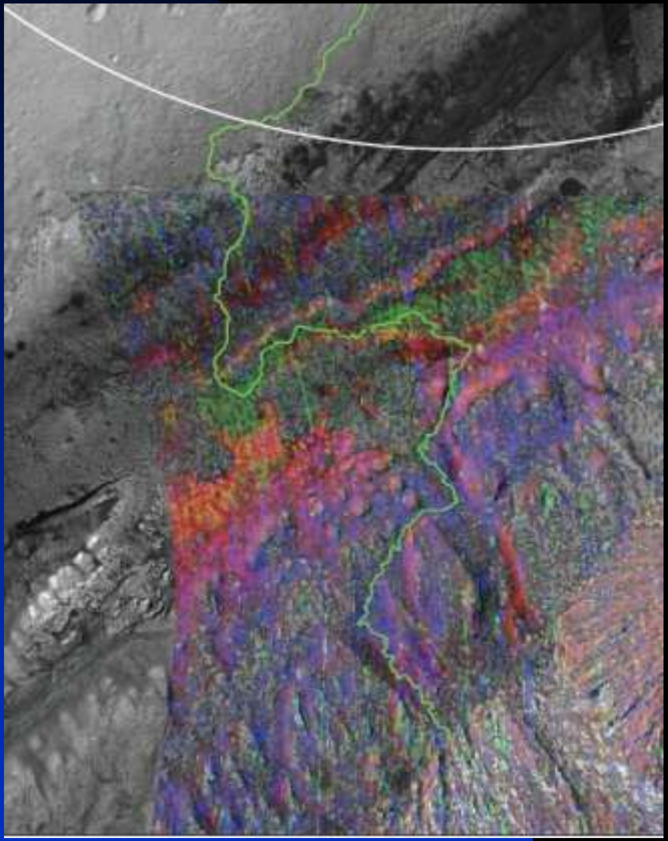
Wavelength	Region	Capability
3.27 µm	Methane	CH_4 to 1 ppb (~20 ppt in SAM) d^{13}C to 10 ‰
2.785 µm	CO_2	CO_2 to 0.2 ppm d^{13}C to 2 ‰ d^{18}O to 1-2 ‰ d^{17}O to 3 ‰
2.783 µm	H_2O	H_2O to 0.1 ppm dD to 2 ‰ d^{18}O to 3 ‰ d^{17}O to 5 ‰

TLS LOD is ~10^{-9} wt% H_2O in rocks

TLS LOD is ~10^{-8} wt% C in rocks

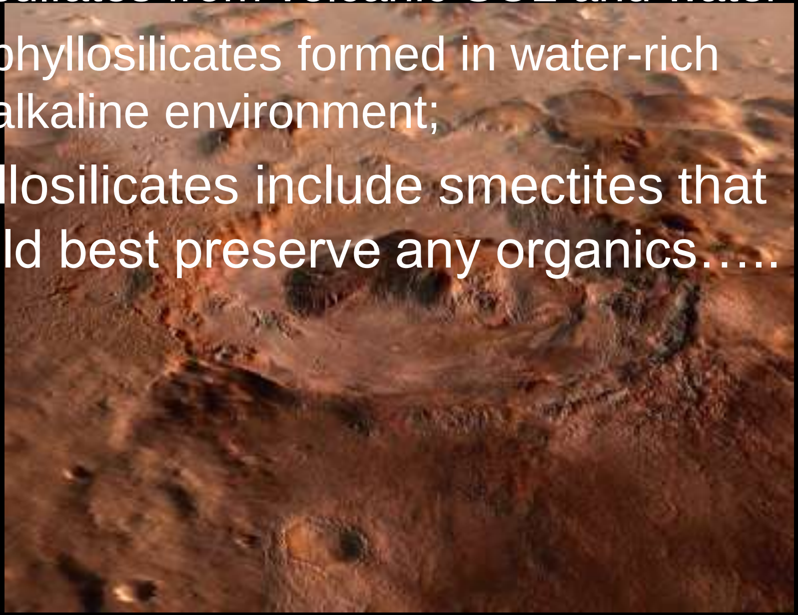
- Will measure δ13C of CO_2 from organics release/ combustion

Gale Crater- a record of past aqueous environments?

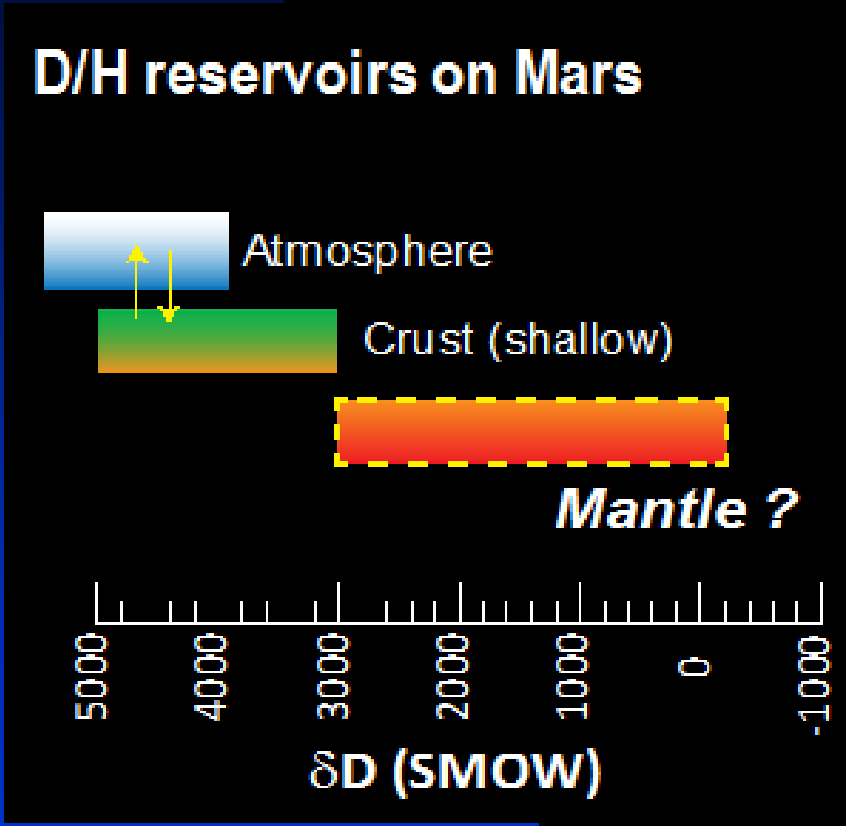


Curiosity will land on the floor of Gale crater (inside the arc) and could rove along the green line, climbing across layered sediments containing clays and sulfates (denoted by their spectral colors).- Kerr, Science, July 2011.

- Gale crater is late Noachian (~4Gya), floor deposits early Hesperian (~3.5Gya)
- 5 km of layered sediments/strata record sequences of aqueous habitable environments over a long time period;
- Strata contain hydrous minerals
  - sulfates from volcanic SO2 and water
  - phyllosilicates formed in water-rich alkaline environment;
- Phyllosilicates include smectites that would best preserve any organics…..



D/H as discriminator of atmosphere, crust, mantle - a tracer of Mars evolution



- Studies of Shergottite meteorites by T. Usui (NASA Johnson);
- Will SAM-TLS see same record across Gale Crater?

T. Usui

Martian water-rock interactions will be revealed in H, O isotope ratios

- Rapid equilibration of CO_2 with liquid water will exchange ^{18}O
- In rocks, H is minor and O is major component, so Water/Rock (W/R) ratio:

  (W/R)Hydrogen >> (W/R)Oxygen
- Thus, small amounts of water can produce significant change in δD of a rock;
- e.g. L-shaped trend, here a product of profound hydrothermal alteration event during Eocene time when exchange with hot infiltrating fluids derived from low meteoric waters produced large changes in δD, but little in $\delta^{18}O$.

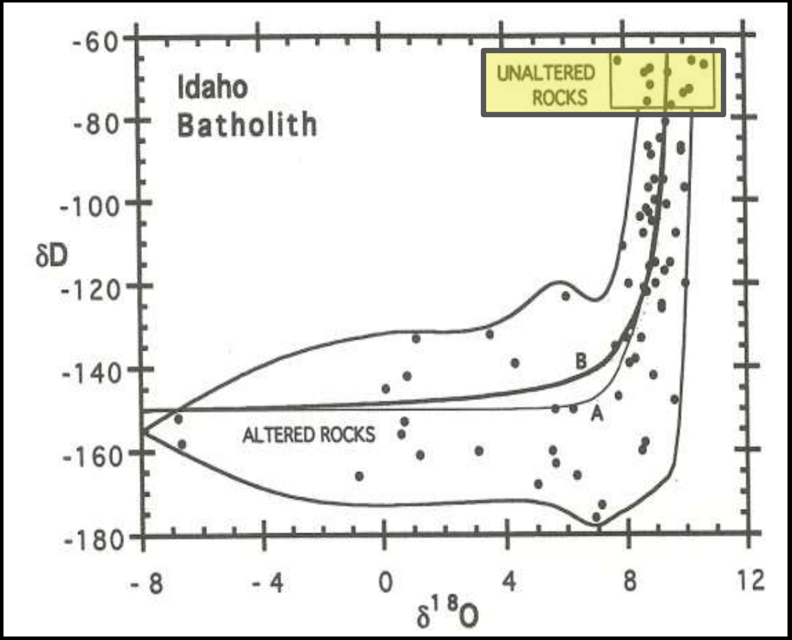
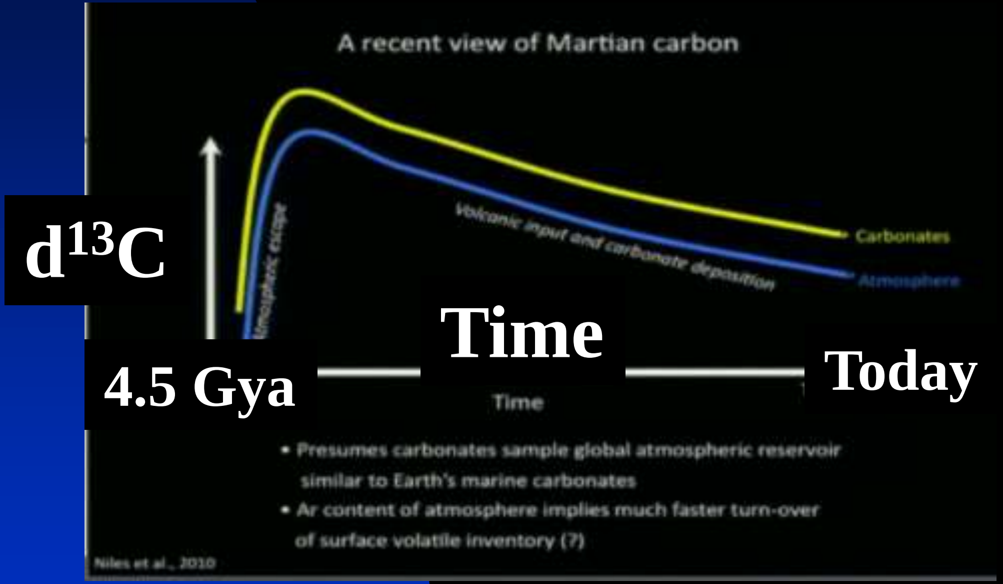


Figure and text after *Robert Criss, 1999*

Reconciling Mars CO_2 isotopes with the meteorite record

- Atmospheric CO_2 produces carbonates enriched in 13C
- Meteorites show d13C ~50‰, but Phoenix reports atmospheric d13C of -2.5‰



A recent view of Martian carbon

- Presumes carbonates sample global atmospheric reservoir similar to Earth's marine carbonates
- Ar content of atmosphere implies much faster turn-over of surface volatile inventory (?)

Niles et al., 2010

Will Gale Crater show evidence of high d^{13}C carbonates?

Clumped Isotopes ($^{18}O^{13}C^{16}O$): Carbonates in the Martian meteorite AH84001 formed at 18 ± 4 °C in a near-surface aqueous environment - Itay Halevy, Woodward Fischer, John Eiler

Summary Requirements

- Carefully identify target body-specific requirements !

Measurement	New bodies*	Earth, Mars, meteorites
Elemental abundances	10%	2%
Mineralogical components	10%	5%
Noble gas isotope ratios	5%	3%
D/H	30%	1%
δ13C	10 ‰	0.1 ‰
δ13C biological	10 ‰	
δ18O, δ17O	20 ‰	0.2 ‰
δ15N	20 ‰	0.2 ‰
δ34S, δ33S	10 ‰	0.2 ‰

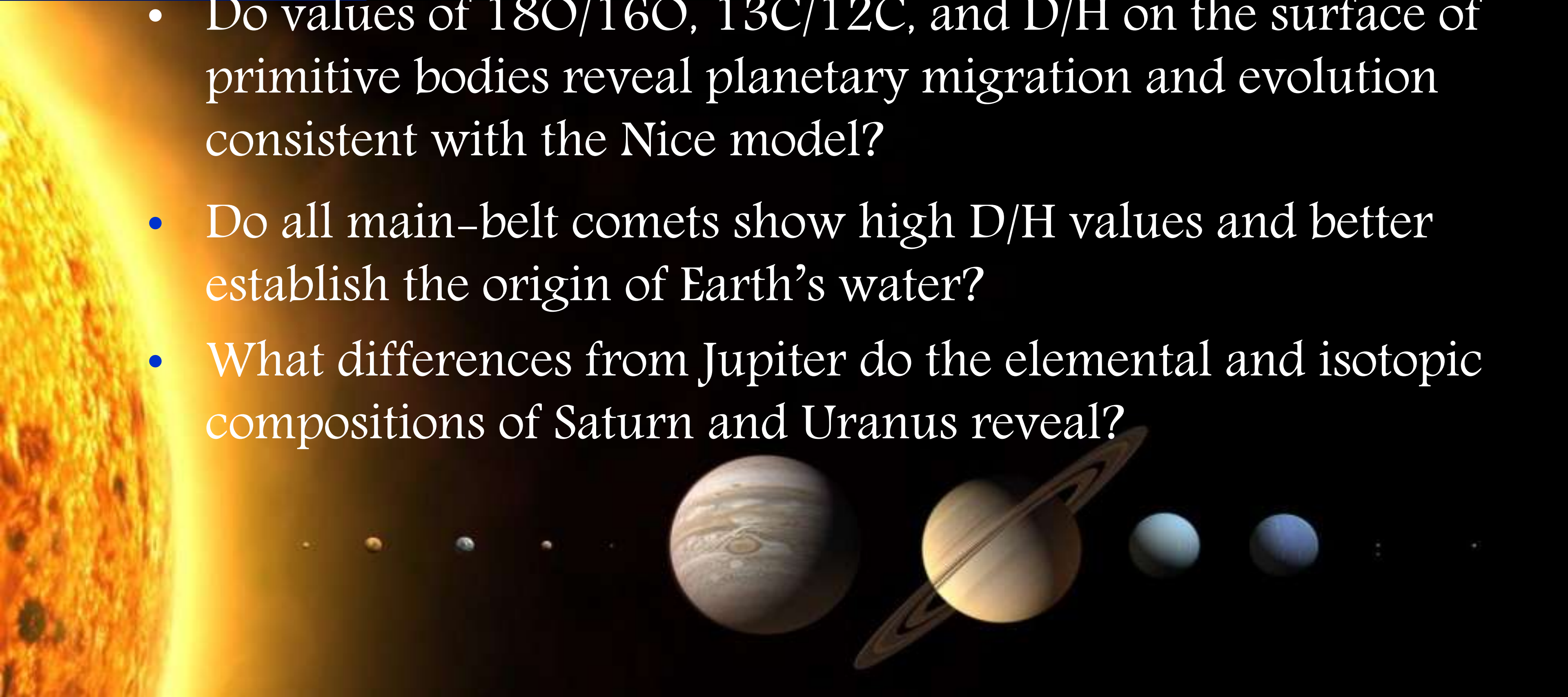
* Inner planets (not Earth), outer planets, satellites, primitive bodies

Where Cavity Ringdown Detection would be of benefit

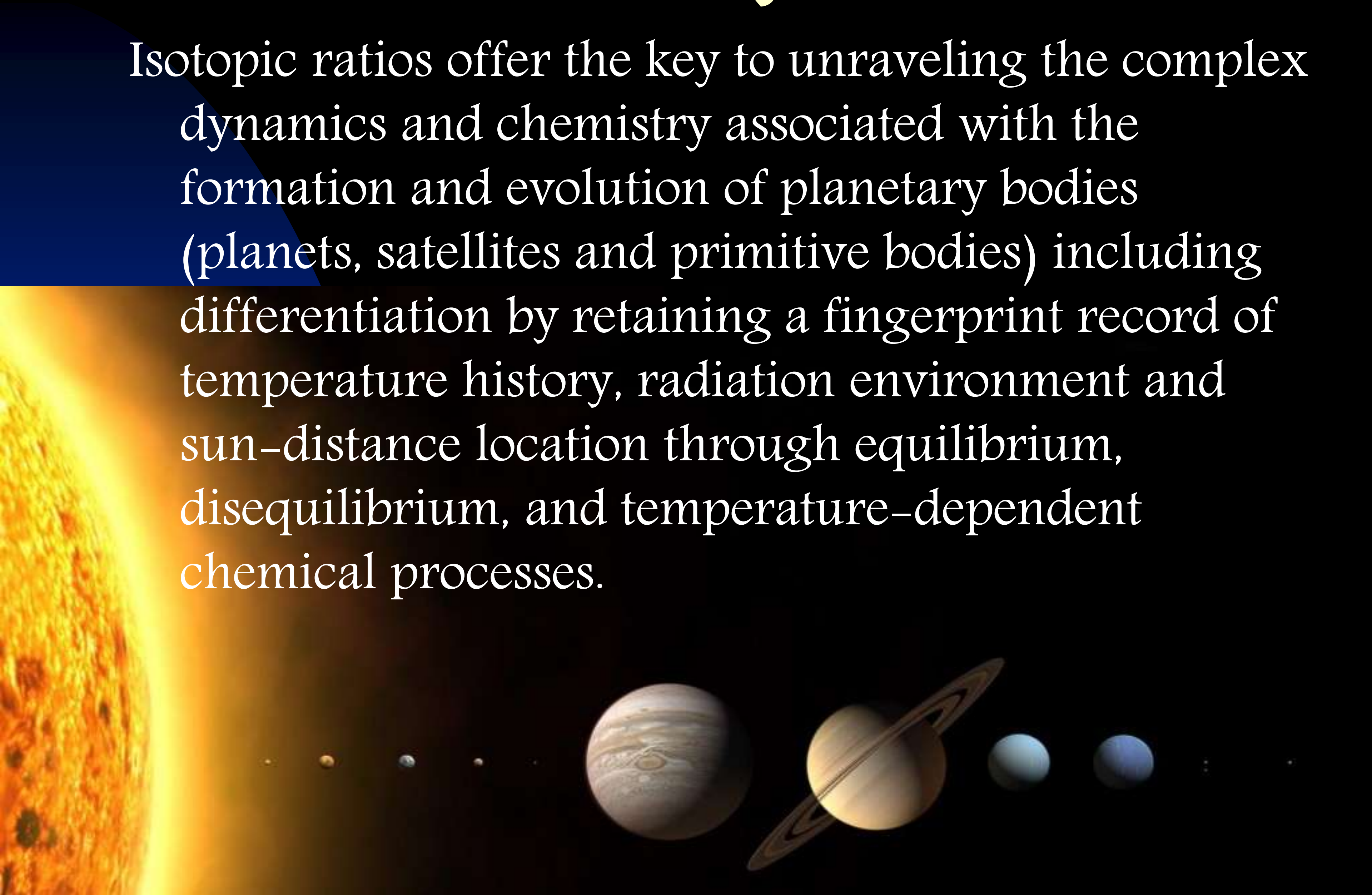
- Earth *stratospheric* water isotope ratios;
- S isotope ratios in (inherently weak) H_2S, SO_2 (e.g. Venus);
- Methane isotope ratios (C, H) in *low abundance* methane (e.g. Mars); *not* Saturn, Titan;
- CO and CO_2 isotopes in *low-abundance* regions (e.g. Saturn, Uranus);
- *Clumped* isotopic measurements in CO_2 (e.g. $^{18}O^{13}C^{16}O$ for Mars environment evolution, primitive body origins;
- ^{17}O measurements to 0.1 per mil to identify sources

Questions

- Will SAM provide the *direct connection* of the SNC meteorites with Mars and establish the timeline of the Martian carbon cycle?
- Will SAM confirm a watery past for Mars?
- Do values of 18O/16O, 13C/12C, and D/H on the surface of primitive bodies reveal planetary migration and evolution consistent with the Nice model?
- Do all main-belt comets show high D/H values and better establish the origin of Earth’s water?
- What differences from Jupiter do the elemental and isotopic compositions of Saturn and Uranus reveal?



Summary



Isotopic ratios offer the key to unraveling the complex dynamics and chemistry associated with the formation and evolution of planetary bodies (planets, satellites and primitive bodies) including differentiation by retaining a fingerprint record of temperature history, radiation environment and sun-distance location through equilibrium, disequilibrium, and temperature-dependent chemical processes.