

Photochemistry in the Early Solar system: Summary of Observations and Explanations

E. D. Young

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ÉCOLE DE PHYSIQUE
Les Houches

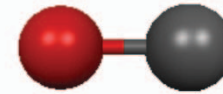


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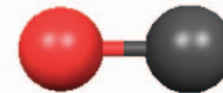
Isotope fractionation

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K_f}{\mu}}$$

Reduced mass
controls frequency



C¹⁶O



C¹⁷O



Harold Urey



Jacob Bigeleisen



Maria Goeppert-Mayer

Harold Urey, *J. Chem. Soc. (London)* (1947)

J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* (1947)

Isotope fractionation

$$v = \frac{1}{2\pi} \sqrt{\frac{K_f}{\mu}}$$

$$\delta^{17}\text{O}_a - \delta^{17}\text{O}_b \cong 10^3 \ln \alpha_{a-b}^{17/16} = \frac{10^3}{24} \left(\frac{h}{k_b T} \right)^2 \left(\frac{1}{m_{16}} - \frac{1}{m_{17}} \right) \left[\sum_{j=1}^{3N_a-3} \frac{K_{f,j,a}}{4\pi^2} - \sum_{j=1}^{3N_b-3} \frac{K_{f,j,b}}{4\pi^2} \right]$$

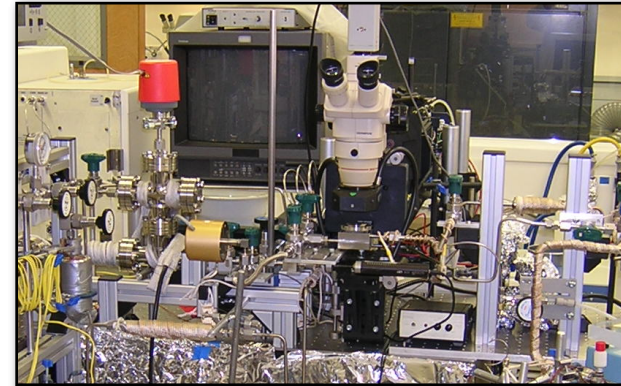
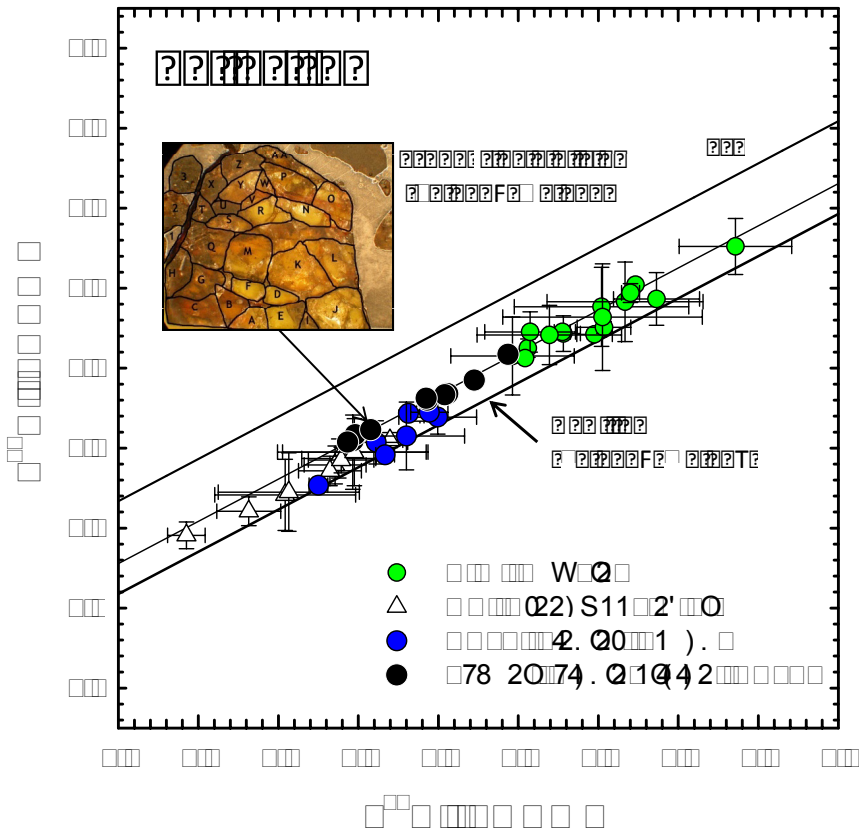
$$\delta^{18}\text{O}_a - \delta^{18}\text{O}_b \cong 10^3 \ln \alpha_{a-b}^{18/16} = \frac{10^3}{24} \left(\frac{h}{k_b T} \right)^2 \left(\frac{1}{m_{16}} - \frac{1}{m_{18}} \right) \left[\sum_{j=1}^{3N_a-3} \frac{K_{f,j,a}}{4\pi^2} - \sum_{j=1}^{3N_b-3} \frac{K_{f,j,b}}{4\pi^2} \right]$$

$$\frac{\delta^{17}\text{O}_a - \delta^{17}\text{O}_b}{\delta^{18}\text{O}_a - \delta^{18}\text{O}_b} = \frac{\left(\frac{1}{m_{16}} - \frac{1}{m_{17}} \right)}{\left(\frac{1}{m_{16}} - \frac{1}{m_{18}} \right)} = 0.531$$

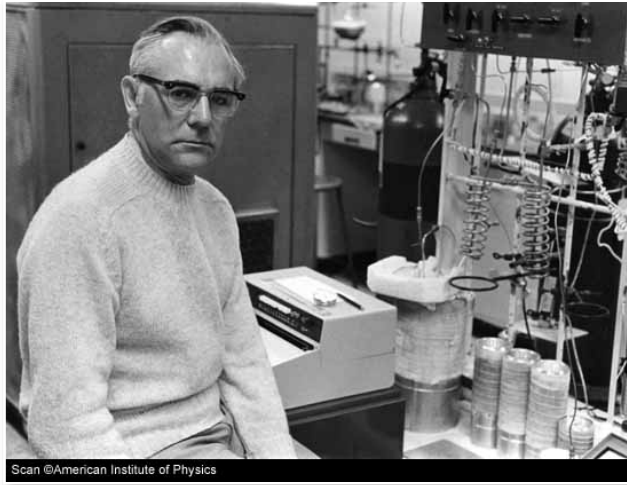
Mass-dependent
fractionation



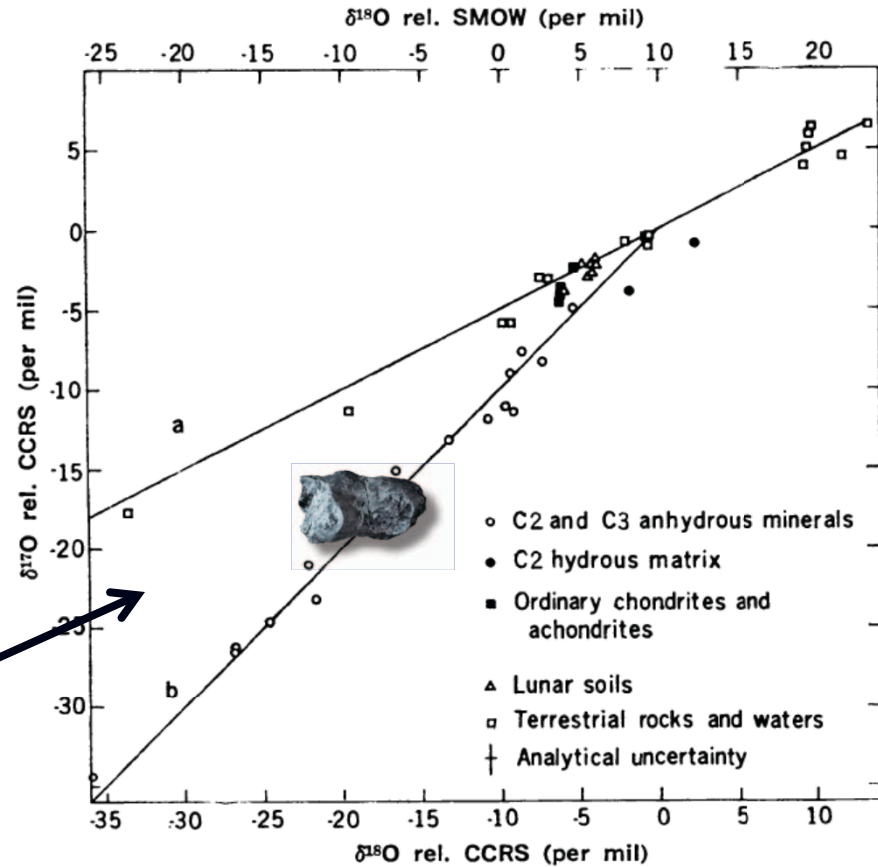
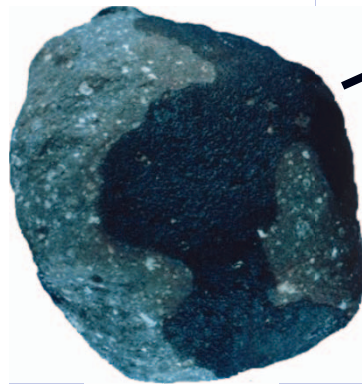
Isotope fractionation



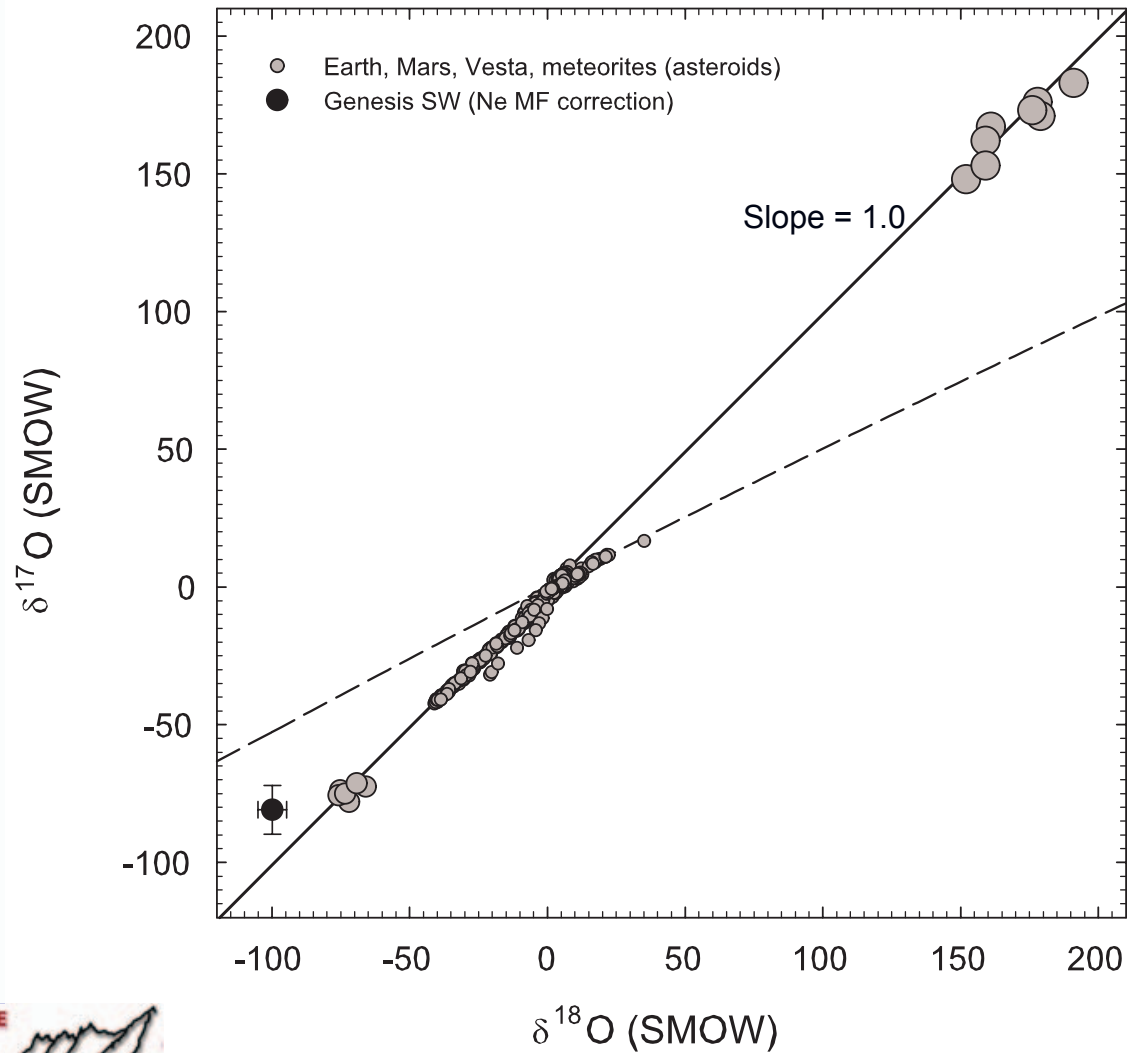
$$\delta^{17}\text{O}/\delta^{18}\text{O} = \frac{\left(\frac{1}{m_{16}} - \frac{1}{m_{17}} \right)}{\left(\frac{1}{m_{16}} - \frac{1}{m_{18}} \right)} = 0.531$$

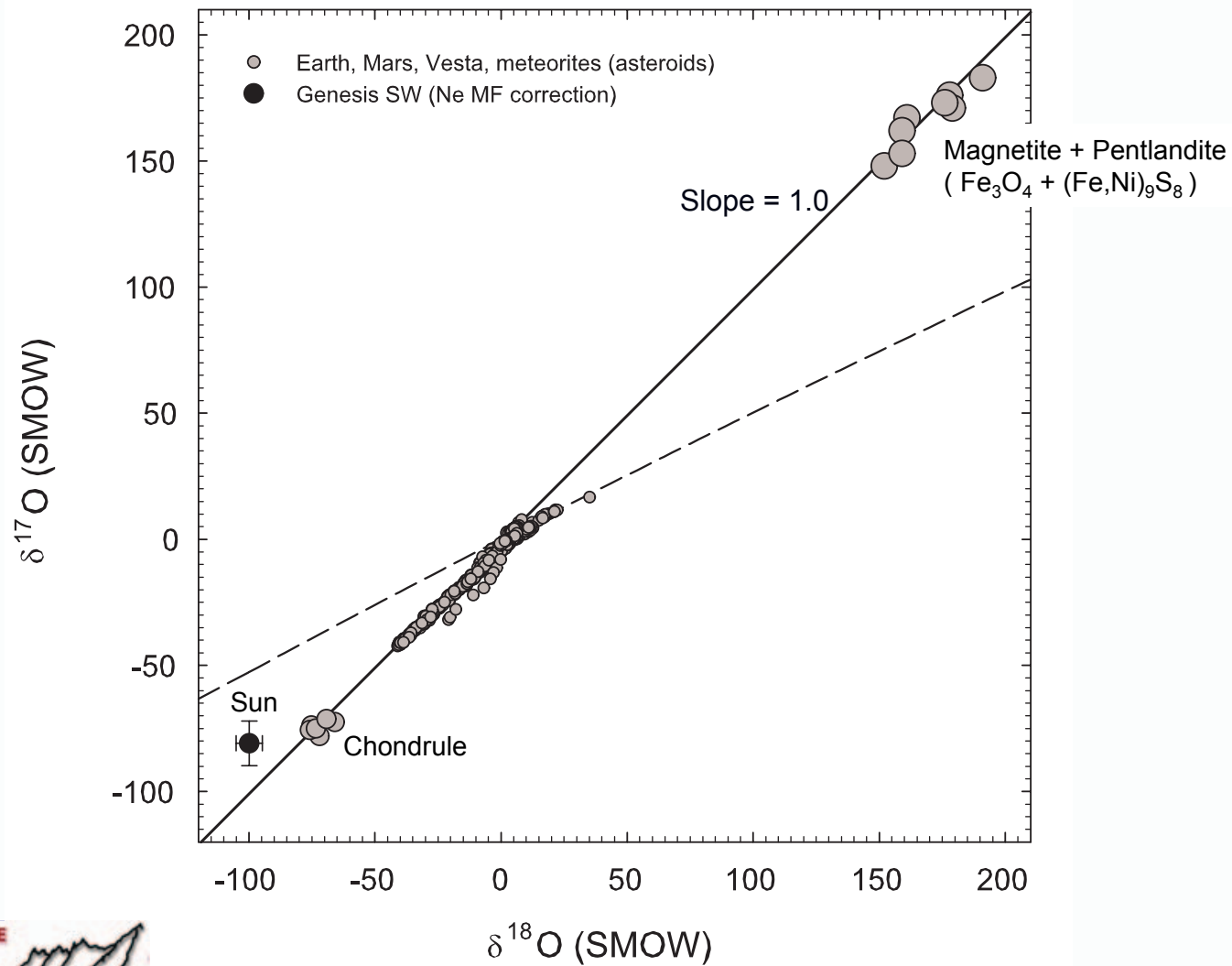


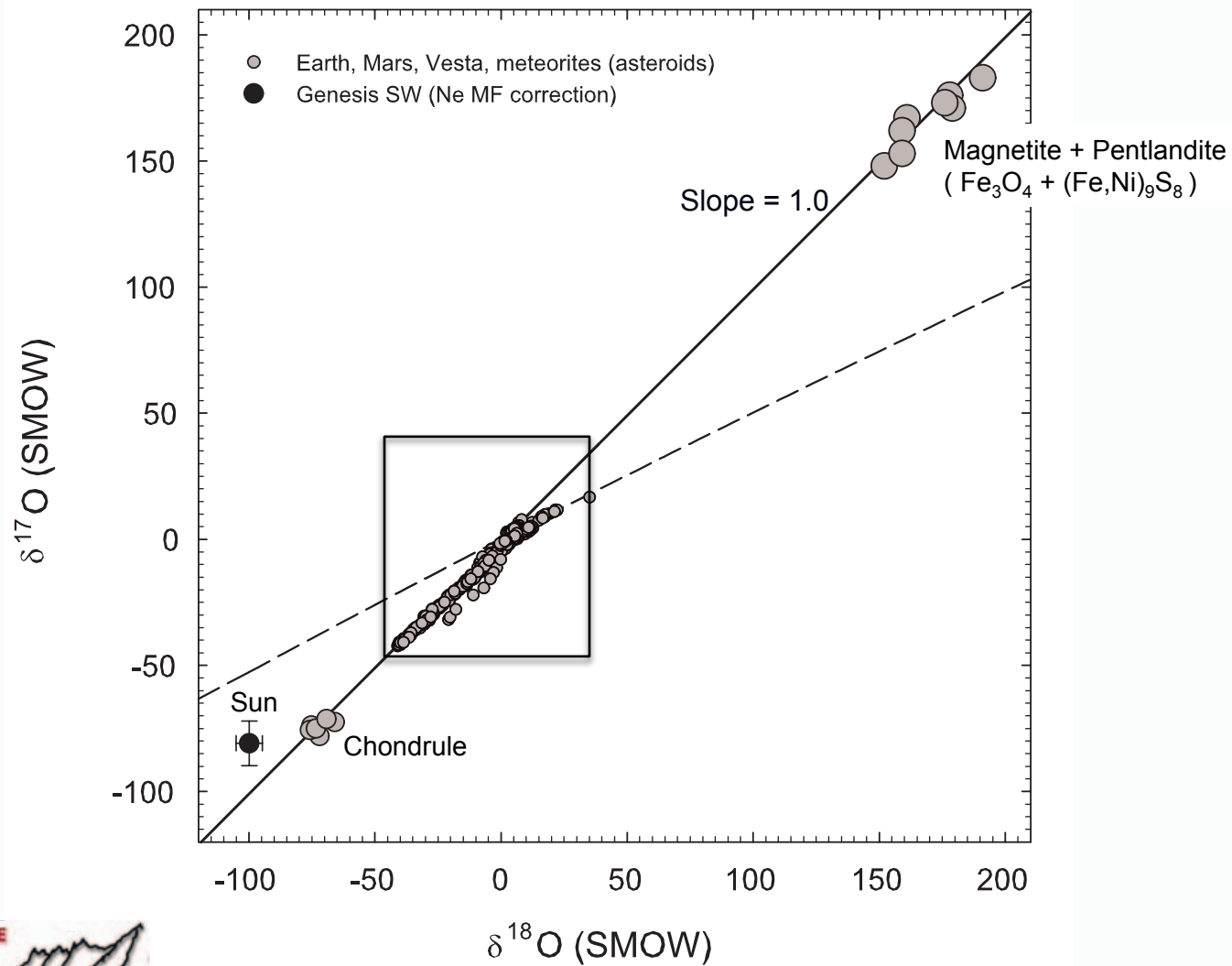
Robert N. Clayton

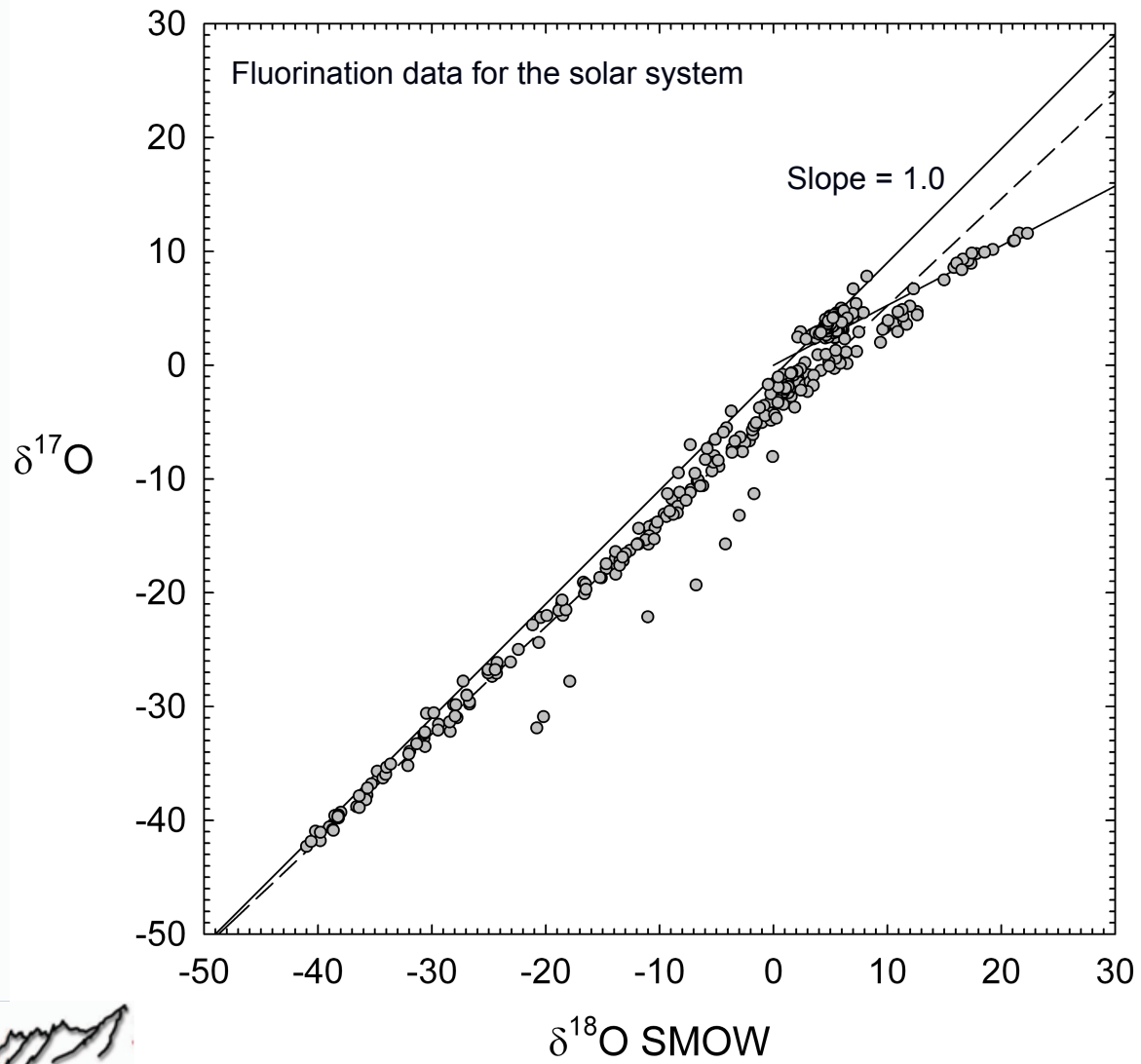


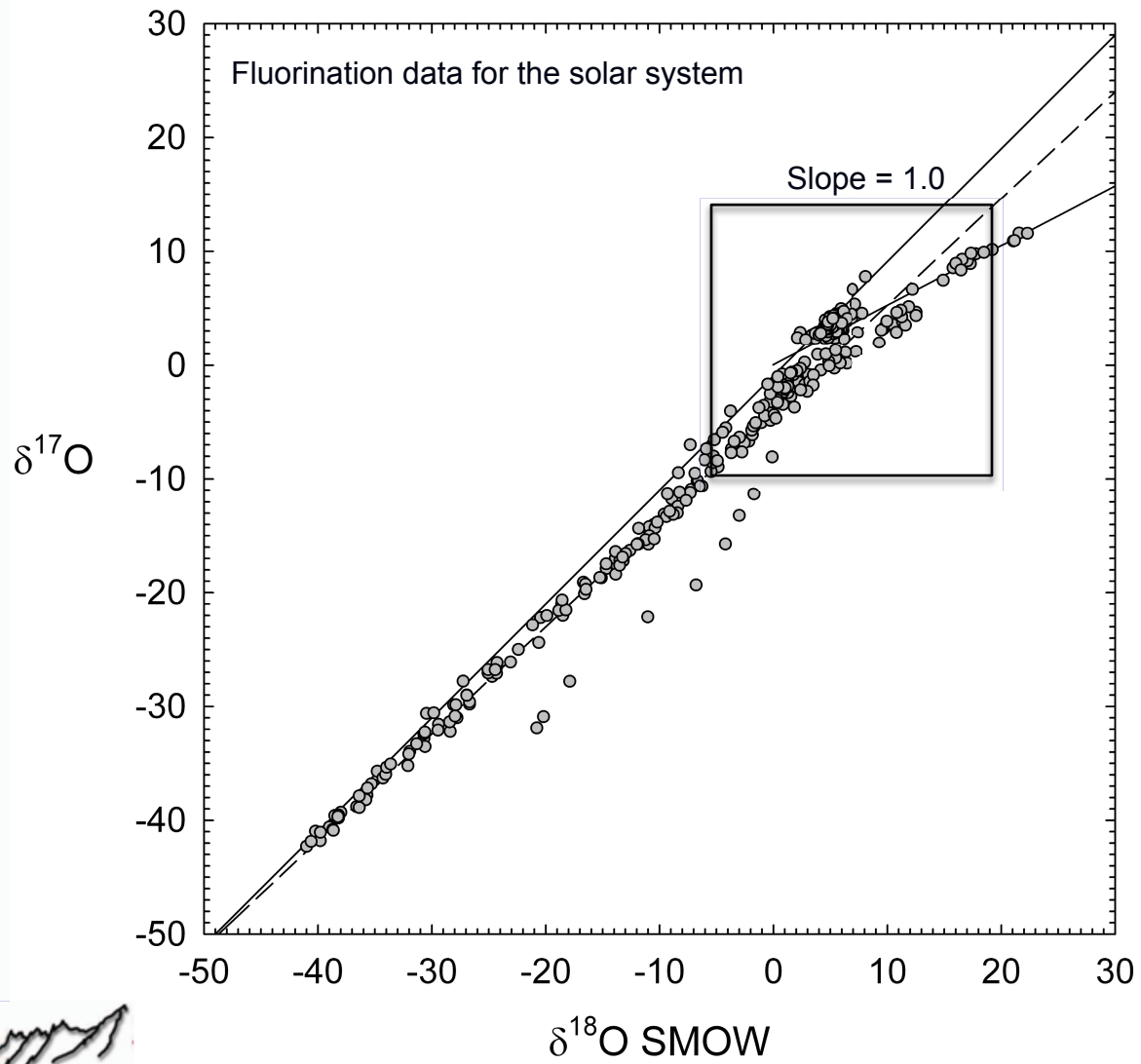
1973: oxygen isotope anomaly in meteorites (CAIs)

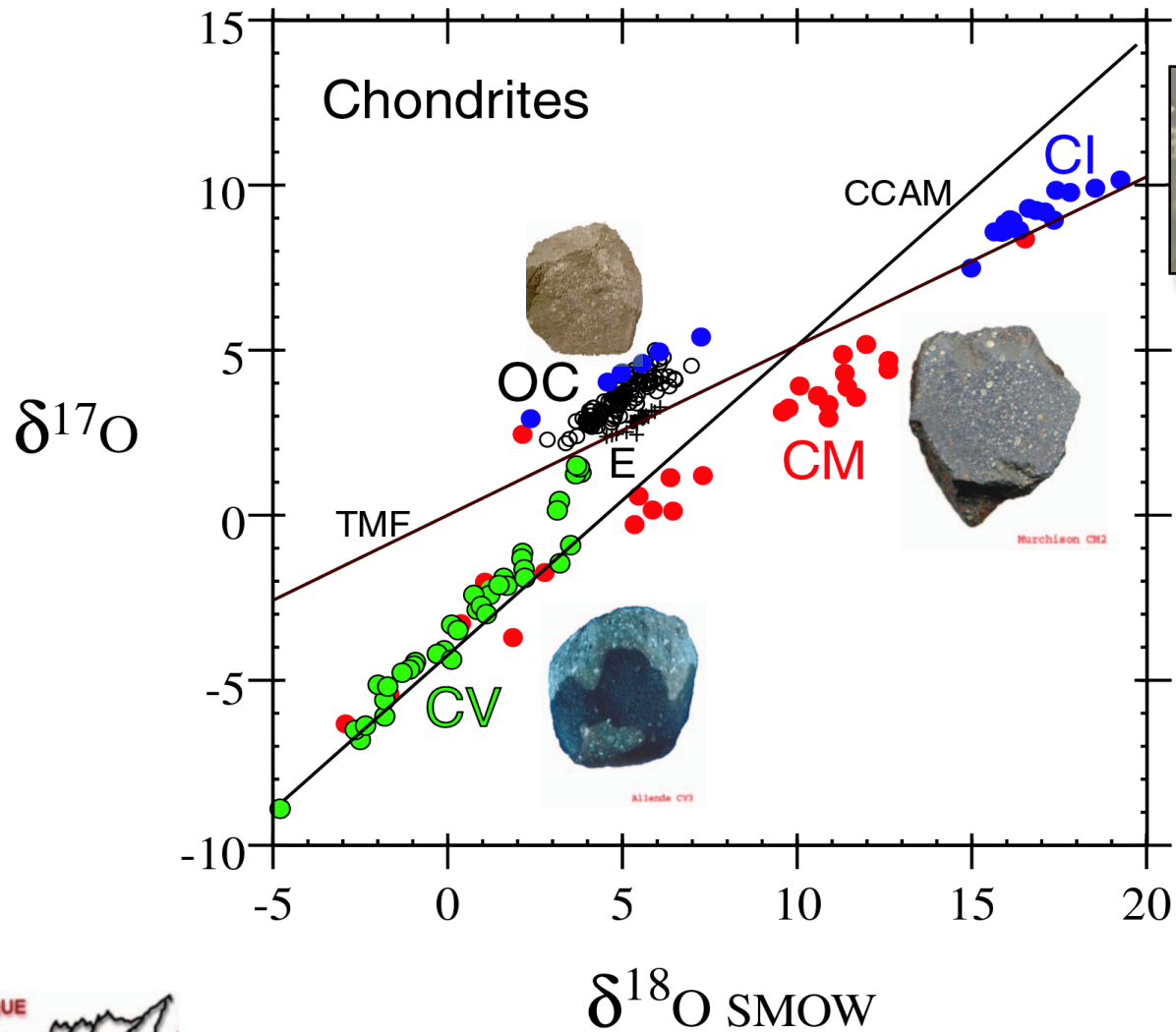




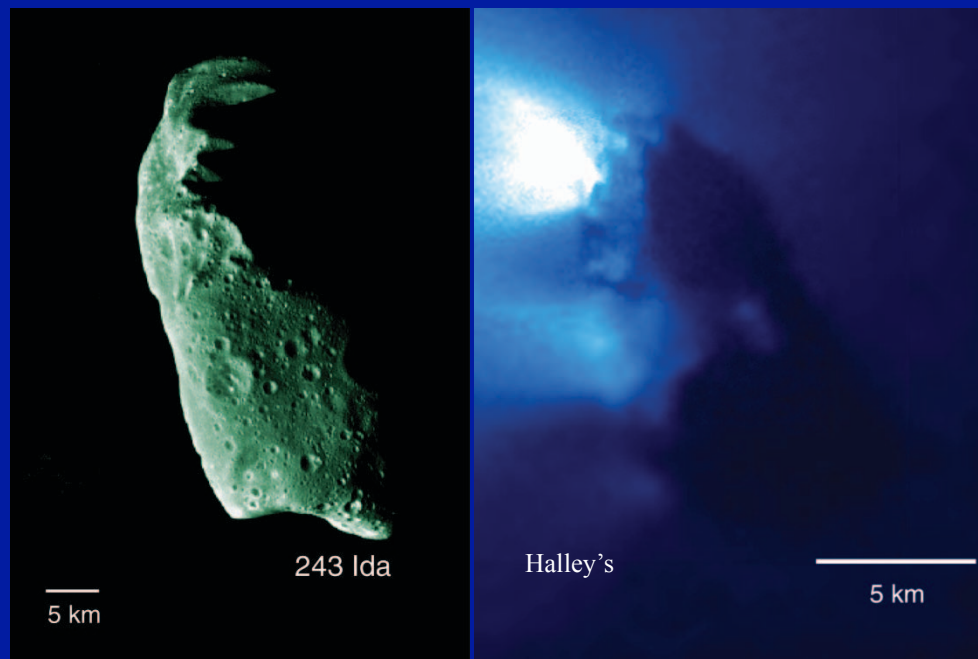








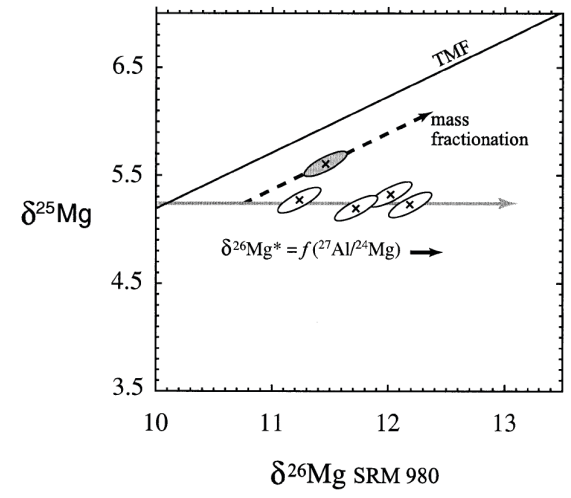
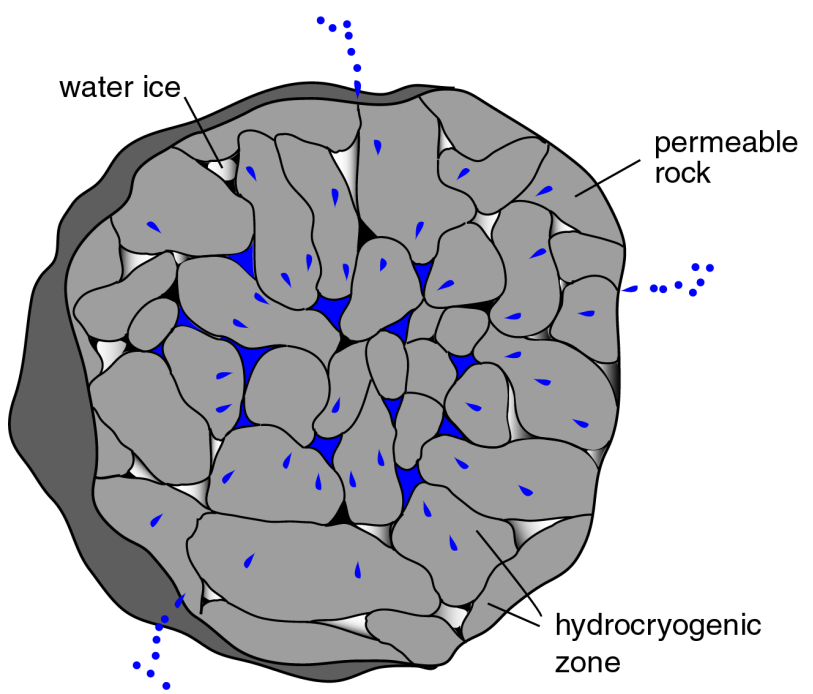
Planetesimal hydrology:



^{26}Al (half life = 0.7 Myr) = heat source in the early solar system

$$^{26}\text{Al} \rightarrow ^{26}\text{Mg}^*$$

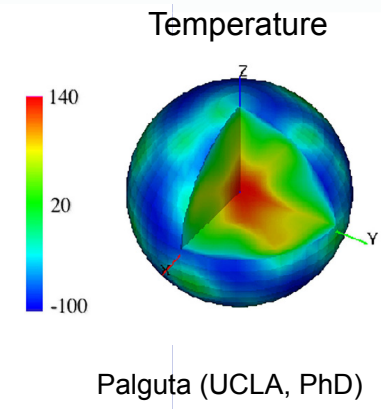
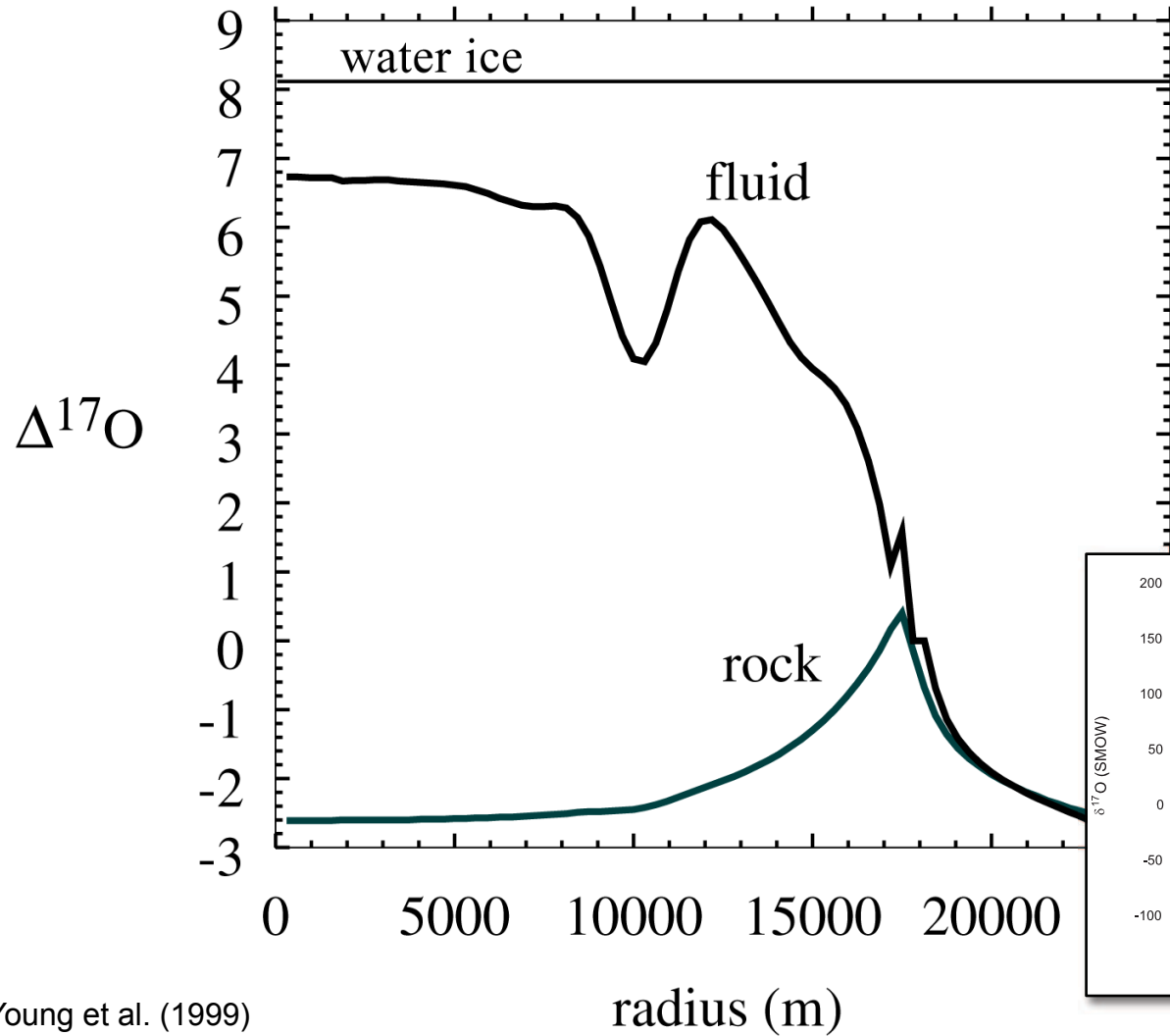
$$Q = 6 \times 10^3 \left(^{26}\text{Al}/^{27}\text{Al} \right) \exp(-\lambda t) \text{ W/kg}$$



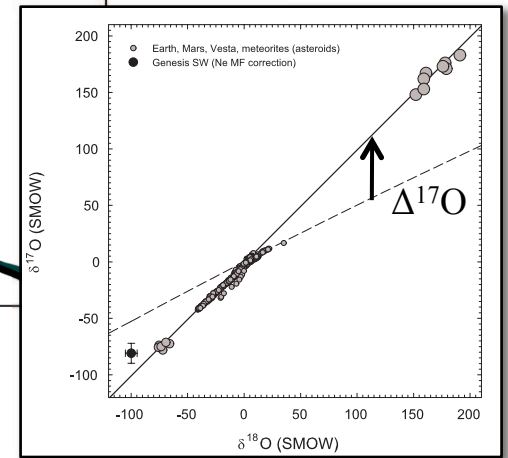
Water ice melts, water flows

Hydrology not unlike terrestrial water-rock systems

Kinetic models for fluid flow

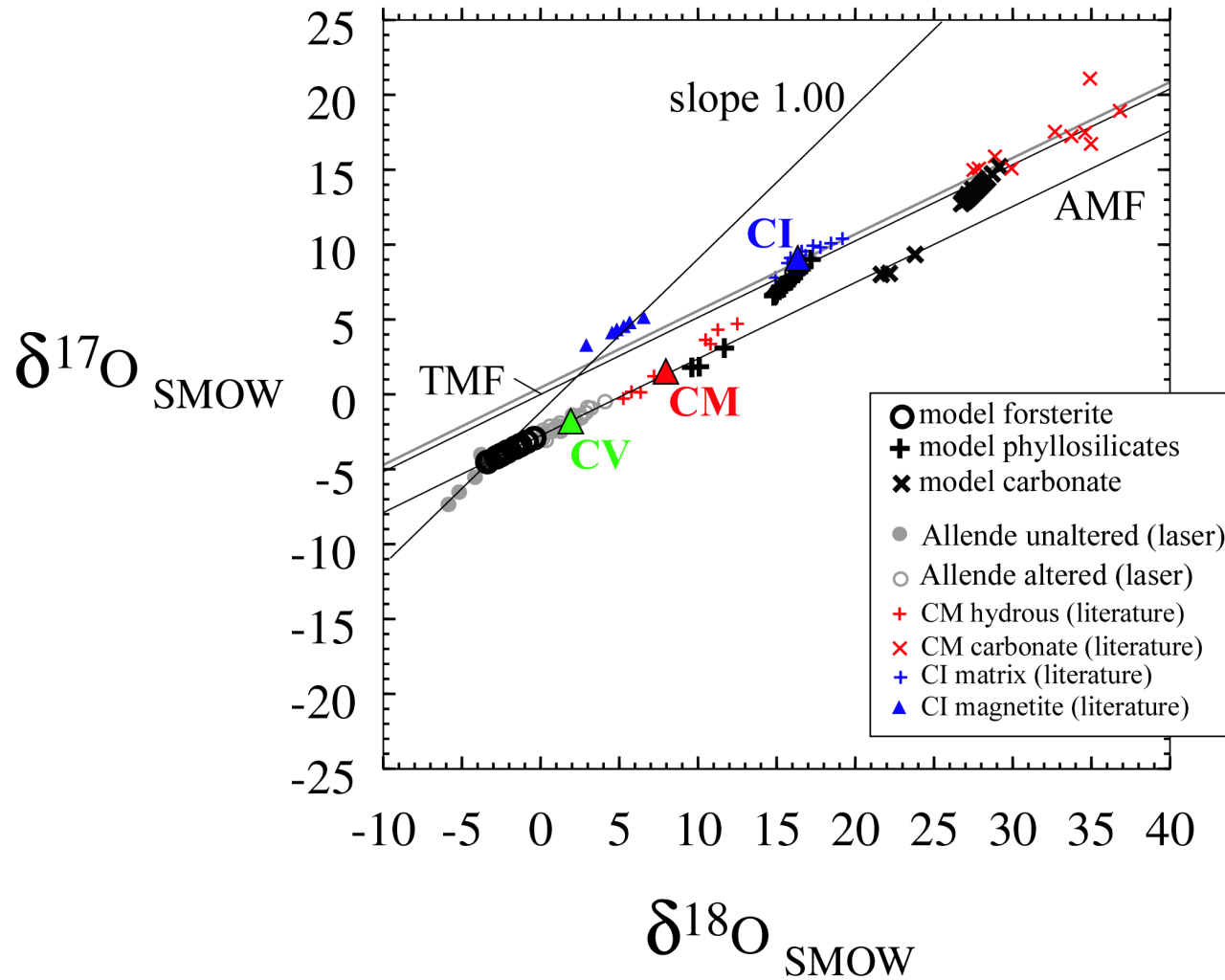


Palguta (UCLA, PhD)



After Young et al. (1999)

Kinetic models for fluid flow



After Young et al. (1999)



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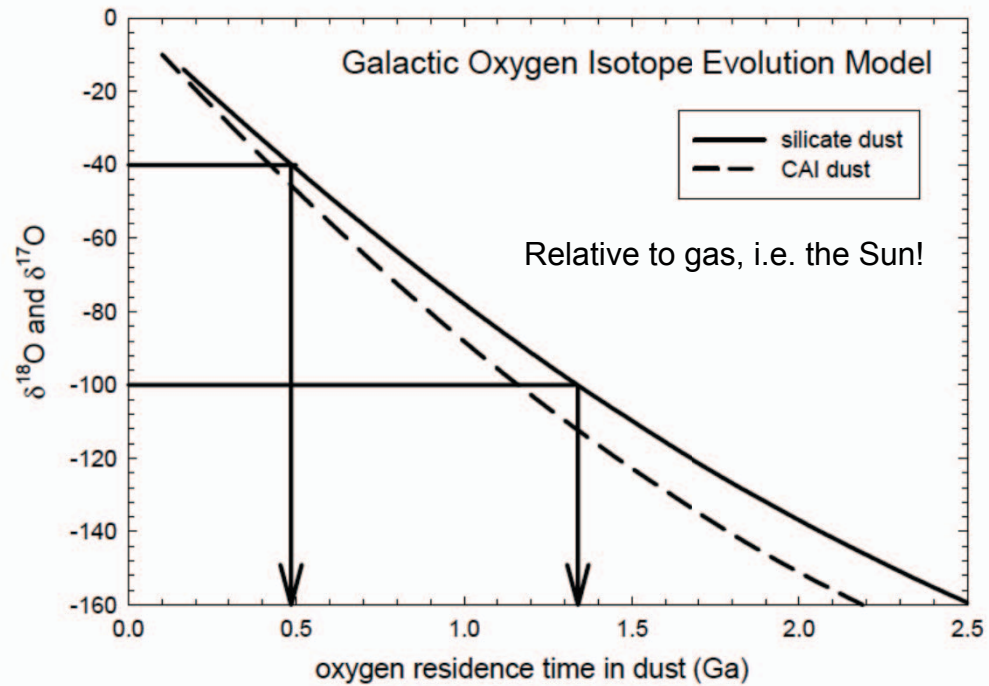
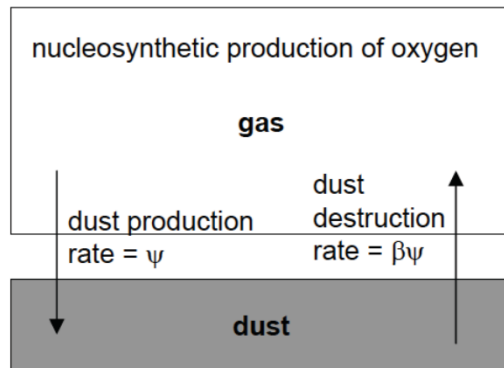
Explanations:



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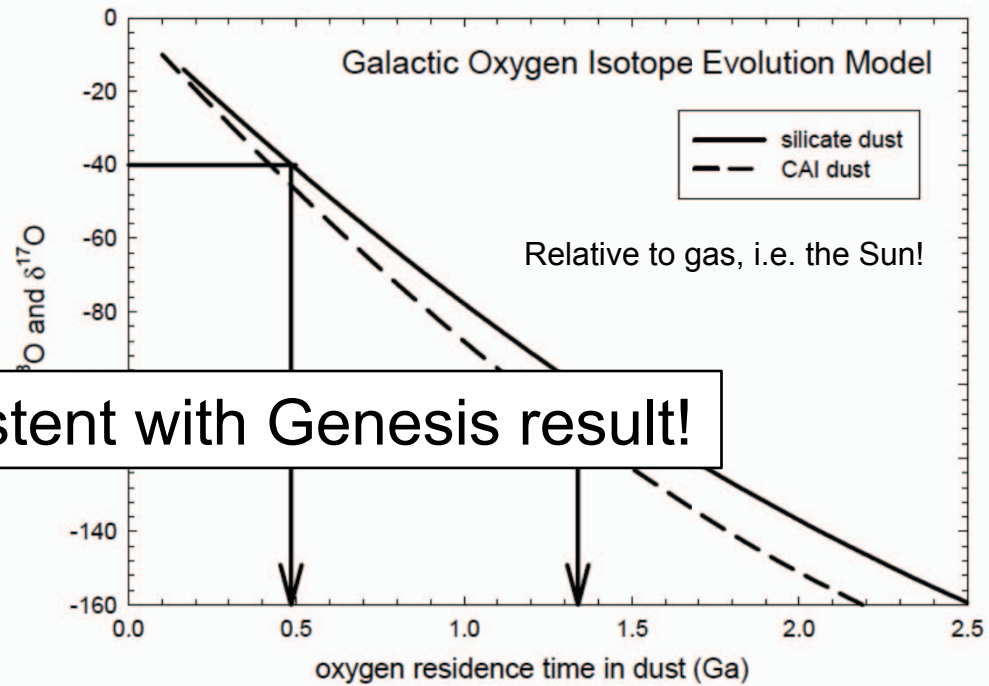
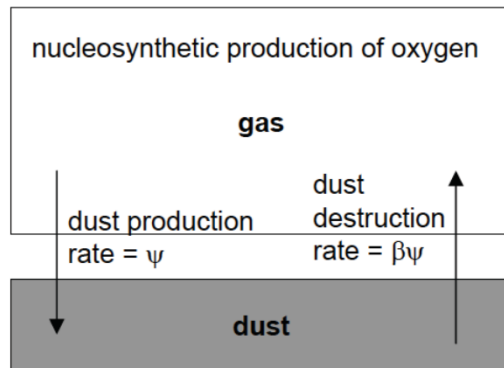
Galactic Chemical Evolution Preserved in Dust and Gas

(e.g., D.D. Clayton 1988; Jacobsen et al. 2007)



Galactic Chemical Evolution Preserved in Dust and Gas

(e.g., D.D. Clayton 1988; Jacobsen et al. 2007)



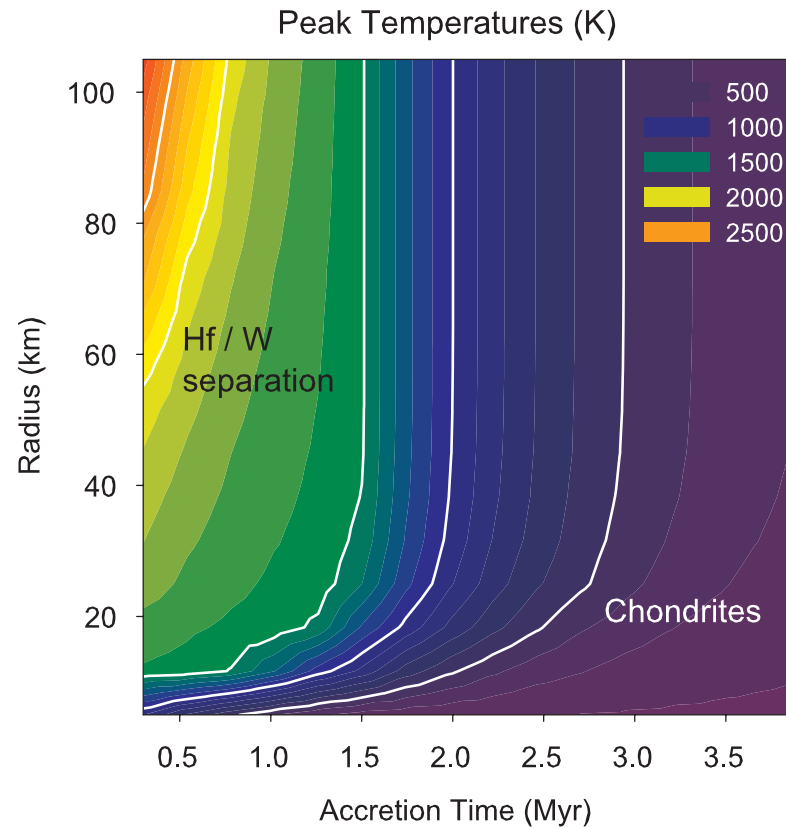
Inconsistent with Genesis result!



Galactic Chemical Evolution Preserved in Dust and Gas

(Krot et al., 2010)

Differentiated asteroids formed early but are ^{16}O poor.

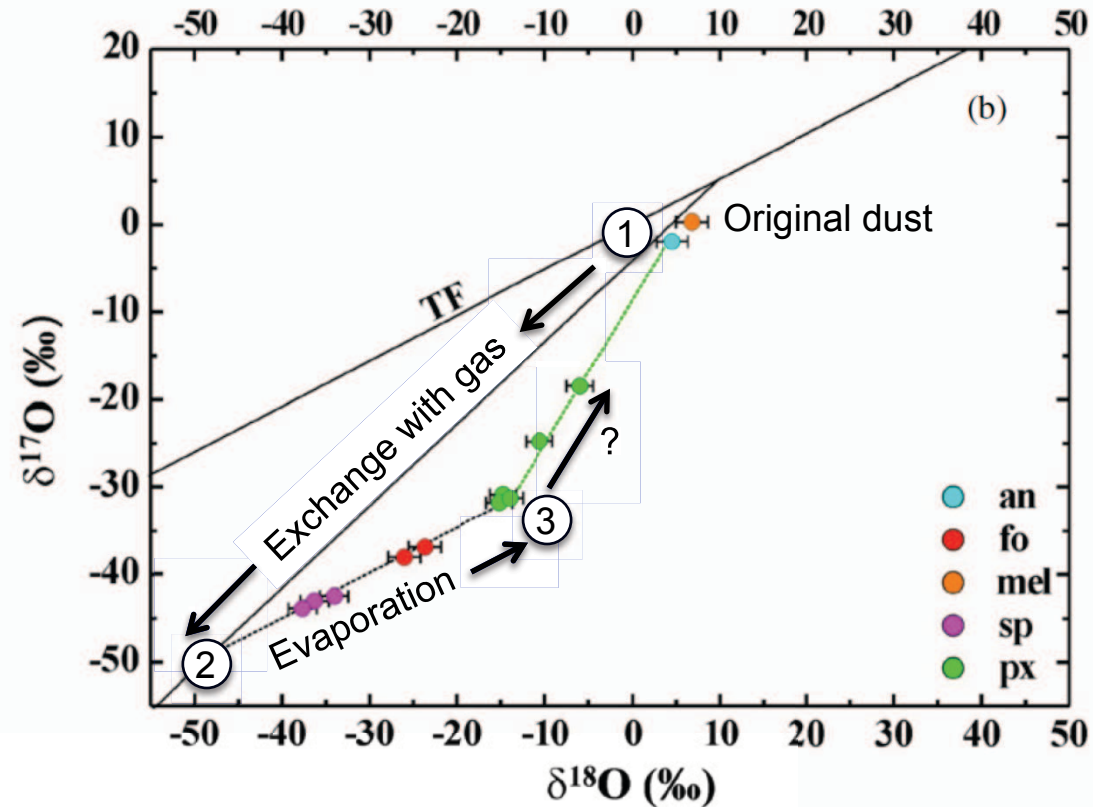


Young (2011, MetSoc)

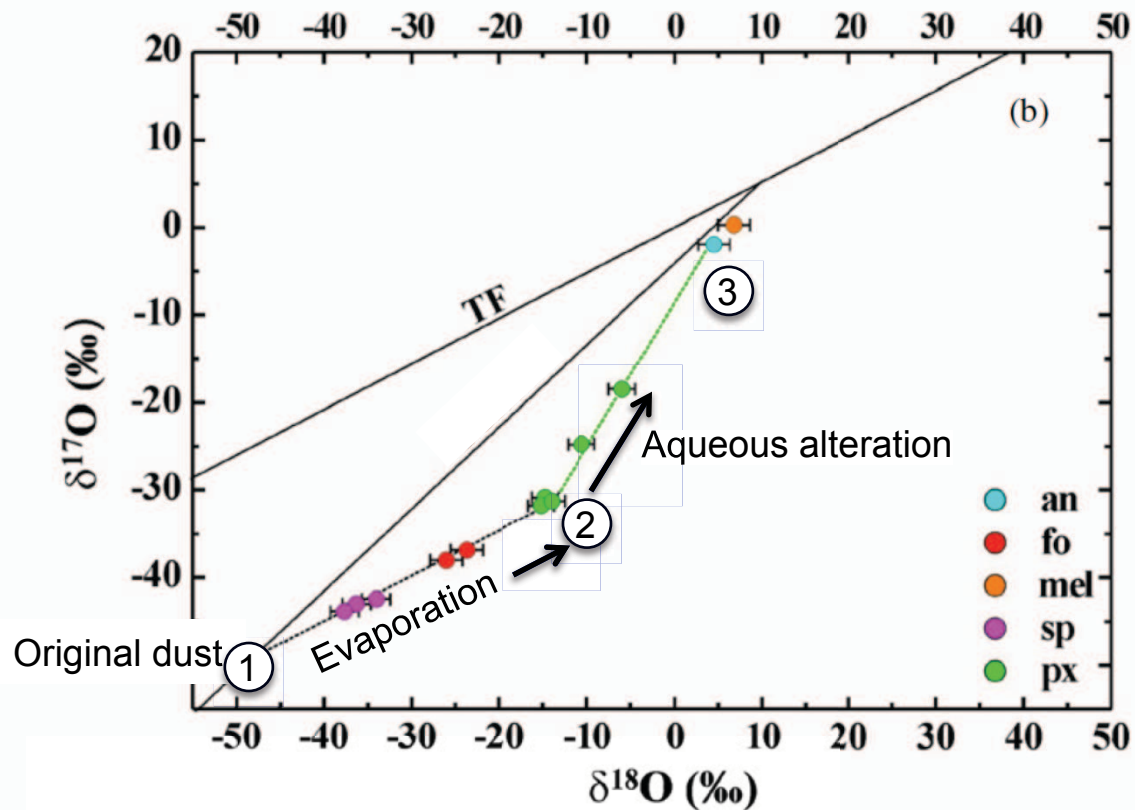


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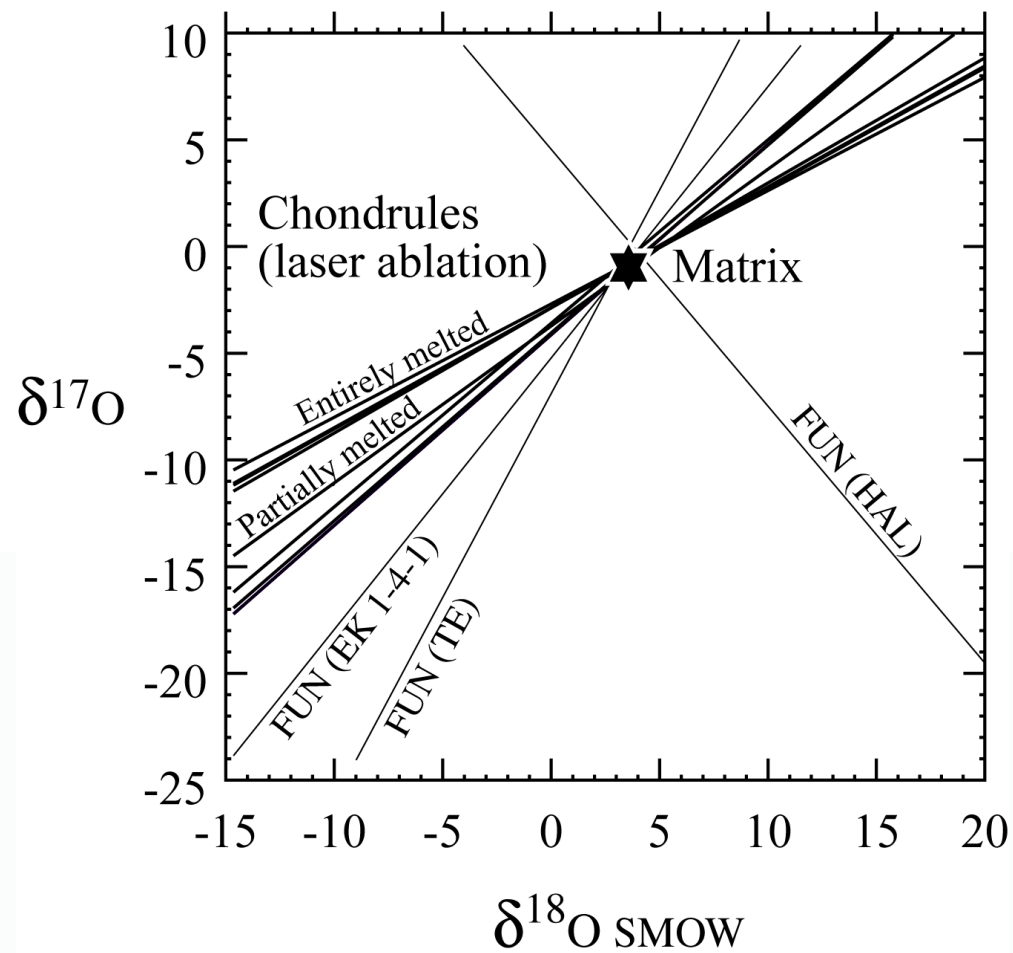
Galactic Chemical Evolution Preserved in Dust and Gas: Dust was ^{16}O poor? (Krot et al., 2010)



Two-stage alternative:



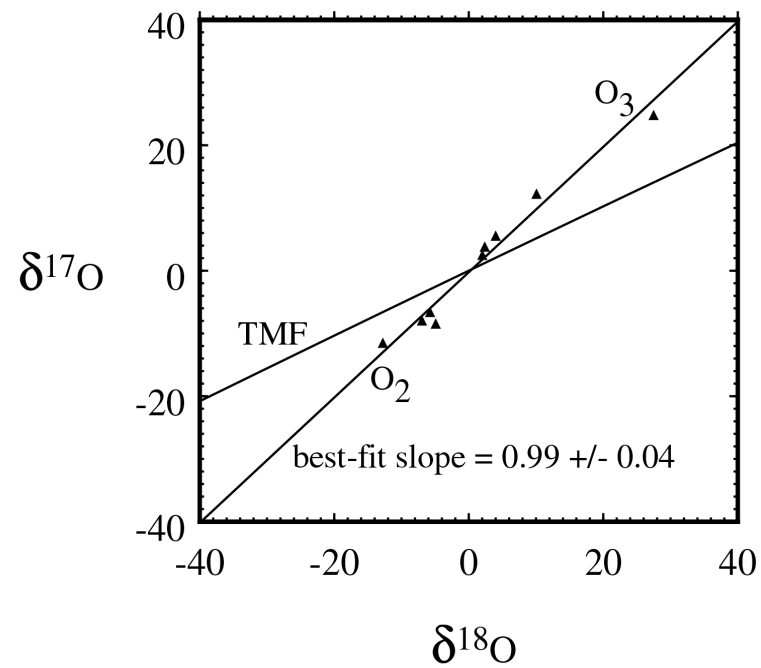
Galactic Chemical Evolution or Simply Aqueous Alteration?



Intramolecular disequilibrium (Non-RRKM) effects

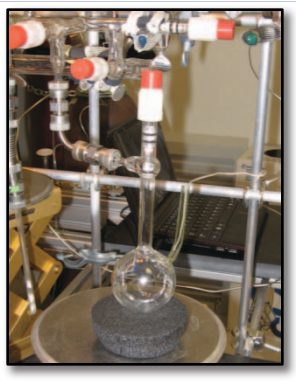
Mass-independent fractionation (MIF)

Thiemens and others, since 1983



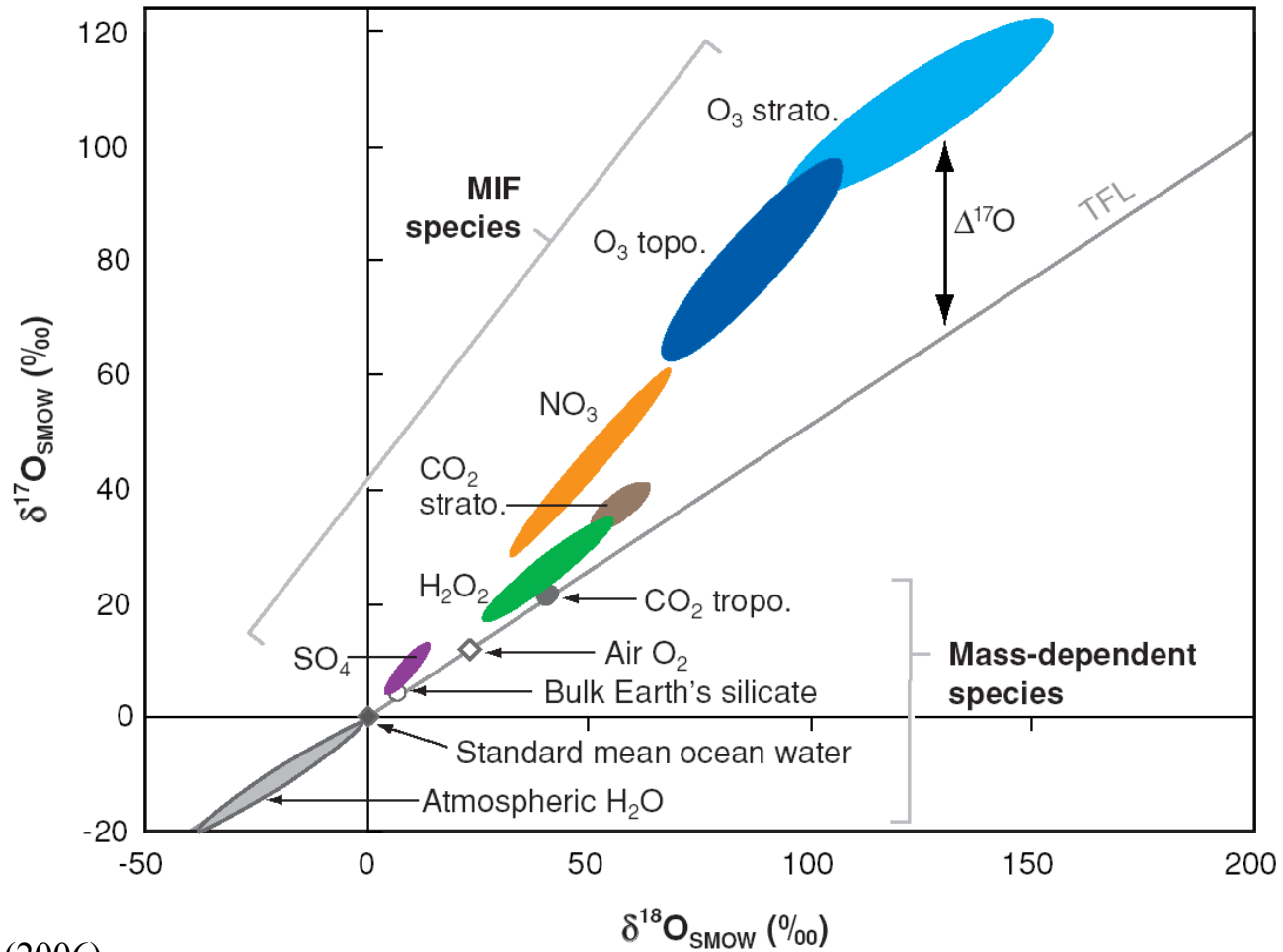
(Young and Hoering, unpub. data 1993)

$P^0 = 44\text{-}101$ torr



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Intramolecular disequilibrium (Non-RRKM) effects



Thiemens (2006)

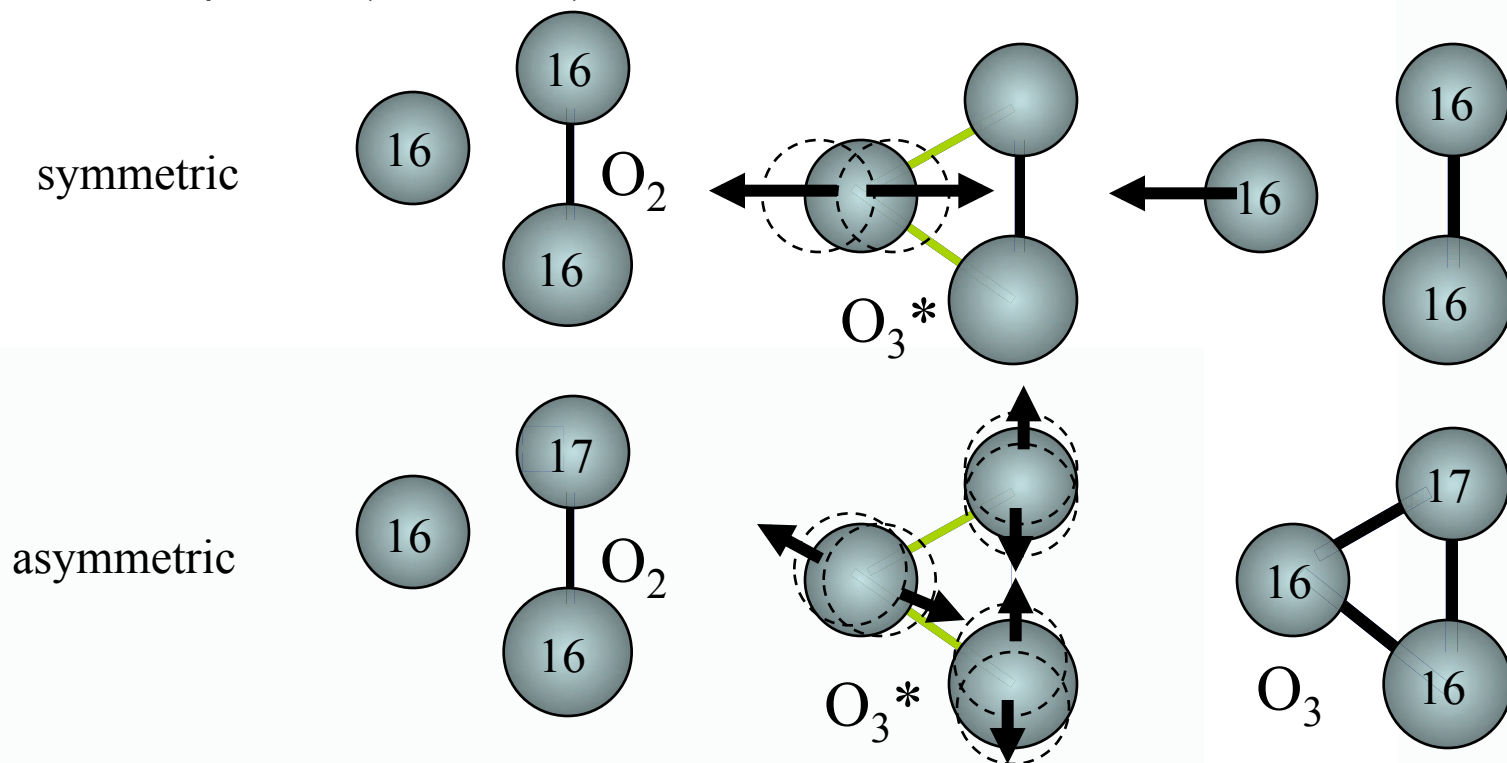


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Intramolecular disequilibrium (Non-RRKM) effects

Rudolph A. Marcus proposes, with coworkers (1999 to 2004):

- A mechanism for the ozone mass independent fractionation (MIF) effect
- Departure from intramolecular equilibrium in the vibrationally excited state of the symmetrical isotopologue
- The so-called η effect... (non RRKM)

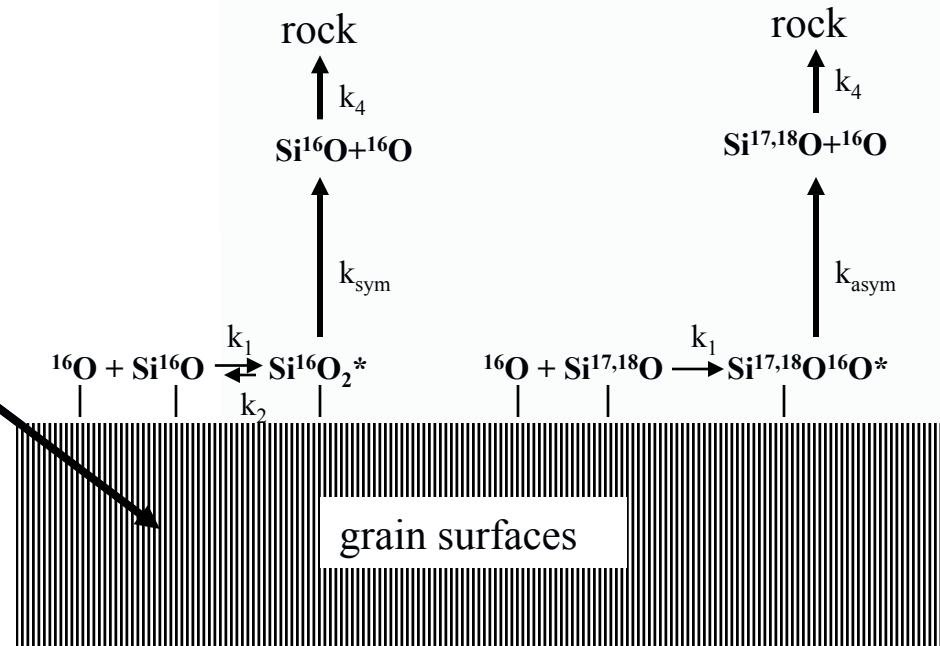


Intramolecular disequilibrium (Non-RRKM) effects

Marcus (2004) – analogous to ozone but mediated by grain surfaces...

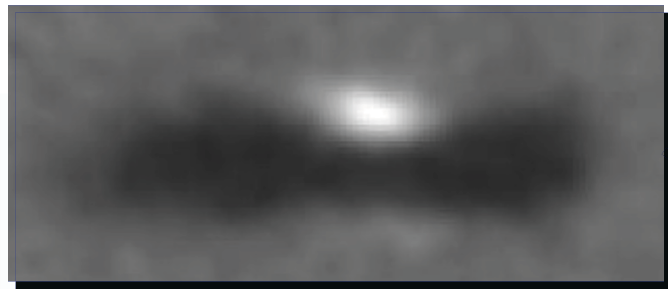


Dusty disk environment

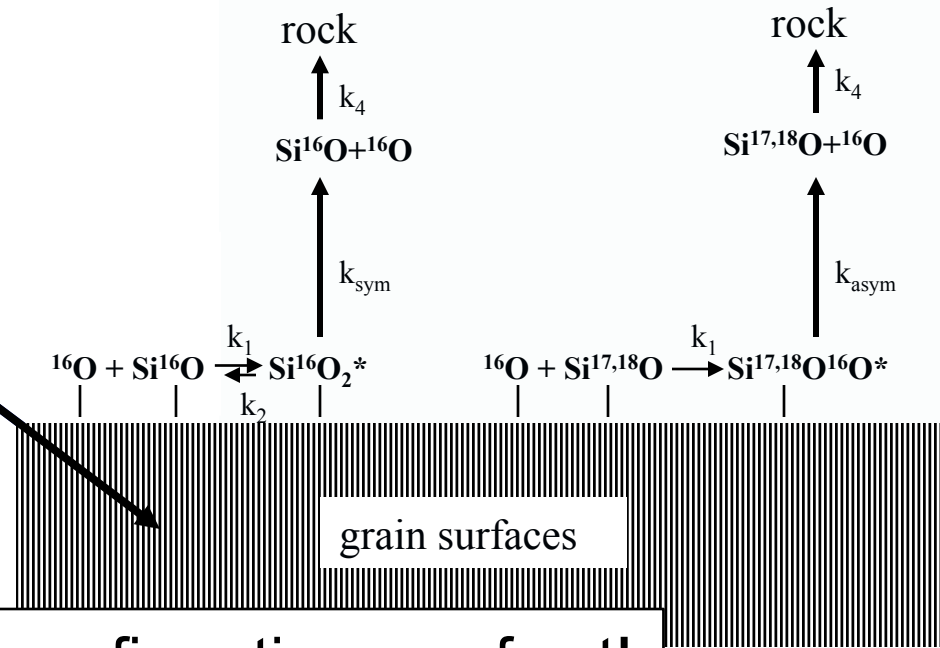


Intramolecular disequilibrium (Non-RRKM) effects

Marcus (2004) – analogous to ozone but mediated by grain surfaces...



Dusty disk environment



No experimental confirmation as of yet!

ISOTOPE-SELECTIVE PHOTODESTRUCTION OF CARBON MONOXIDE

JOHN BALLY AND WILLIAM D. LANGER

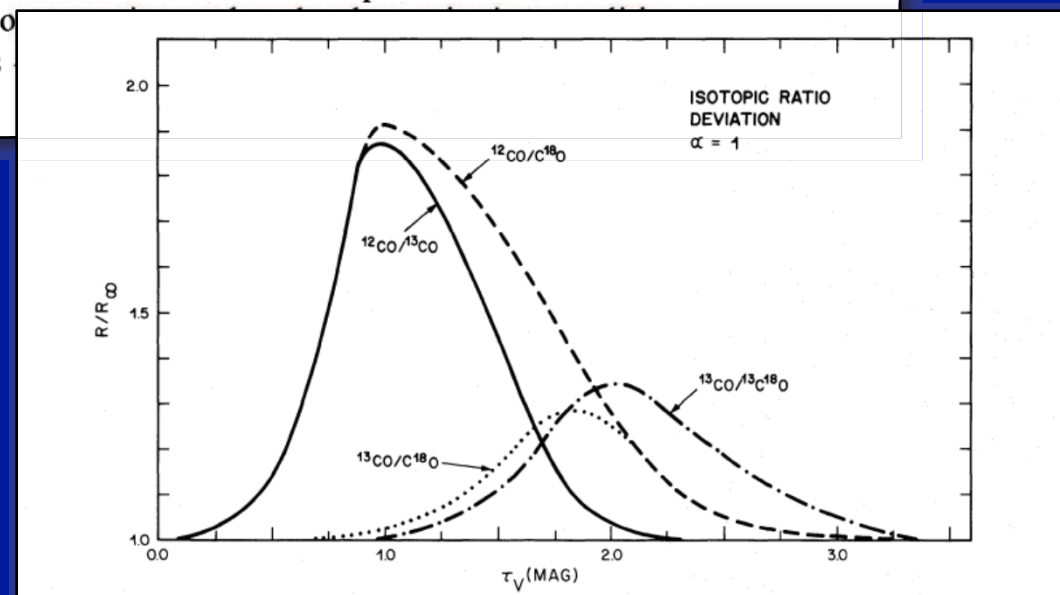
Crawford Hill Laboratory, Bell Laboratories, Holmdel, New Jersey

Received 1981 August 19; accepted 1981 October 19

ABSTRACT

Observations of the molecular cloud boundary layer near the H II region S68 reveal an overabundance of ^{12}CO and ^{13}CO relative to C^{18}O consistent with a simple model of isotope-selective photodestruction of the rarer CO species. Self-shielding and the isotopic shift of the UV dissociative transitions increase the lifetime of the more abundant isotopes of carbon monoxide in a UV irradiated environment. As a result, large variations occur in the abundance ratios of CO isotopes in the surface layer of clouds and near internal UV sources. This effect is important for the determination of molecular abundances, cloud masses, iso

Subject headings: interstellar: molecules
nebulae: H II regions



$$N_i = \int_0^z n_i(Z) dz$$



$$\sigma_{\nu} = \phi_{\nu} \frac{\pi e^2}{m_e c} f_{\nu}$$



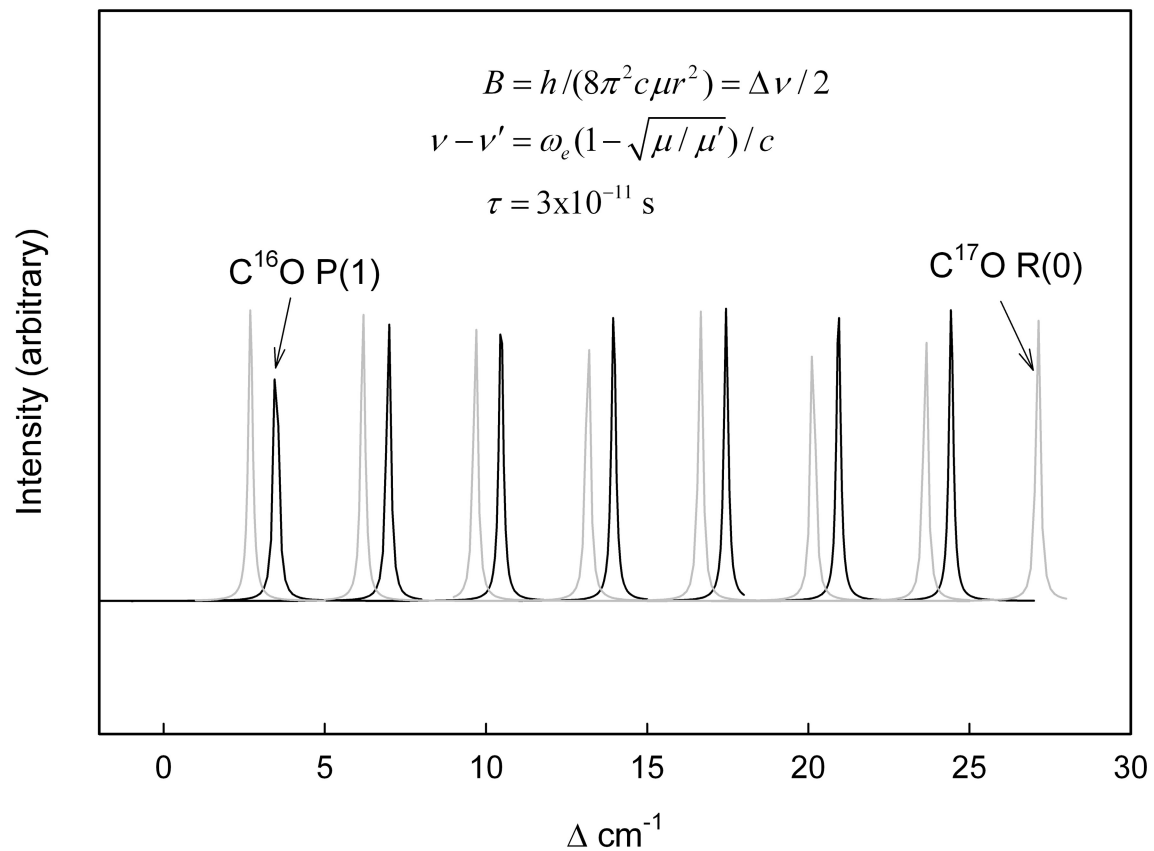
$$\begin{aligned}\frac{I_\lambda}{I_\lambda^o} &= \prod_i \Theta_i(N_i) \\ &= \prod_i \exp(-\tau_i) \\ &= \prod_i \exp(-\sigma_i N_i)\end{aligned}$$



$$k = J^\circ \prod_i \exp(-\tau_i)$$

$$\alpha = \frac{k'}{k} = \frac{\prod_i \exp(-\sigma_i N'_i)}{\prod_i \exp(-\sigma_i N_i)}$$





CO photodissociation self shielding

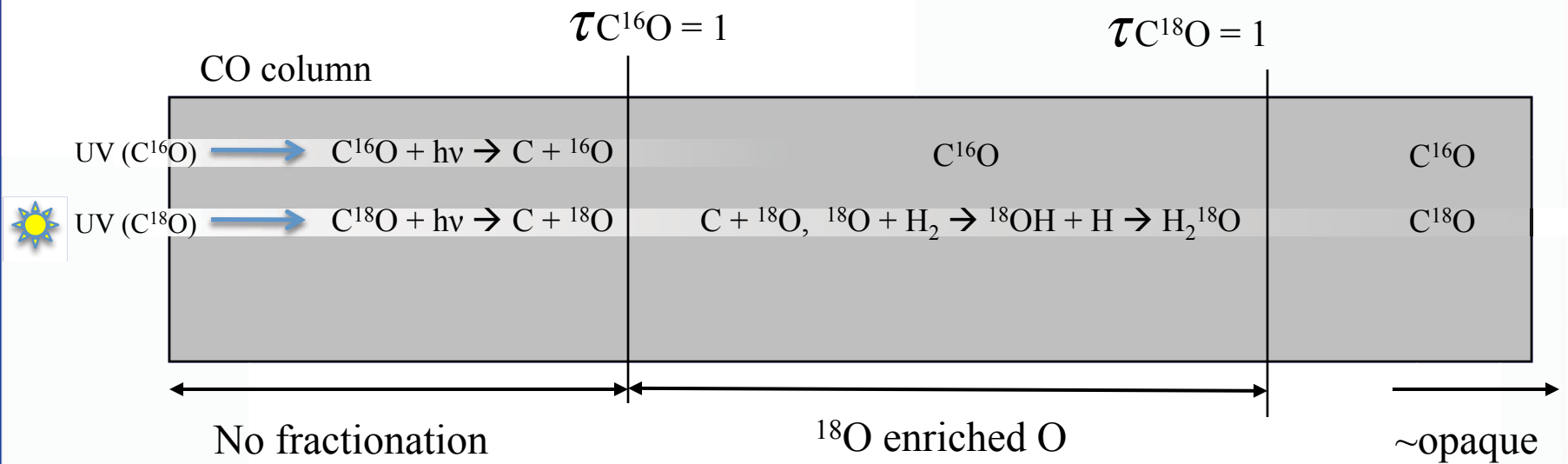
$$I_{\nu} / I_{\nu}^0 = e^{-\tau}$$

$$\tau_{C^{16}O} = 1$$



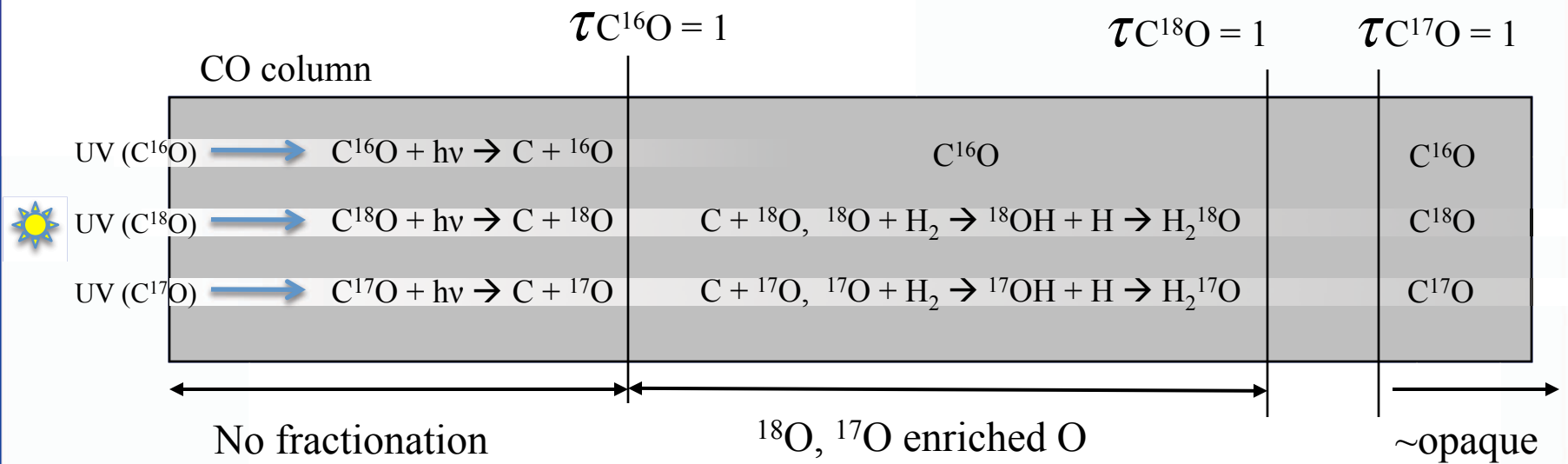
CO photodissociation self shielding

$$I_v / I_v^0 = e^{-\tau}$$

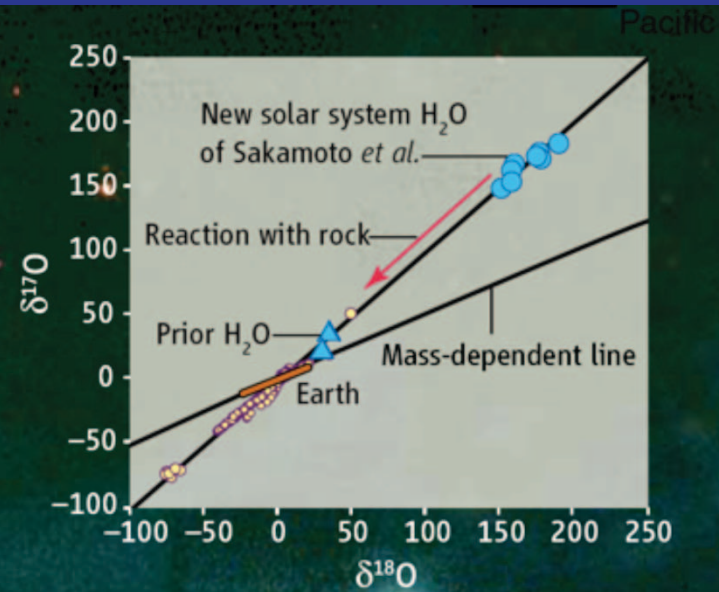


CO photodissociation self shielding

$$I_v / I_v^0 = e^{-\tau}$$

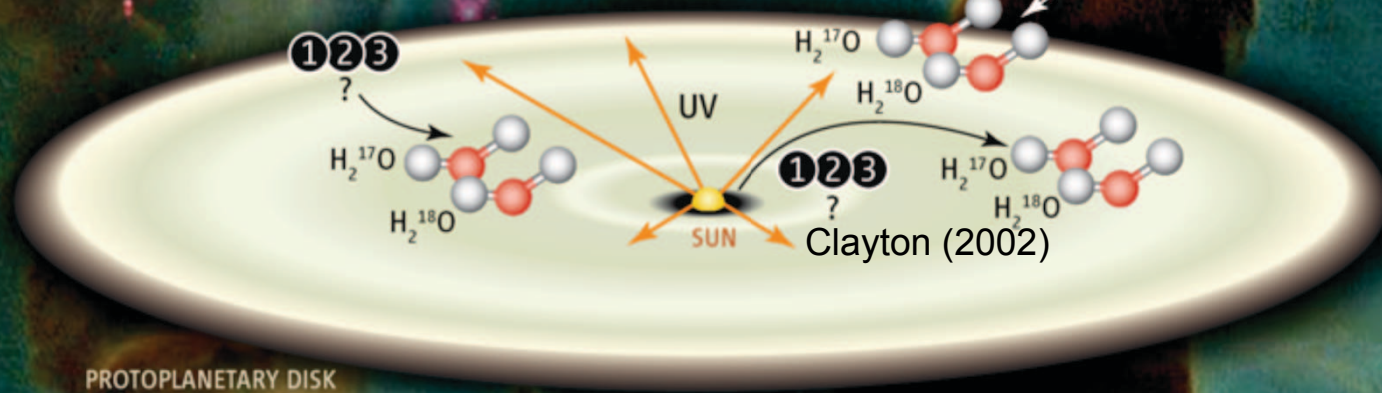


- ① $\text{CO} + \text{uv} \rightarrow \text{C} + \text{O}$
- ② $\text{O} + \text{H} \rightarrow \text{OH}$
- ③ $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$



Lyons and Young (2005)

Yurimoto and Kuramoto (2004)

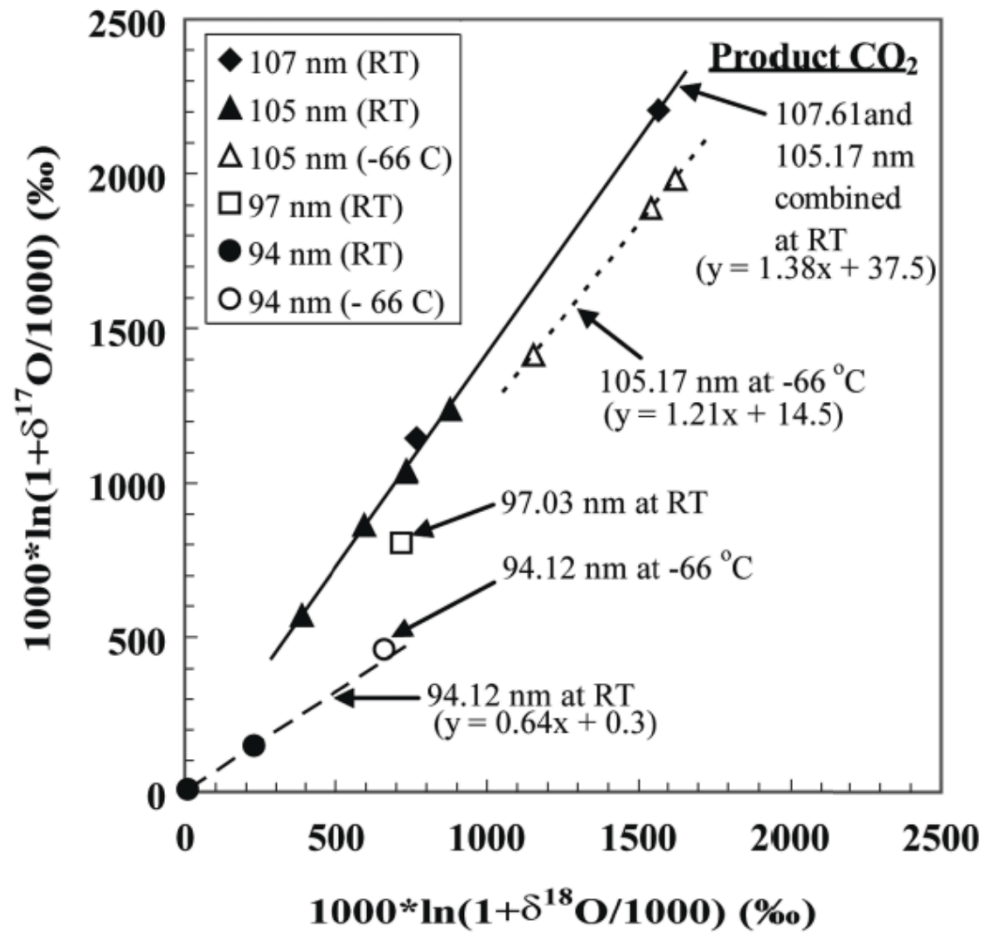


Young (2007)



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Chakraborty et al. (2009)



REPORTS

Experimental Test of Self-Shielding in Vacuum Ultraviolet Photodissociation of CO

Subrata Chakraborty,¹ Musahid Ahmed,² Teresa L. Jackson,¹ Mark H. Thiemens^{1*}

Self-shielding of carbon monoxide (CO) within the nebular disk has been proposed as the source of isotopically anomalous oxygen in the solar reservoir and the source of meteoritic oxygen isotopic compositions. A series of CO photodissociation experiments at the Advanced Light Source show that vacuum ultraviolet (VUV) photodissociation of CO produces large wavelength-dependent isotopic fractionation. An anomalously enriched atomic oxygen reservoir can thus be generated through CO photodissociation without self-shielding. In the presence of optical self-shielding of VUV light, the fractionation associated with CO dissociation dominates over self-shielding. These results indicate the potential role of photochemistry in early solar system formation and may help in the understanding of oxygen isotopic variations in Genesis solar-wind samples.

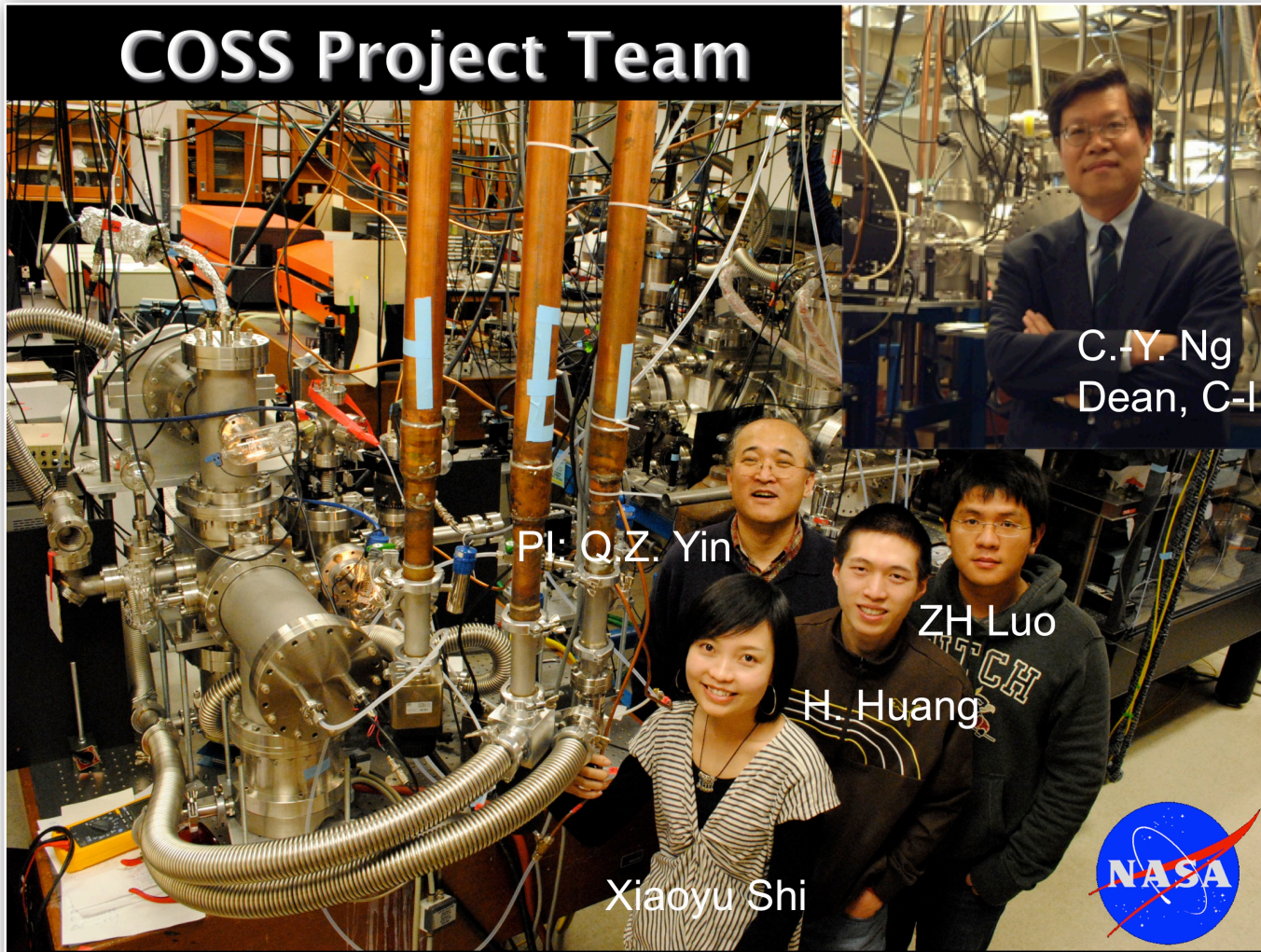
fect associated that has not been
Isotopically invoked as an in interstellar medium the observed at topomers of CO self-shielding by the observed isotopic anomalies proposed to account for the proto-Sun [with and the heavy elements transported through forming zone, inclusions (CAIs) from the residual avoid the erosion change (δ), it self-shielding occur molecular cloud Another me

Isotope-selective photodissociation, or self-dissociation of the minor species results with



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COSS Project Team



C.Y. Ng
Dean, C-I

PI: Q.Z. Yin

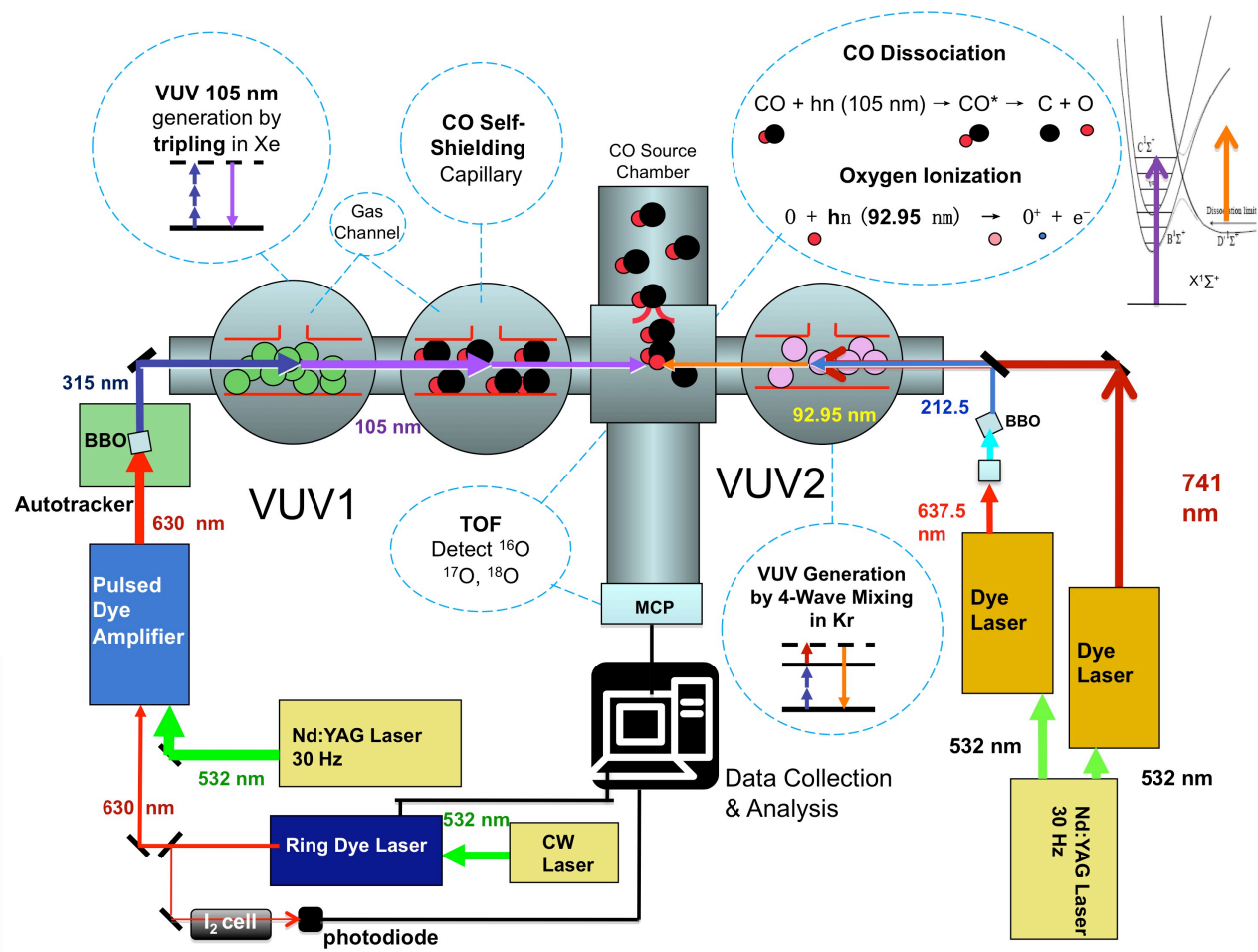
ZH Luo

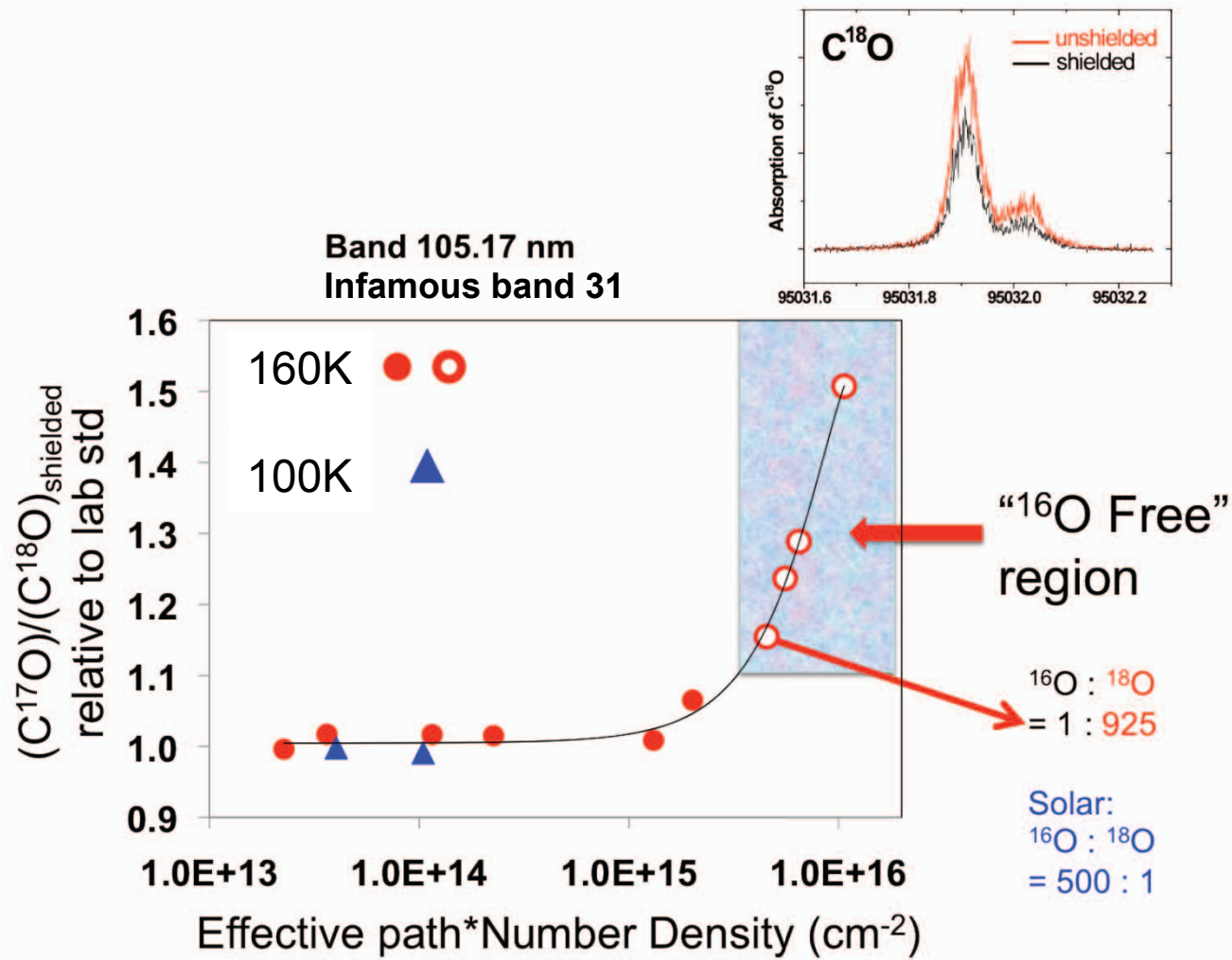
H. Huang

Xiaoyu Shi



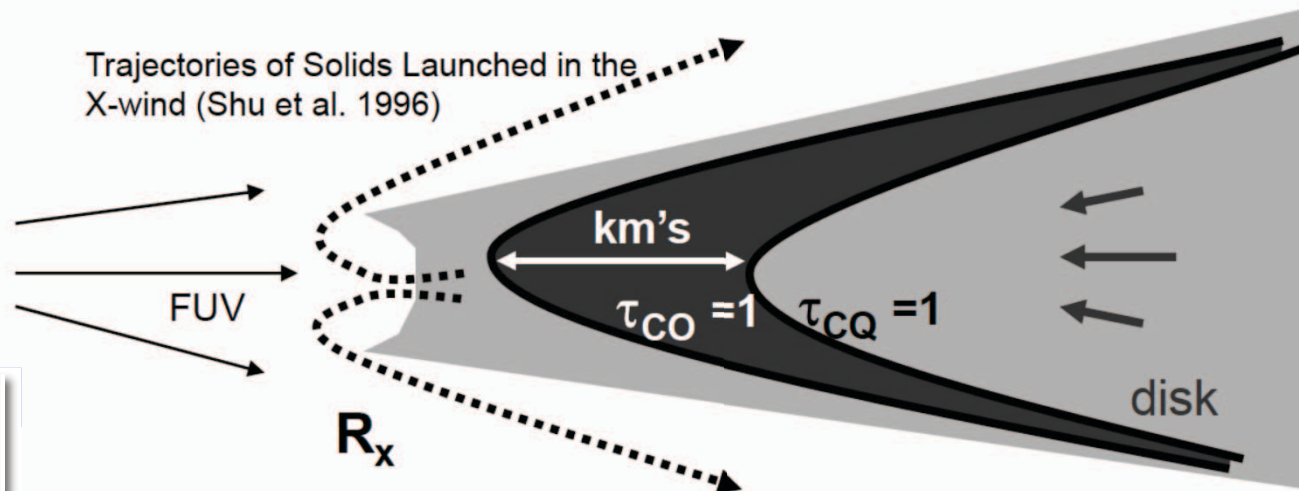
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Inner Edge of Disk Clayton (2002)

Self shielding by CO near R_x (high T)



Solar System Self-shielding in the solar nebula

Variations in the abundance of isotopes of elements in primitive meteorites carry the record of chemical and nuclear processes that occurred during the formation of the Solar System. Here we explore the possibility that photochemical self-shielding of carbon monoxide, a process that is known to occur in molecular clouds, may also have been important in the solar nebula. In the solar nebula, the process is based on far-ultraviolet radiation from the growing Sun, which is effective over a small distance in the inner part of the nebula. In order to acquire their observed isotope compositions, all of the solid matter in the present inner Solar System must have been processed through this region, and subsequently expelled to greater distances by an X-wind or similar mechanism.

Self-shielding in the ultraviolet photo-dissociation of CO is thought to be responsible for large isotopic fractionation effects that are apparent in carbon and oxygen in molecular clouds. Dissociation of CO, in the wavelength range 91–110 nm, occurs almost entirely by a predissociation that corresponds to ^{16}O is more rapidly attenuated than that which corresponds to the less abundant ^{18}O . As a consequence, the interior of the cloud continues to undergo photodissociation of ^{16}CO , but not of ^{18}CO . This results in an increase in the ^{18}C atoms/ ^{12}C atoms ratio of the dissociation products in the cloud interior. Millimeter-wavelength observations reveal the complementary enhancement of $^{13}\text{C}/^{12}\text{C}$ in the cloud interior. The same effect must occur for oxygen isotopes, and even more strongly, because of the larger isotope ratios: $^{18}\text{O}/^{16}\text{O} \approx 500$, $^{17}\text{O}/^{16}\text{O} \approx 2.500$.

The same type of isotopic self-shielding effect should occur in the T-Tauri stage of solar evolution. The proto-Sun provides a strong source of ultraviolet radiation, and it has a gaseous disk in which the gas predominantly consists of H_2 , CO and N_2 . Irradiation of the disk produces isotopically nondiscriminatory dissociation of CO at the inner edge, and preferential production of ^{18}O and ^{17}O atoms in the interior (in approximate proportion to their overall abundances). Further chemical processing within the disk, to produce solid and/or liquid condensates, should preferentially involve the heavy isotope-enriched, reactive atoms rather than the more inert CO molecules. I have thus elucidated a process for enriching the rocky components and water

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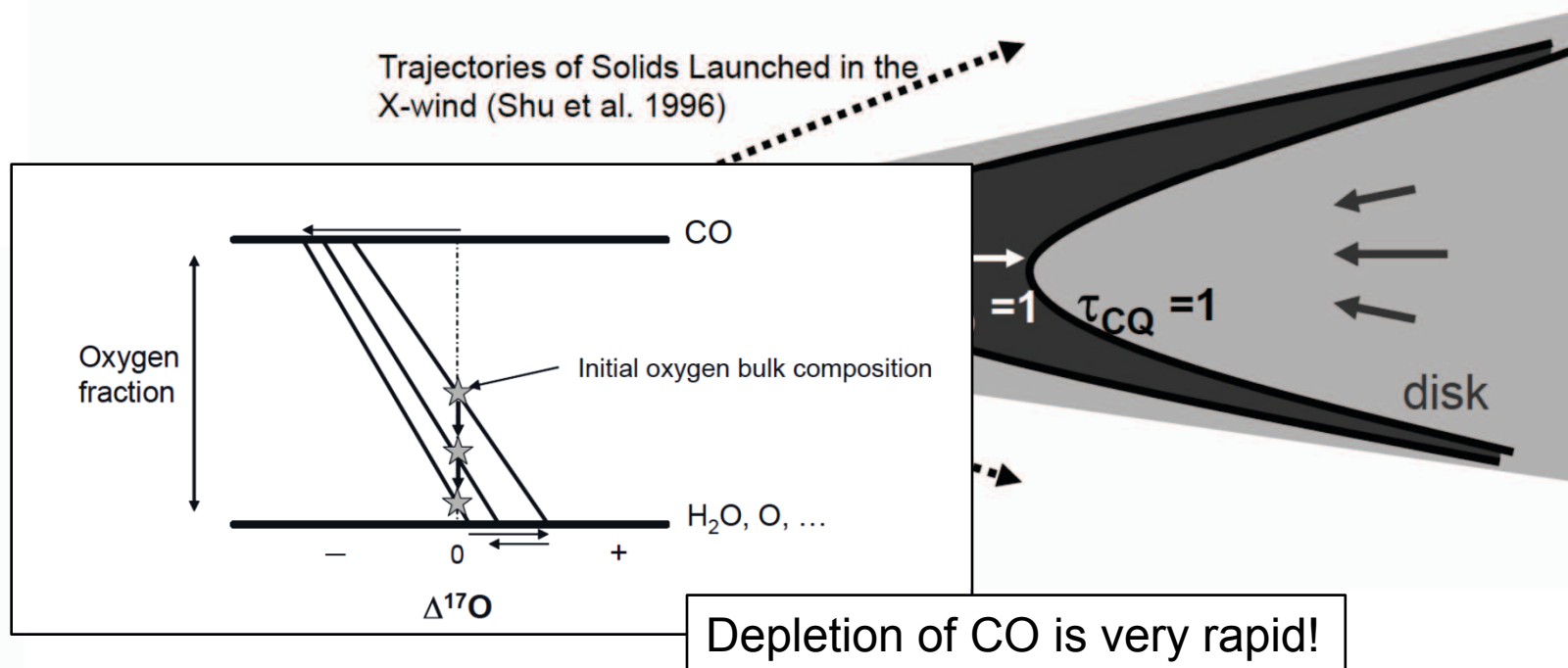


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Inner Edge of Disk

Clayton (2002)

Self shielding by CO near R_x (high T)



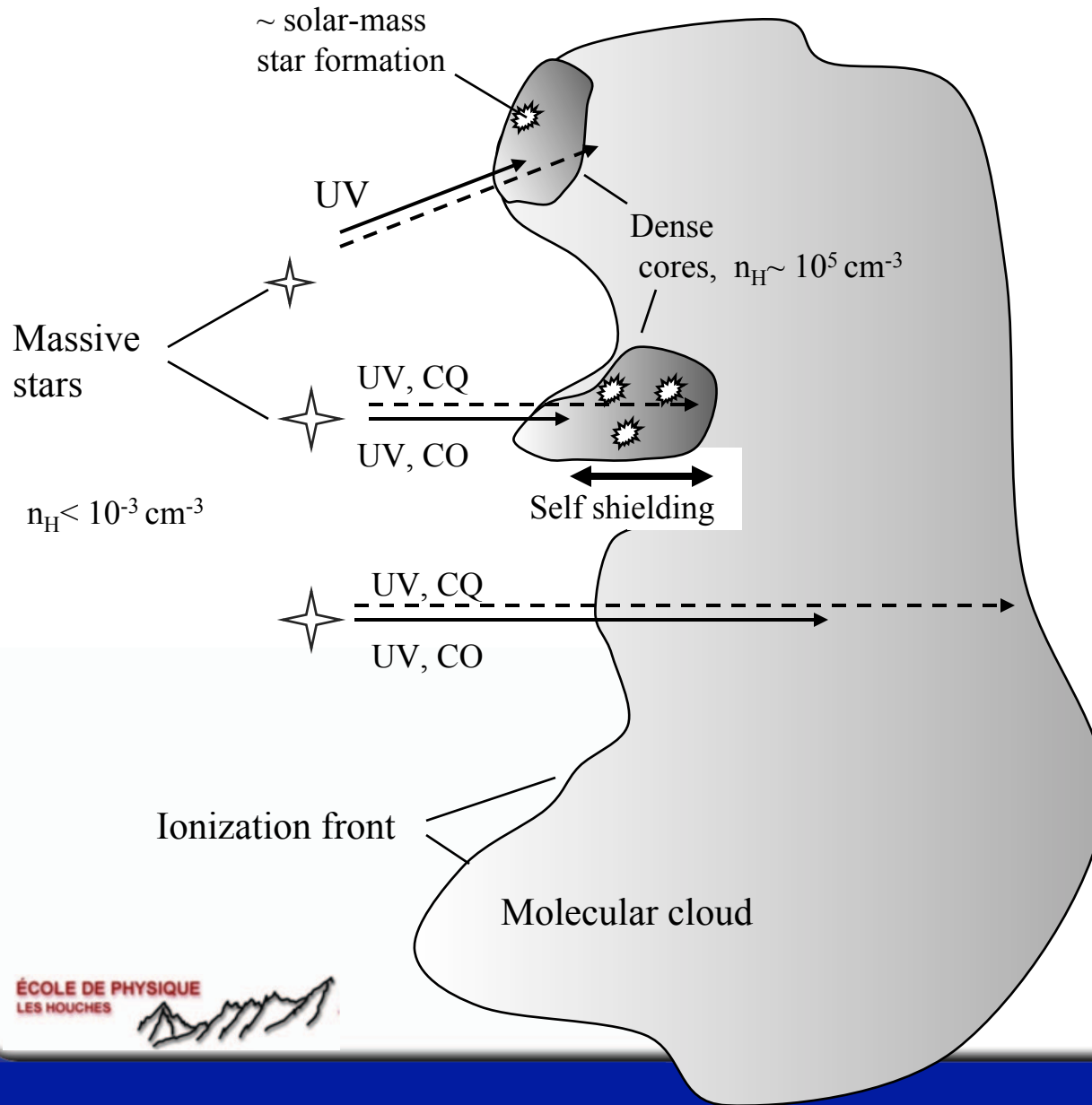
Molecular Cloud

Yurimoto and Kuramoto (2004)

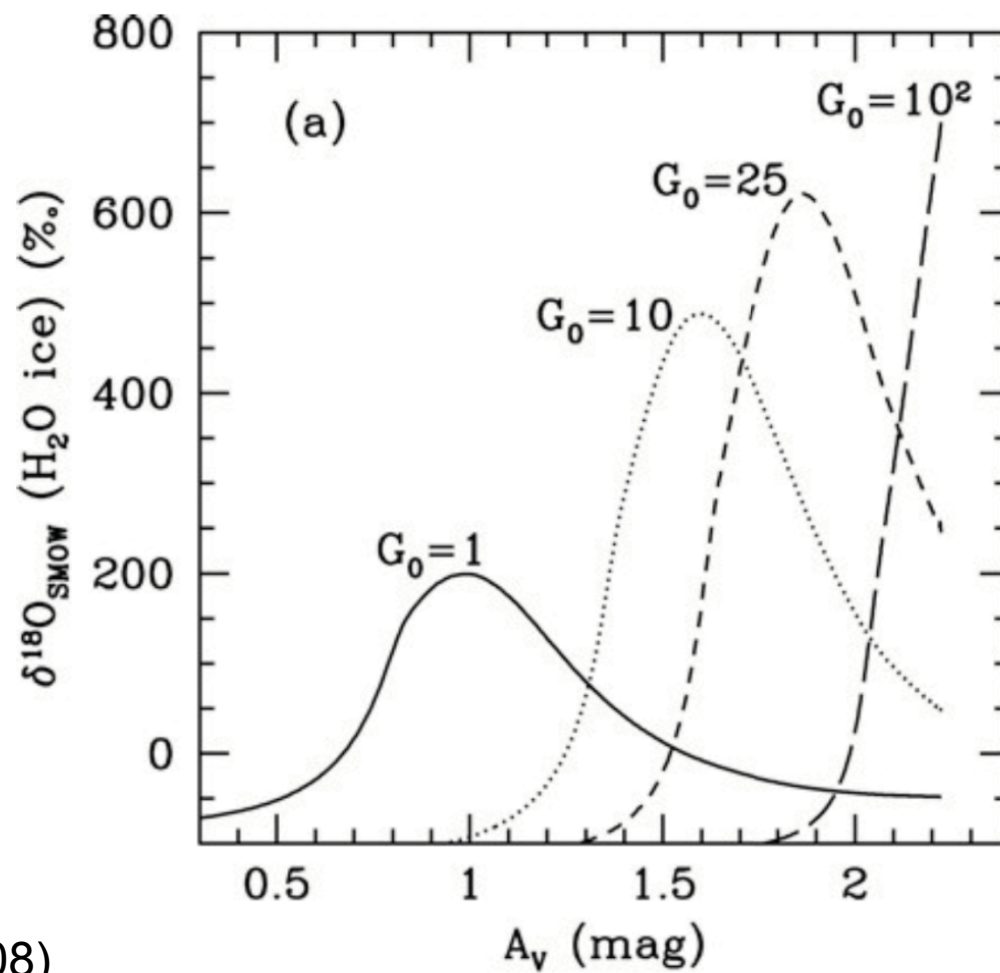
Molecular Cloud Origin for the Oxygen Isotope Heterogeneity in the Solar System

Hisayoshi Yurimoto^{1*} and Kiyoshi Kuramoto²

Meteorites and their components have anomalous oxygen isotopic compositions characterized by large variations in $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios. On the basis of recent observations of star-forming regions and models of accreting protoplanetary disks, we suggest that these variations may originate in a parent molecular cloud by ultraviolet photodissociation processes. Materials with anomalous isotopic compositions were then transported into the solar nebula by icy dust grains during the collapse of the cloud. The icy dust grains drifted toward the Sun in the disk, and their subsequent evaporation resulted in the ^{17}O - and ^{18}O -enrichment of the inner disk gas.



Molecular Cloud

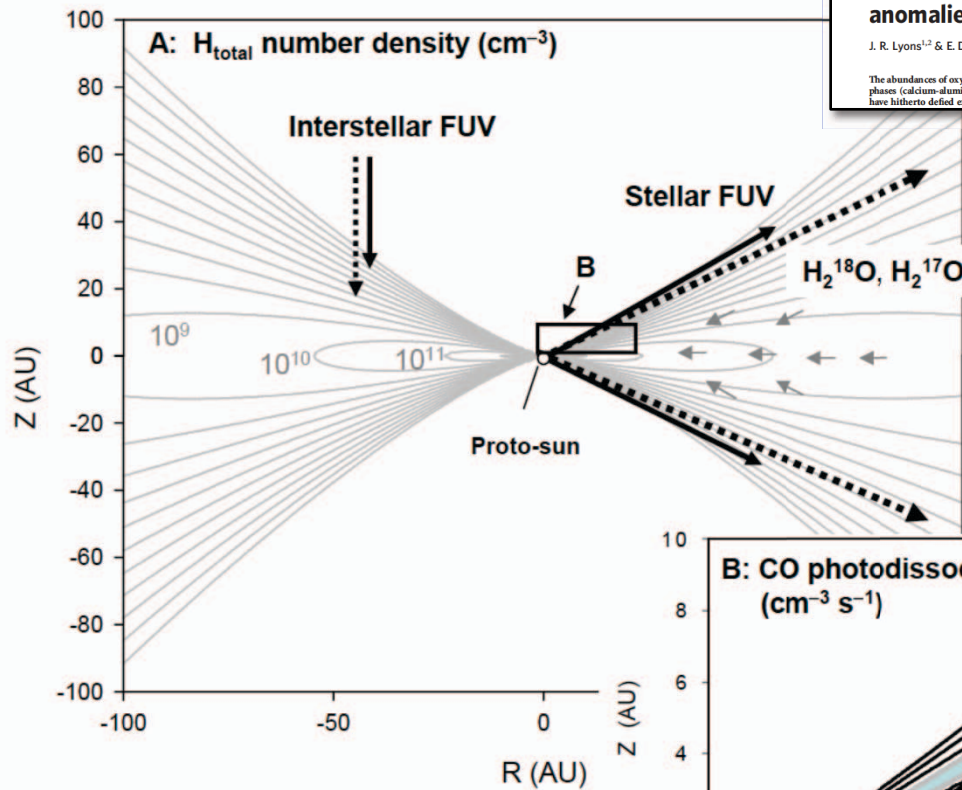


Lee et al. (2008)



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Disk Surfaces



Vol 435/19 May 2005/doi:10.1038/nature03557 nature

LETTERS

CO self-shielding as the origin of oxygen isotope anomalies in the early solar nebula

J. R. Lyons^{1,2} & E. D. Young^{1,2}

The abundances of oxygen isotopes in the most refractory mineral phases (calcium-aluminum-rich inclusions, CAIs) in meteorites have hitherto defied explanation. Most processes fractionate iso- CO self-shielding on oxygen isotope ratios in the early Solar System, we used a one-dimensional photochemical model to compute the time-dependent oxygen isotope profiles in a two-dimensional, axi-

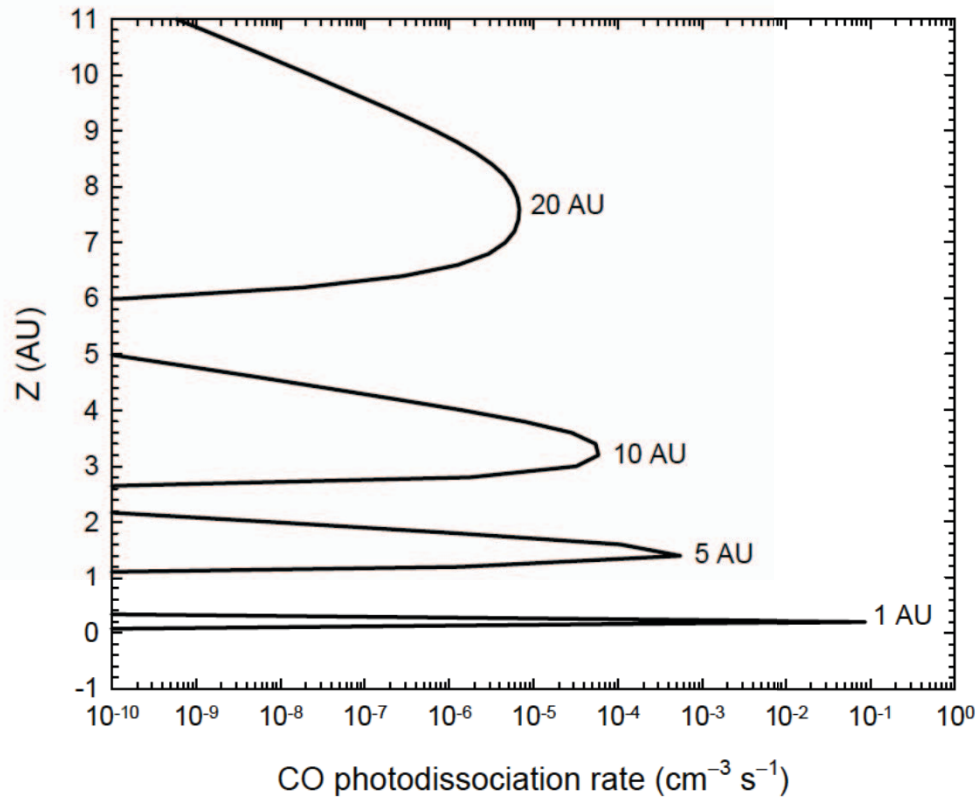
Young (2007)



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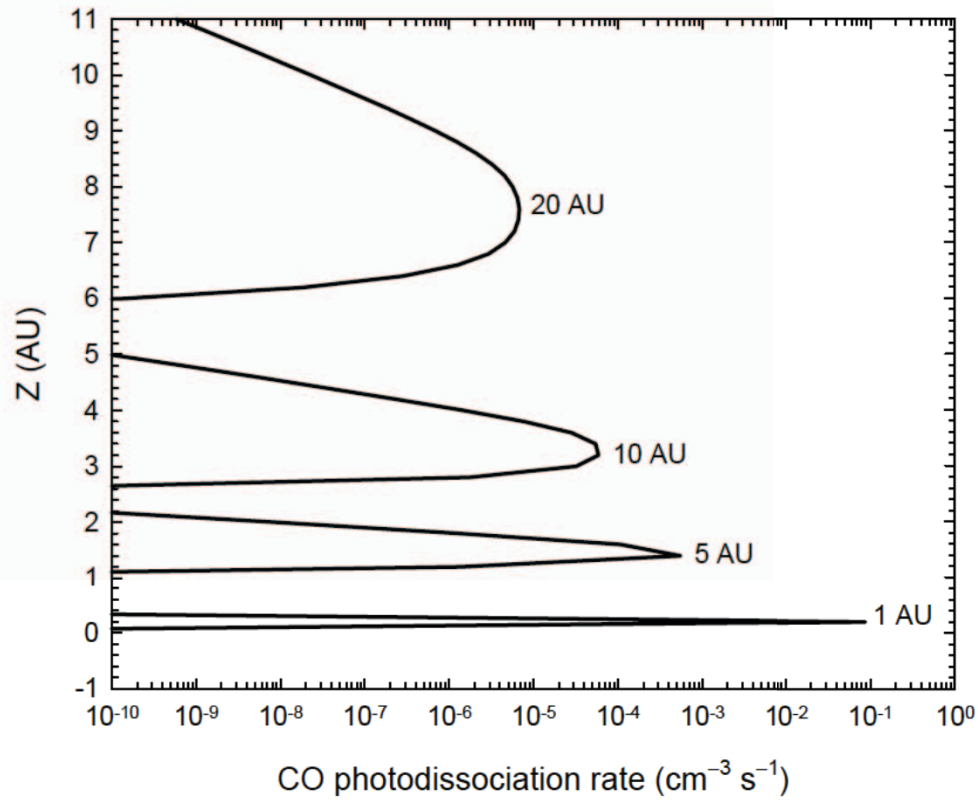
Disk Surfaces

Reaction rate vs. height at different R
stellar sight line



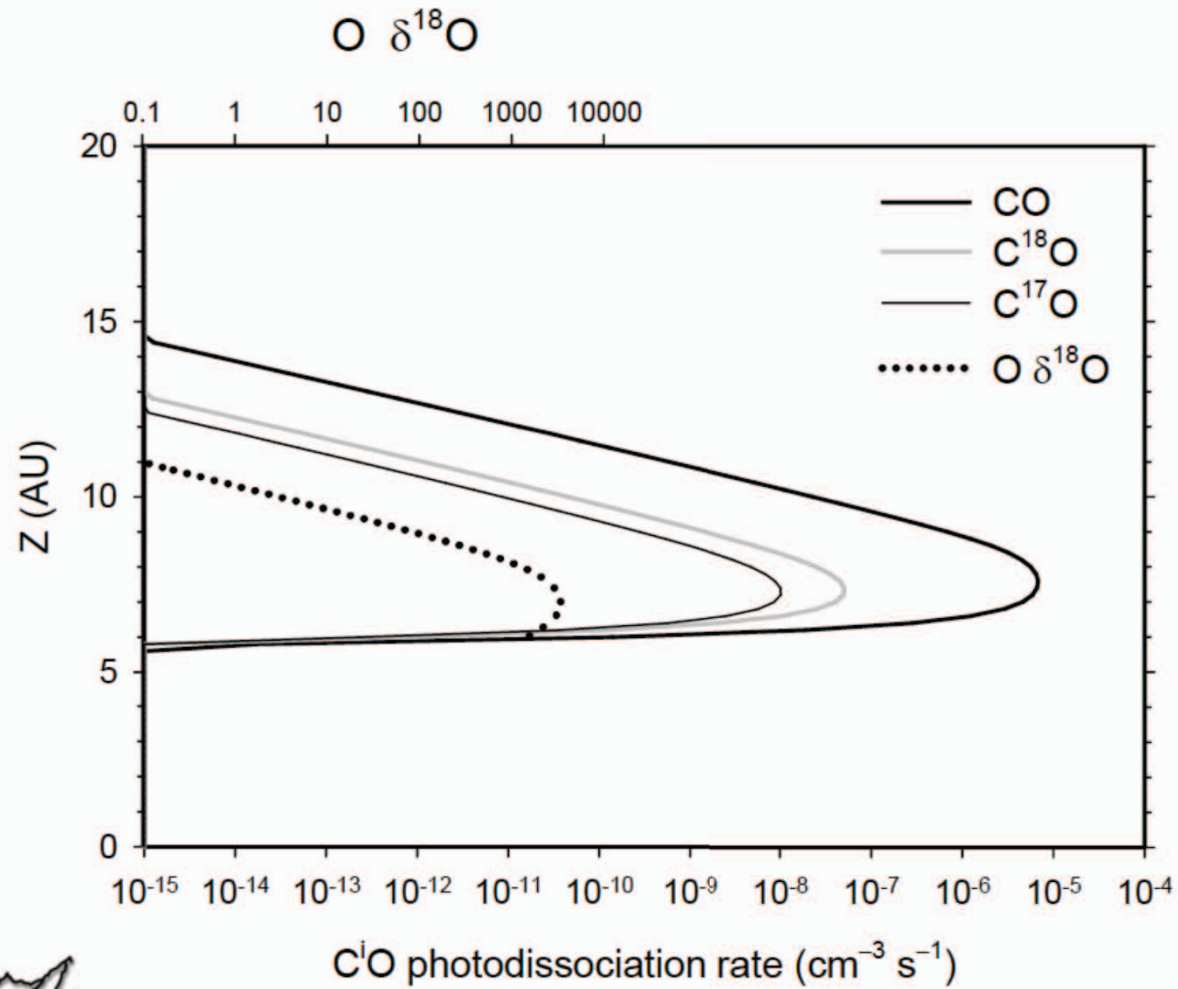
Disk Surfaces

Reaction rate vs. height at different R
stellar sight line



Disk Surfaces

Young (2007)



Disk Surfaces

Reaction network – oxygen isotopologues

7603 reactions, 546 species, oxygen isotopologues, gas-grain reactions

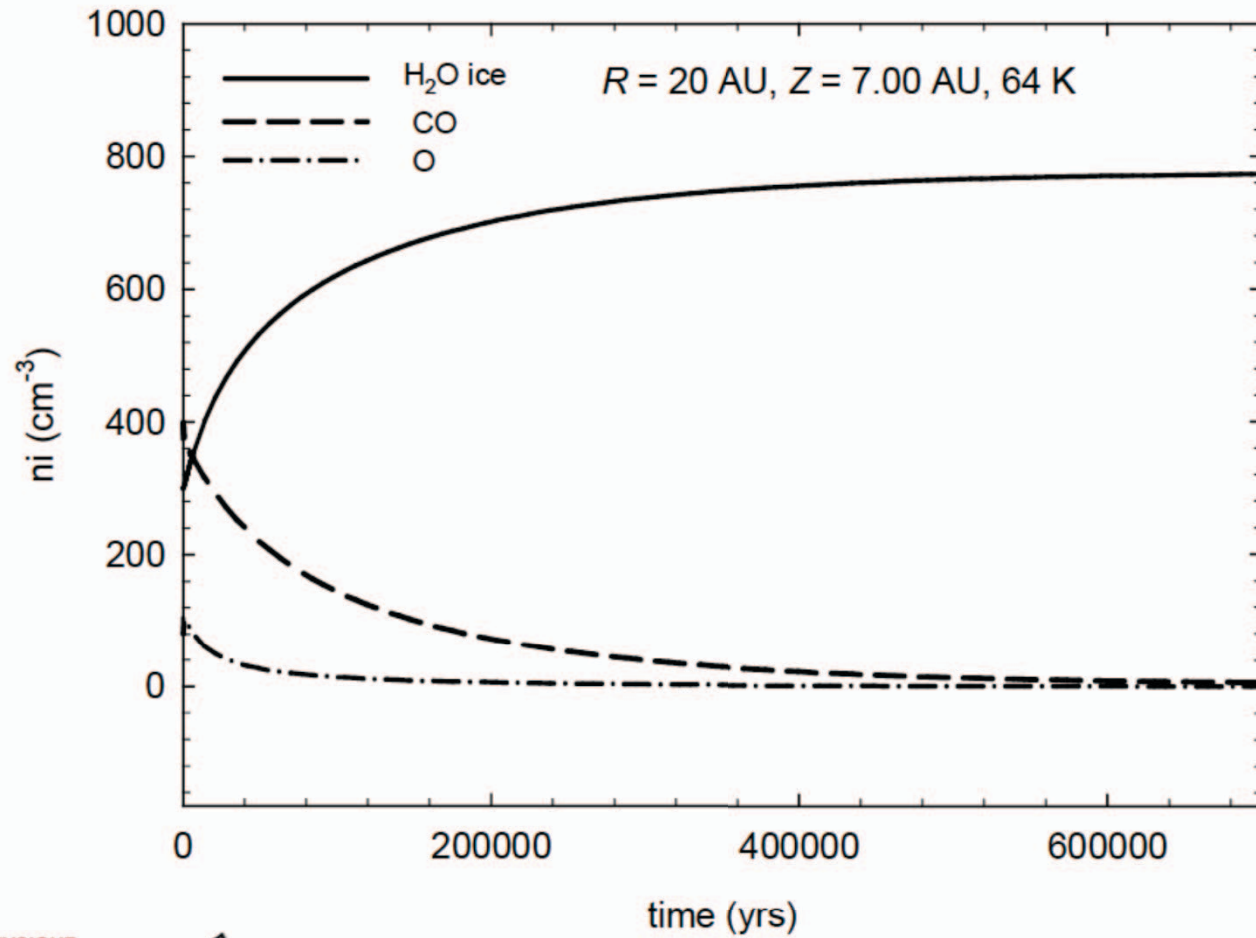
| | | | | | | | | | |
|----|---|------|------|----|------------|------|----------|------------|-----------|
| 1 | H | CH | C | H2 | 2.7000E-11 | 0.38 | 0.0C | 300 | 2000BHG93 |
| 2 | H | CH2 | CH | H2 | 6.6400E-11 | 0.00 | 0.0L | 300 | 2500ANIST |
| 3 | H | NH | N | H2 | 1.7300E-11 | 0.50 | 2400.0L | 80 | 300C |
| 4 | H | CH3 | CH2 | H2 | 1.0000E-10 | 0.00 | 7600.0L | 300 | 2500ANIST |
| 5 | H | NH2 | NH | H2 | 5.2500E-12 | 0.79 | 2200.0L | 73 | 300C |
| 6 | H | CH4 | CH3 | H2 | 5.9400E-13 | 3.00 | 4045.0L | 300 | 2500ANIST |
| 7 | H | OH | O | H2 | 6.9900E-14 | 2.80 | 1950.0L | 300 | 2500ANIST |
| 8 | H | QH | Q | H2 | 6.9695E-14 | 2.80 | 1950.0L | 300 | 2500ANIST |
| 9 | H | XH | X | H2 | 6.9792E-14 | 2.80 | 1950.0L | 300 | 2500ANIST |
| 10 | H | NH3 | NH2 | H2 | 7.8000E-13 | 2.40 | 4990.0M | 200 | 2500CNIST |
| 11 | H | H2O | OH | H2 | 1.5900E-11 | 1.20 | 9610.0L | 250 | 3000ANIST |
| 12 | H | H2Q | QH | H2 | 1.5858E-11 | 1.20 | 9610.0L | 250 | 3000ANIST |
| 13 | H | H2X | XH | H2 | 1.5878E-11 | 1.20 | 9610.0L | 250 | 3000ANIST |
| 14 | H | C2 | CH | C | 4.6700E-10 | 0.50 | 30450.0L | 101541000C | |
| 15 | H | HCN | CN | H2 | 6.2000E-10 | 0.00 | 12500.0L | 300 | 2500CNIST |
| 16 | H | C2H3 | C2H2 | H2 | 3.3200E-11 | 0.00 | 0.0L | 300 | 2500ANIST |
| 17 | H | CO | OH | C | 1.1000E-10 | 0.50 | 77700.0L | 259041000C | |
| 18 | H | CQ | QH | C | 1.0987E-10 | 0.50 | 77700.0L | 259041000C | |
| 19 | H | CX | XH | C | 1.0993E-10 | 0.50 | 77700.0L | 259041000C | |

| | | | | | | | | | |
|------|-------|--------|--------|-----|------------|-------|---------|--------------|----------|
| 7580 | H2ADS | | H2 | | 1.0000E+12 | 0.00 | 450.0L | 10 | 300EHH93 |
| 7581 | HADS | HADS | H2ADS | | 3.8800E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7582 | HADS | OADS | OHADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7583 | HADS | QADS | QHADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7584 | HADS | XADS | XHADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7585 | HADS | OHADS | H2OADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7586 | HADS | QHADS | H2QADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7587 | HADS | XHADS | H2XADS | | 1.9400E+12 | 0.00 | 0.0L | 10 | 300EH92 |
| 7588 | QH | H2O | OH | H2Q | 2.3000E-13 | 0.00 | 2100.0C | 10 | 300EGH89 |
| 7589 | XH | H2O | OH | H2X | 2.3310E-13 | 0.00 | 2100.0C | 10 | 300EGH89 |
| 7590 | OH | H2Q | QH | H2O | 2.3000E-13 | 0.00 | 2100.0C | 10 | 300EGH89 |
| 7591 | OH | H2X | XH | H2O | 2.3280E-13 | 0.00 | 2100.0C | 10 | 300EGH89 |
| 7592 | QH | CO | OH | CQ | 1.0000E-15 | 0.50 | 0.0C | 10 | 300EGH89 |
| 7593 | XH | CO | OH | CX | 1.0160E-15 | 0.50 | 0.0C | 10 | 300EGH89 |
| 7594 | OH | CQ | QH | CO | 1.0000E-15 | 0.50 | 0.0C | 10 | 300EGH89 |
| 7595 | OH | CX | XH | CO | 1.0060E-15 | 0.50 | 0.0C | 10 | 300EGH89 |
| 7596 | HCO+ | CQ | HCO+ | CO | 2.3800E-10 | -0.29 | 0.0C | 10 | 300LGF84 |
| 7597 | HCO+ | CO | HCO+ | CQ | 2.3800E-10 | -0.29 | 14.0C | 10 | 300LGF84 |
| 7598 | HCO+ | CX | HCO+ | CO | 2.3990E-10 | -0.29 | 0.0C | 10 | 300LGF84 |
| 7599 | HCO+ | CO | HCO+ | CX | 2.3990E-10 | -0.29 | 14.0C | 10 | 300LGF84 |
| 7600 | H2O | PHOTON | OH | H | 5.9000E-10 | 0.00 | 1.7L | 1041000BRJ91 | |
| 7601 | H2Q | PHOTON | QH | H | 5.9000E-10 | 0.00 | 1.7L | 1041000BRJ91 | |
| 7602 | H2X | PHOTON | XH | H | 5.9000E-10 | 0.00 | 1.7L | 1041000BRJ91 | |
| 7603 | H2 | PHOTON | H | H | 2.0000E-17 | 0.00 | 1.7L | 1041000EEDY | |

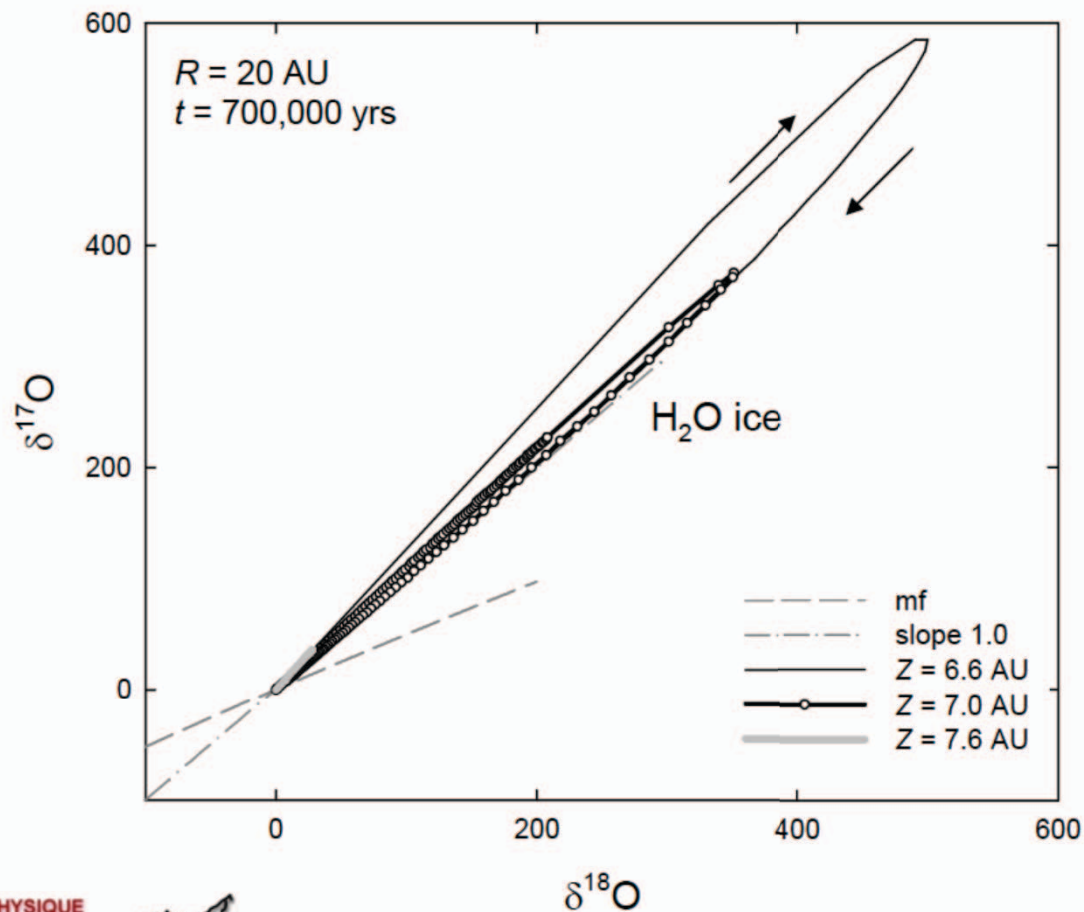


Disk Surfaces

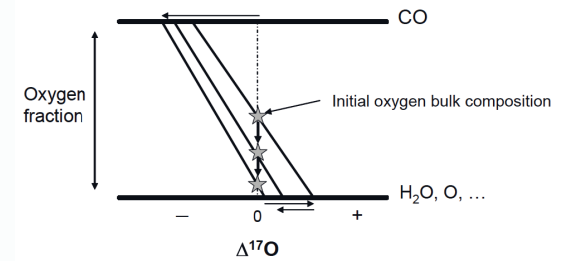
Young (2007)

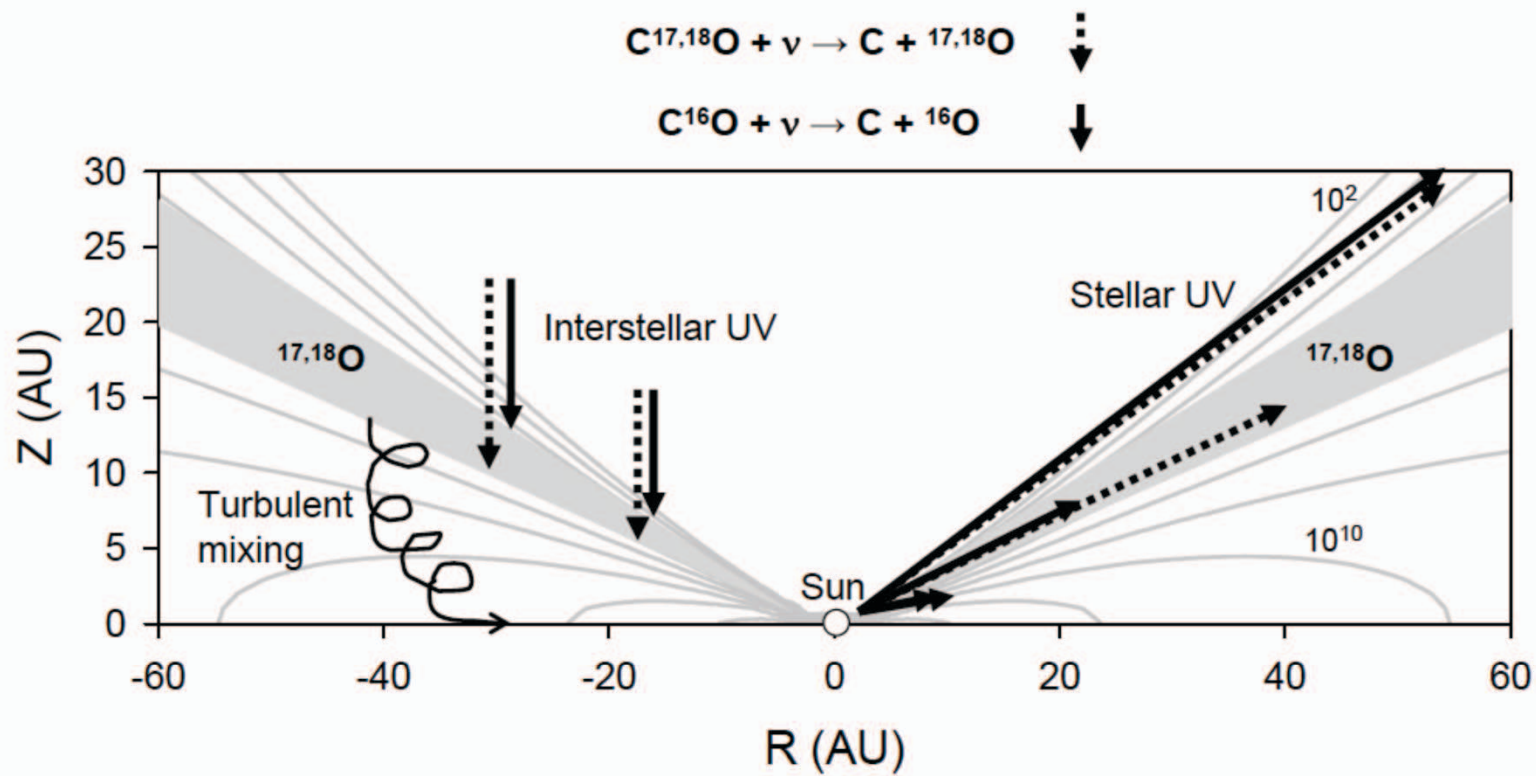


Calculated H₂O evolution in the early solar system

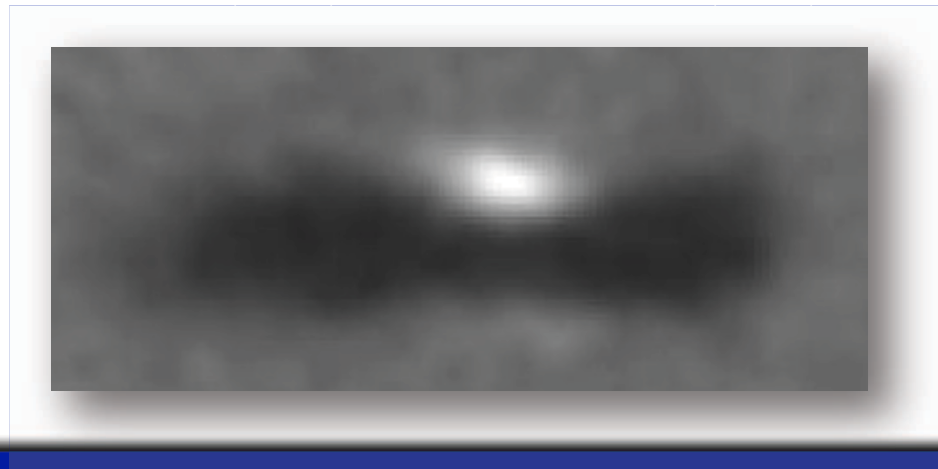
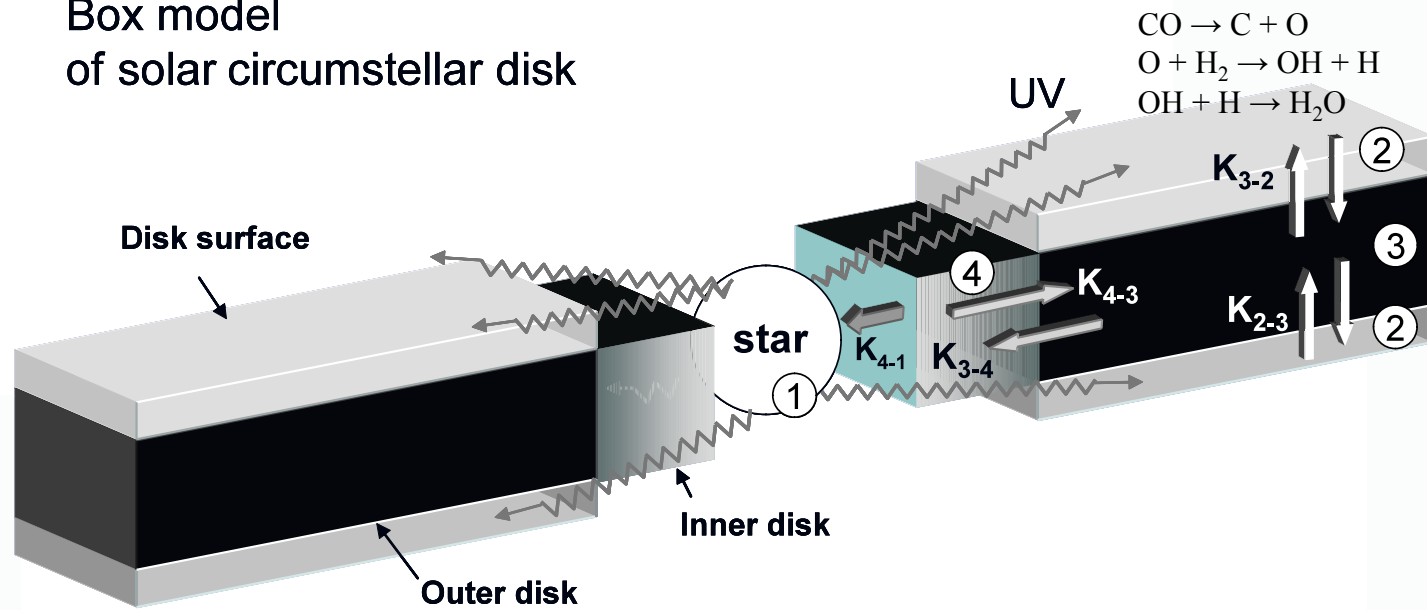


Young (2007)

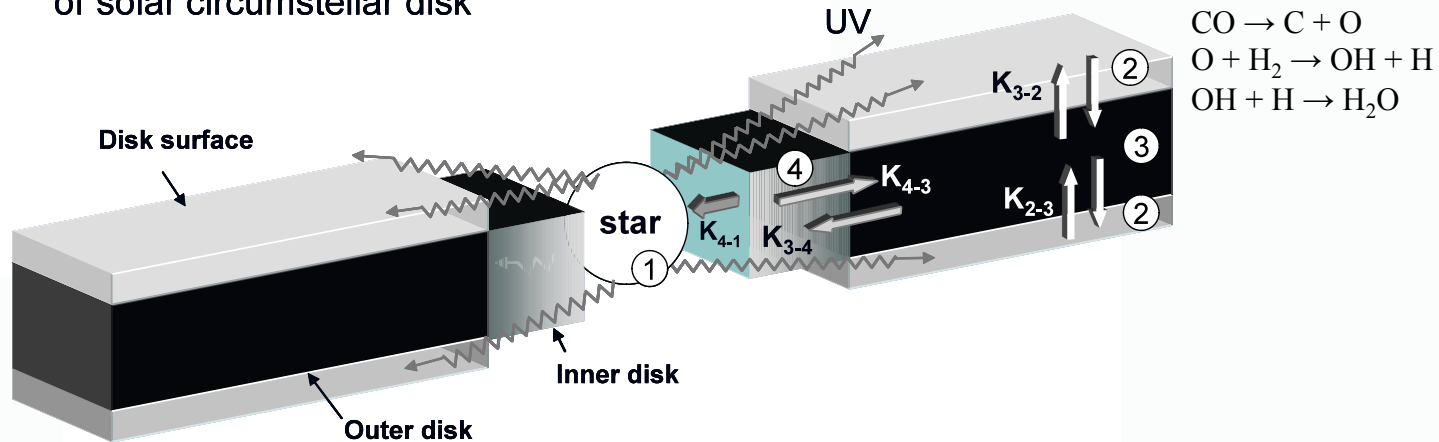




Box model of solar circumstellar disk



Box model
of solar circumstellar disk



Equations

$$\frac{dn_{l,j}}{dt} = \sum_i k_{ij} n_{l,i} - n_{l,j} \sum_i k_{ji}$$

⋮

$$\frac{dn_{m,j}}{dt} = \sum_i k_{ij} n_{m,i} - n_{m,j} \sum_i k_{ji}$$

⋮

$$\frac{dn_{m,p}}{dt} = \sum_i k_{ip} n_{m,i} - n_{m,p} \sum_i k_{pi}$$

Input transport rate constants

$$k_{4-1} = 10^{-7} \text{ yr}^{-1} (10^{\square} M_{\odot} \text{ yr}^{\square} \text{ OK, disk drains faster})$$

$$k_{3-4} = 10^{-5} \text{ yr}^{-1} (R/100 \text{ AU}) \text{ (Hartmann, 2000)}$$

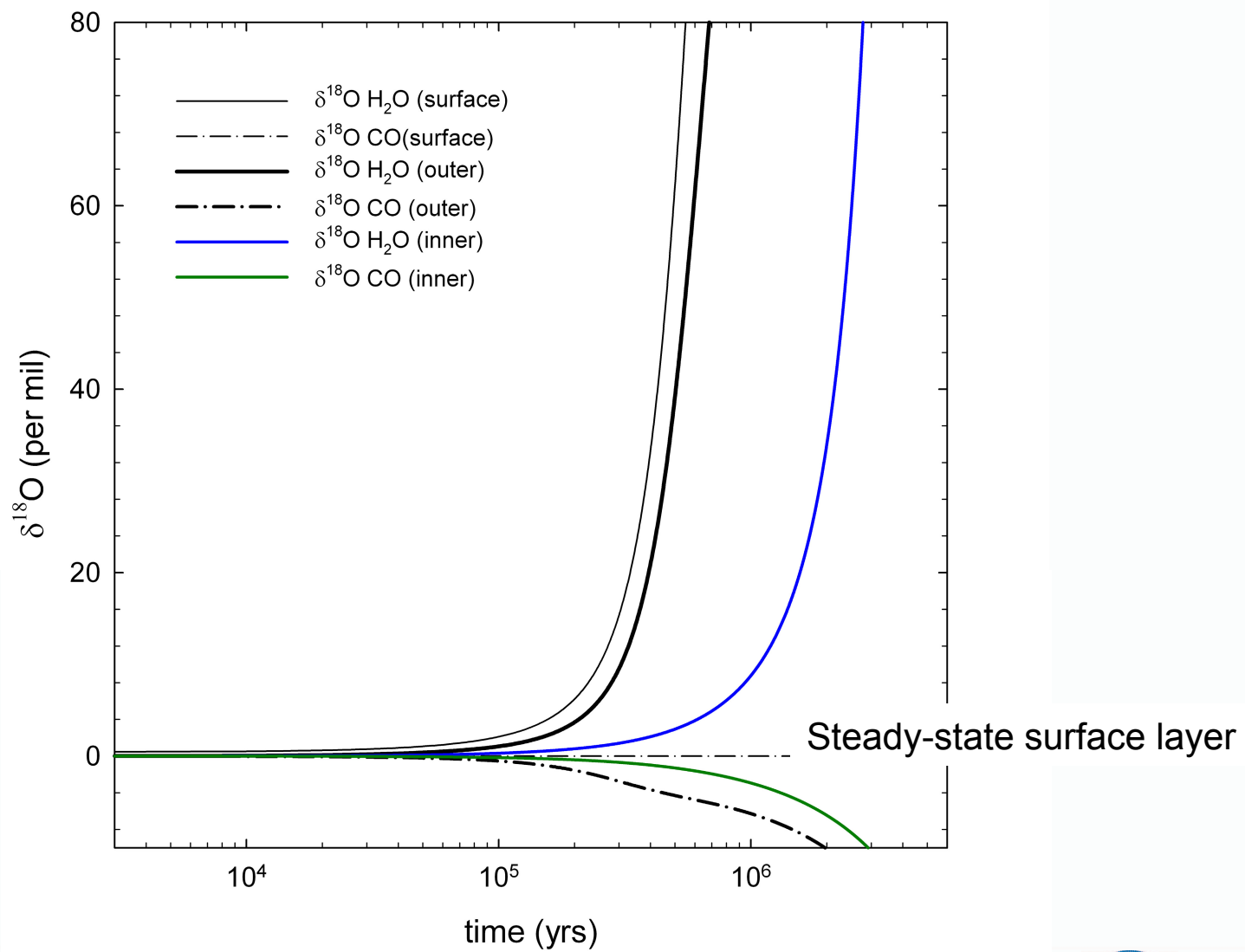
$$k_{4-3} = k_{3-4}/10 \text{ (radial mixing)}$$

$$k_{3-4(\text{H}_2\text{O})} > k_{3-4} \text{ (Cuzzi and Zahnle, 2004)}$$

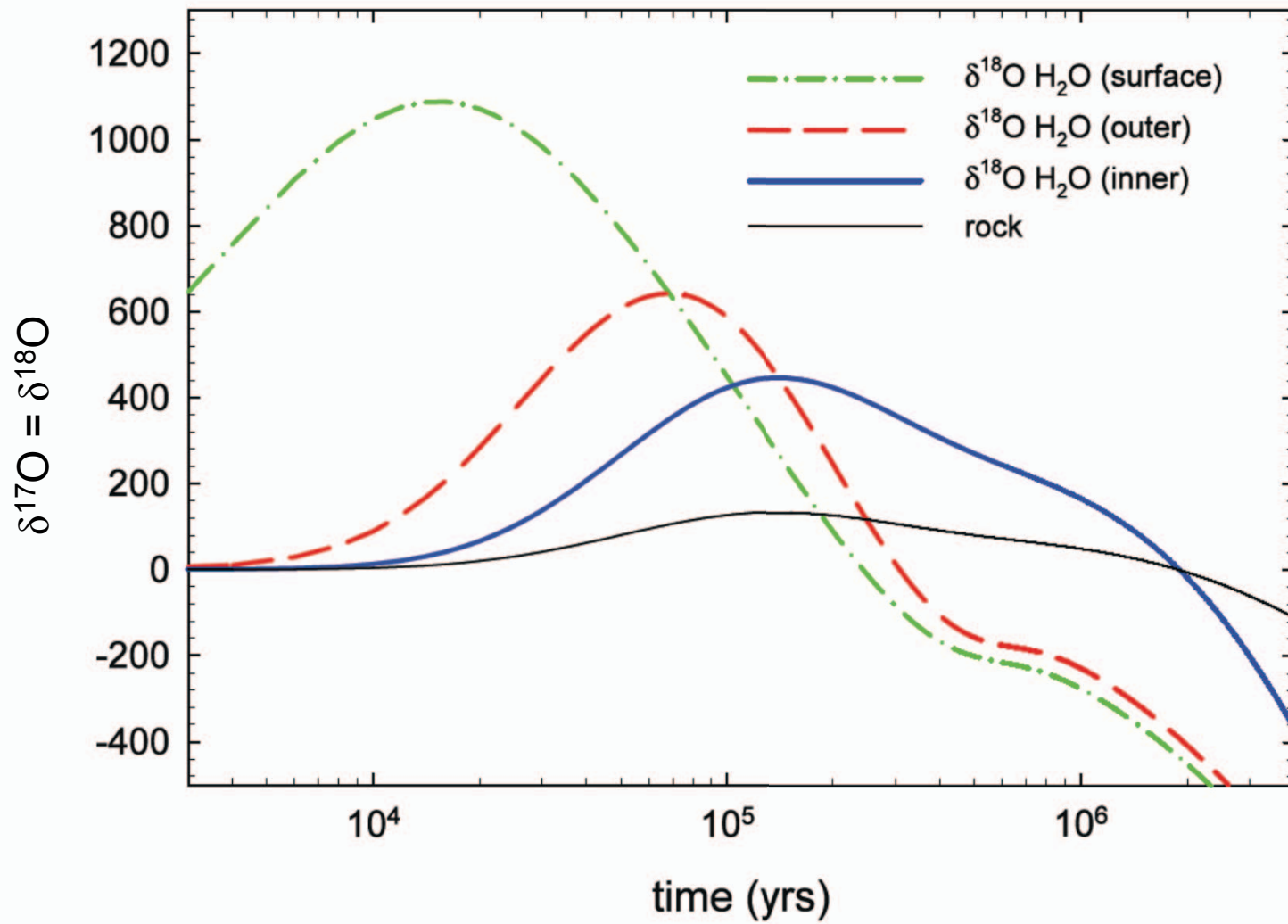
$$k_{3-2} = k_{2-3} \sim 1/(\Omega\alpha) \text{ (}\Omega = \text{angular velocity)}$$

$$R = 20 \text{ AU}, \alpha = 10^{\square}, (\tau_v)^{\square} = 1 \times 10^{-4} \text{ yr}^{-1}$$

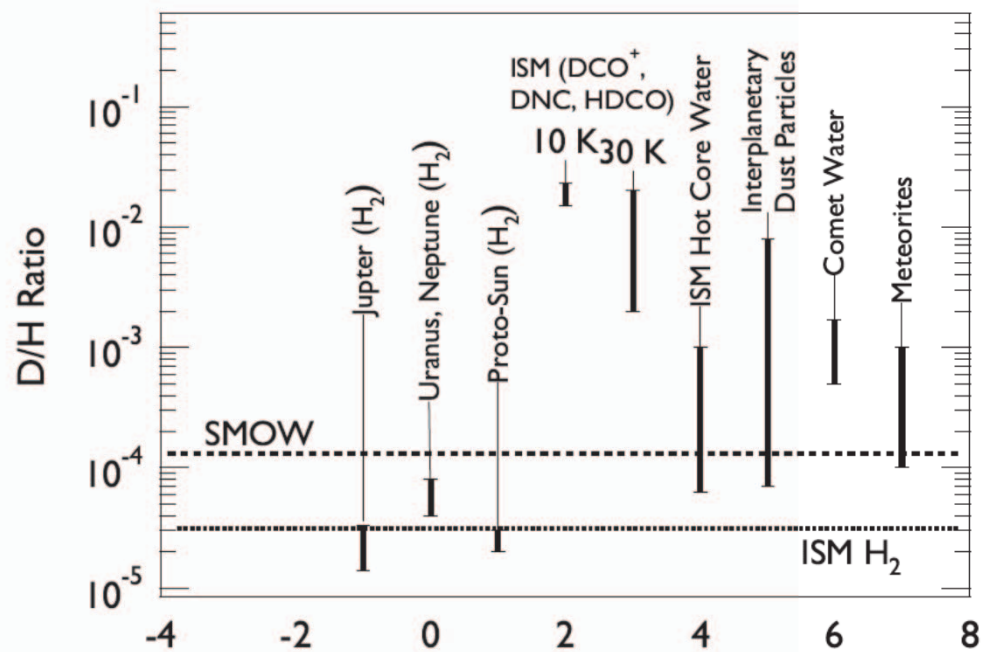




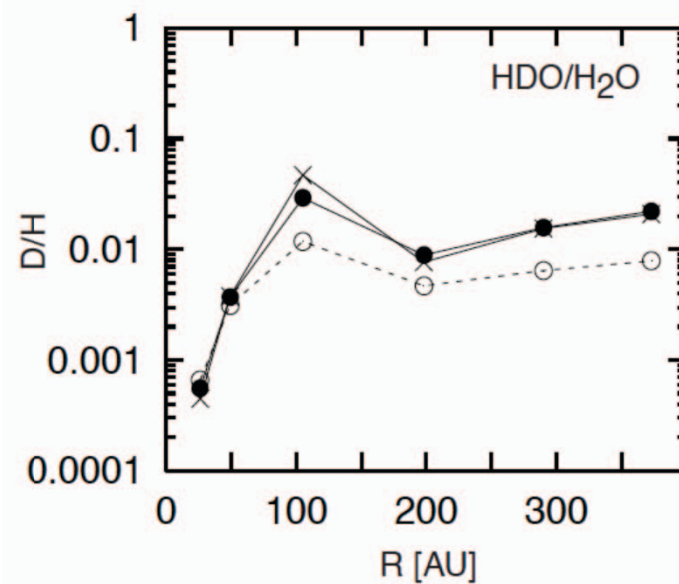
Young (2007)



Is there a D/H signature of inward H₂O migration?



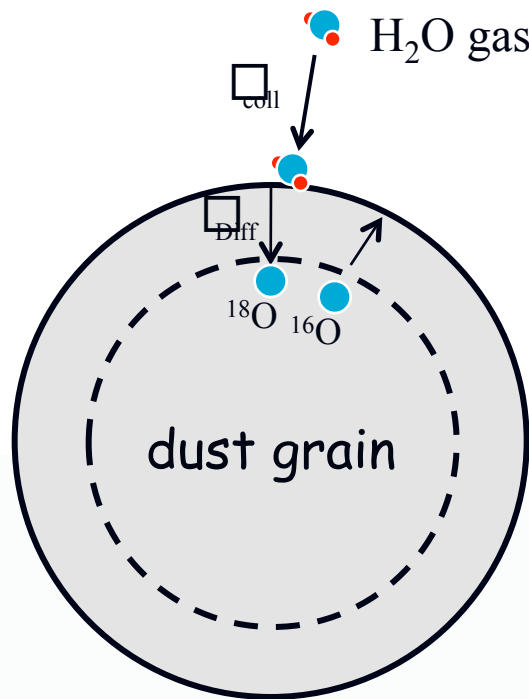
Bergin (2009)



Aikawa et al. (2002)



Timescale for oxygen isotopic equilibration of dust



H₂O gas – dust grain collision frequency

$$J_{i,\text{gas}} = \frac{\alpha n_{i,\text{gas}}}{4} v_{\text{gas}}$$

$$v_{\text{gas}} = \left(\frac{8kT}{\pi\mu_{\text{gas}}} \right)^{1/2}$$

$$v_{\text{coll}} = J_{i,\text{gas}} A_{\text{dust}}$$

$$\tau_{\text{coll}} = \frac{n_{i,\text{dust}} \left(\frac{4}{3} \pi r_{\text{dust}}^3 L / \hat{V}_{\text{dust}} \right)}{v_{\text{coll}}}$$

Self diffusion of O in dust grain

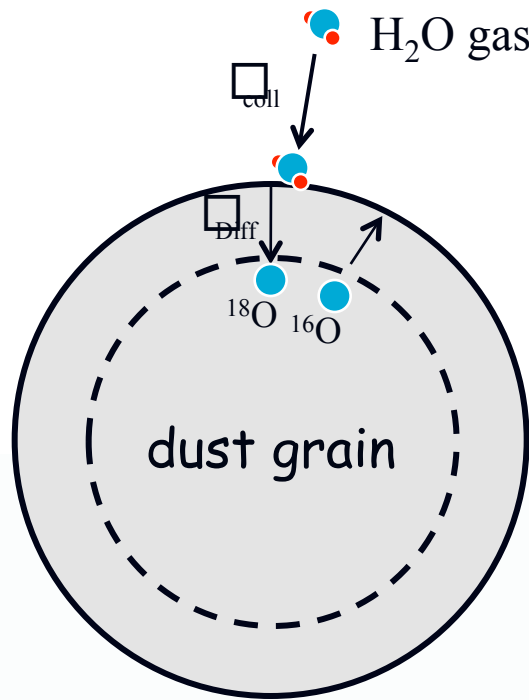
$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n\pi^2 \xi)$$

$$\xi = \frac{Dt}{r^2}$$

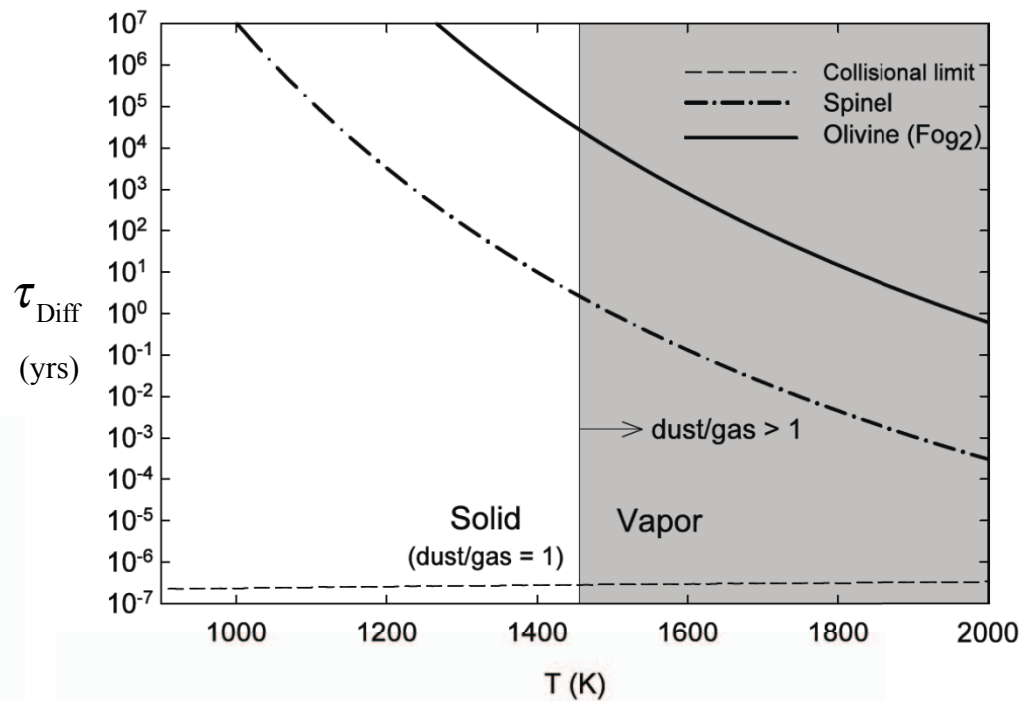
$$\tau_{\text{Diff}} = \frac{1.5 \xi r^2}{D(T)}$$



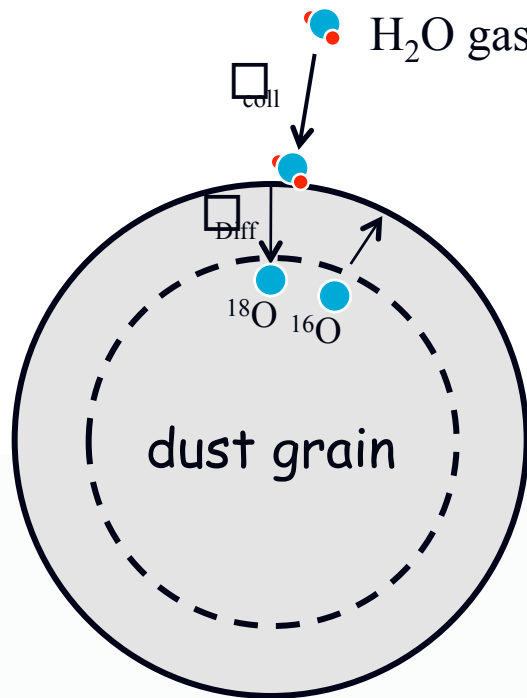
Timescale for oxygen isotopic equilibration of dust



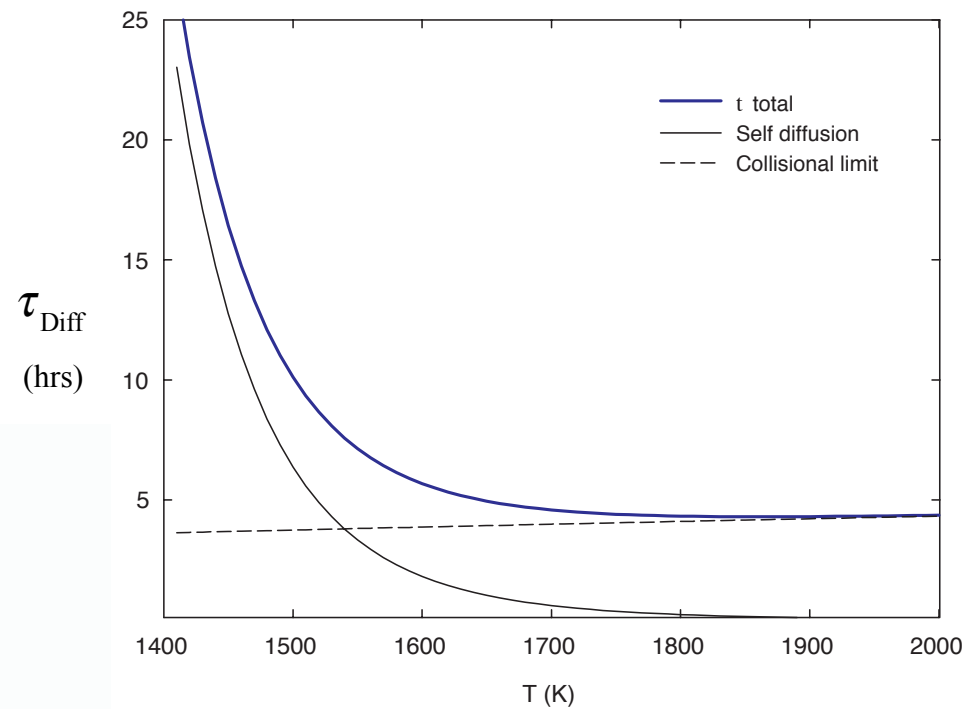
1 μm dust grains, 10^{-3} bar total pressure, $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 2 \times 10^{-4}$

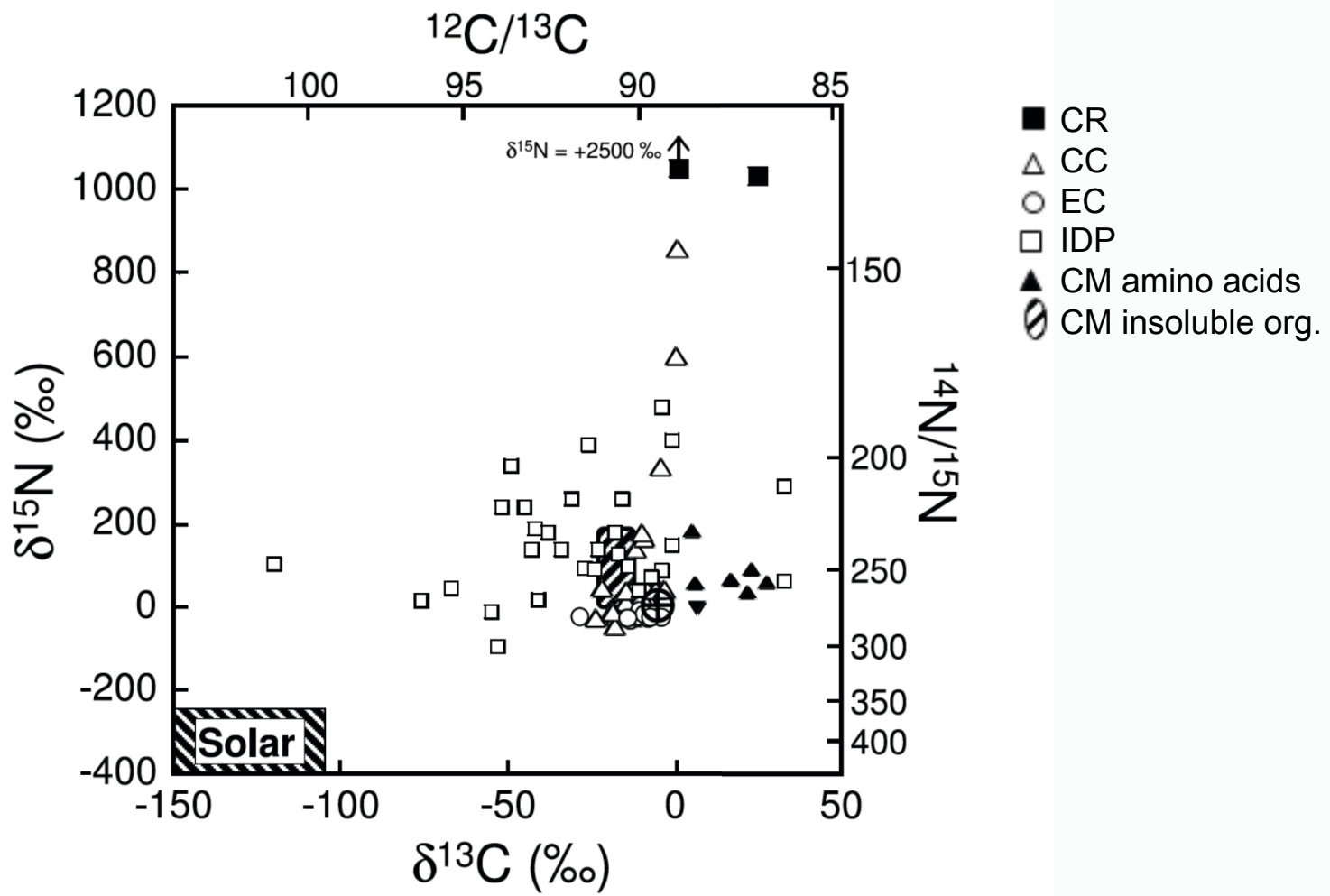


Timescale for oxygen isotopic equilibration of melt



1 mm chondrule, 10^{-3} bar total pressure, $P_{H_2O}/P_{H_2} = 2 \times 10^{-4}$

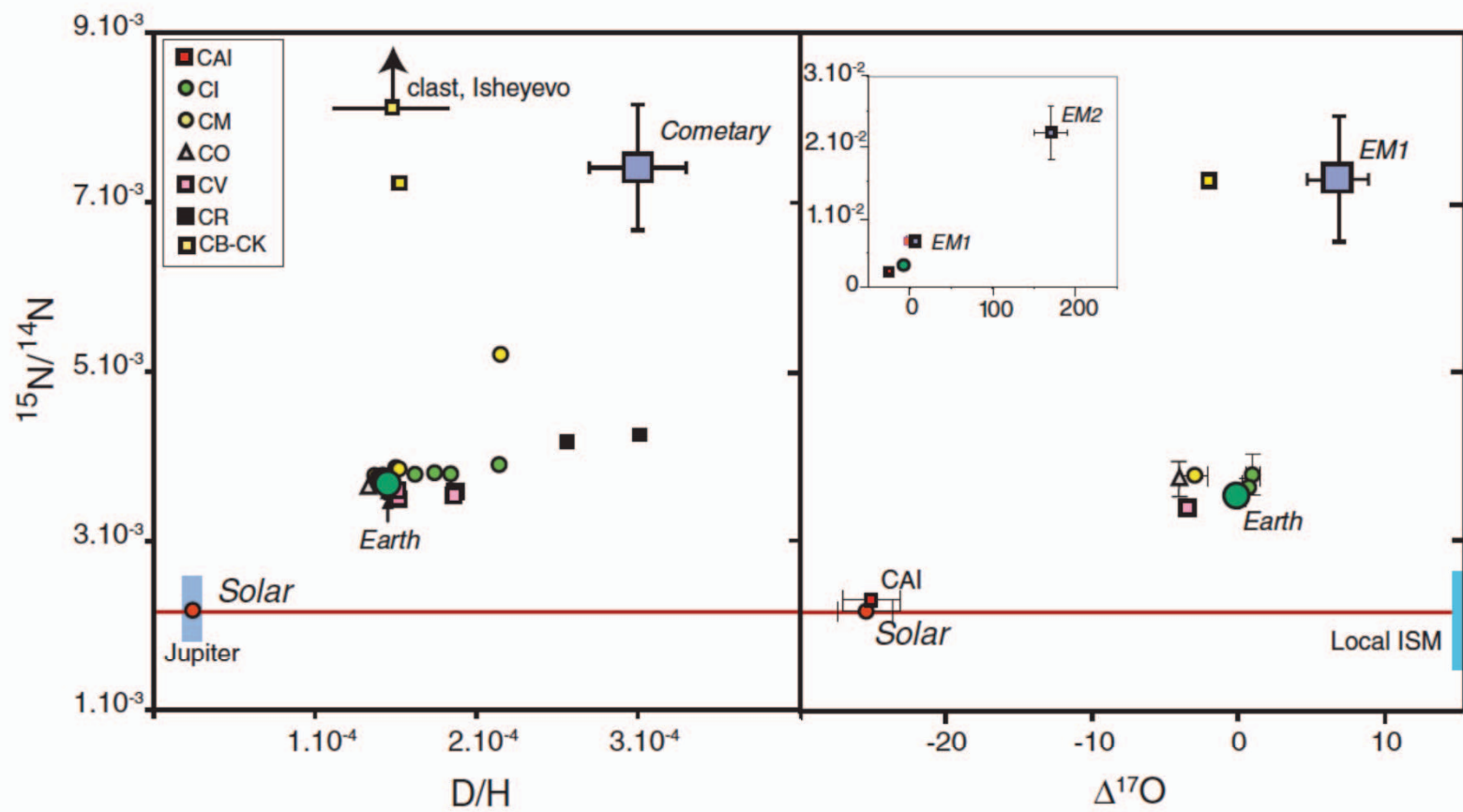




Hashizumet et al. (2004)



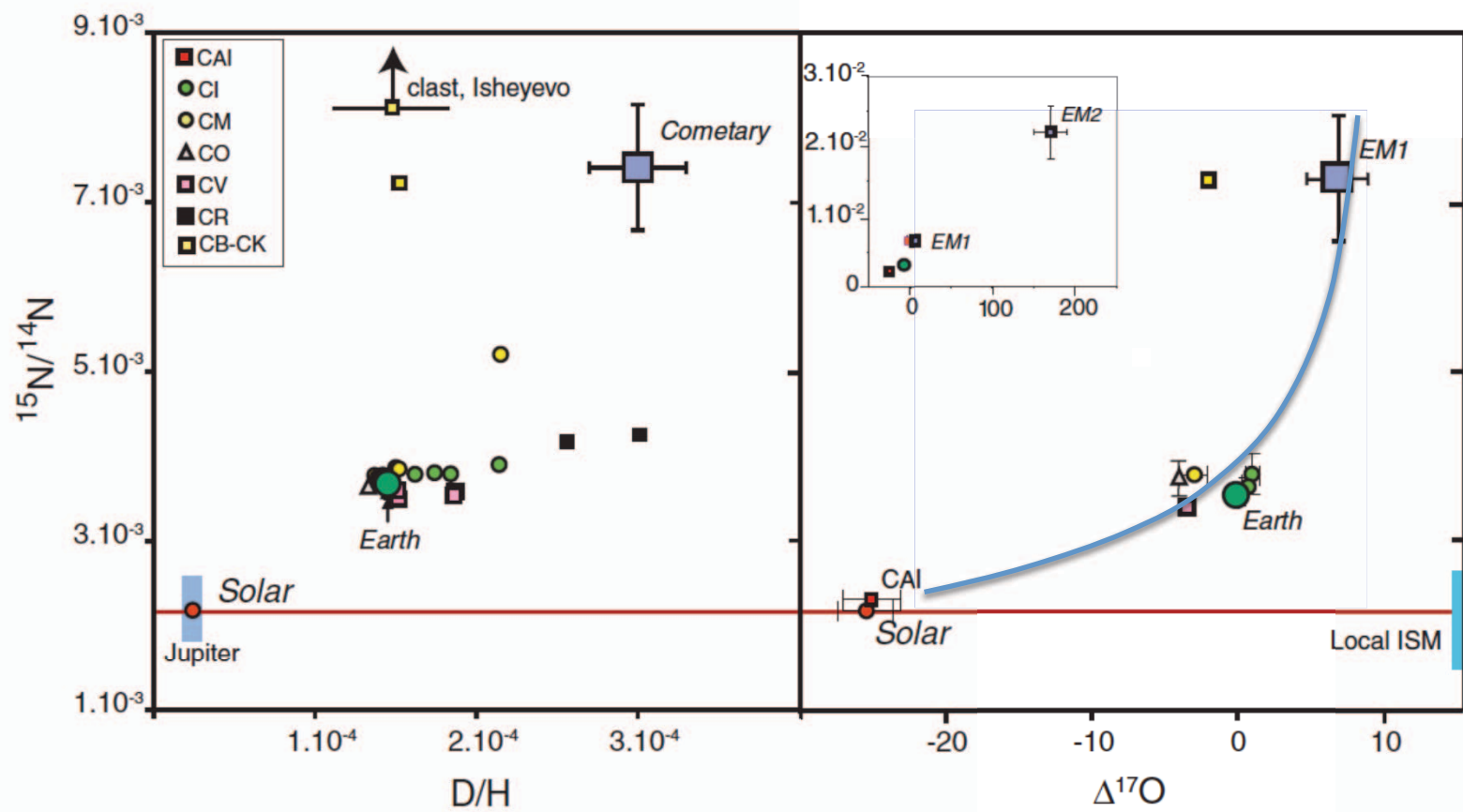
UCLA



Marty et al. (2011)

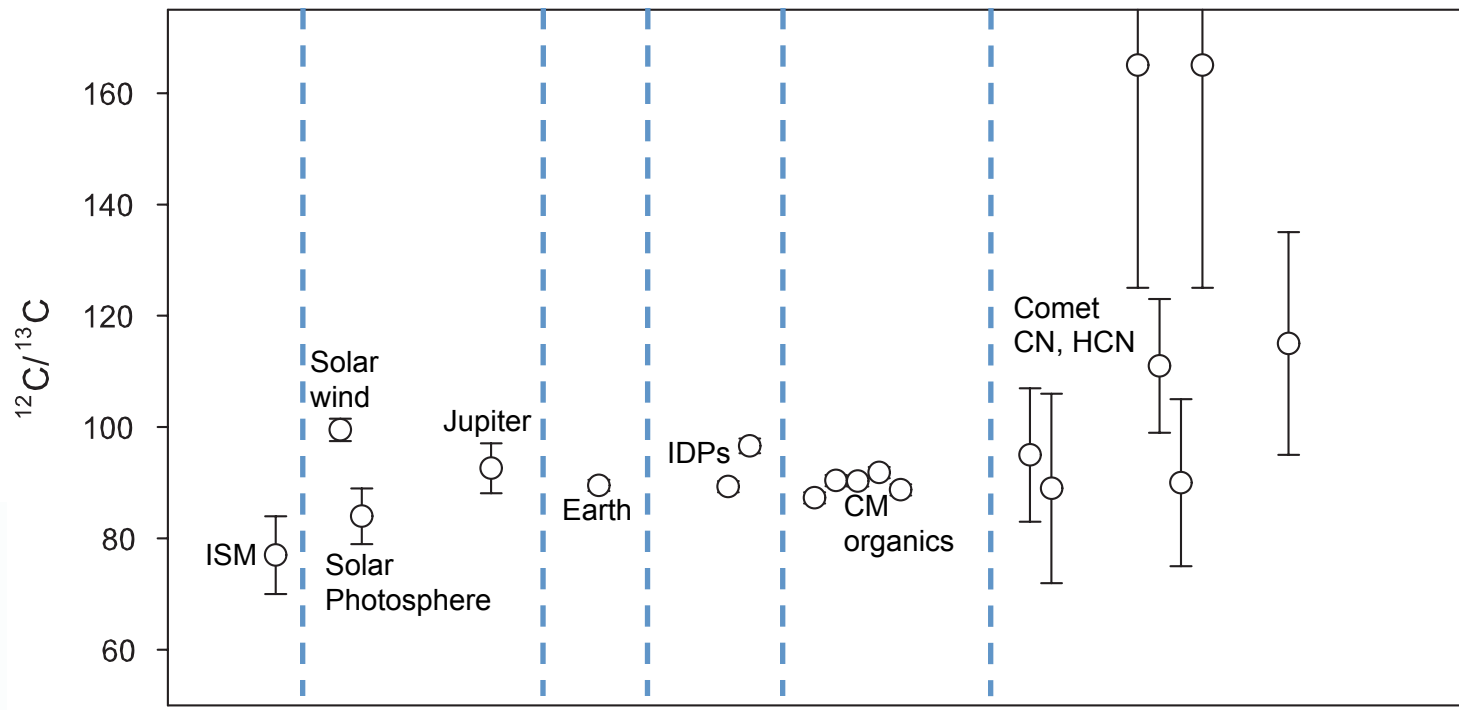


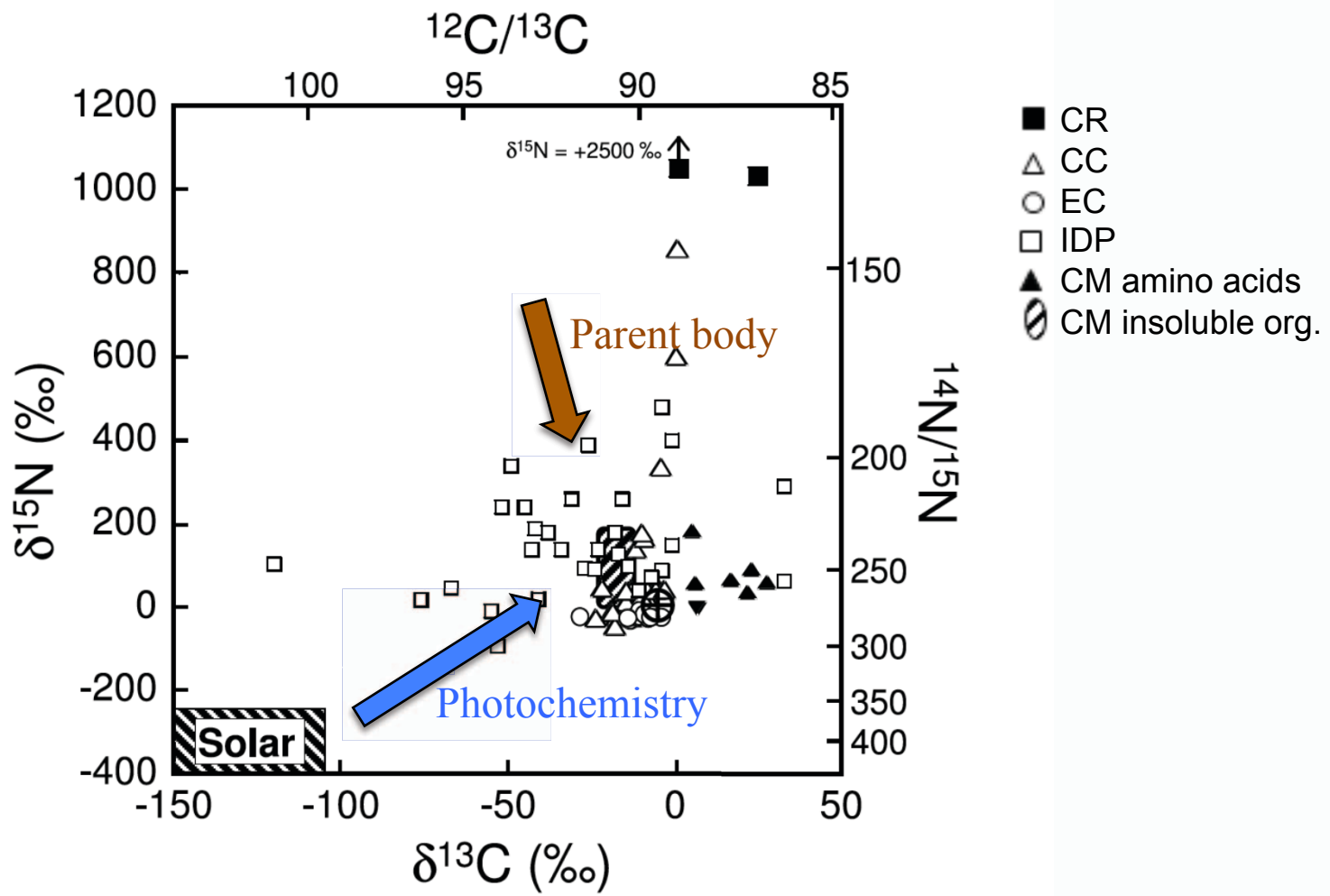
UCLA



Marty et al. (2011)







Hashizumet et al. (2004)