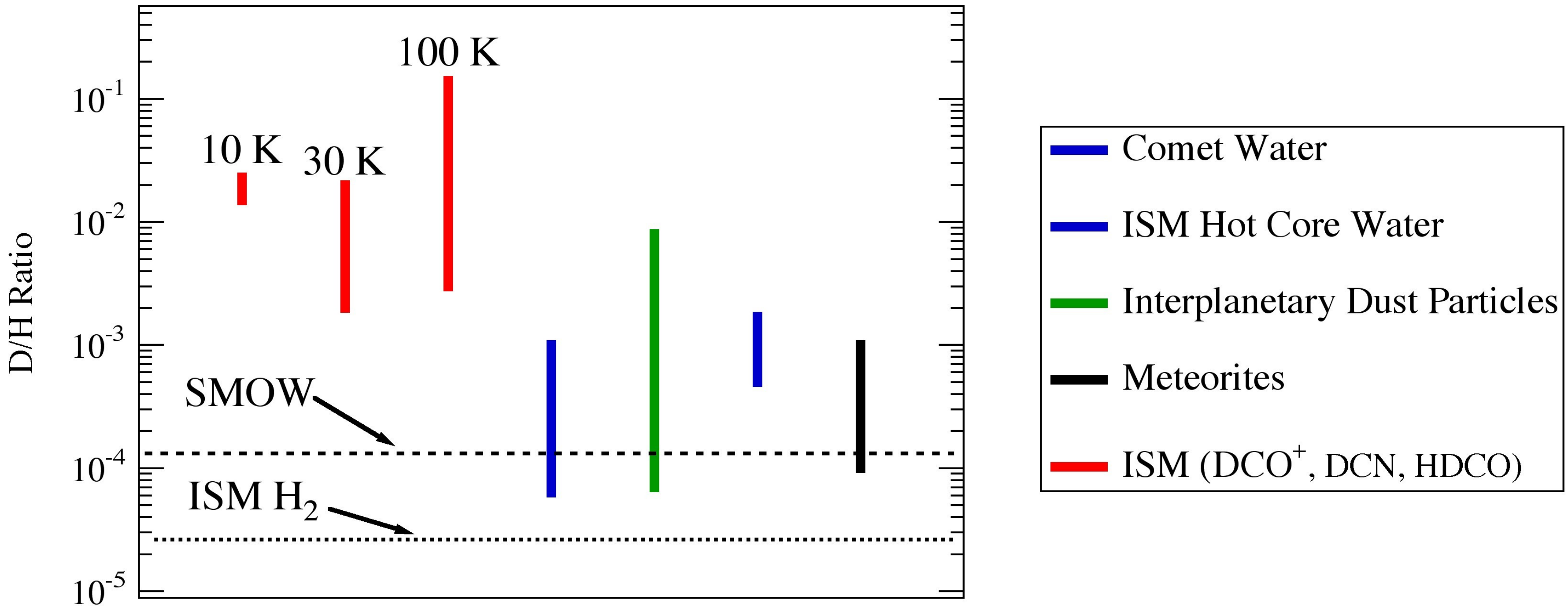
Deuterium Fractionation: Fossils



adapted from Messenger 2000

Deuterium Fractionation

- Because of difference in zero–point energy chemical reactions between molecules favor the deuterium bond relative to the hydrogen bond.
- $(D/H)_{ism,lb} = (1.5 \pm 0.1) \times 10^{-5}$ Linsky 1998
- Ratio roughly constant with 100 pc (lb: local bubble)
- Shows variations beyond with average value in local galactic disk:

$(D/H)_{ism} > (2.3 \pm 0.2) \times 10^{-5}$

Linsky et al. 2006

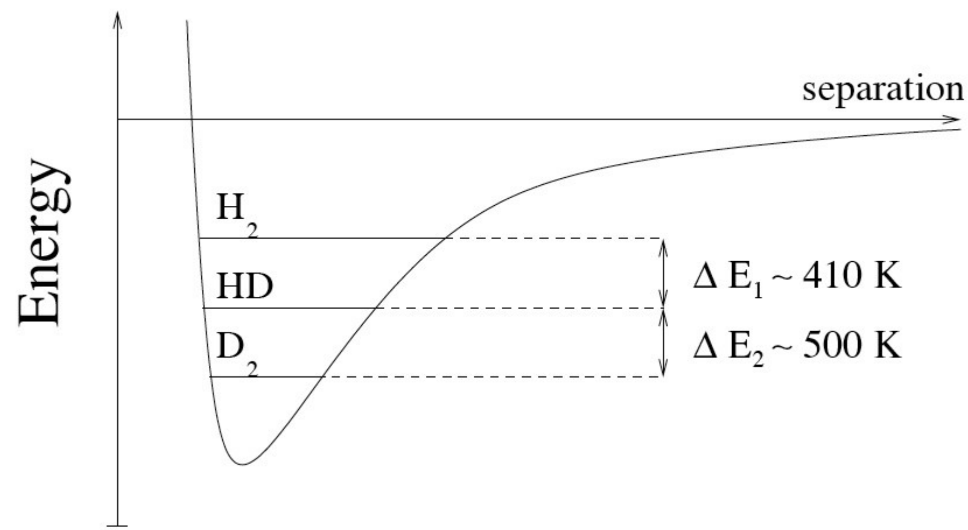


Figure 7. H_2, HD and D_2 potential energy diagram. ΔE_i is the difference between the zero point energies relative to the minimum of the molecular potential curve.

Phillips and Vastel 2003

Deuterium Fractionation

- Deuterium fractionation in ISM and in disks starts with the following reaction:

$$H_3^+ + HD \leftrightarrow H_2D^+ + H_2 + 230K. \tag{1}$$

The rate for this reaction is generally taken as:

$$k_f = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

$$k_r = 2.0 \times 10^{-9} (\frac{T}{300})^{-0.8} exp(-230/T) \text{ cm}^3 \text{ s}^{-1}$$

However, recent lab measurements at 10 K (Gerlich et al. 2002) find:

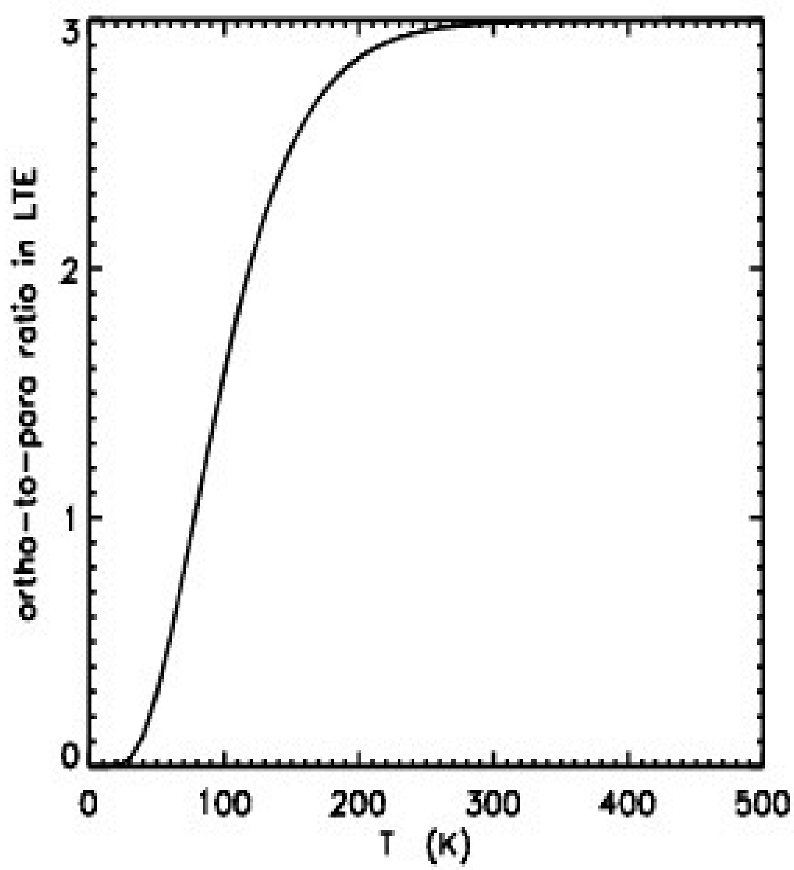
$$k_r = 4.9 \times 10^{-11} \text{ for nomal } H_2 \text{ (o:p = 3:1)}$$

$$k_r = 7.3 \times 10^{-13} \text{ for para-}H_2$$

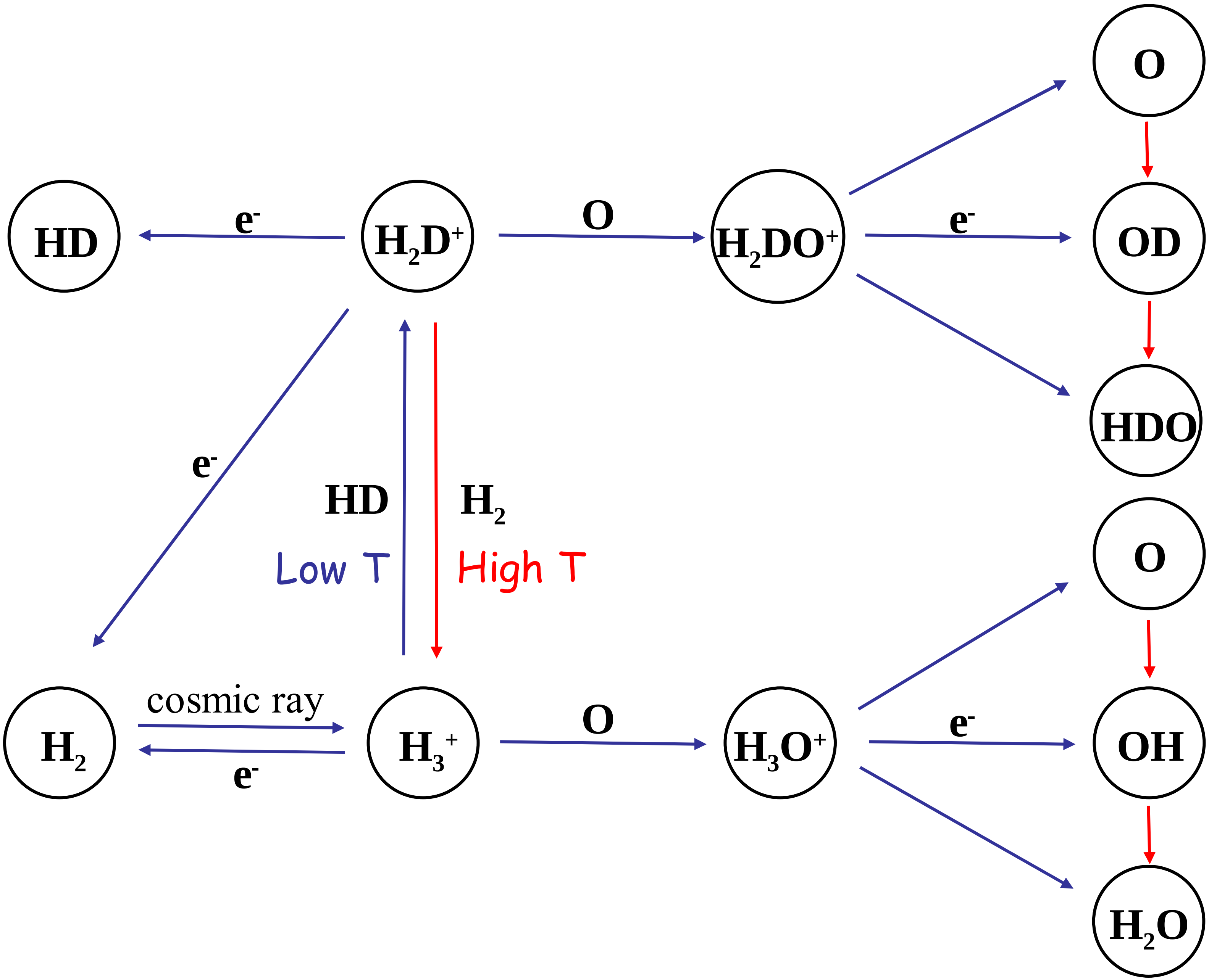
???? what happens at 20 K ????

H_2 Equilibrium Ortho/Para Ratio

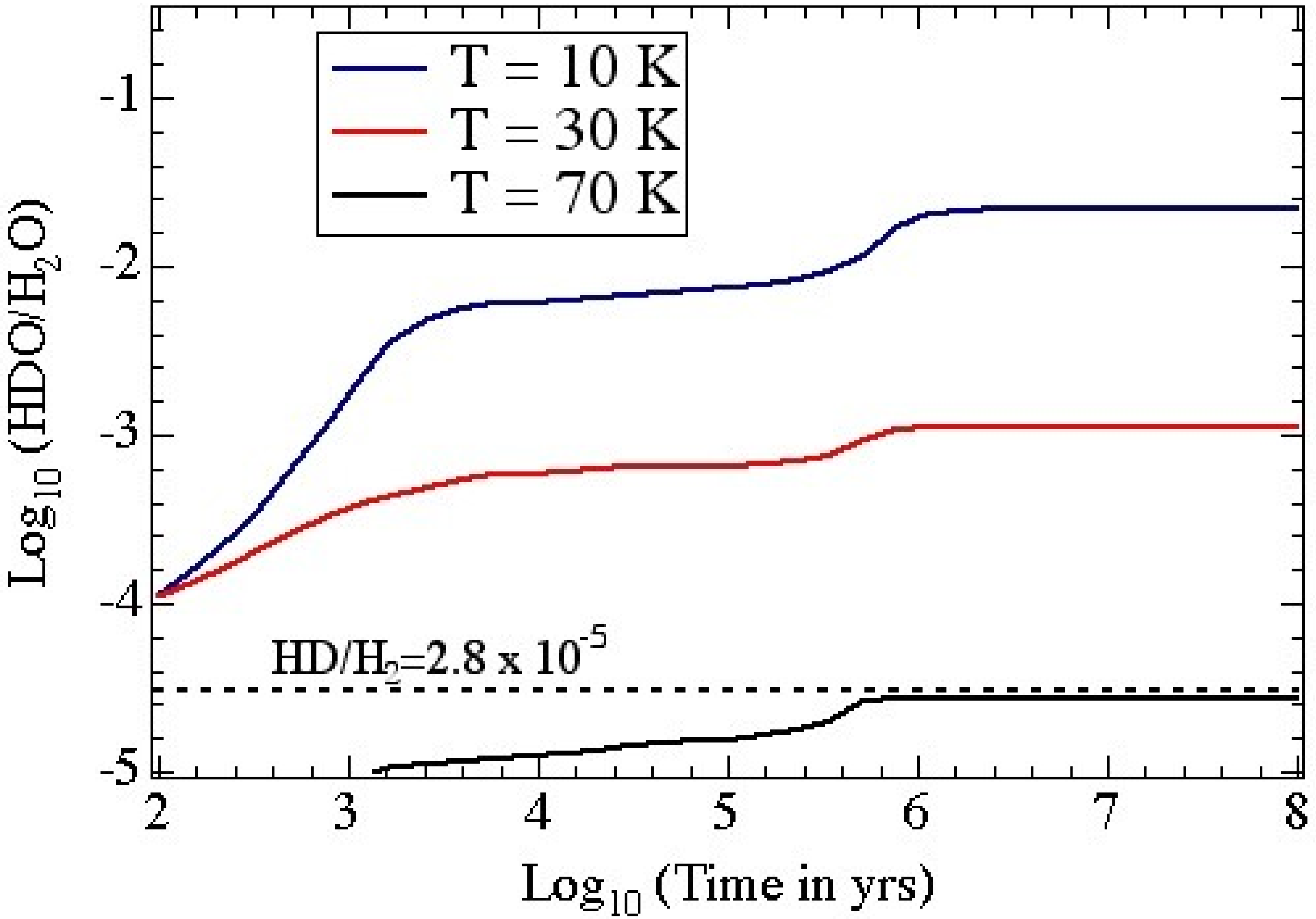
- D/H ratio will therefore track temperature twice - but o/p dependence is not clear at present
- H_2 ortho/para ratio almost unknown in ISM -- and certainly in disks
- In ISM at the front of shocks where H_2 rotational emission is detected the smallest ratio is ~ 0.1 (Neufeld et al. 2006).



Deuterium Fractionation of Water



Deuterium Fractionation of Water



Expanded D. Network

Detection of NHD_2 in pre-stellar cores led to a rethink of interstellar dueterium fractionation theory.

Reaction sequence does not stop with H_2D^+

$$H_2D^+ + HD \leftrightarrow D_2H^+ + H_2 + 180K. \tag{1}$$

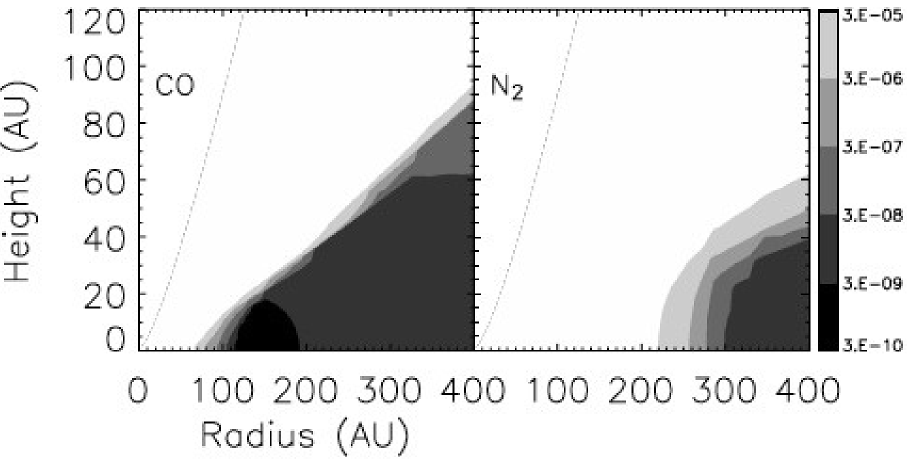
$$D_2H^+ + HD \leftrightarrow D_3^+ + H_2 + 230K. \tag{2}$$

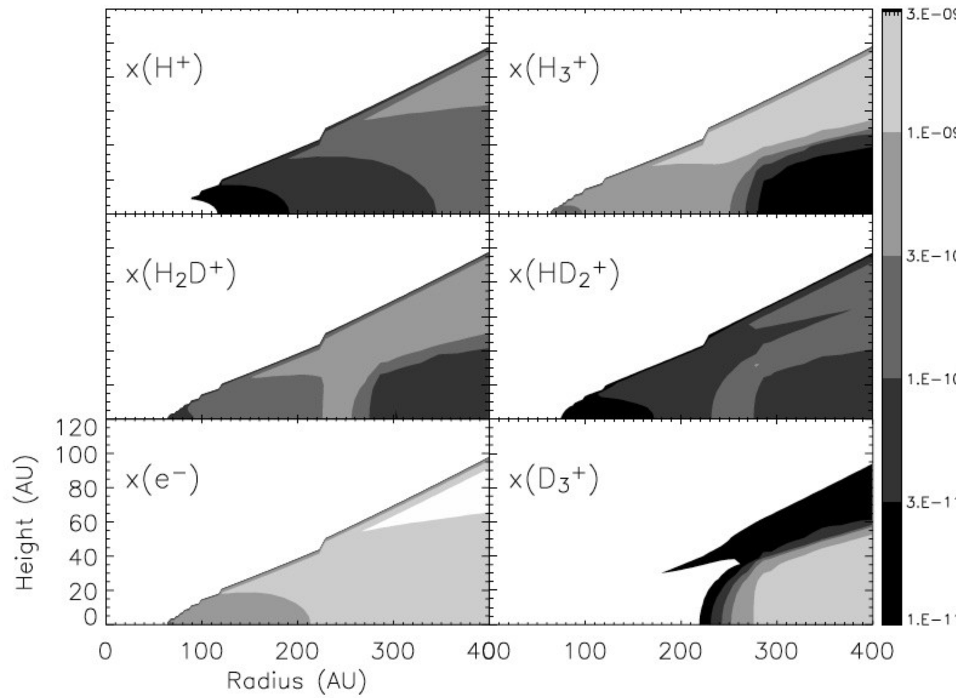
Leads to the production of doubly and triply deuterated molecules.

D_3^+ may be the dominant ion in the midplane.

Expanded D network can be found in Roberts et al. (2004)

D Fractionation in Disks





Ceccarelli and Dominik 2005

Deuterium Fractionation in Disks

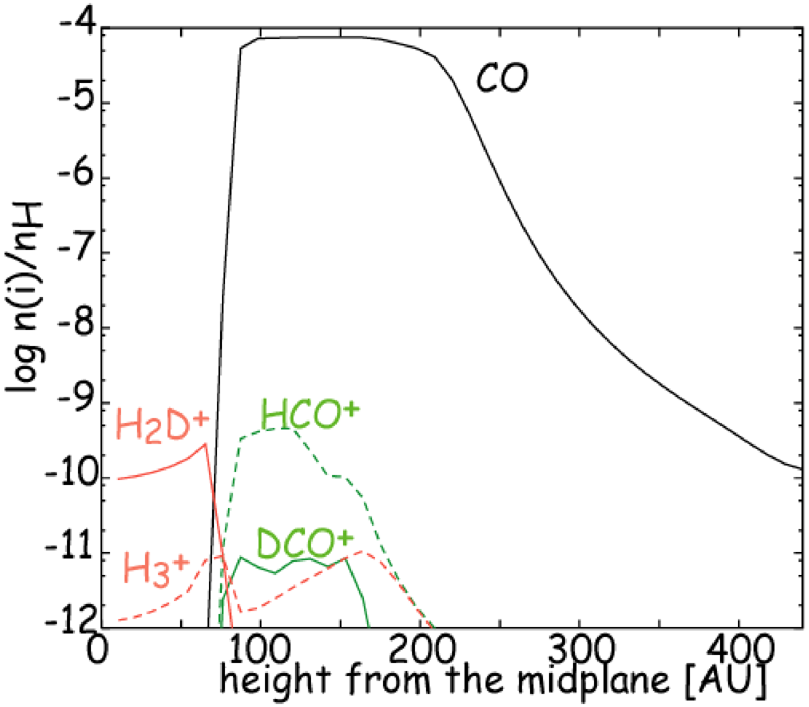
- What happens to D chemistry in a disk:
  - Strong depletion of neutrals in the midplane
  - Low ionization fraction

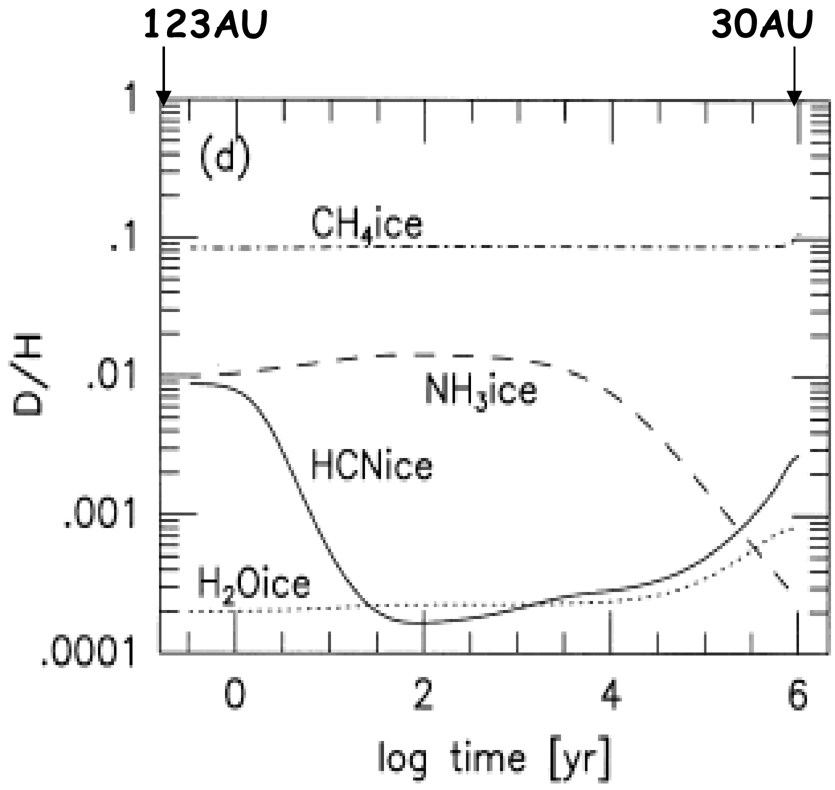
$$\frac{dn(H_3^+)}{dt} = \zeta n - (kn(CO) + \beta n_e)n(H_3^+)$$

$$n(H_3^+) = \frac{\zeta n}{kn(CO) + \beta x_e}$$

  - Abundance of H_3^+ rises (if ionization present) and gas-phase D fractionation will take off
  - Caveat: will create species like HDCO, DCN, etc in gaseous layers where CO and other neutrals are freezing onto grains
  - These neutrals then freeze onto grains

D Fractionation in Disks

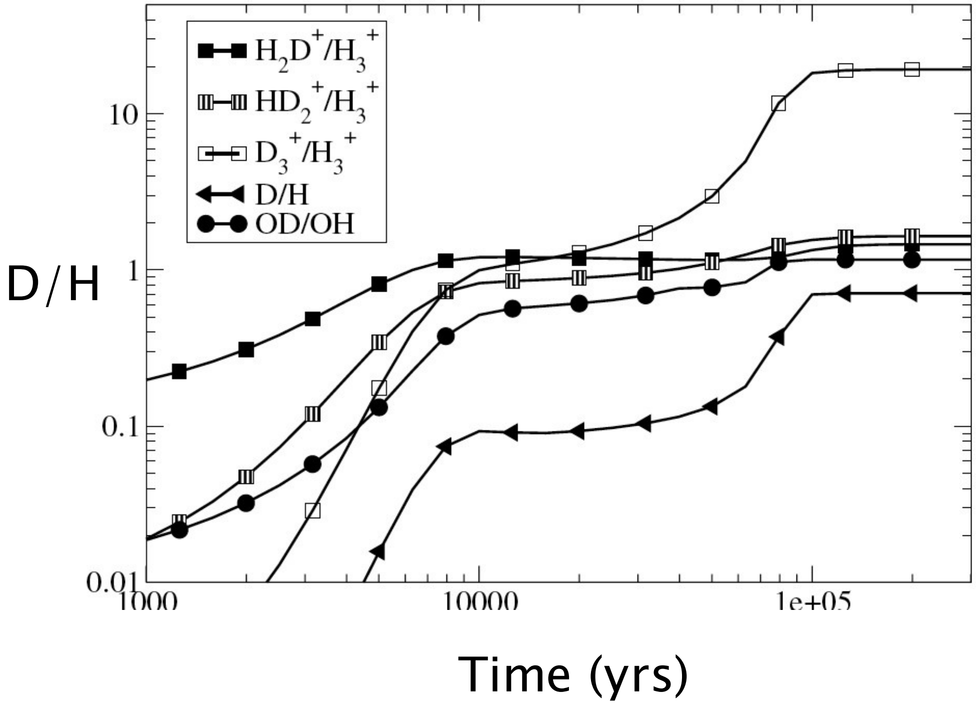




Aikawa and Herbst 1999 – no mixing

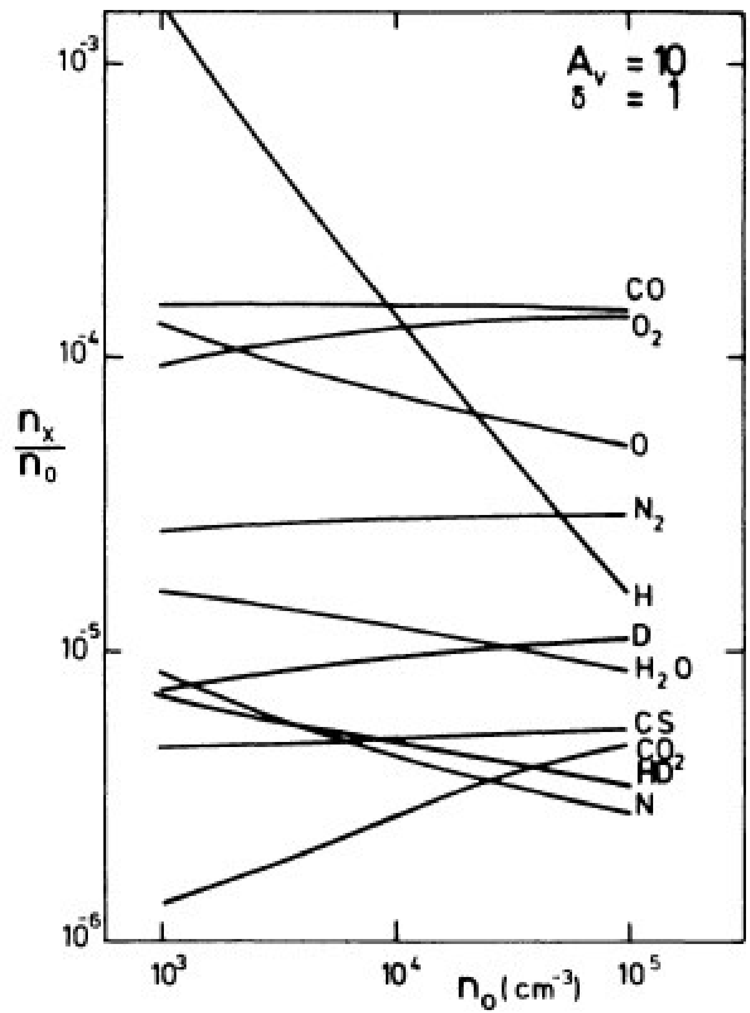
D Fractionation in Disks

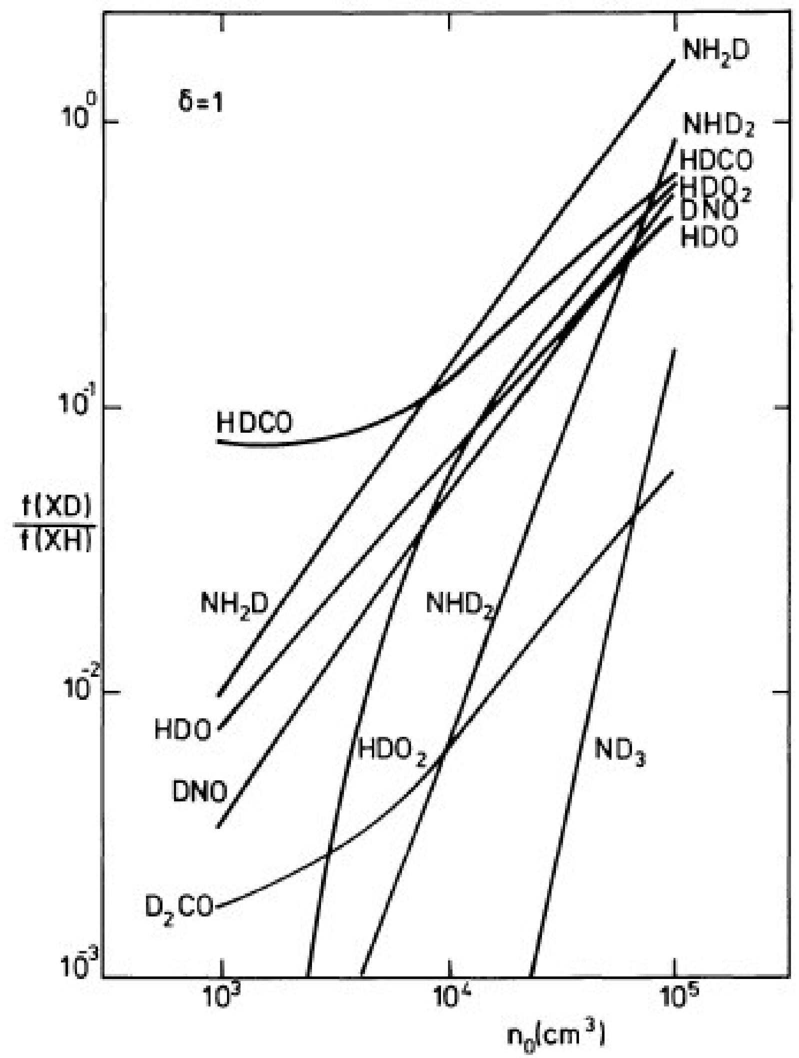
Produces an increase in atomic D/H ratio



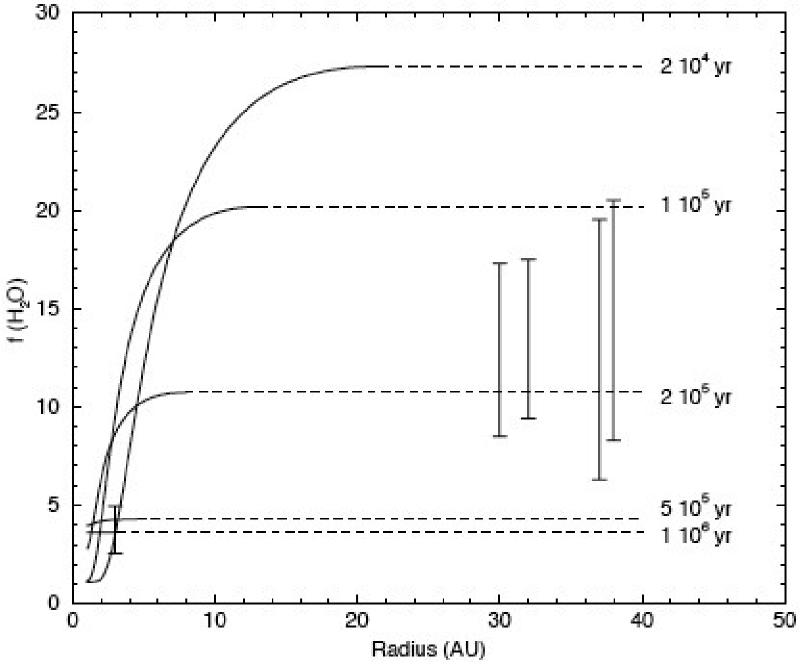
Roberts et al. 2004

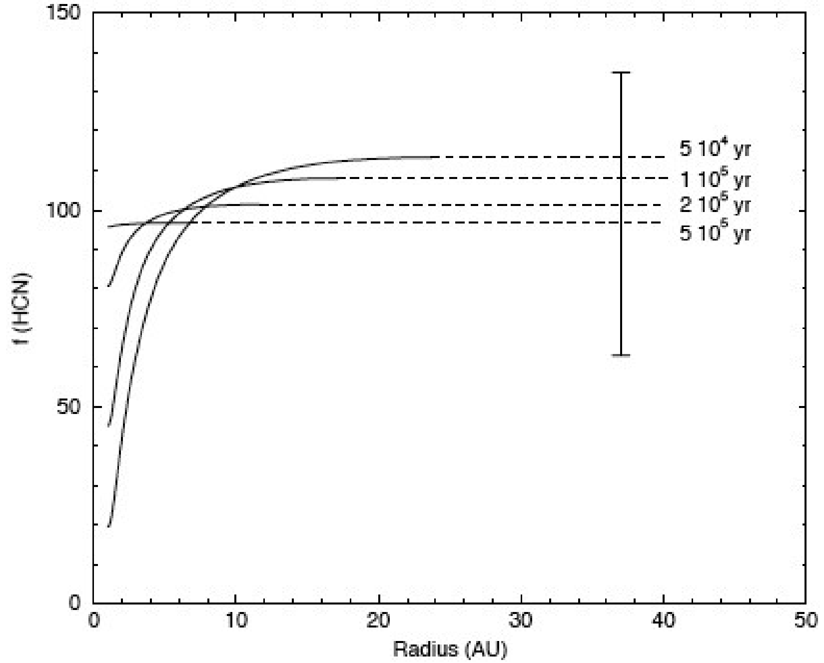
Enhanced Surface Chemistry





Thermochemistry as well…

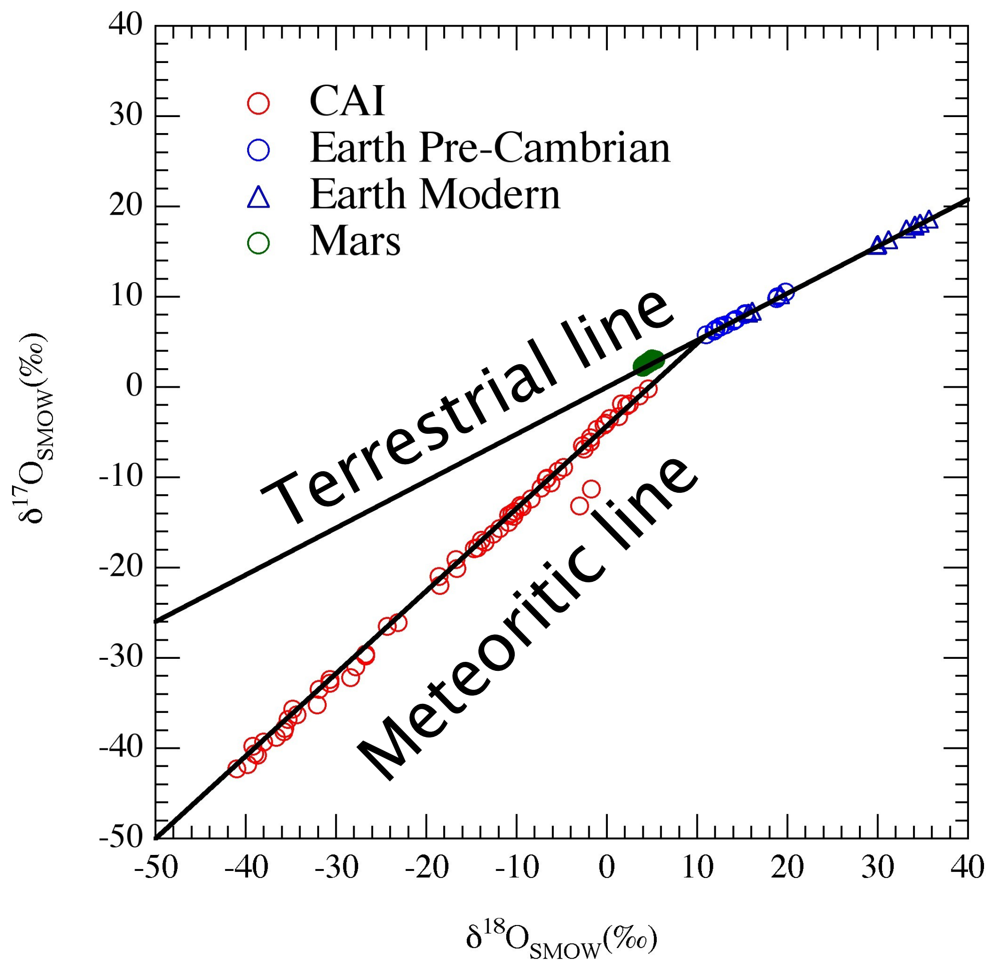




- Hersant et al. 2001
  - Thermochemistry
  - Vigorous radial mixing of inner disk to cometary formation zones

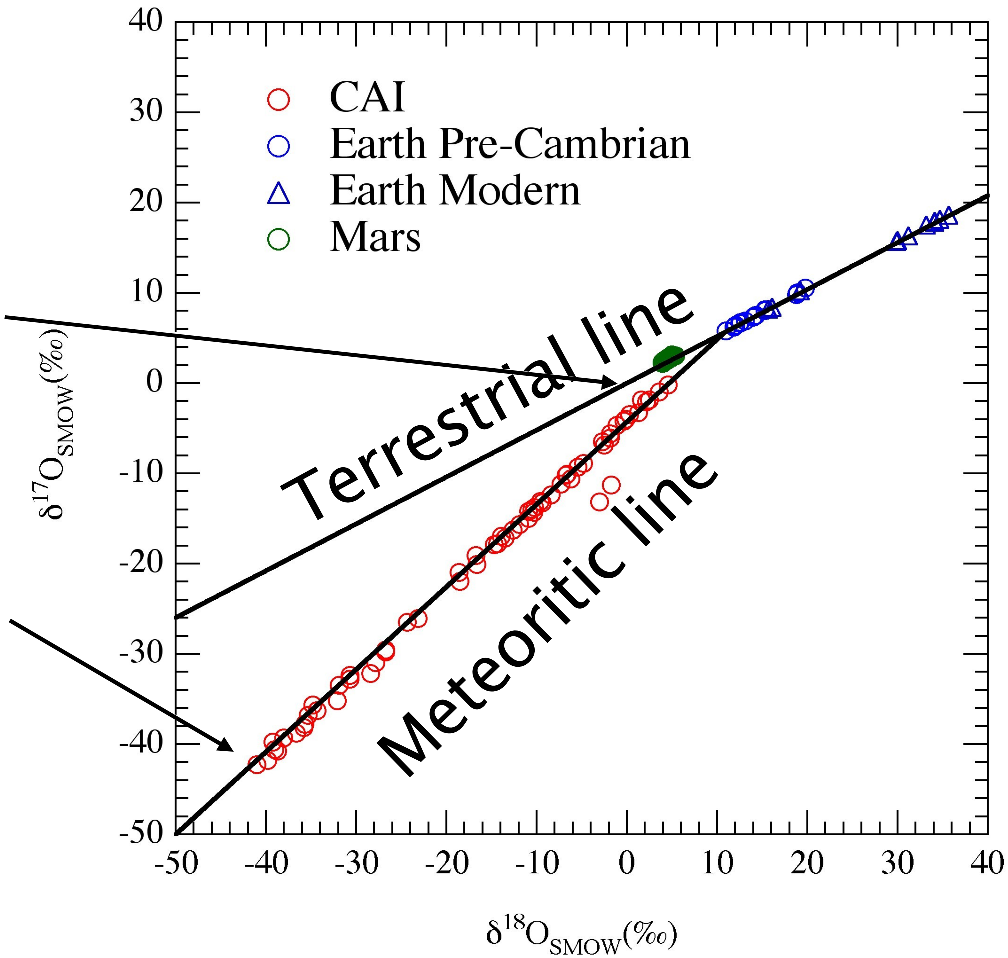
Oxygen Isotopes in Meteorites

- 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.



Oxygen Isotopes in Meteorites

- meteoritic results can be from mixing of 2 reservoirs

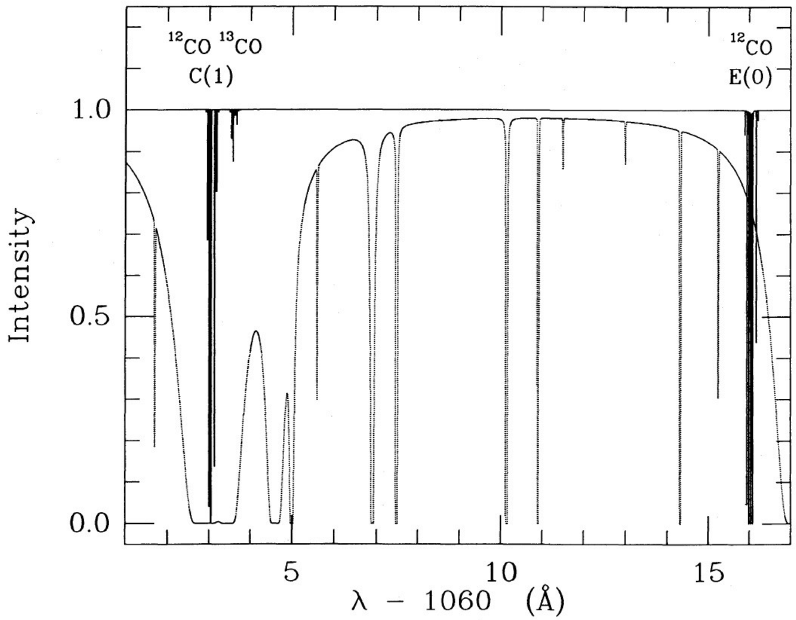


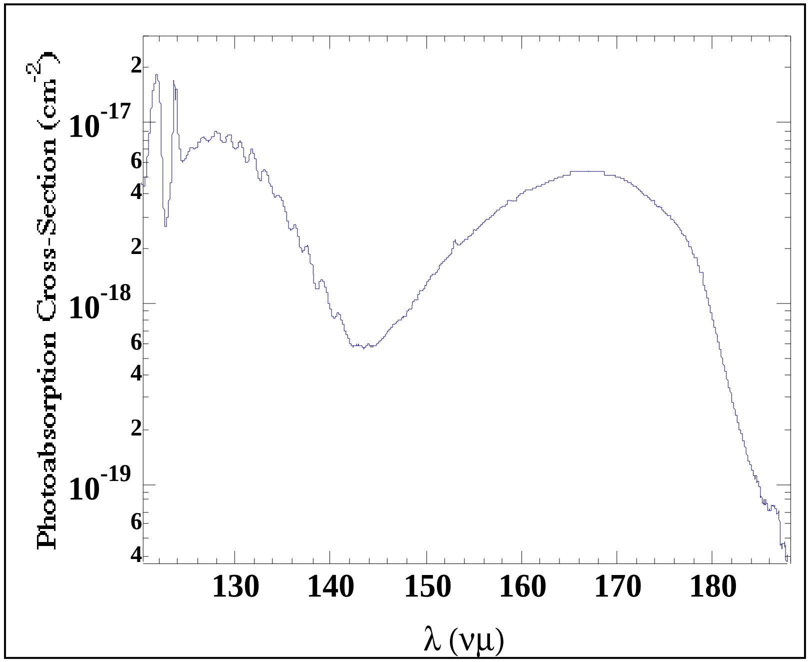
- thought ^{16}O poor state in gas (Clayton 1993, etc.)

Oxygen Isotopes Theory

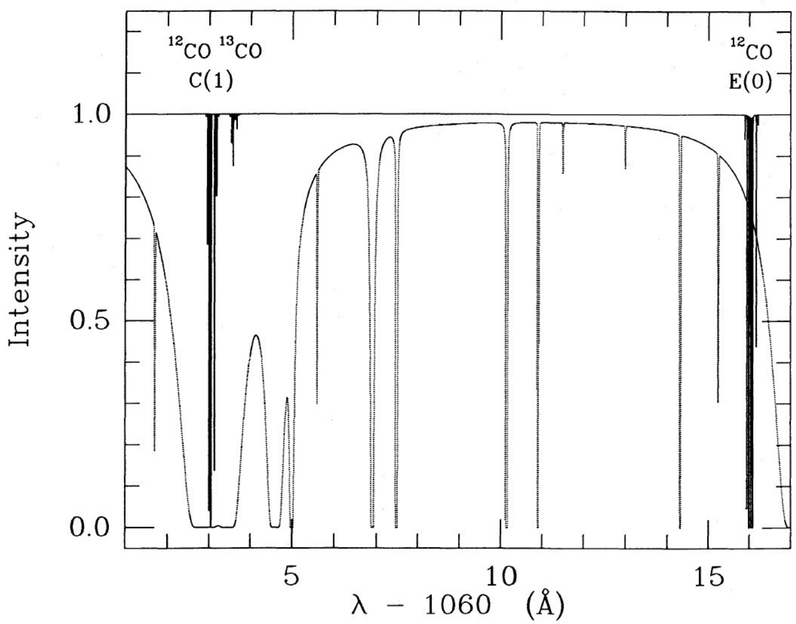
- stellar nucleosynthesis
  - lack of similar trend seen in outer elements
- chemical reactions that are non-mass dependent (Thiemens and Heidenreich 1983)
  - known to happen in the Earth's atmosphere (for ozone)
  - no theoretical understanding of other reactions that can link to CO and H_2O
- photo-chemical CO self-shielding
  - suggested by Clayton 2002 at in the inner nebula at the edge of the disk (X point)
  - active on disk surface (Lyons and Young 2005)
  - active on cloud surface and provided to disk (Yurimoto and Kuramoto 2004)

How Does Isotope Selective Photodissociation Work?





How Does Isotope Selective Photodissociation Work?



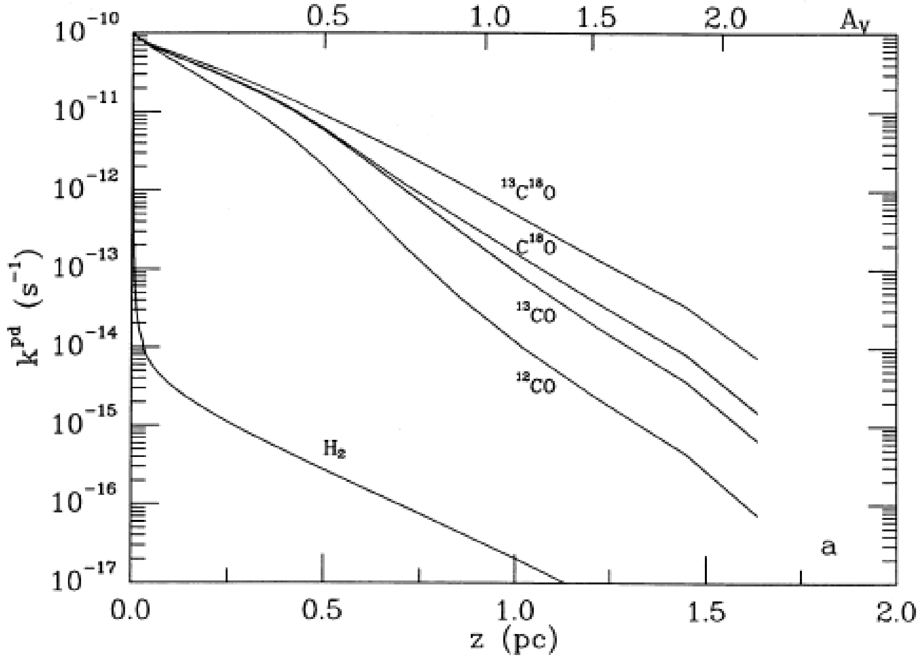
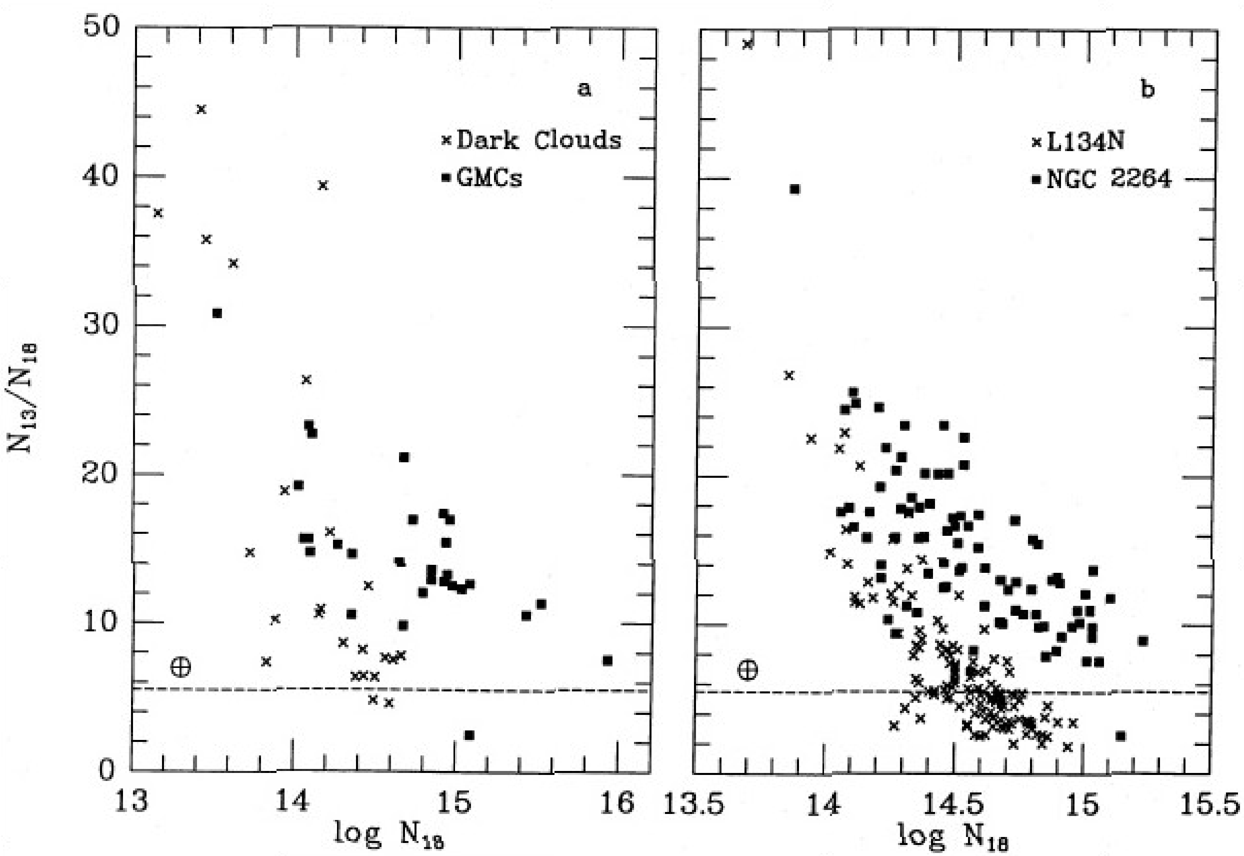


FIG. 5*a*

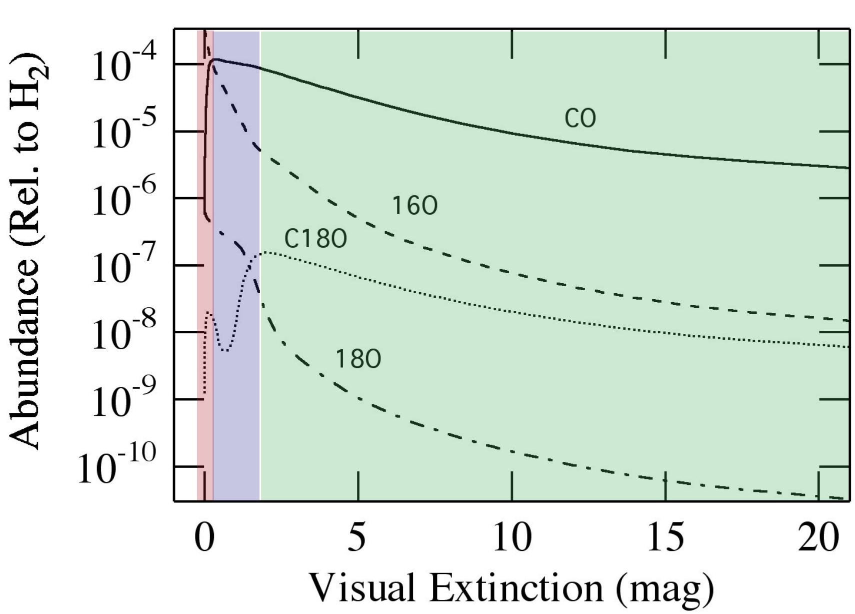
Isotopic Selective Photodissociation:

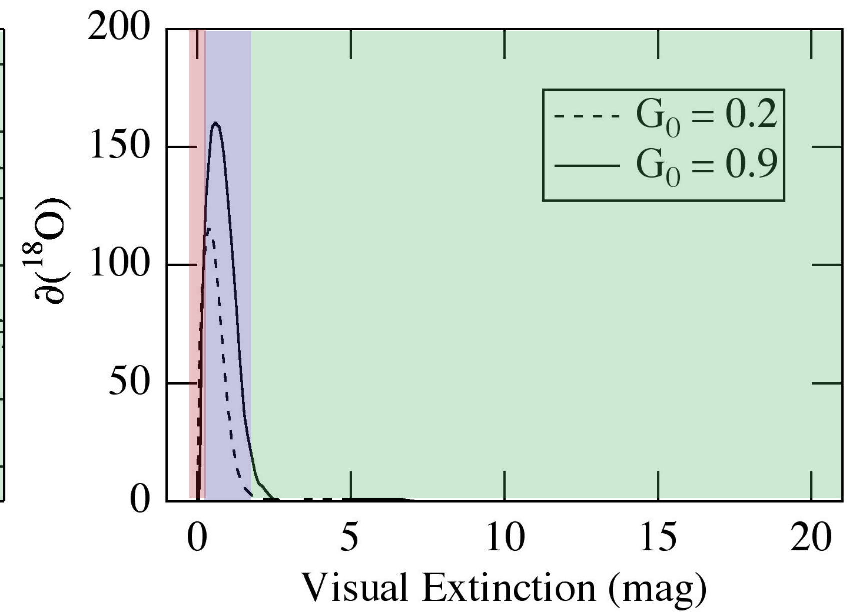


- Observed in ISM
- Strength of effect depends on radiation field.
- Can expect gradient along disk surface.

Taylor and Dickman 1989

CO Photodissociation and Oxygen Isotopes



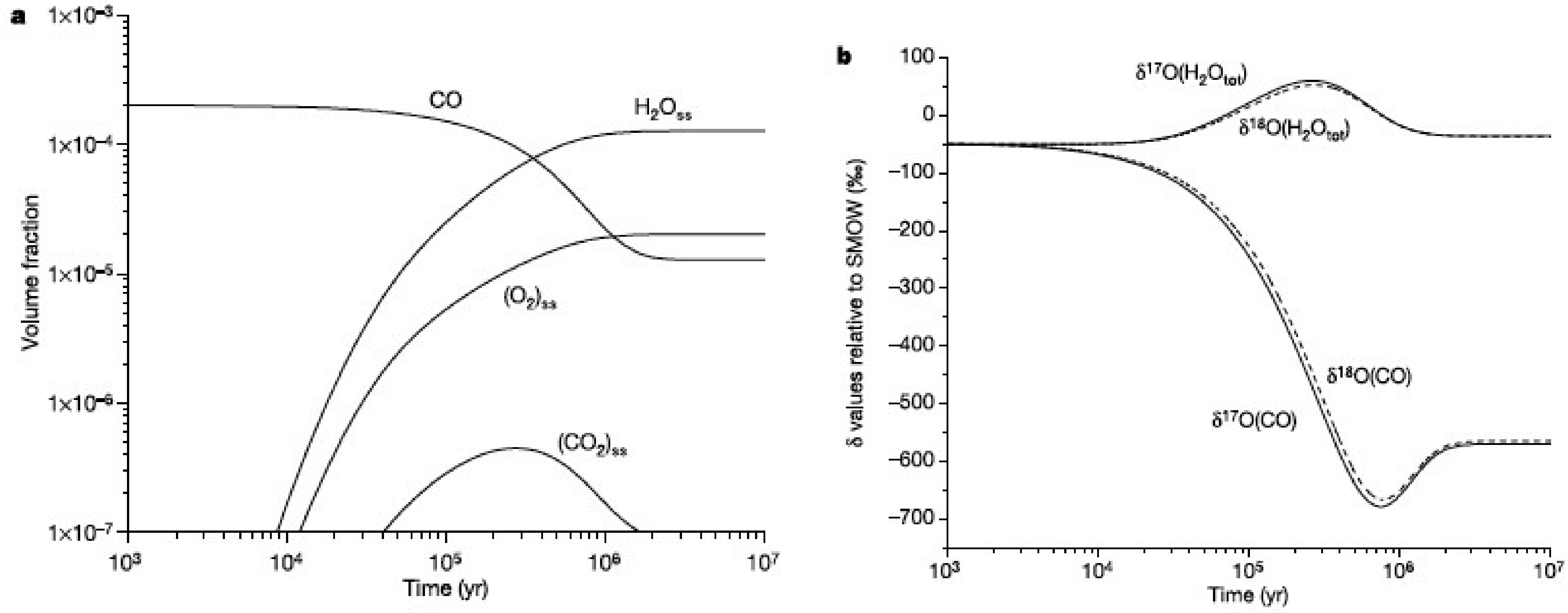


$A_v < 0.5$	$0.5 < A_v < 2$	$A_v > 2$
CO + hν -> C + O	CO	CO
C^{18}O + hν -> C + ^{18}O	C^{18}O + hν -> C + ^{18}O	C^{18}O
	^{18}O + gr -> $H_2{}^{18}O_{ice}$	

CO Self-Shielding Models

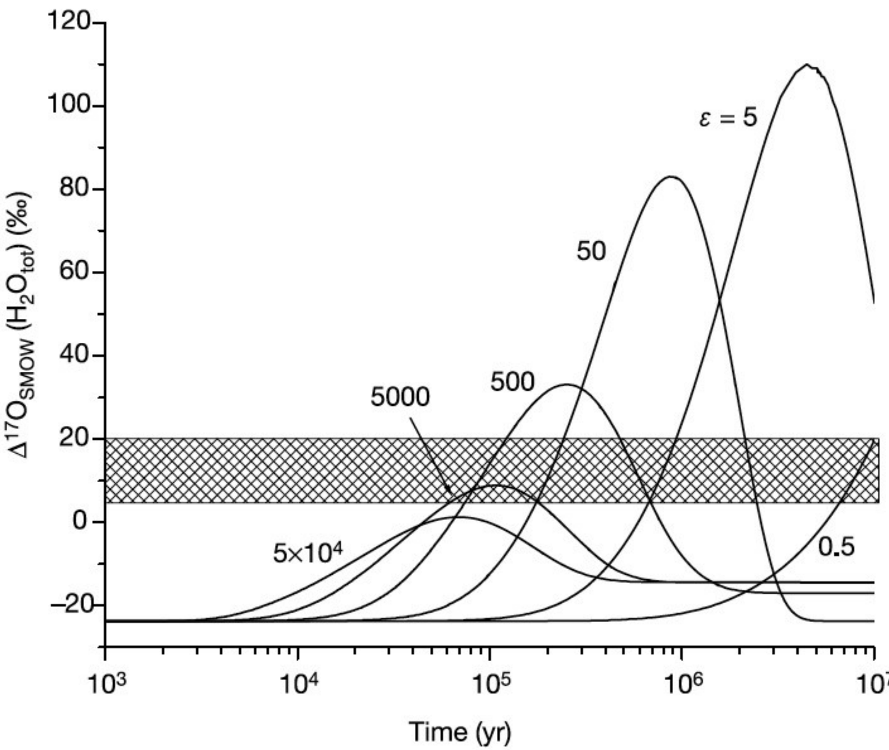
- active in the inner nebula at the edge of the disk (Clayton 2002)
  - only gas disk at inner edge, cannot make solids as it is too hot
- active on disk surface and mixing to midplane (Lyons and Young 2005)
  - credible solution
  - mixing may only be active on surface where sufficient ionization is present
  - cannot affect Solar oxygen isotopic ratio
- active on cloud surface and provided to disk (Yurimoto and Kuramoto 2004)

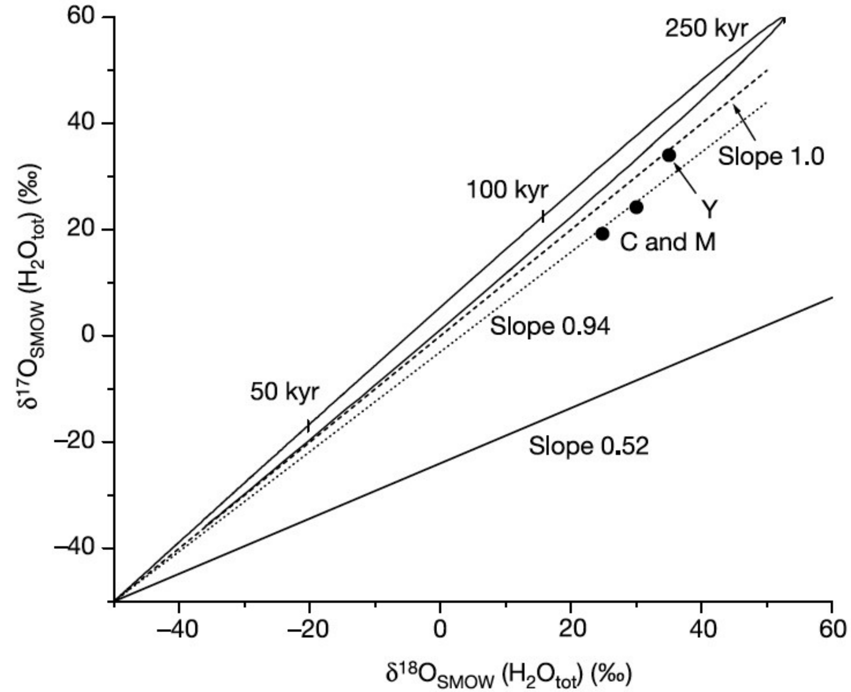
Oxygen Isotopes



Lyons and Young 2005

Oxygen Isotopes





Lyons and Young 2005
Also see poster by J.E. Lee

Summary – Open Questions

- Observations and theory suggest that disk surfaces are photon-dominated regions similar to those seen in ISM.
  - UV field is has different wavelength dependence (Lyman alpha)
  - Rough characteristics of the vertically stratified chemistry are established
- Two regimes for chemistry exist within the disk: T. eq. and kinetic
  - Not entirely clear how distinct these reservoirs are -- although the outer disk is out of equilibrium
- What happens in gas/what happens on grains? How can we tell?
  - Where do complex molecules seen in meteorites originate -- is the disk a complex organic molecule factory?
- What happens prior to stellar birth/what happens in the disk?
  - Signatures of cold chemistry are the same
  - Mixing will be a large difference – what are the signatures?
- Can we find a way to determine how important grains are in determining the charge balance?
- <u>Lots of work to do -- even better before ALMA tells us where we are wrong….</u>