Disk Chemistry

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Chemistry of Protoplanetary Disks

1. Observational constraints
   - planets, comets, meteorites, protoplanetary disks
- Thermochemical equilibrium and kinetic models
  - how are these models created and what are the limitations
- Key Ingredients and Our Current View of Disk Chemistry
  - Cosmic ray, X-ray, UV irradiation
  - models of illuminated disks
- Chemical Fractionation Effects
  - deuterium chemistry and oxygen isotopic fractionation

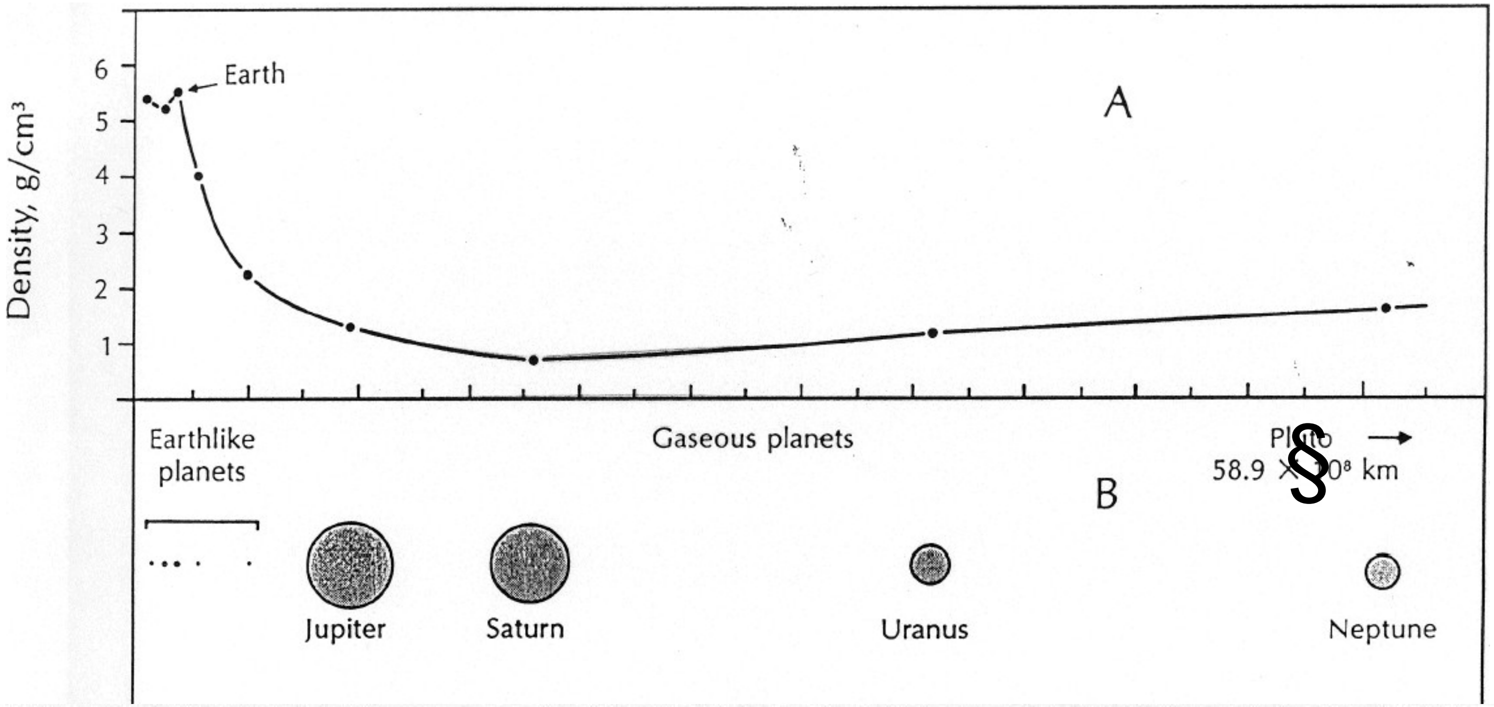
Two recent reviews: Ciesla and Charnley (MESS II) and Bergin et al. (PPV)

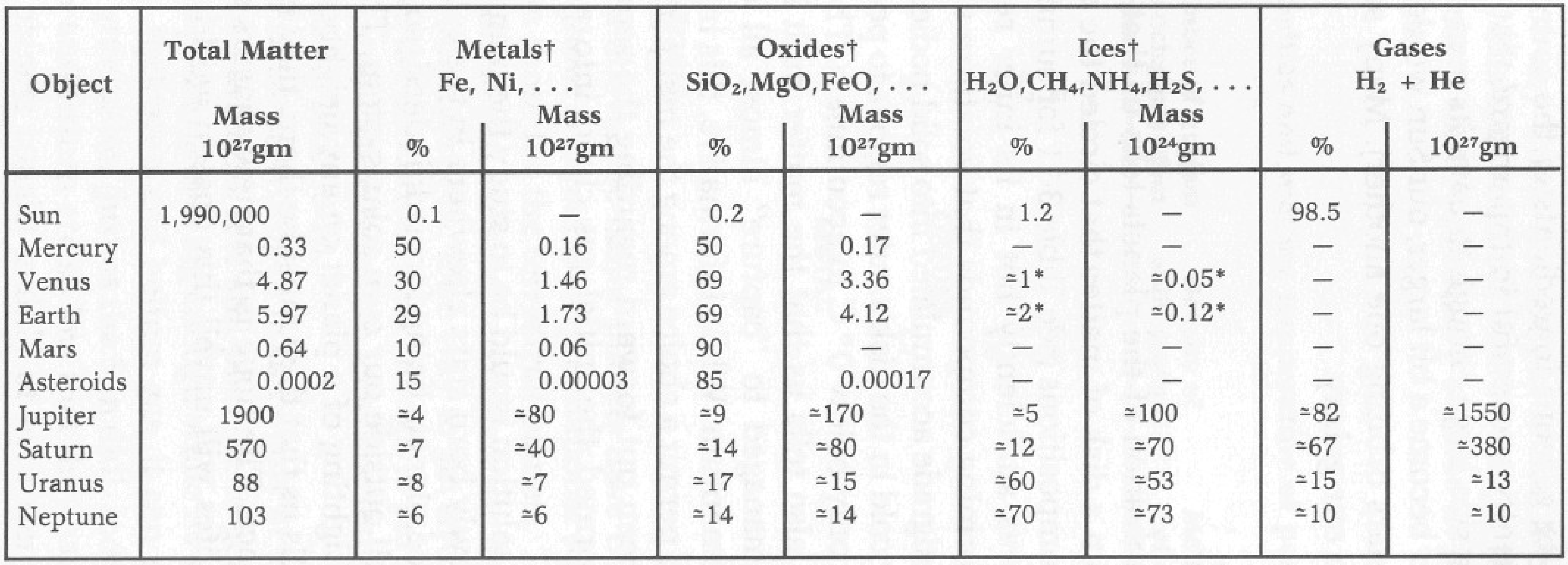
Edwin (Ted) Bergin/Univ. of Michigan

Observational Constraints

- planetary composition
- meteoritic record
- cometary composition
- chemical fractionation within above classes
- observations of distant protoplanetary disks

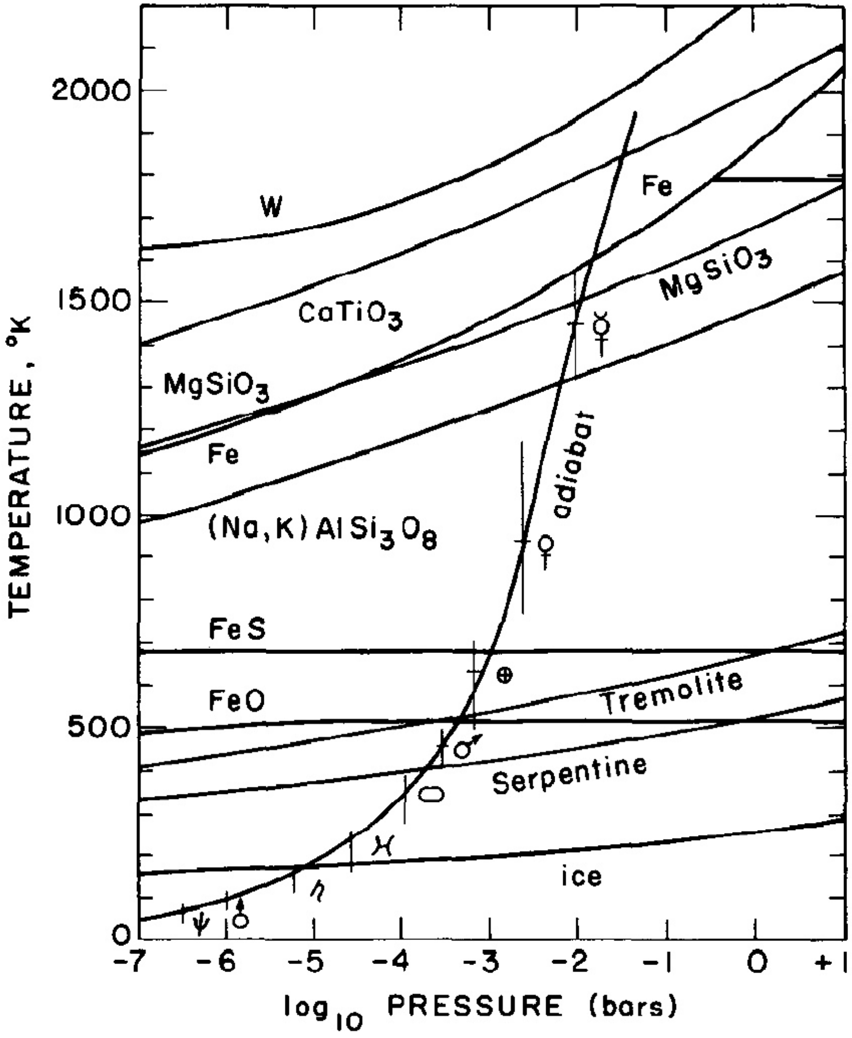
Solar System

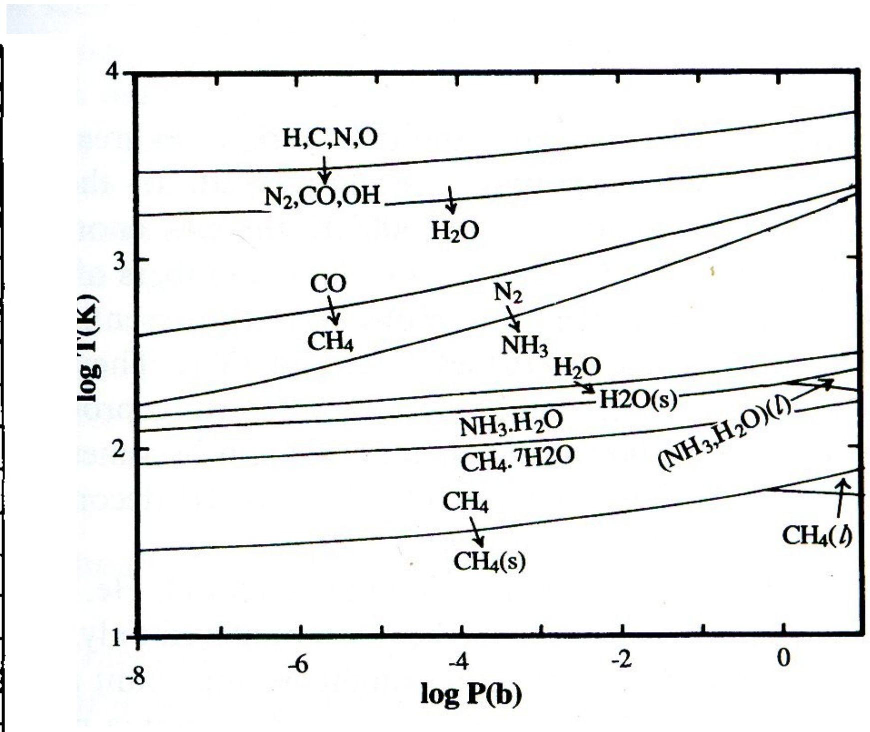




Object	Total Matter Mass 10^{27}gm	Metals† Fe, Ni, . . . %	 Mass 10^{27}gm	Oxides† SiO_2, MgO, FeO, . . . %	 Mass 10^{27}gm	Ices† H_2O, CH_4, NH_4, H_2S, . . . %	 Mass 10^{24}gm	Gases H_2 + He %	 10^{27}gm
Sun	1,990,000	0.1	—	0.2	—	1.2	—	98.5	—
Mercury	0.33	50	0.16	50	0.17	—	—	—	—
Venus	4.87	30	1.46	69	3.36	≃1*	≃0.05*	—	—
Earth	5.97	29	1.73	69	4.12	≃2*	≃0.12*	—	—
Mars	0.64	10	0.06	90	—	—	—	—	—
Asteroids	0.0002	15	0.00003	85	0.00017	—	—	—	—
Jupiter	1900	≃4	≃80	≃9	≃170	≃5	≃100	≃82	≃1550
Saturn	570	≃7	≃40	≃14	≃80	≃12	≃70	≃67	≃380
Uranus	88	≃8	≃7	≃17	≃15	≃60	≃53	≃15	≃13
Neptune	103	≃6	≃6	≃14	≃14	≃70	≃73	≃10	≃10

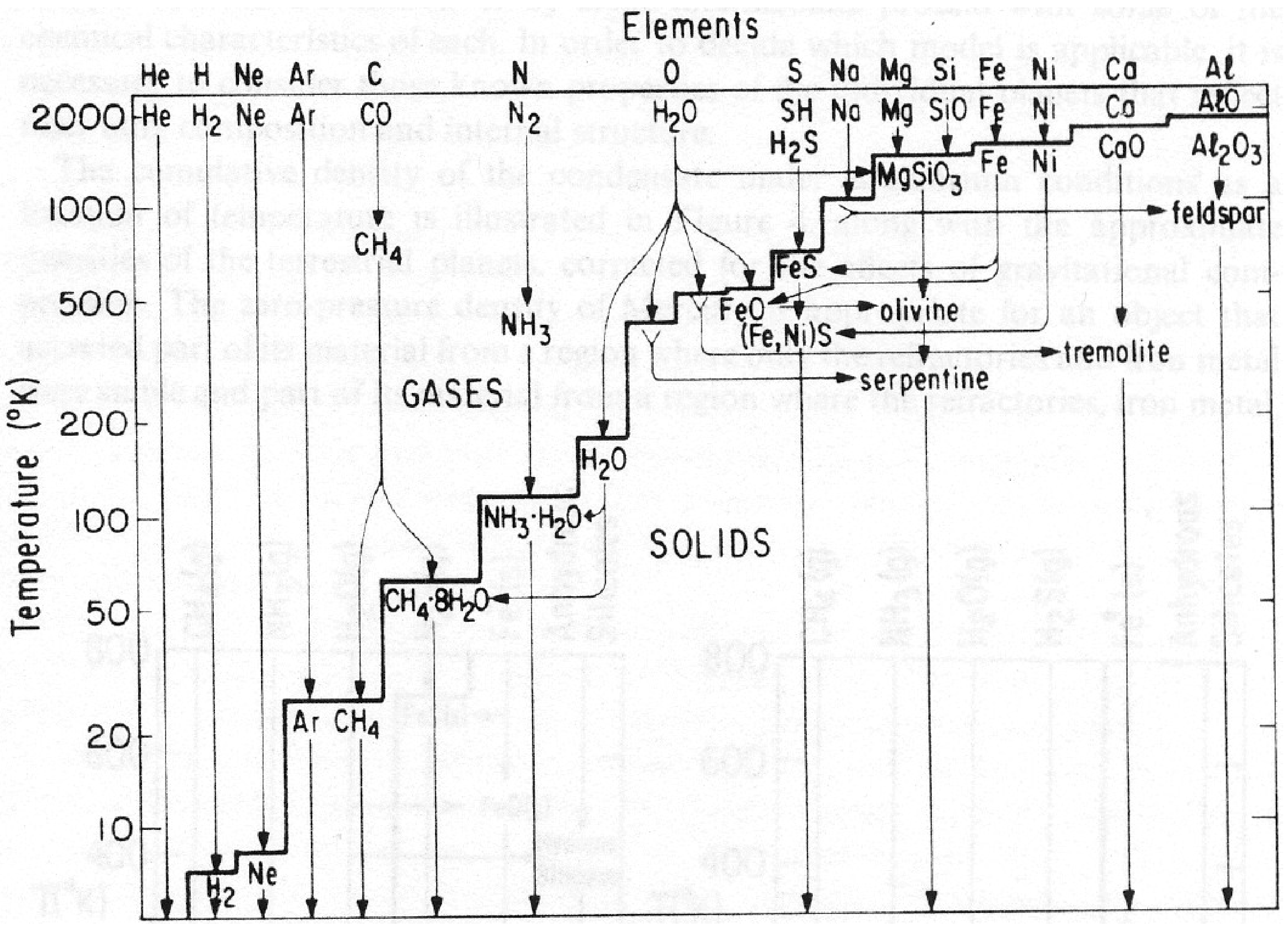
Condensation Sequence





Barshay and Lewis 1976 (ARAA); Lewis 1997 (Physics and Chemistry of the Solar System)

Condensation Sequence



Mercury

Venus

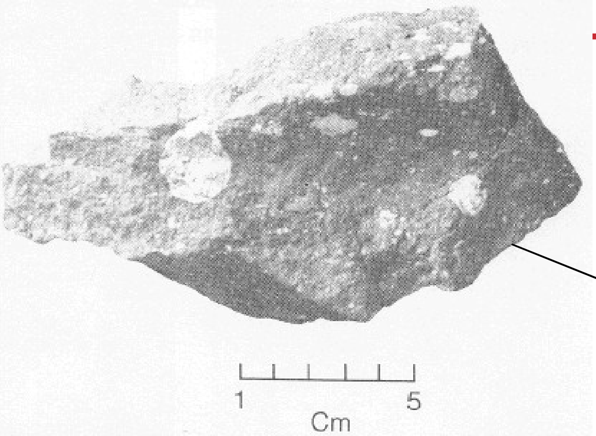
Earth

Mars

Jupiter

Saturn

Meteorite Classification



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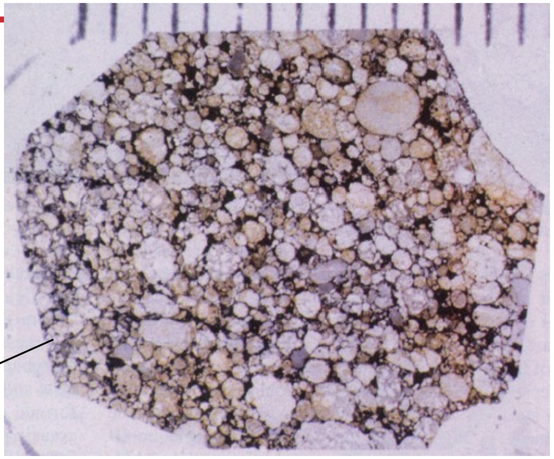

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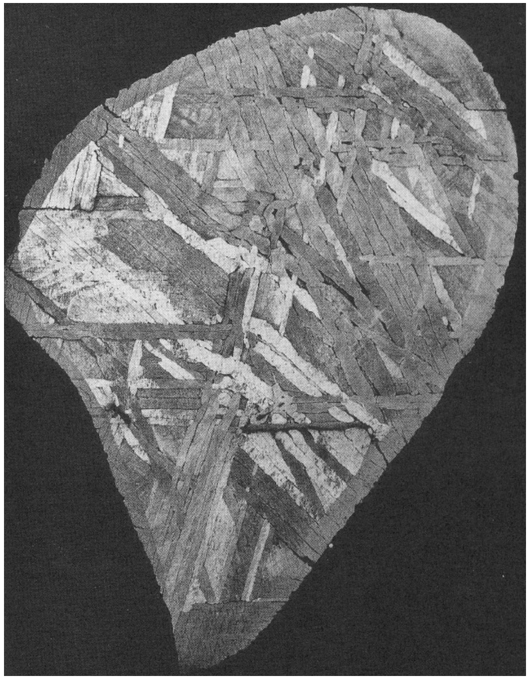
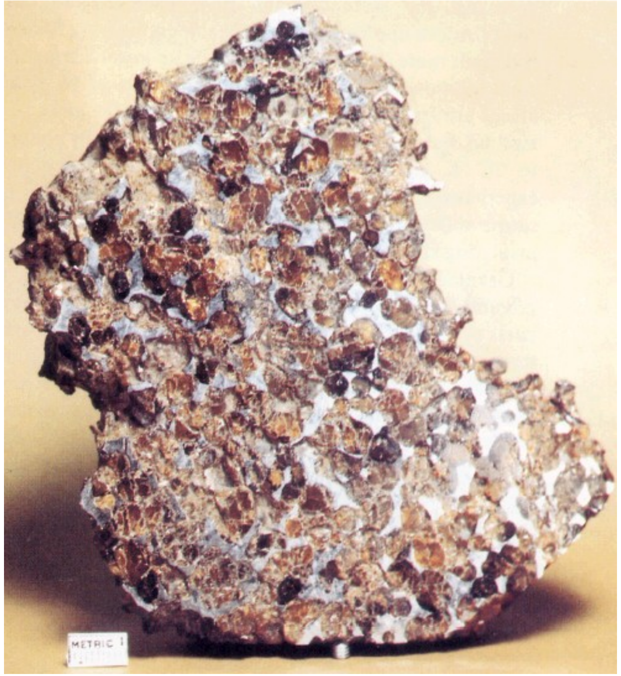
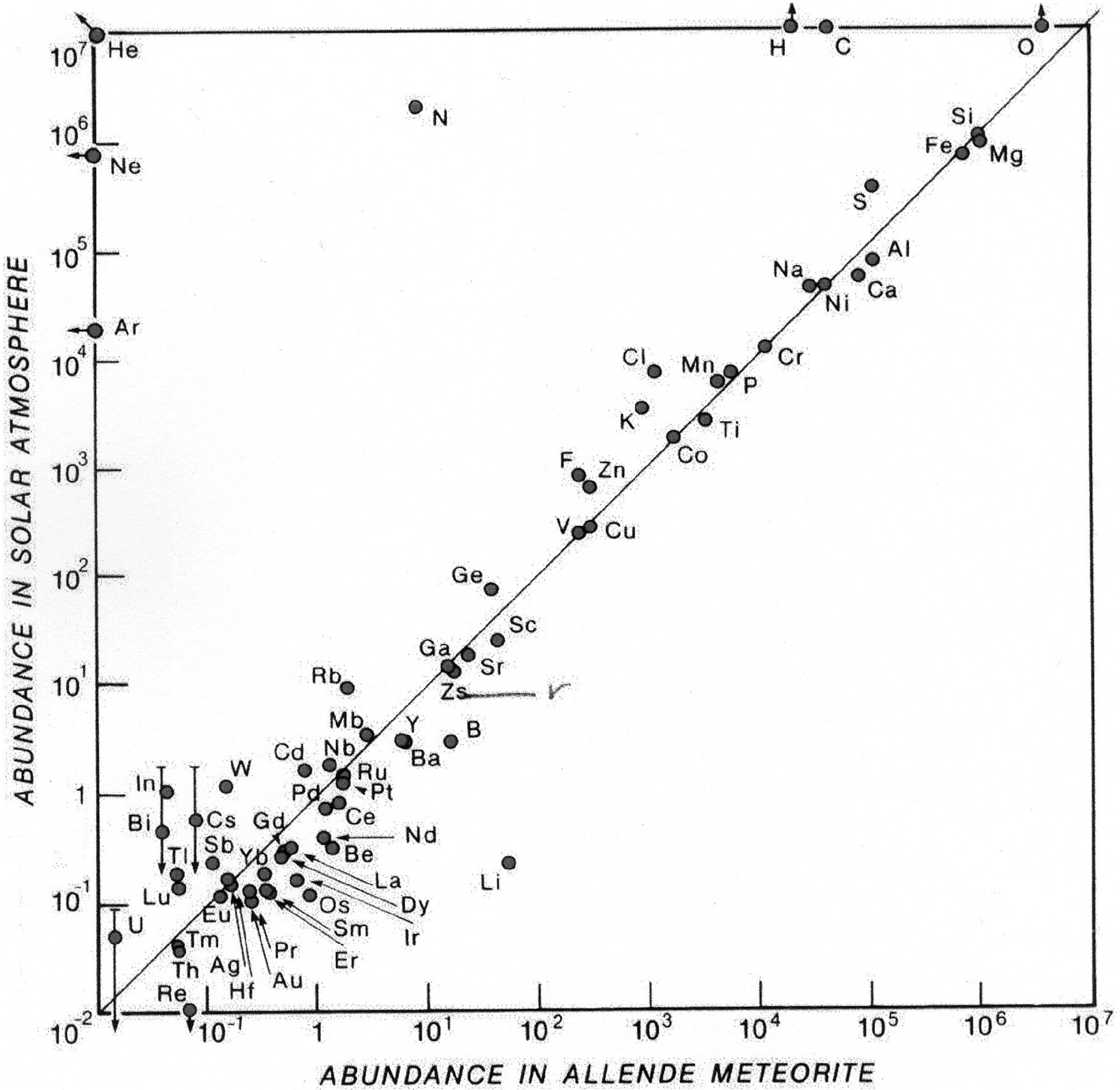




from
P. Asimow
web lecture

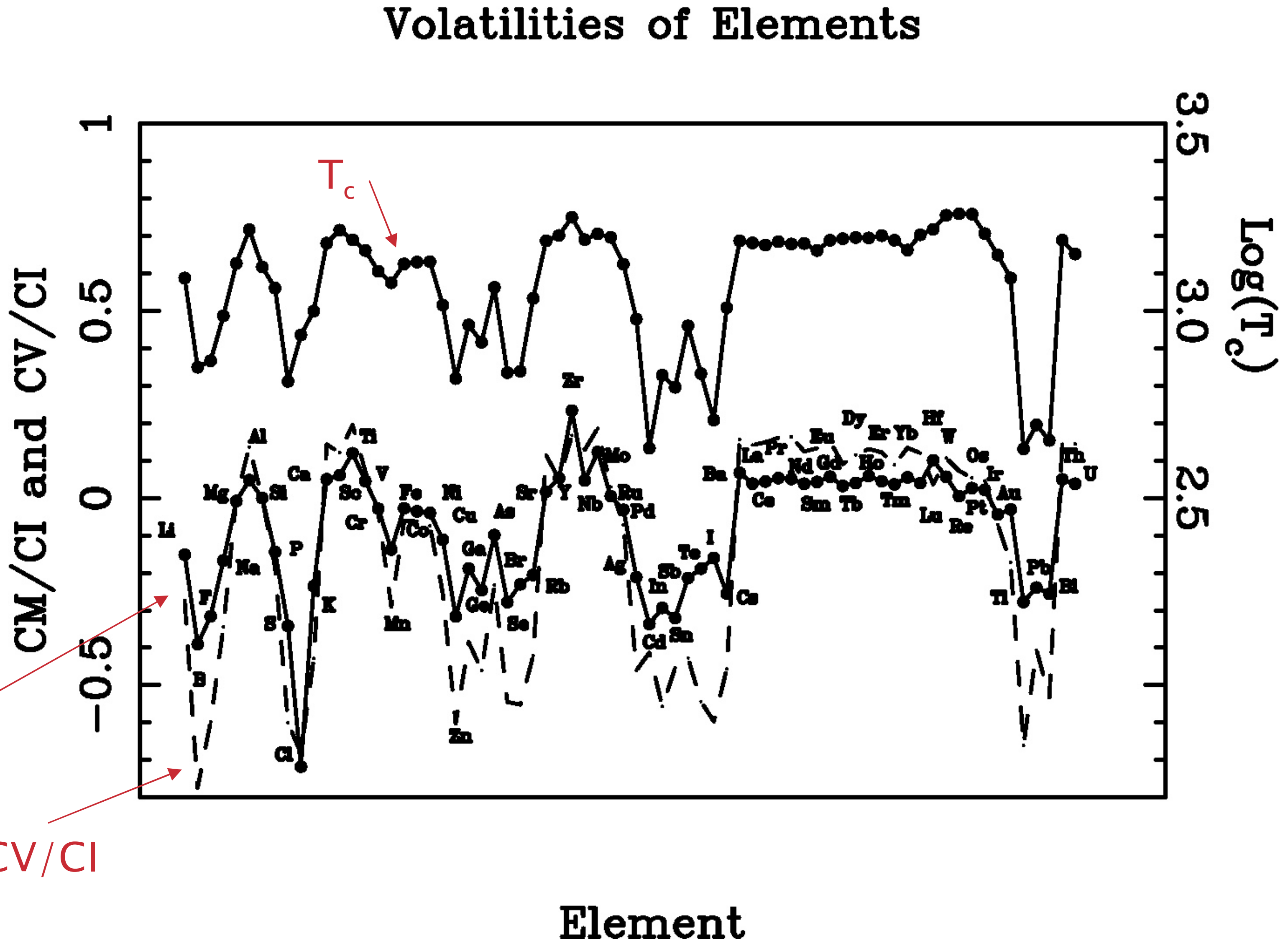
Carbonaceous Chondrites



Except for most volatile elements (i.e., more volatile than nitrogen), CI carbonaceous chondrites are excellent models of bulk solar system composition.

CI chondrites are the "most primitive" and are used to examine abundance trends.

Carbonaceous Chondrites



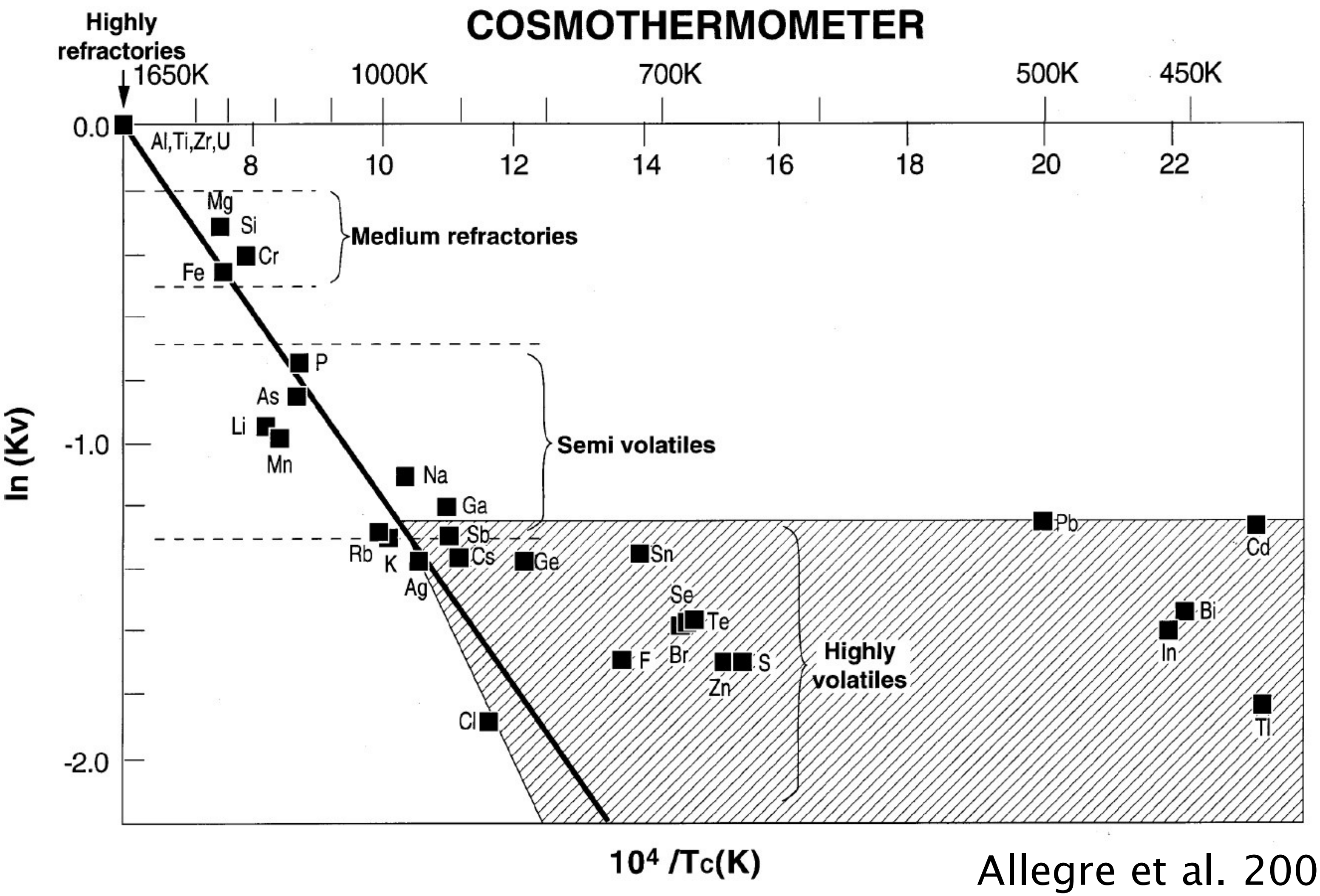
T_c

CM/CI

CV/CI

CV (Allende -- rich in refractory material) relative to CI chondrites. Among the several classes of carbonaceous chondrites, relative abundance of all elements are controlled by condensation temperature.

Carbonaceous Chondrites



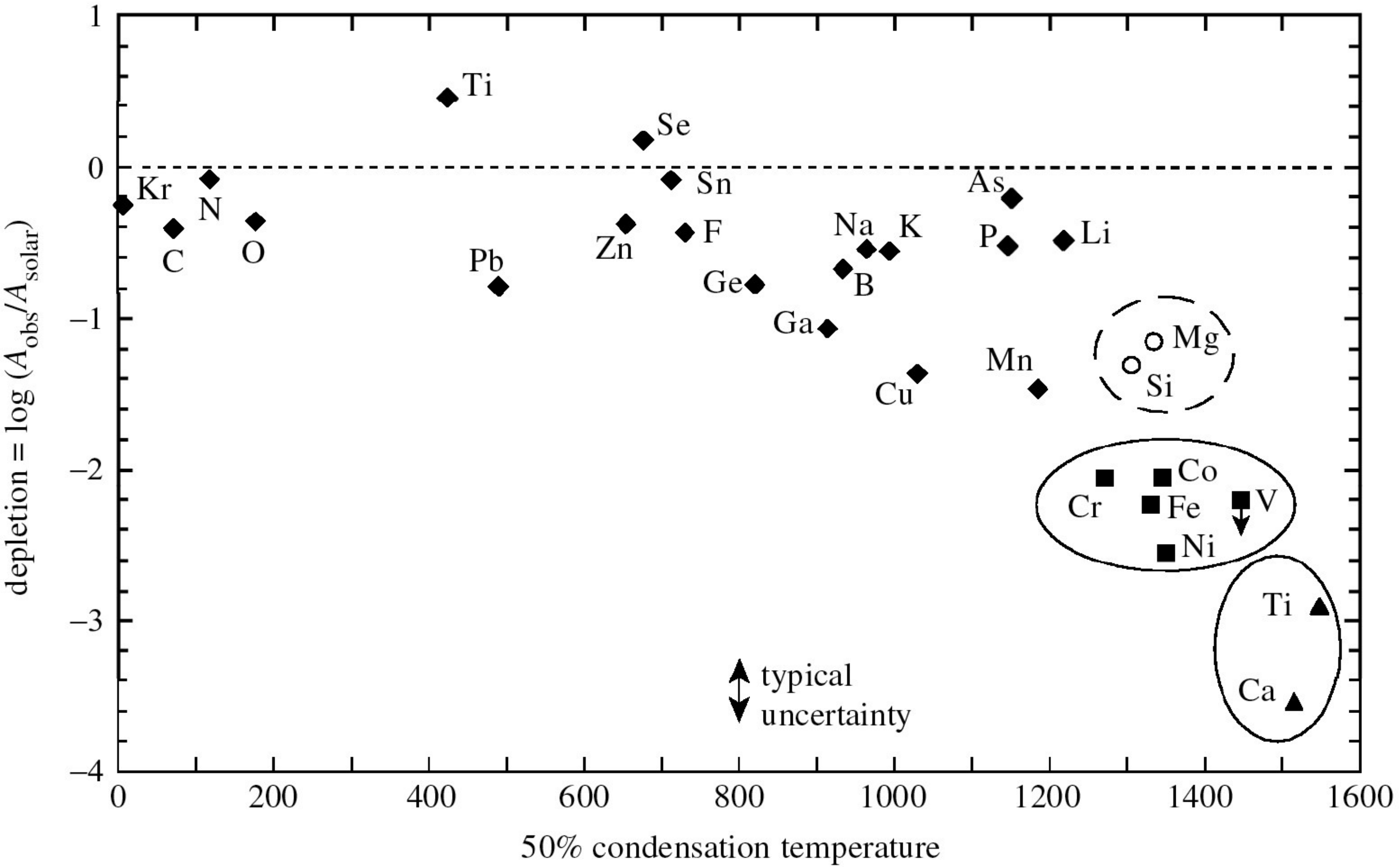
Allegre et al. 2001

Kv = volatile fractionation factor in CV relative to CI

Laboratory quantification of volatility by condensation temperature shows that relative abundance in carbonaceous chondrites is controlled by **pure vapor-solid equilibrium** down to ~900 K, then **adsorption** must become significant for retaining many highly volatile elements.

from
P. Asimow
web

Some Similarity to ISM



Ebel 2000

The Earth

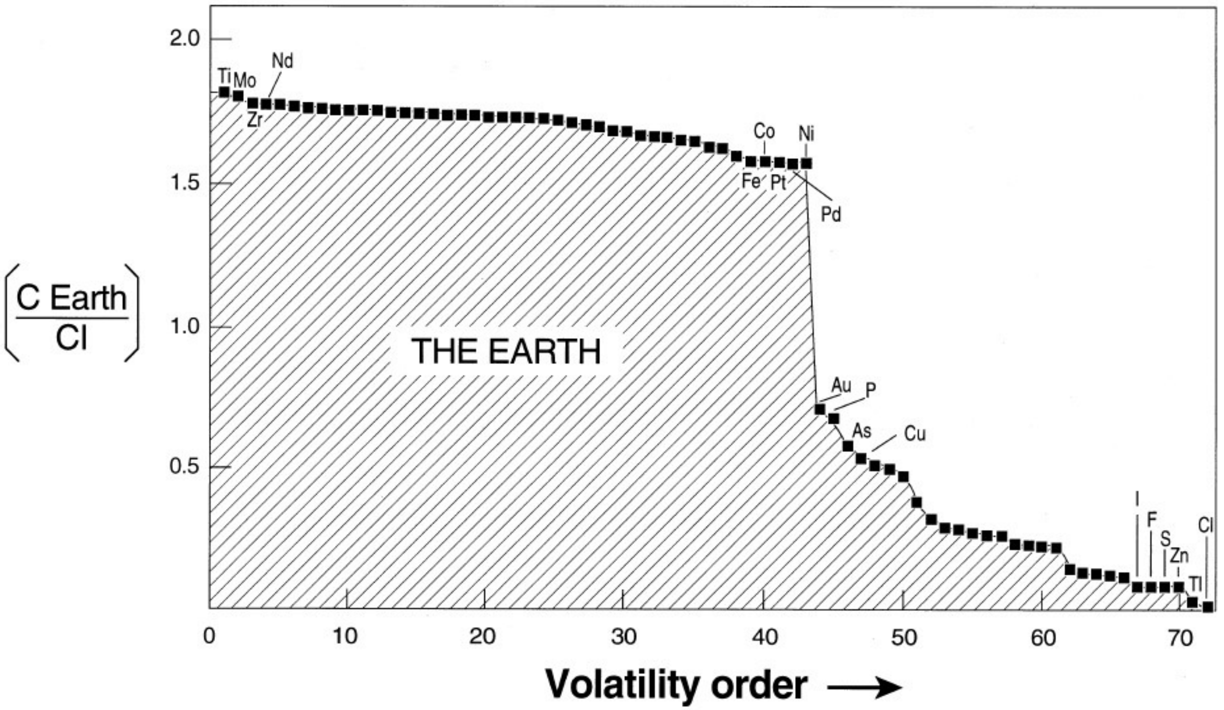


Fig. 7. The composition of the Earth normalised to CI chondrites plotted as a 'spidergram', which is therefore directly comparable with the K_V pattern of Fig. 4.

Nobel Gases

- Noble gases:
    - inert
    - heavy
    - do not participate in biology
- Condense at very low temperatures and can be used to probe conditions in early solar system
- Measure abundances of noble gases in planetary atmospheres and examine question of origin (outgassing/contributions from impacts)

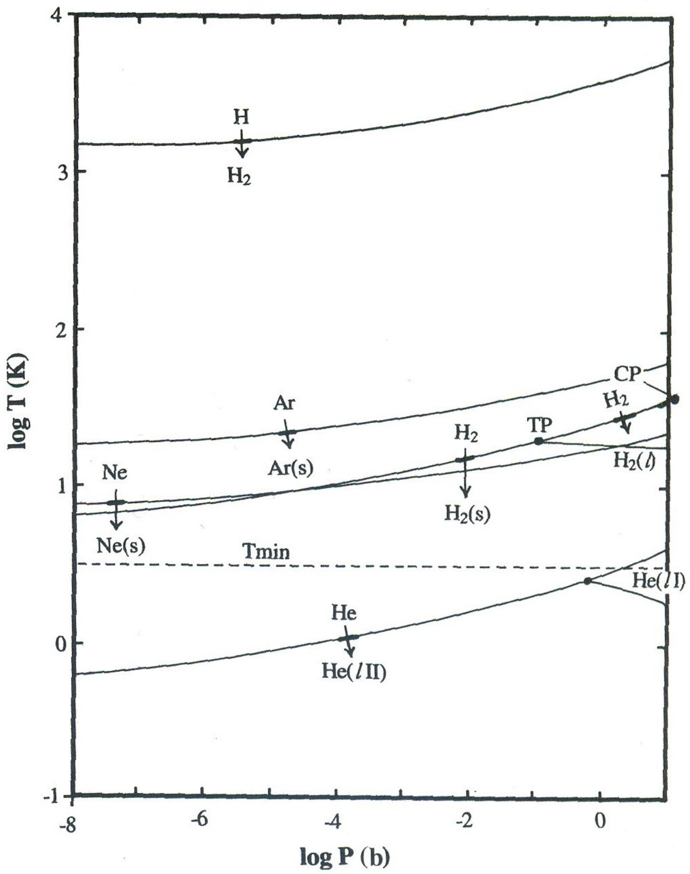


Figure IV.14 Hydrogen, helium, and neon chemistry. The top line is the locus of equal H and H_2 pressures: below it, H_2 is the dominant gas. The saturation temperatures for H_2, Ne, Ar, and He are illustrated. Note the triple point (TP) and critical point (CP) of H_2 and the He gas-liquid I–liquid II pseudo-triple point ("TP"). The horizontal dashed line labeled T_{min} is the microwave background temperature of the Universe. Lower temperatures, although not wholly impossible, require artificial (or natural) refrigeration.

Nobel Gases

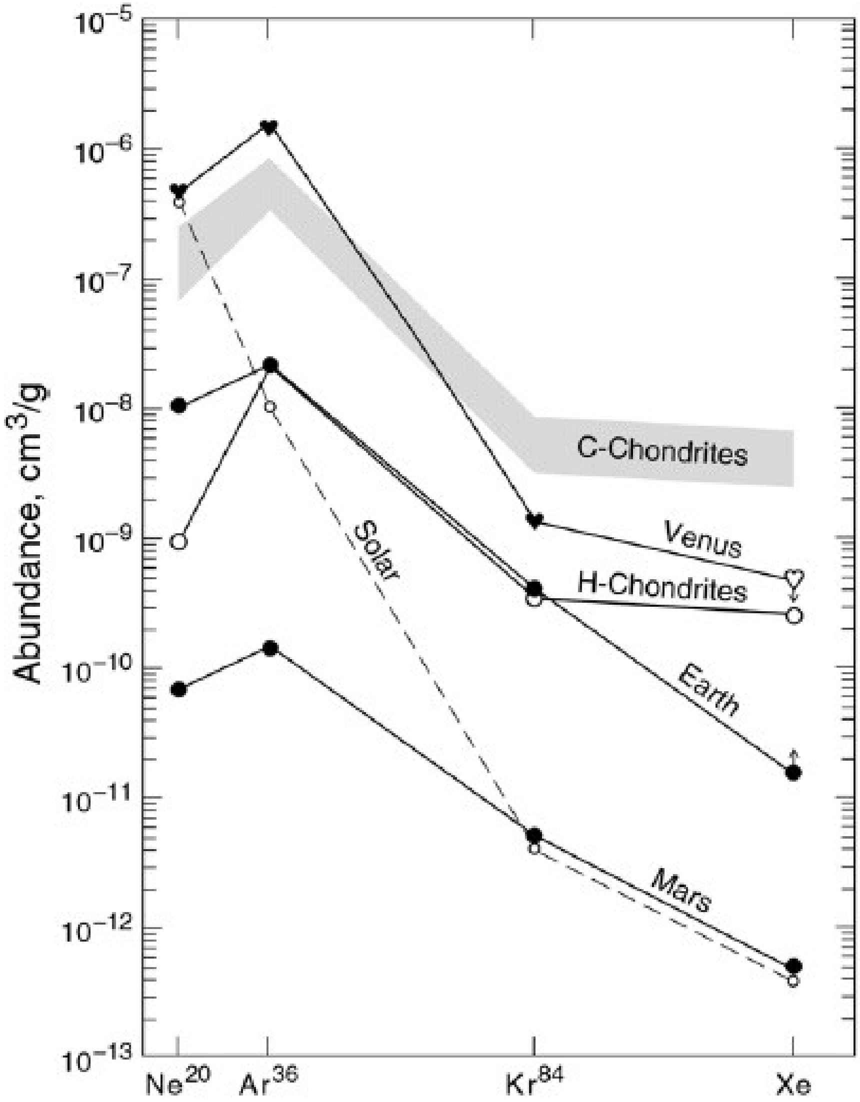


Figure 1. Chondritic meteorites contain about as much xenon as krypton. The meteoritic noble gas abundances therefore do not match the abundance patterns found in inner planet atmospheres, despite the apparent agreement for Ne, Ar, and Kr. (Solar values are normalized for ^{84}Kr on Mars). Note the high abundances of Ne and Ar per gram of rock and the solar type ^{36}Ar/^{84}Kr on Venus (Owen and Bar-Nun, 1995a).

- solar nebula concentration ruled out as planets enriched in Kr and Xe
- chondrites not exact match either
- chondrites not only source
- argue for a contribution from something cold (comets?)

Owen and Bar-Nun 2001

Oxygen Isotopes in the Solar System

- Oxygen isotope production
  - ^{16}O produced in stellar nucleosynthesis by He burning
    - provided to ISM by supernovae
  - rare isotopes ^{17}O and ^{18}O produced in CNO cycles
    - novae and supernovae
- Expected that ISM would have regions that are inhomogeneous
- Is an observed galactic gradient (Wilson and Rood 1992)
- Solar values $^{16}O/^{18}O \approx 500$ and $^{16}O/^{17}O \approx 2600$

Oxygen Isotopes in the Solar System

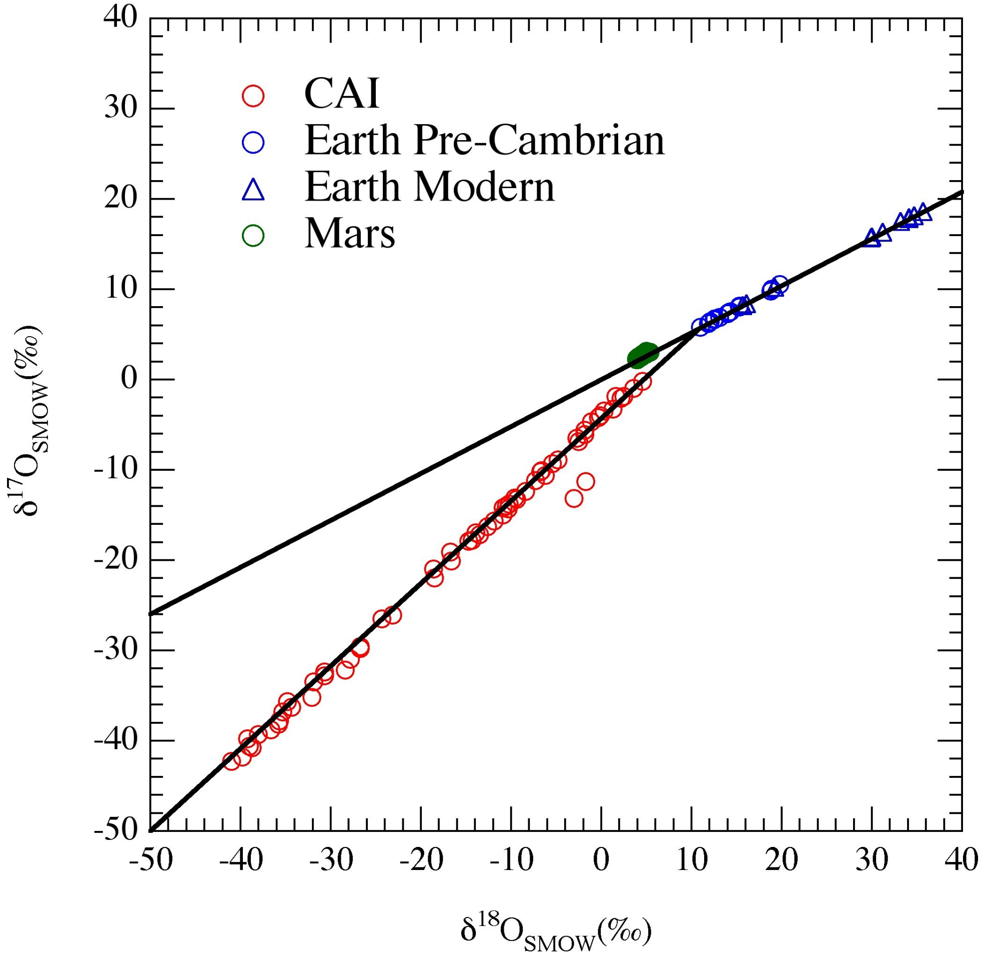
- chemical fractionation can also occur in ISM
  - *except for H, kinetic chemical isotopic effects are in general of order a few percent*
  - distinguishes fractionation from nuclear sources of isotopic enrichment
  - almost linearly proportional to the differences in mass between the isotopes
    - Ex: a chemical process that produces a factor of x change in the $^{17}O/^{16}O$ ratio produces a factor of 2x change in the $^{18}O/^{16}O$
  - so if you plot $\Delta(^{17}O/^{16}O)/\ \Delta(^{18}O/^{16}O)$ then the slope would be 1/2
- for more information see Clayton 1993, Ann. Rev. Earth. Pl. Sci.

Oxygen Isotopes in Meteorites

- In 1973 Clayton and co-workers discovered that calcium-aluminum-rich inclusions (CAI) in primitive chondrite meteorites had anomalous oxygen isotopic ratios.

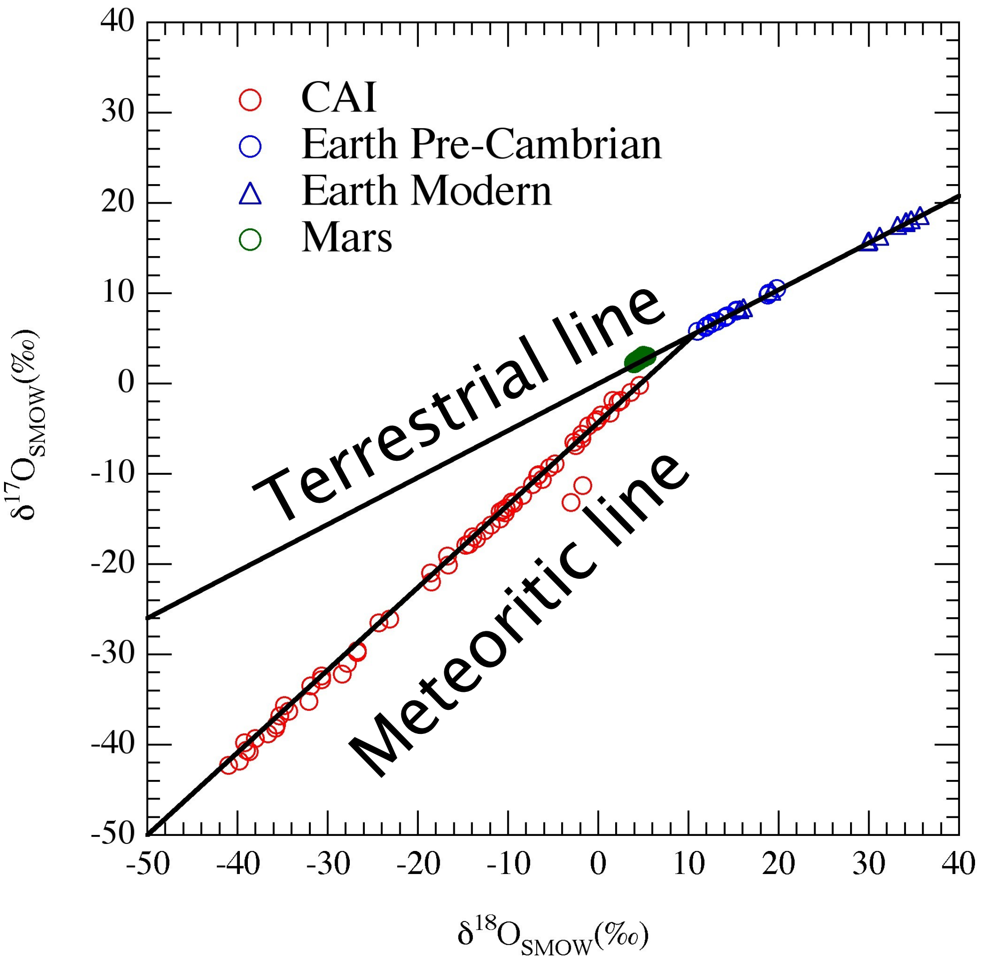
- Definition:

$$\delta({}^{x}O) = \left\{ \frac{\left({}^{x}O / {}^{16}O\right)_{source}}{\left({}^{x}O / {}^{16}O\right)_{s\tan dard}} - 1 \right\} 1000$$



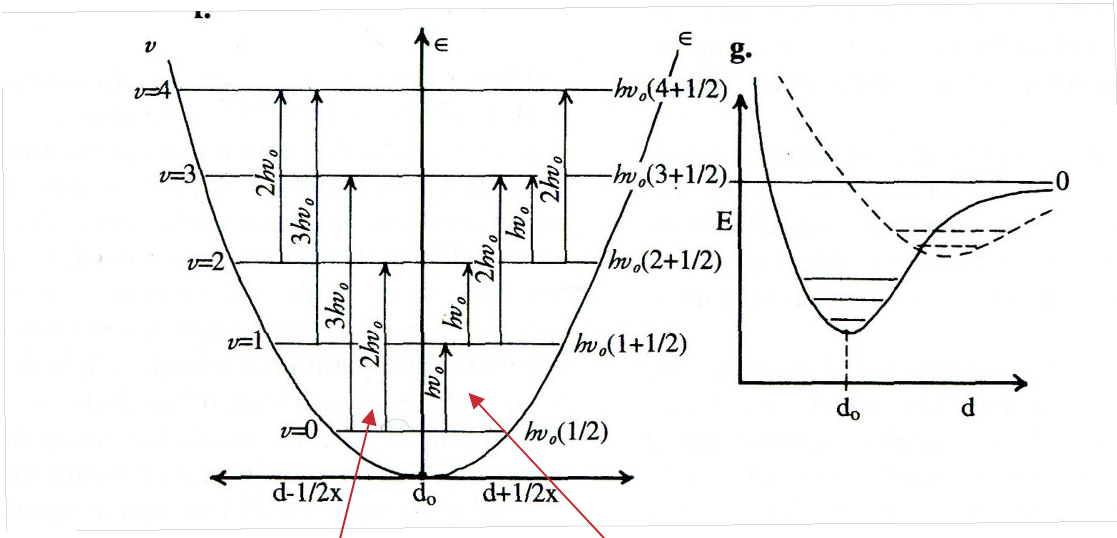
Oxygen Isotopes in Meteorites

- Earth, Mars, Vesta follow slope 1/2 line indicative of mass-dependent fractionation
- primitive CAI meteorites (and other types) follow line with slope ~ 1 indicative of mass independent fractionation
- meteorites have oxygen isotope ratios where the rare isotopes are slightly more abundant (50 per mil) than ^{16}O.



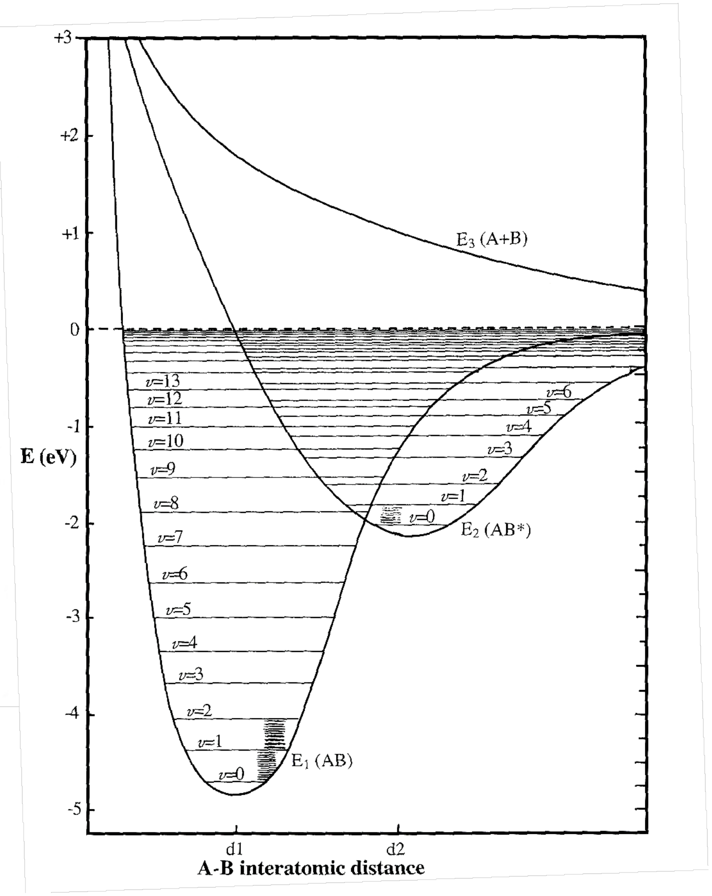
Origin is uncertain -- more later....

Aside: Molecular Spectra

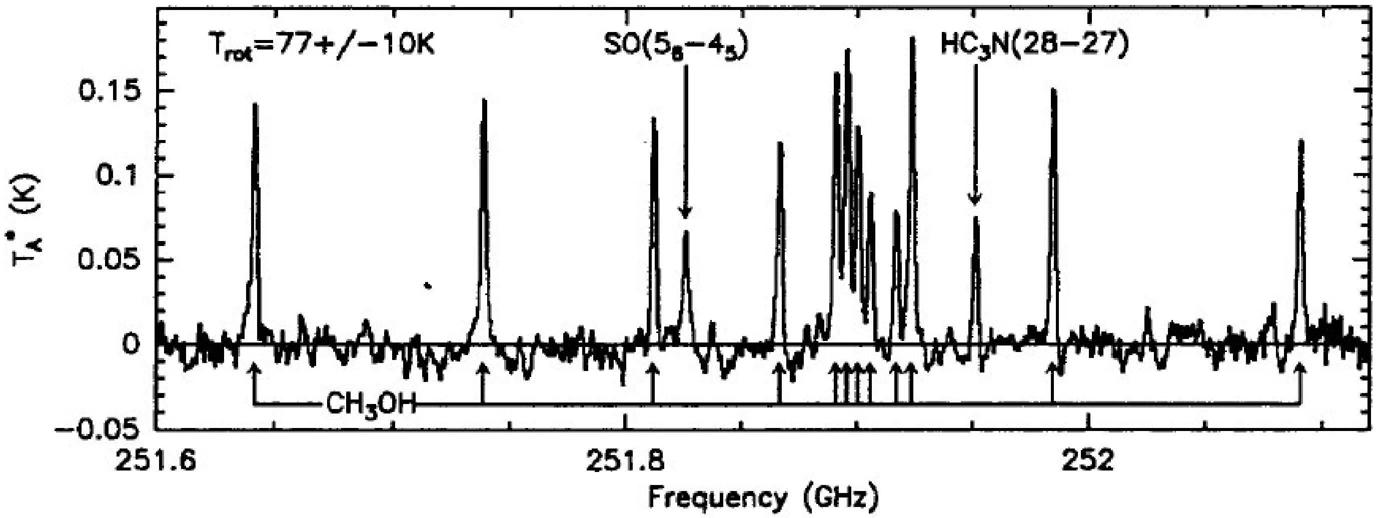


1st overtone

fundamental

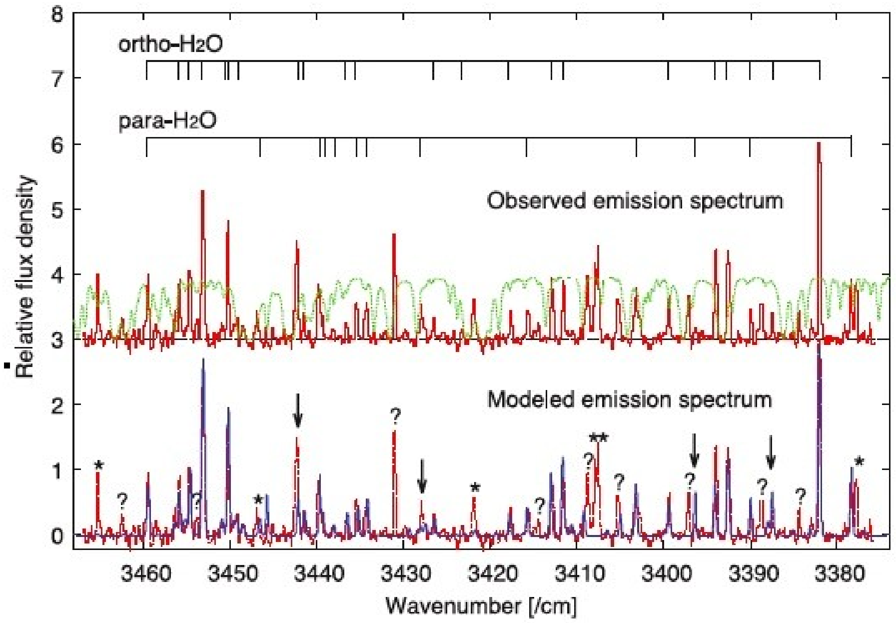


Cometary Observations



mm/sub-mm Spectroscopy
Crovisier, Bockelee-Morvan
Lis, Biver, et al.

IR Spectra: H_2O, CH_4, …
Mumma, Dello Russo, et al.



Cometary Composition

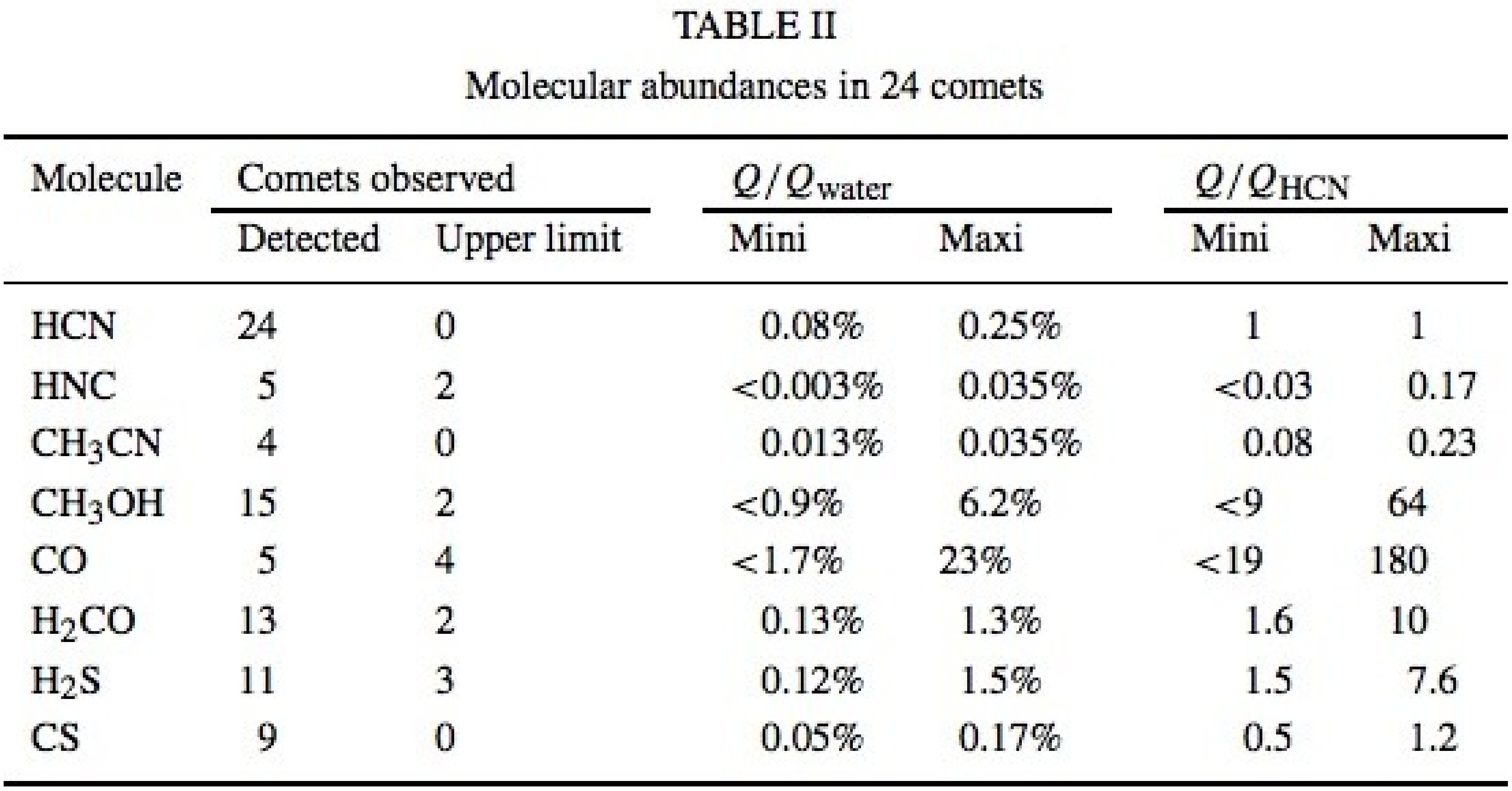


TABLE II

Molecular abundances in 24 comets

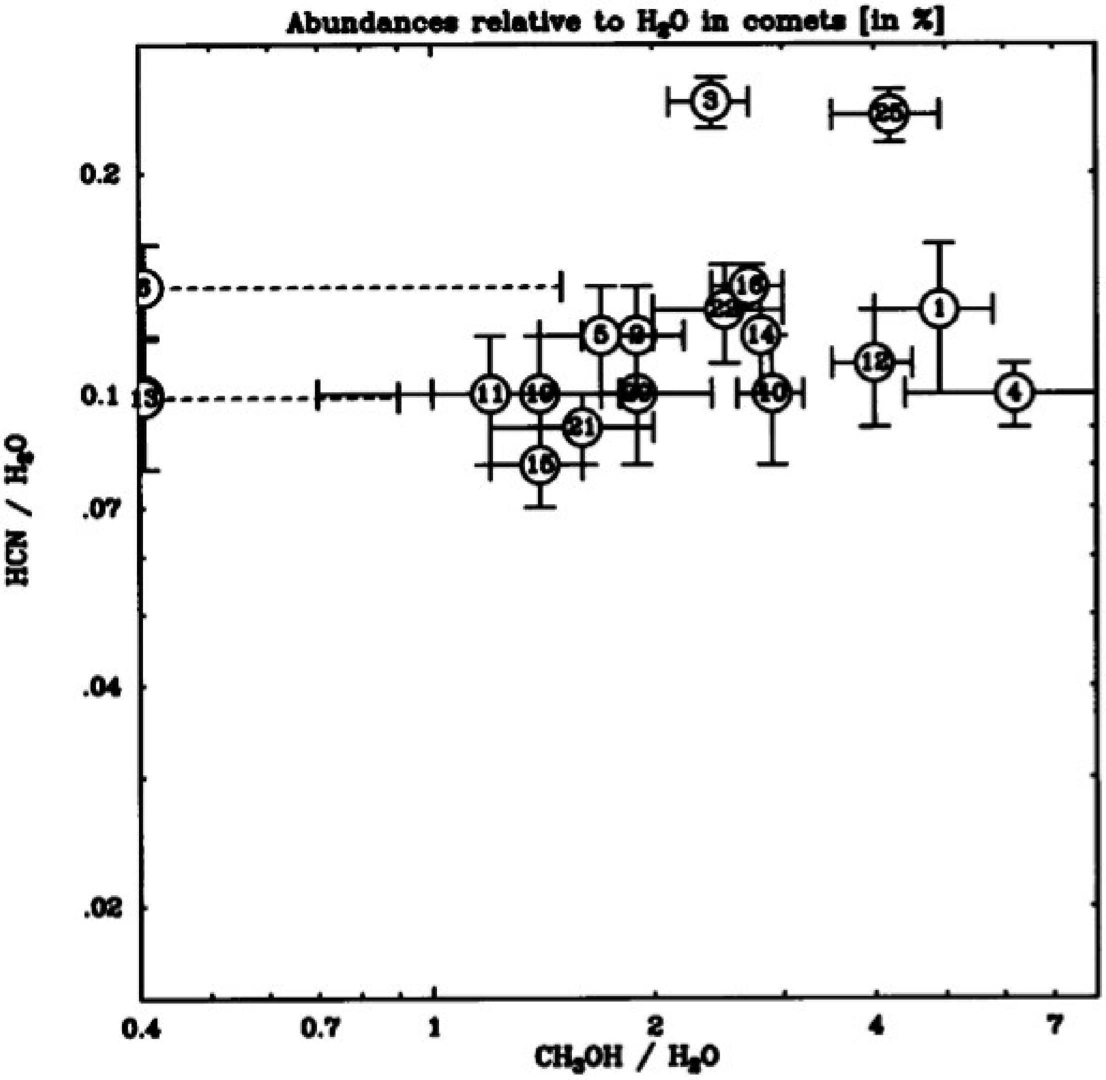
Molecule	Comets observed		Q/Q_{water}		Q/Q_{HCN}	
	Detected	Upper limit	Mini	Maxi	Mini	Maxi
HCN	24	0	0.08%	0.25%	1	1
HNC	5	2	<0.003%	0.035%	<0.03	0.17
CH_3CN	4	0	0.013%	0.035%	0.08	0.23
CH_3OH	15	2	<0.9%	6.2%	<9	64
CO	5	4	<1.7%	23%	<19	180
H_2CO	13	2	0.13%	1.3%	1.6	10
H_2S	11	3	0.12%	1.5%	1.5	7.6
CS	9	0	0.05%	0.17%	0.5	1.2

Biver et al. 2002

Cometary Composition

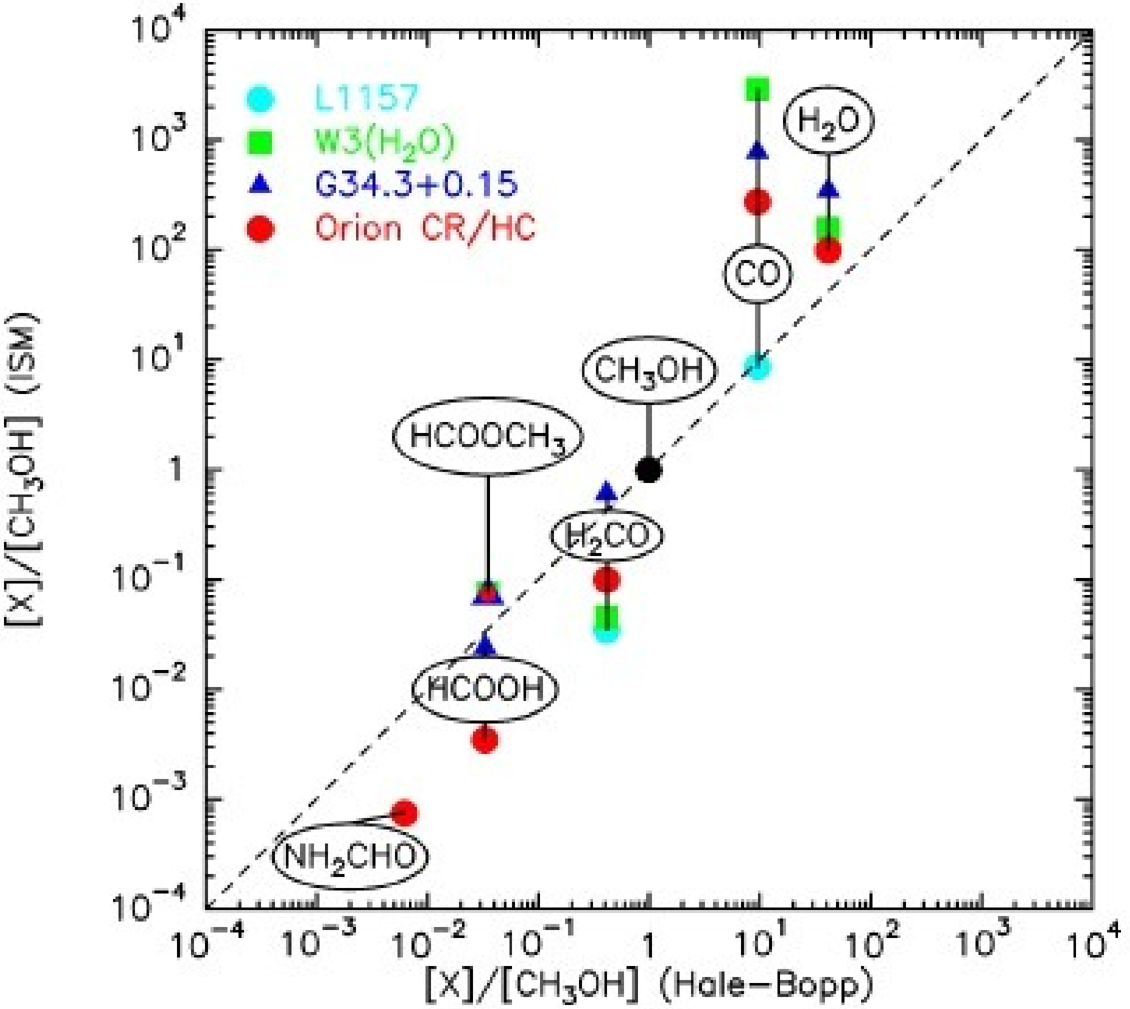
Example of trends:

- Comets show larger variation in methanol abundances than HCN.
- Implies extra source of CH_3OH production.
- In ISM CH_3OH ice is detected only towards embedded sources (perhaps a link to radiation).



Biver et al. 2002

Comparison to ISM “Ices”

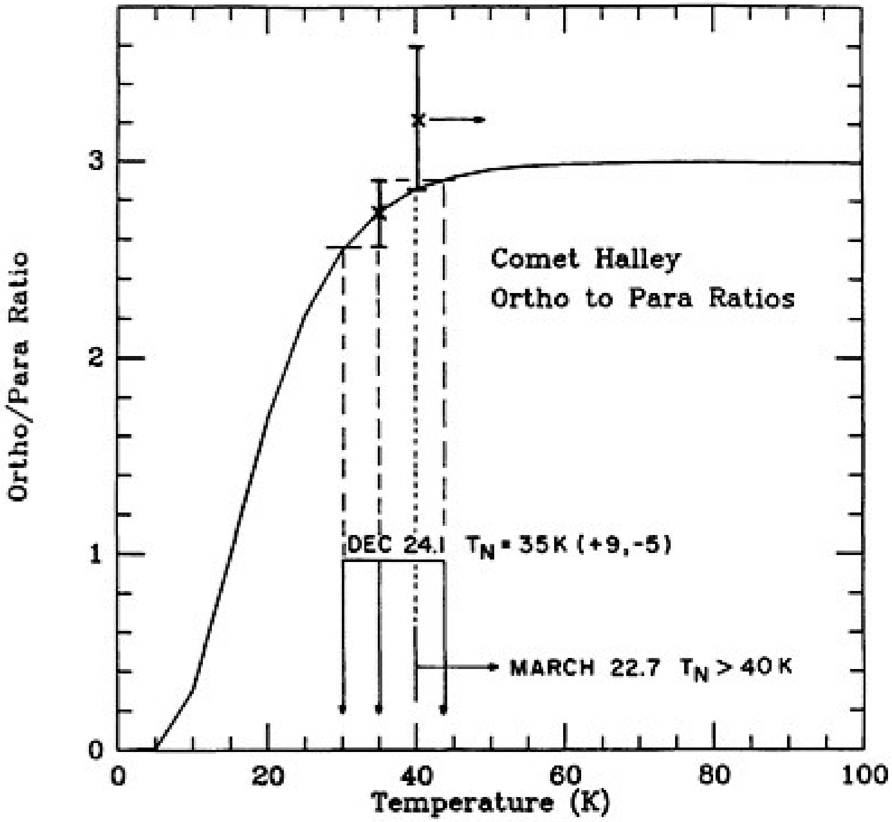


Comparison between the abundance ratios measured in comet Hale-Bopp and those measured in the molecular hot cores and the bipolar flow L1157

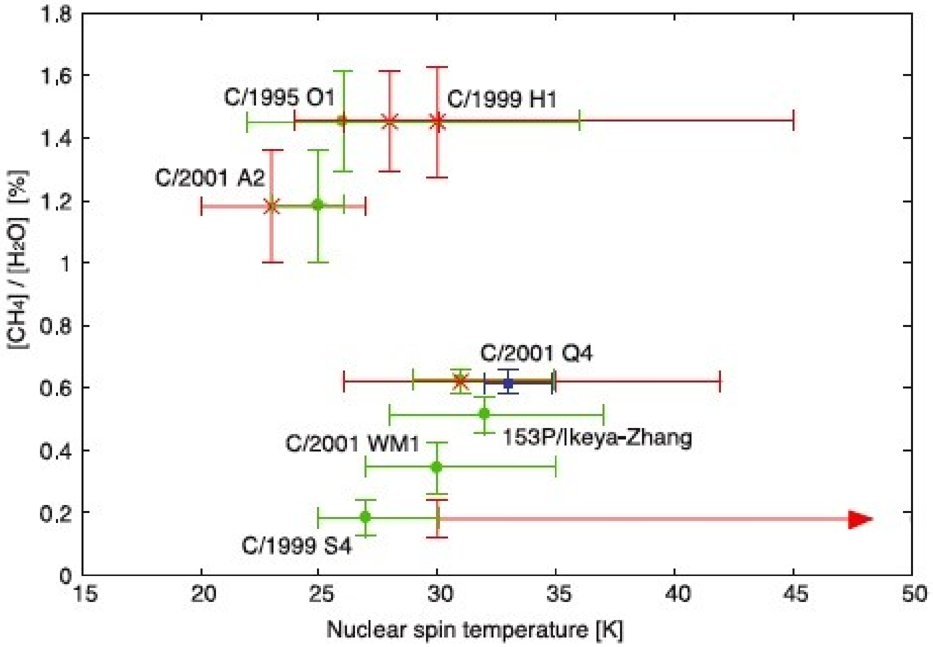
Bockelee-Morvan et al. 2000

Ortho/Para Ratio of Water

Mumma et al. 1987

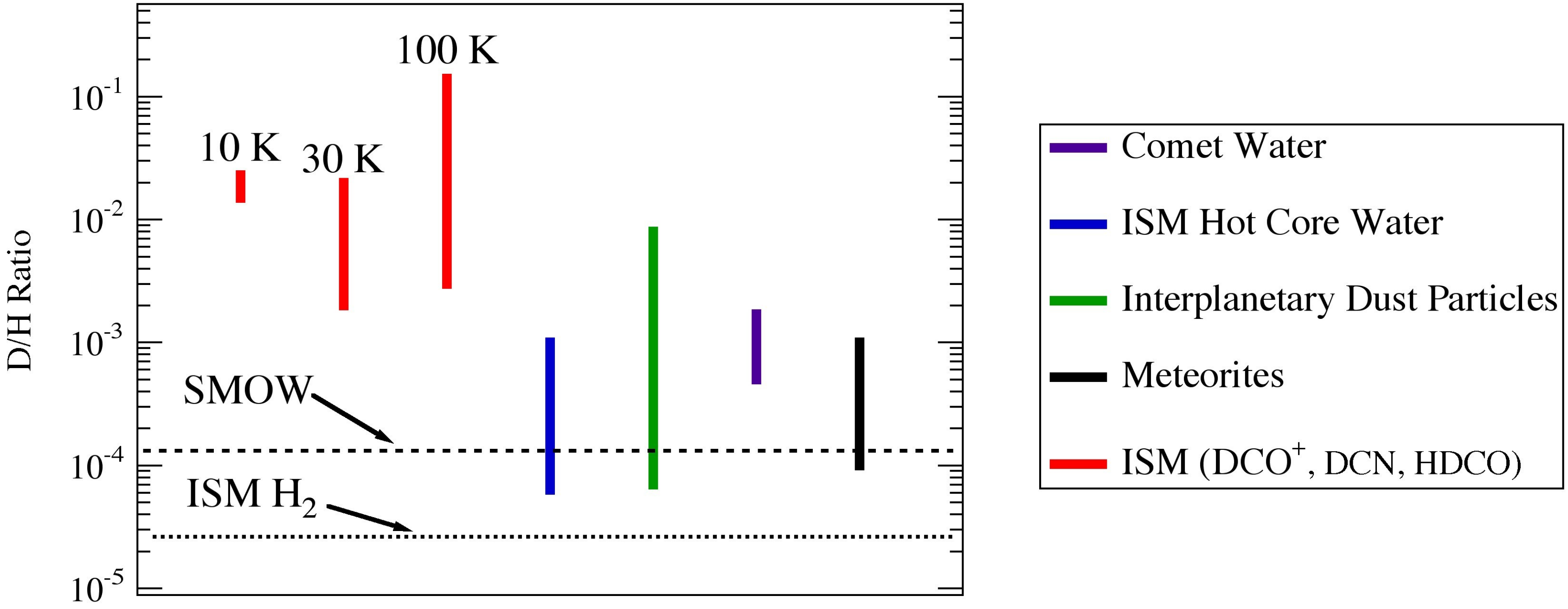


Kawakita et al. 2006



- Ground state of ortho-water is 34.2 K above that of para-water in equilibrium the ratio is 3:1 (spin statistics)
- If water formed in the gas phase the excess energy of reaction likely would produce 3:1 ratio.
- If water formed on grains then the energy could be provided to the matrix and a low temperature o/p ratio may be preserved.

Deuterium Fractionation: Fossils



consistent with low temperature formation -- prior to stellar birth?

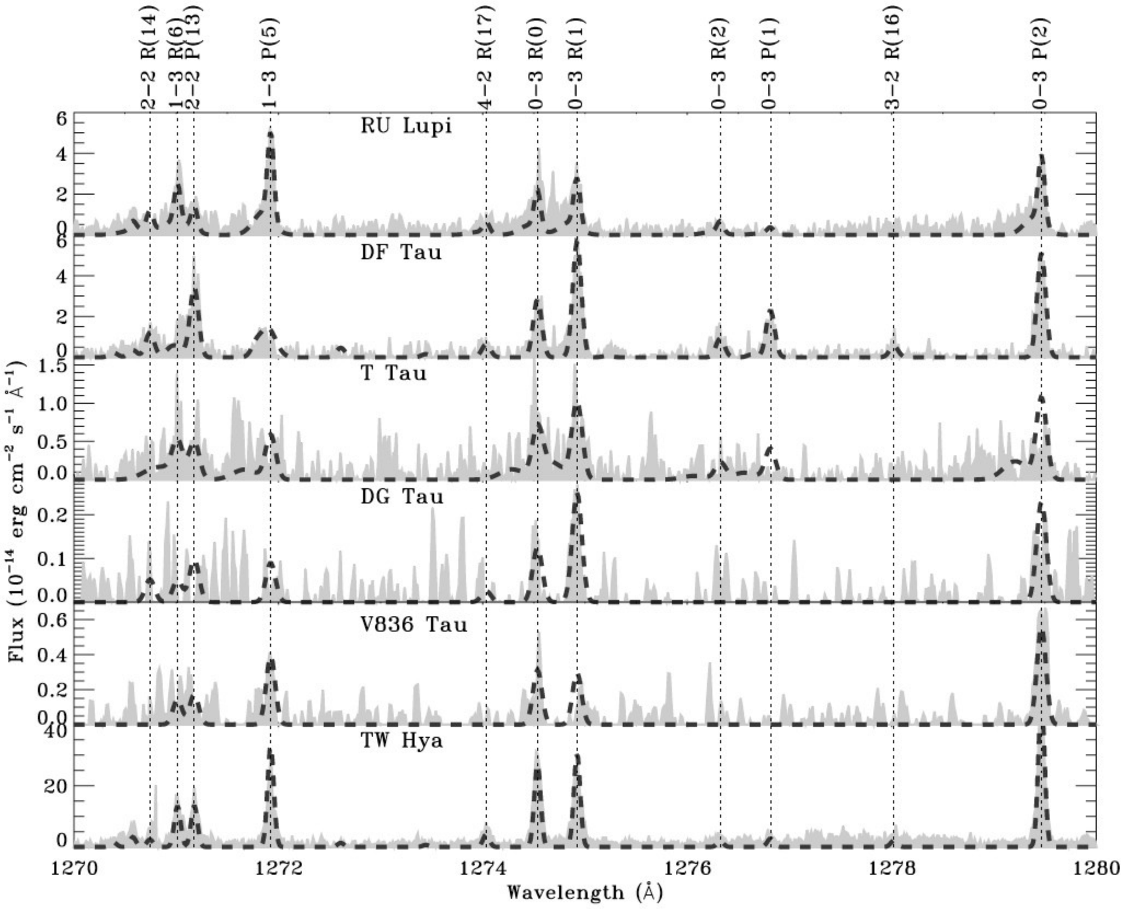
adapted from Messenger 2000

mm/sub-mm wave Observations of Protoplanetary Disks

- New field that has emerged over the past decade.
- Different Wavelength Regimes
  - UV: H_2 in hot inner disk (within a few AU)
  - Optical: O I emission
  - IR: H_2, CO, H_2O, OH in warm inner disk (1-10 AU)
  - mm/submm: CO, HCN, CN, …. in cold outer disk (>> 10 AU)
    - Sensitivity limited –
      - small angular sizes at distance of nearest S.F. region (60-120 pc): 1-4”
      - observing technique requires interferometry which is inherently less sensitive than a big light bucket.
- Some clear trends seen
- ALMA will revolutionize this field

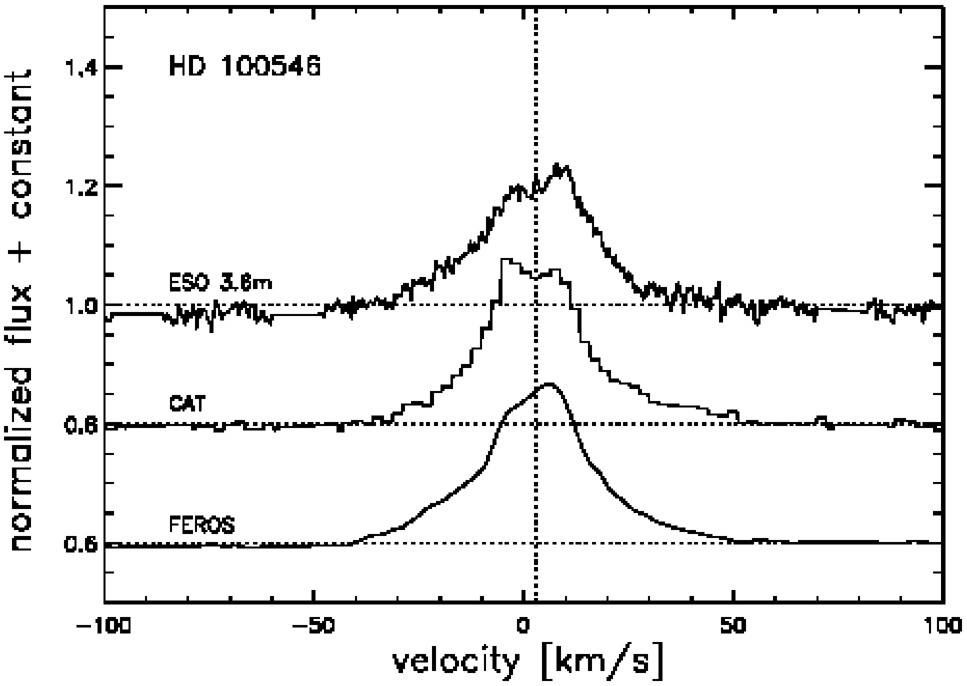
UV: H_2 Fluorescence

- Herczeg et al. 2006 summarizes HST/STIS observations of H_2 fluorescence in T Tauri stars
  - UV illuminated (Ly α pumped)
  - hot: 2000–3000 K
  - in some cases clearly associated with the disk (in others outflow origin)



Optical Spectroscopy

Optical [O I] 6300 Å

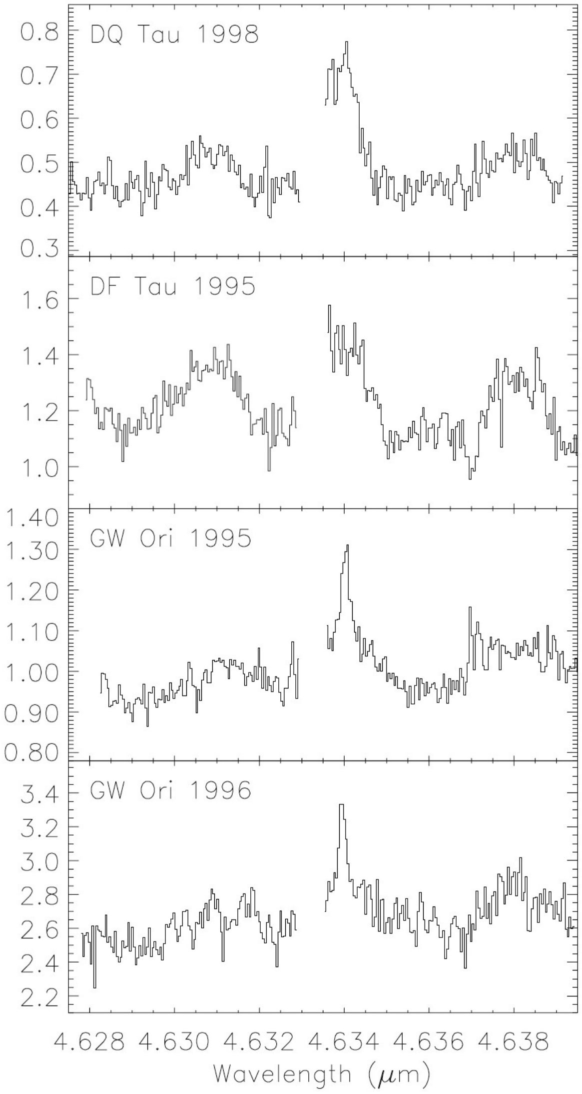


Acke et al. 2005

- double peaked profile -- Keplerian rotation
- likely from photodissociation of OH on surface
- requires OH abundances 10^{-7} – 10^{-6} – orders of magnitude above seen in ISM

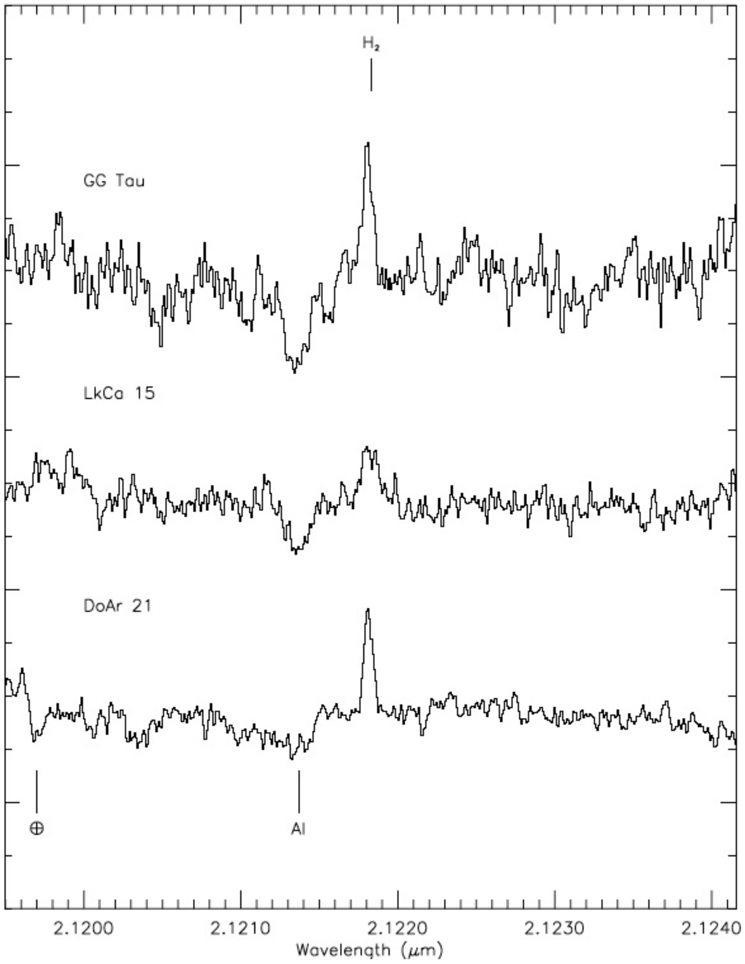
IR Spectroscopy: H_2 + CO

CO Fundamental



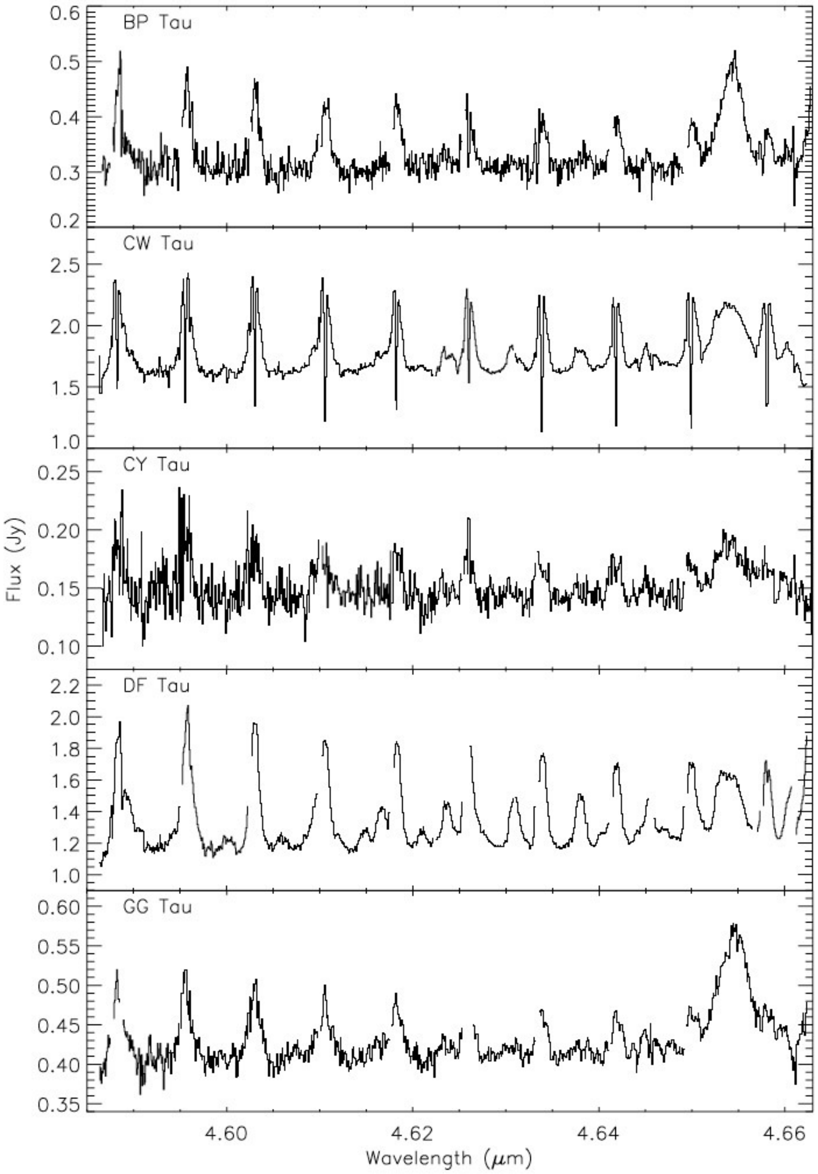
Najita et al. 2003

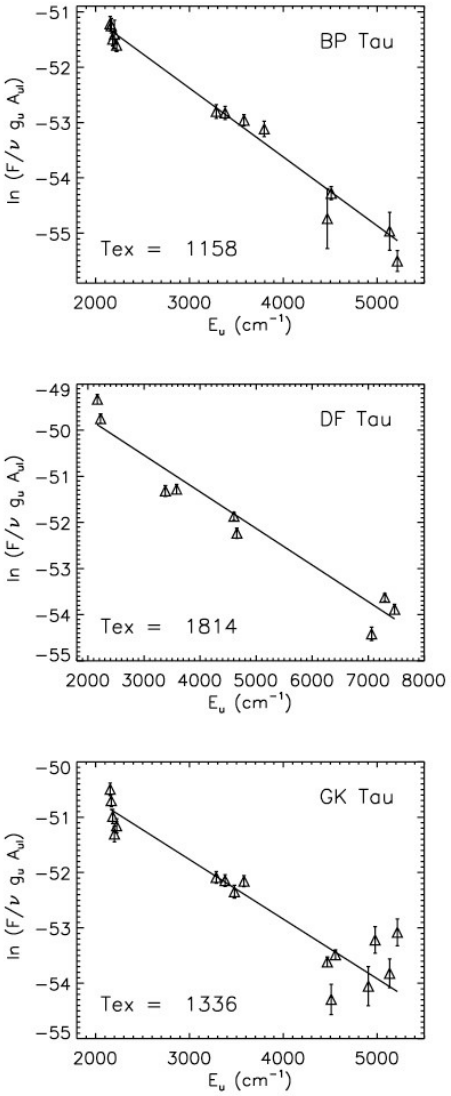
H_2 1–0



Bary et al. 2003

IR Spectroscopy: CO

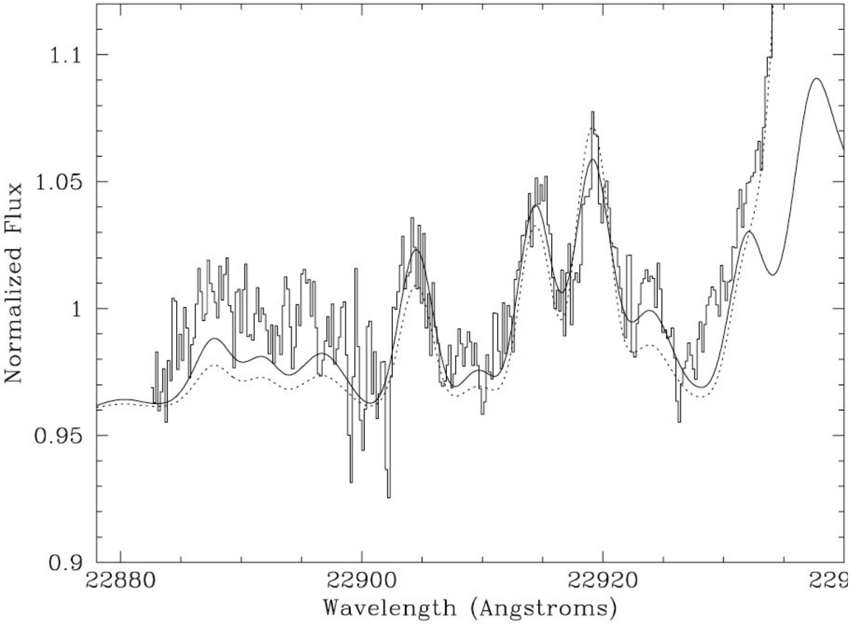




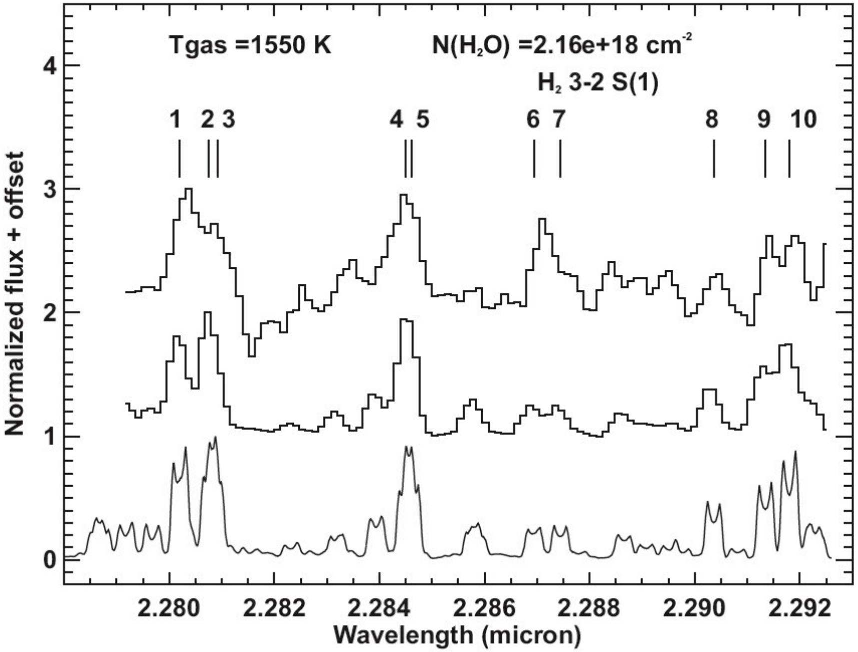
Najita et al. 2003

IR Spectroscopy: H_2O

Carr et al. 2004



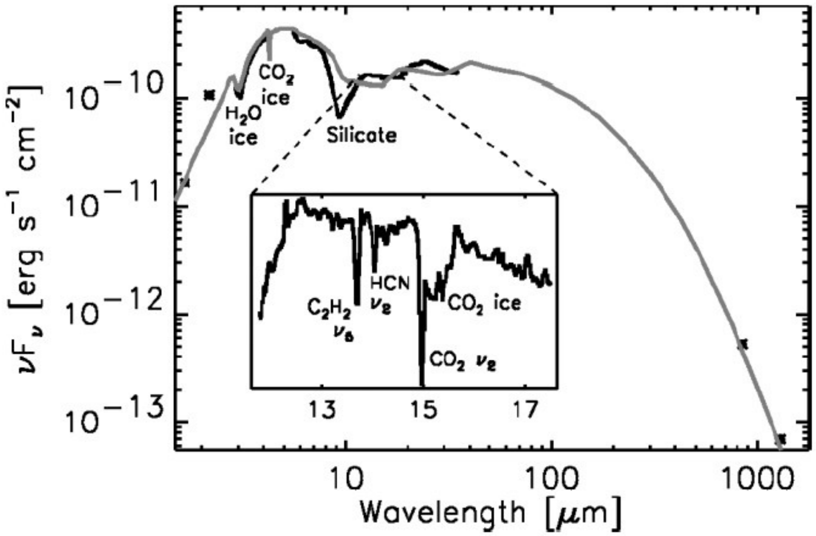
Thi and Bik 2005



- CO/H_2O not consistent with thermochemical equilibrium – reduced by factors of 2–10
  - indicative of radiation dominance
- summarized in Najita et al. 2006, PPV; but see also work of Brittain and Rettig

IR Spectroscopy: Complex Chemistry

Lahuis et al. 2006



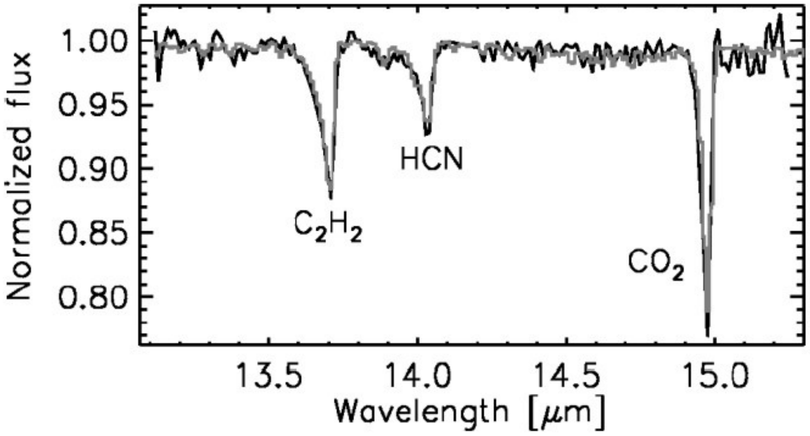
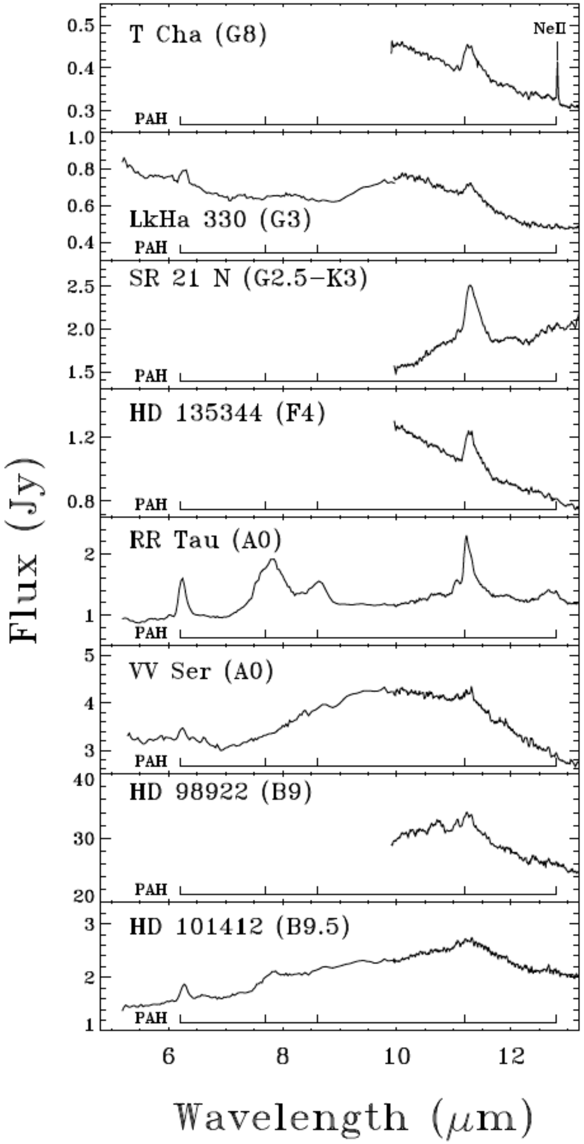


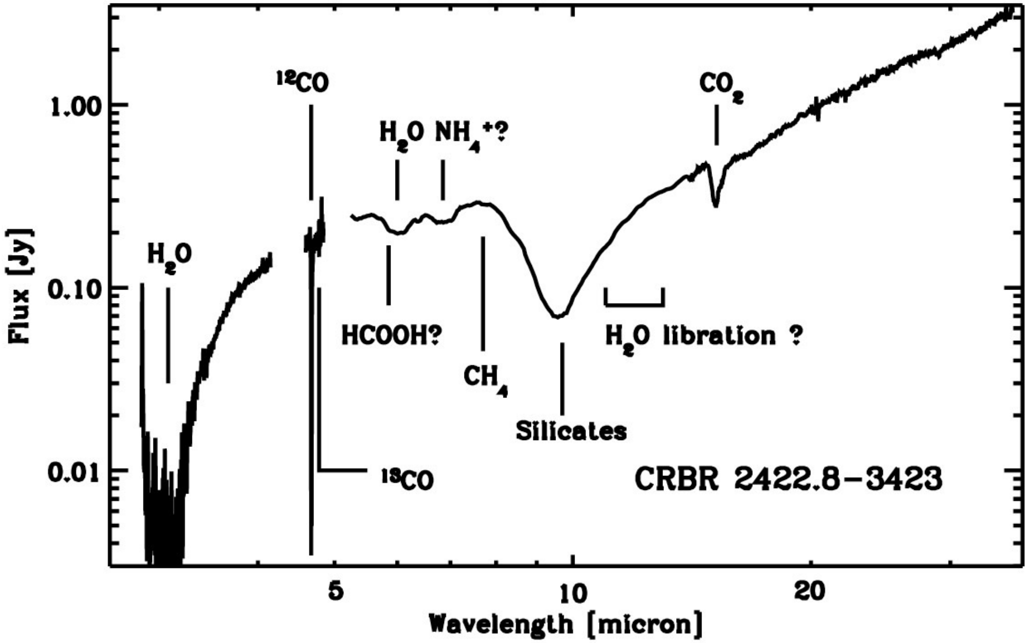
FIG. 2.—Blowup of the IRS 46 normalized *Spitzer*-IRS spectrum covering the C_2H_2 $\nu_5 = 1$–0, HCN $\nu_2 = 1$–0, and CO_2 $\nu_2 = 1$–0 bending mode rovibrational absorption bands. Included in gray is a best-fit synthetic spectrum.

- HCN and C_2H_2 detected around a young low mass star
- T ▯350 K
- abundances several orders of magnitude higher than ISM dark clouds.
- suggest arise in inner (< 6 AU) disk or in wind

Geers et al. 2006

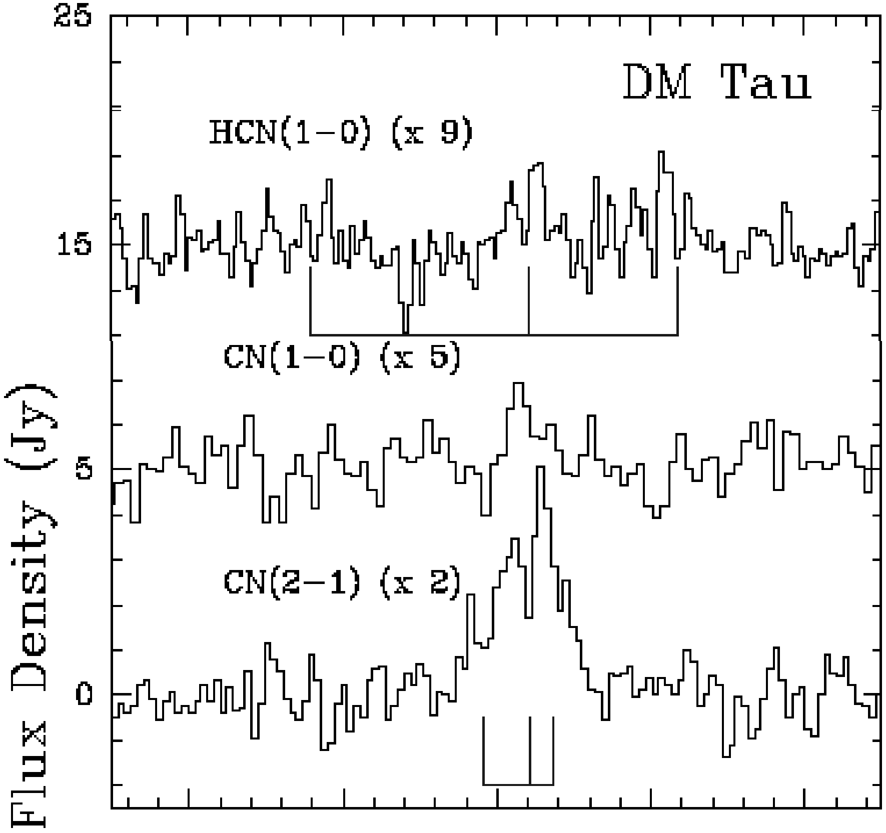


Pontoppidan et al. 2005

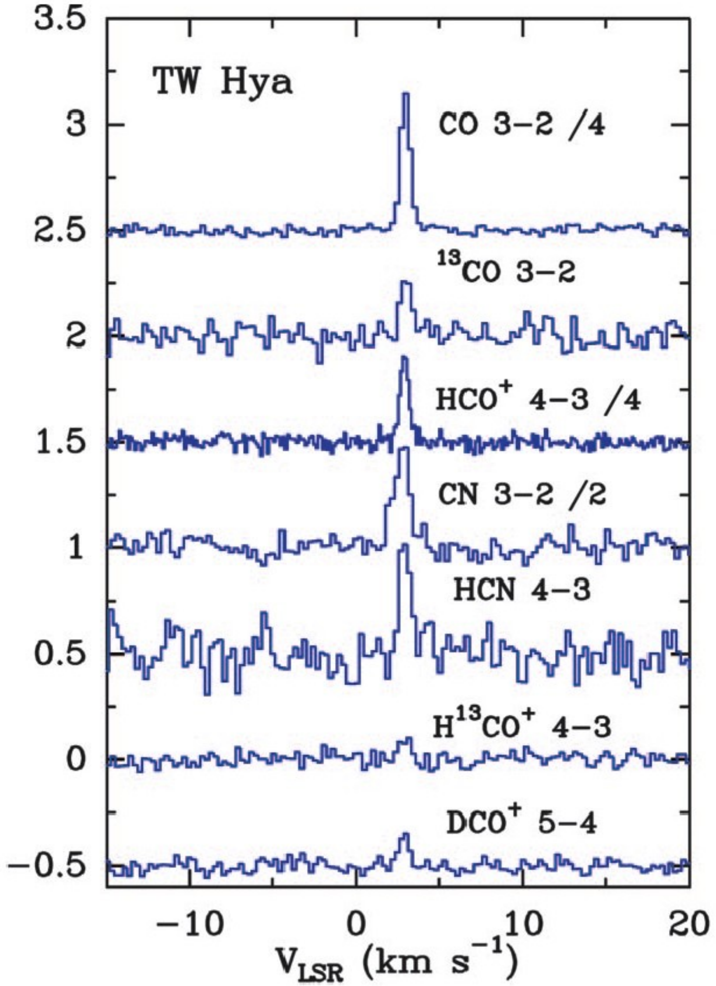


- PAHs
  - require UV excitation
  - TTS have lower estimated abundances
  - not seen towards many TTS (lack of UV or lack of PAH?)
- Ices
  - H_2O dominates with CO and CO_2
  - difficult - need to peer through disk

mm/submm Spectroscopy



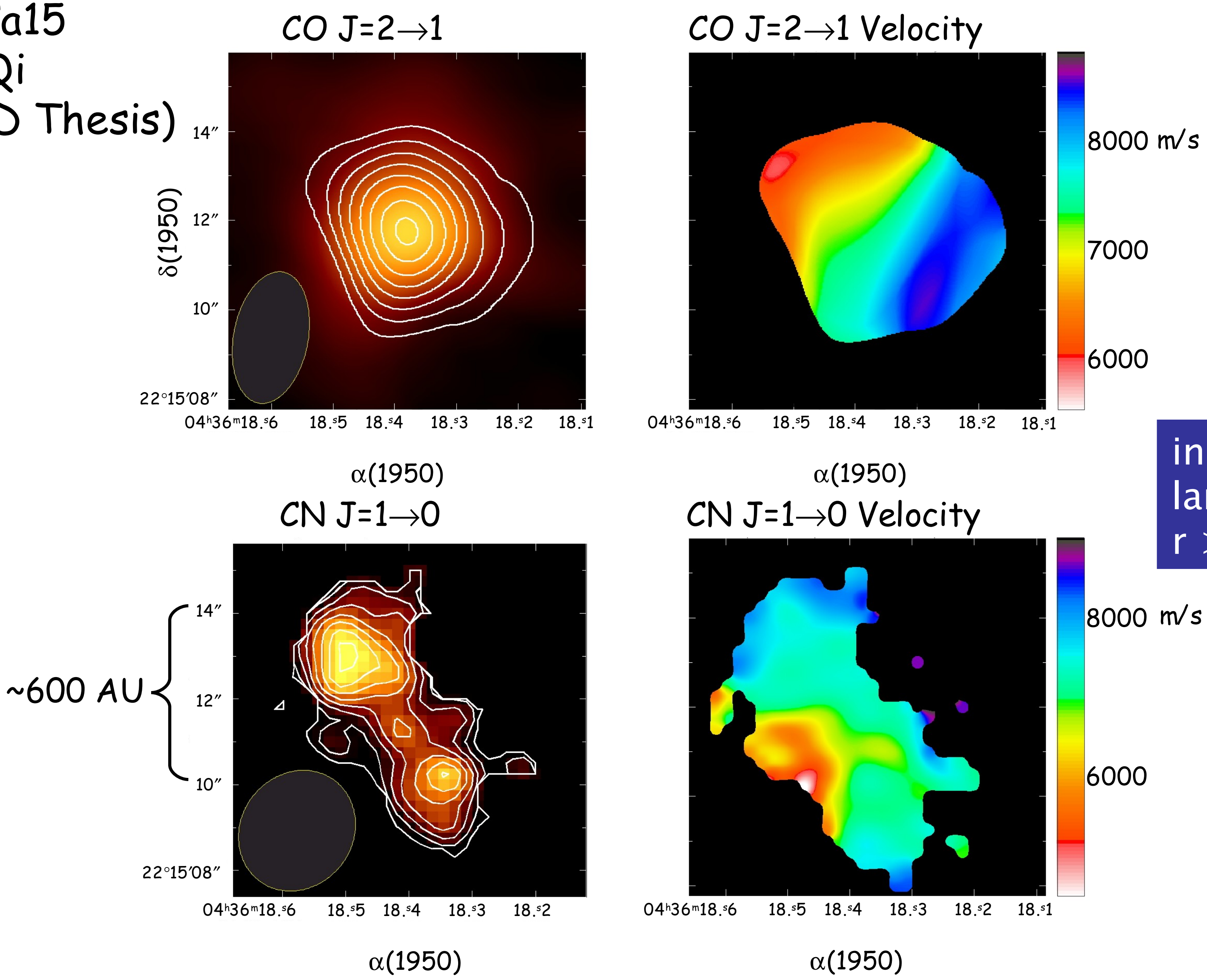
Dutrey et al. 1997



Thi et al. 2004;
Kastner et al. 1997

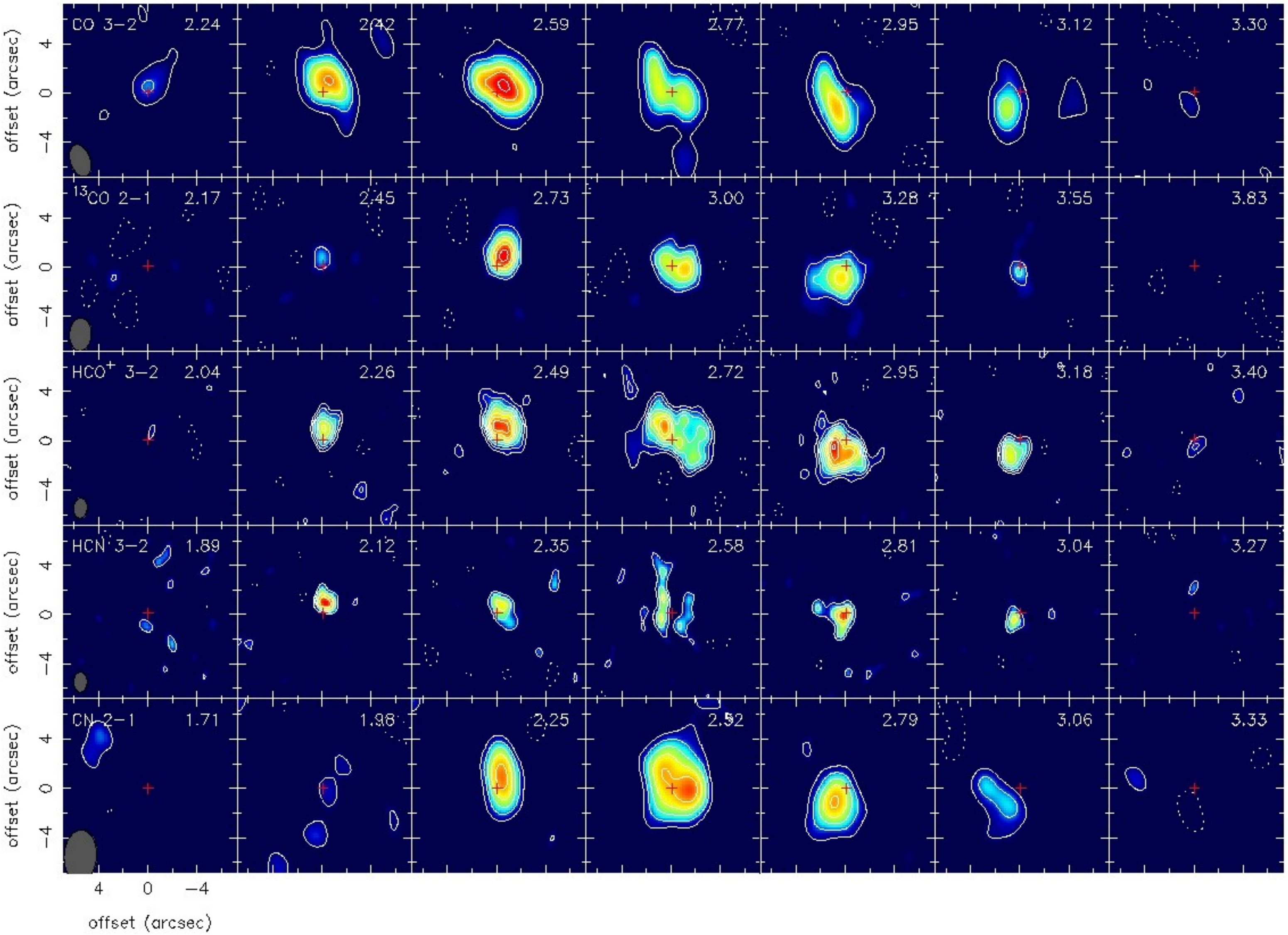
The Future: Interferometry

LkCa15
C. Qi
(PhD Thesis)



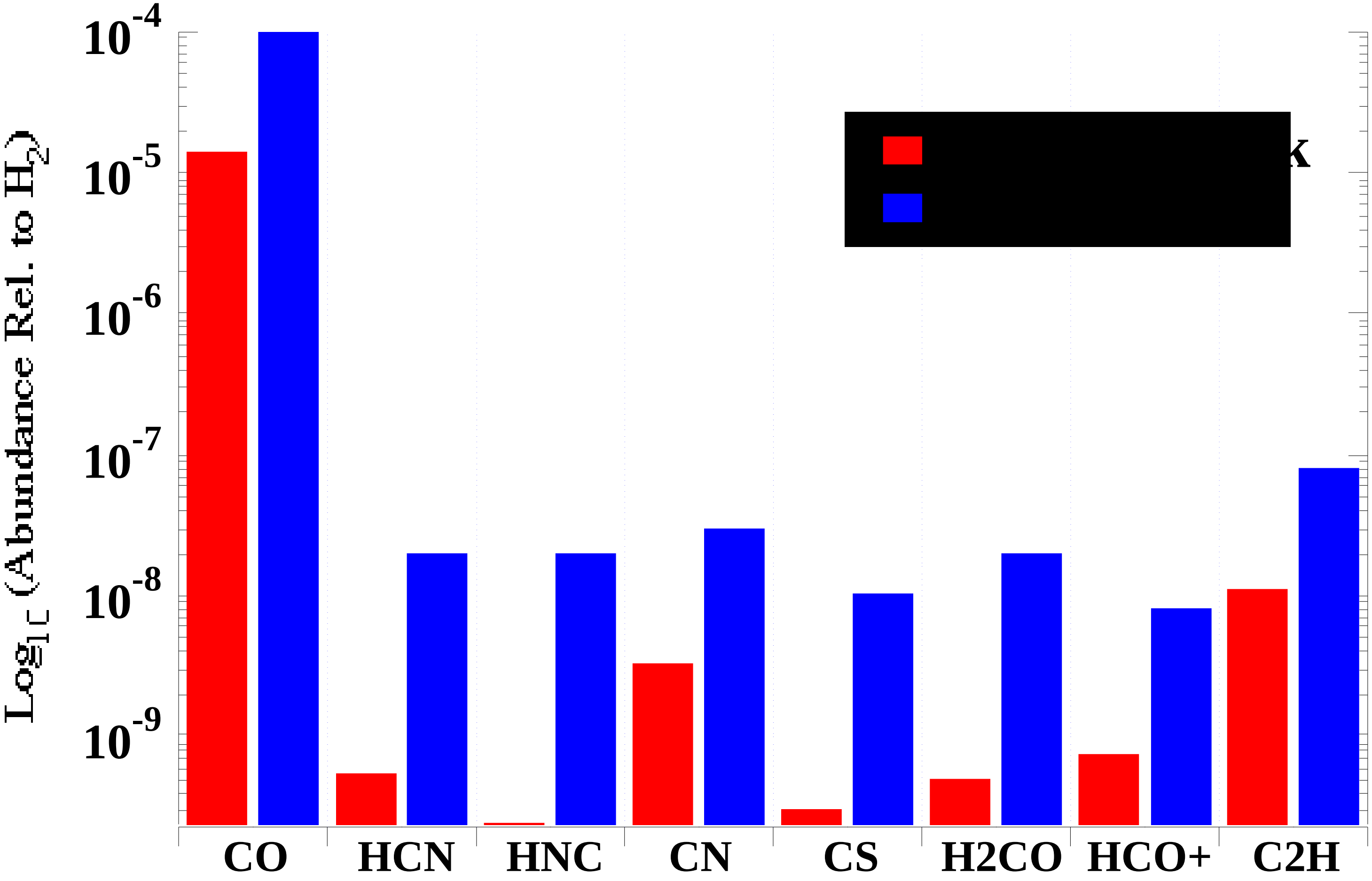
inferring
large sizes
r > 150 AU

Kinematical Chemistry



TW Hya: from SMA: Qi et al., in prep.

Molecular Abundances in Disks



Note: elevated ratio of CN/HCN seen towards all disks, indicative of PDR
see Rodriguez-Franco et al. 1998 for ISM example

Summary

- Solar system
  - clear evidence for temperature gradient
  - volatility a key issue – condensation sequence
  - evidence that even planets were not made of single reservoir
  - oxygen isotopes are difficult to understand (new theories!)
  - cometary composition shows some similarity to ISM, but…
  - cometary D/H ratios and H_2O o/p ratios consistent with cold temperature formation of ices

- Protoplanetary Disks:
  - both simple (CO, CN, CS) and complex (H_2CO, CH_3OH) molecules are detected implying a rich chemistry.
  - abundances are typically depleted by factors of 100 when compared to molecular cloud gas
  - finding large -- r > 150 AU -- disks.
  - evidence for photon-dominated chemistry (PAH emission, elevated CN/HCN ratios; [O I], CO/H_2O)
  - chemistry is quite similar to that seen in dense ISM exposed to enhanced UV fields
  - Future is bright (SMA, CARMA, PdB, and ALMA)