Some thoughts on isotope fractionation

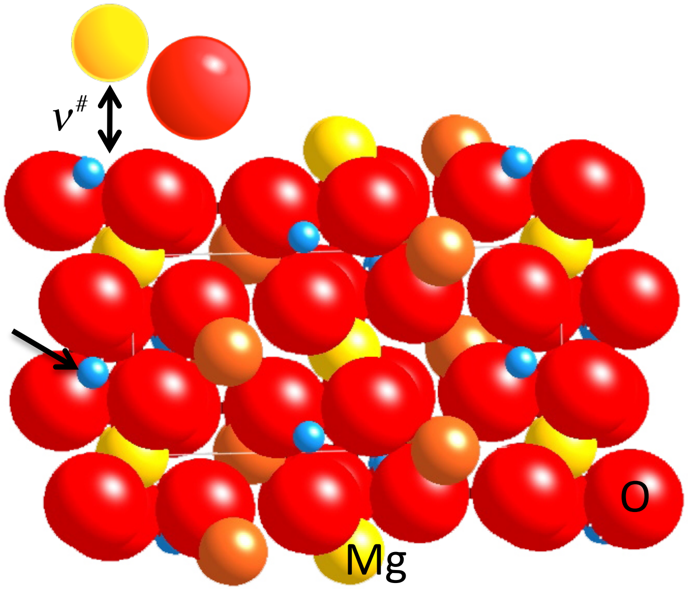
(mainly phase changes and transport, less chemistry)

1. Saturation:
    - Equilibrium
    - Condensation
    - Evaporation
2. Atmospheric escape
3. Steady-state atmospheres
4. Multiply-substituted isotopologues: opportunities
5. Photochemistry

Saturation

Fractionation – kinetics is bidirectional independent of transport

Evaporation



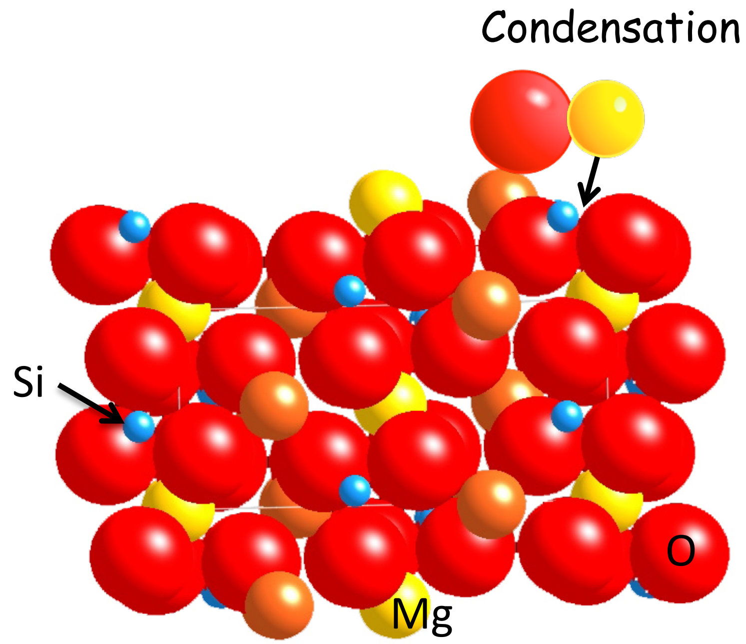
Easily measured in the laboratory and theory is reasonable:

$$\alpha_{\mathrm{EVAP}} = \frac{\nu'^{\#}}{\nu^{\#}} \frac{(Q'^{\dagger}/Q^{\dagger})_{\mathrm{Condensed}}}{(Q'/Q)_{\mathrm{Condensed}}}$$

$$(Q'/Q)_{\mathrm{Condensed}} = \alpha_{\mathrm{EQ}}(Q'/Q)_{V}$$

Saturation

Fractionation – kinetics is bidirectional independent of transport



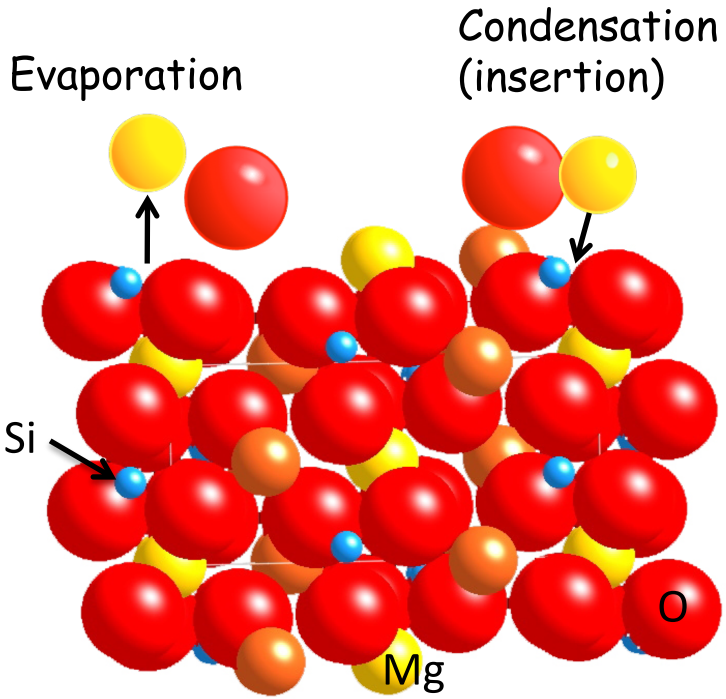
Difficult to resolve from transport effects, theory is not well developed:

$$\ln \alpha_{\mathrm{Condensation}} = \ln\left(\frac{k'}{k}\right) = \ln\left(\frac{\nu'}{\nu}\right) + \left(-(E_{\mathrm{a}}^{'} + E_{\mathrm{a}})/(k_{\mathrm{b}}T)\right)$$

…some analogies with electrochemistry and reorganization energy.

Saturation

Fractionation – law of mass action



Vapor → Condensate

$$\alpha_{\mathrm{EQ}} = \frac{\alpha_{\mathrm{INSERTION}}}{\alpha_{\mathrm{EVAP}}}$$

$$\alpha_{\mathrm{INSERTION}} = \alpha_{\mathrm{EQ}}\ \alpha_{\mathrm{EVAP}}$$

Calculated ↗ α_{EQ}, Measured ↖ α_{EVAP}

Saturation

$$S_i = \frac{P_i}{P_{\mathrm{EQ},i}}$$

$$S_i = 1, \text{ Equilibrium}$$
$$S_i > 1, \text{ Condensation}$$
$$S_i < 1, \text{ Evaporation}$$

Equilibrium

$$S_i = 1$$

For crystalline phases A and B at high T:

$$\ln \alpha_{\text{A-B}} = \frac{1}{24}\left(\frac{h}{k_b T}\right)^2 \left(\frac{1}{m} - \frac{1}{m'}\right)\left[\frac{\hat{K}_{f,\text{A}}}{4\pi^2} - \frac{\hat{K}_{f,\text{B}}}{4\pi^2}\right]$$

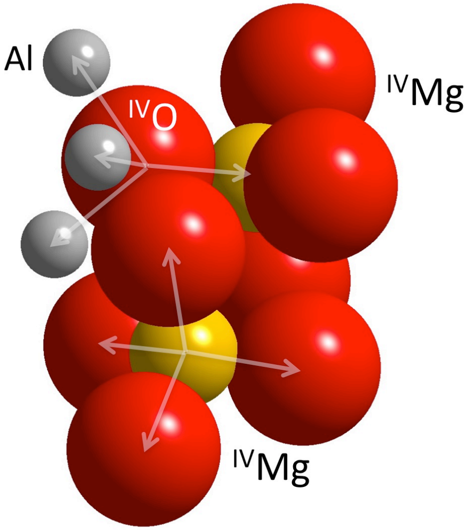
Key is differences in bond stiffness!

Equilibrium

$S_i = 1$

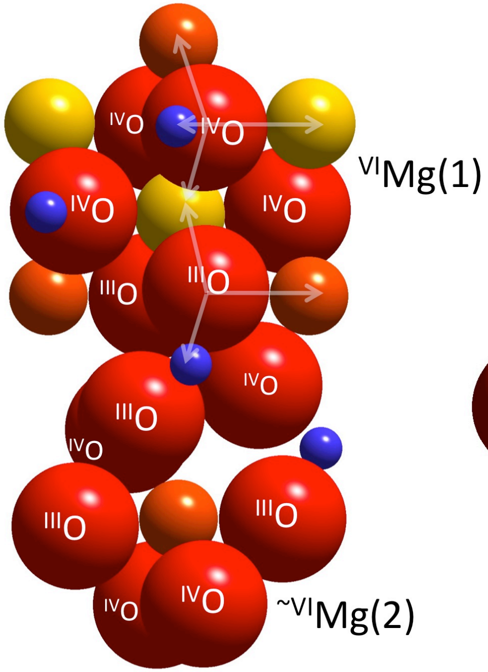
decreasing ^{26}Mg/^{24}Mg →

Spinel



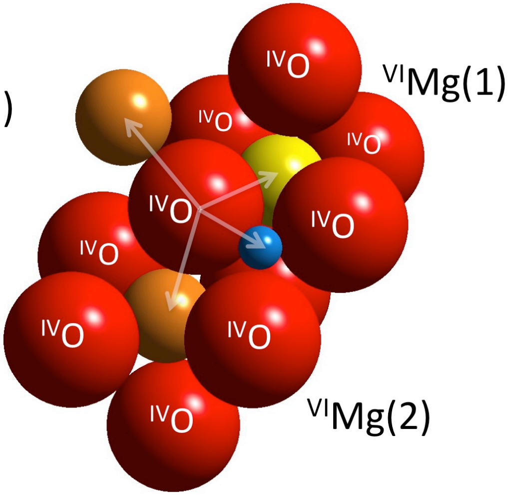
mean $r_{Mg\text{-}O}$ = 0.195 nm

Orthopyroxene



mean ionic $r_{Mg\text{-}O}$ = 0.209 nm

Forsterite



mean ionic $r_{Mg\text{-}O}$ = 0.210 nm

Equilibrium

$$S_i = 1$$

For gas molecules:

$$\frac{Q'}{Q} = \frac{\sigma}{\sigma'} f$$

$$k_{\mathrm{eq}} = \frac{f_a}{f_b} \frac{\sigma_a \sigma'_b}{\sigma'_a \sigma_b}$$

Equilibrium

$S_i = 1$

$$\mathrm{CO} + \mathrm{O}^{18}\mathrm{O} \rightleftharpoons \mathrm{C}^{18}\mathrm{O} + \mathrm{O}_2$$

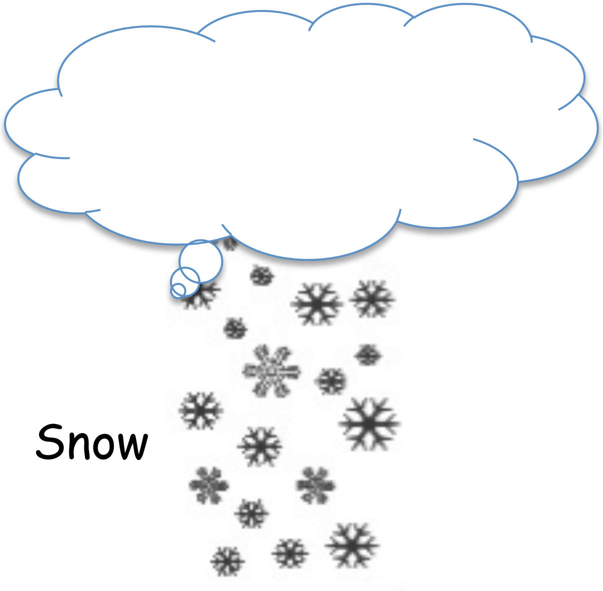
$$k_{\mathrm{eq}} = \frac{Q^{1}_{\mathrm{O}^{18}\mathrm{O}}\; Q^{1}_{\mathrm{CO}}}{Q^{1}_{\mathrm{O}_2}\; Q^{1}_{\mathrm{C}^{18}\mathrm{O}}} = \frac{Q'_{\mathrm{O}_2}\; Q_{\mathrm{CO}}}{Q_{\mathrm{O}_2}\; Q'_{\mathrm{CO}}} = \alpha$$

$$\lim_{T\to\infty} \alpha = \frac{\sigma_{\mathrm{O}_2} \sigma'_{\mathrm{CO}}}{\sigma'_{\mathrm{O}_2}\; \sigma_{\mathrm{CO}}} = \frac{2\times 1}{1\times 1} = 2$$

Condensation

$S_i > 1$

Expanding on Jouzel and Merlivat (1984)
and Simon and DePaolo (2010)



Snow

$$J_i = \frac{\gamma_i \left(P_{i,\mathrm{EQ}} - P_i\right)}{\sqrt{2\pi m_i RT}}$$

Hertz-Knudsen equation

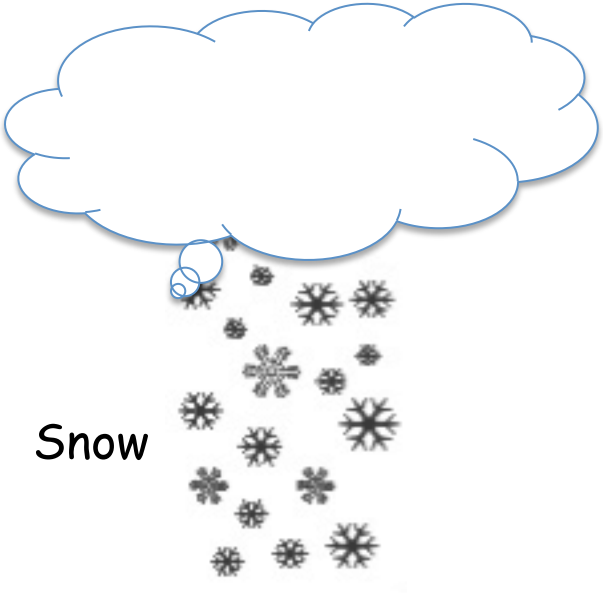
$$\frac{R_{\mathrm{condensate}}}{R_{\mathrm{o}}} = \frac{1}{R_{\mathrm{o}}} \frac{J'}{J} \underbrace{\alpha_{\mathrm{EVAP}} \alpha_{\mathrm{EQ}}}_{\longleftrightarrow}$$

Insertion

Condensation

$S_i > 1$

Expanding on Jouzel and Merlivat (1984)
and Simon and DePaolo (2010)



$$\alpha_{\mathrm{COND}} = \frac{\alpha_{\mathrm{EVAP}}\alpha_{\mathrm{KIN}}\, S_i}{\alpha_{\mathrm{EQ}}(S_i - 1) + \alpha_{\mathrm{KIN}}}$$

$$\alpha_{\mathrm{KIN}} = \sqrt{\frac{\mu_{i,j}}{\mu_{i,j}'}}\; \alpha_{\mathrm{EVAP}}\; \alpha_{\mathrm{EQ}}$$

transport insertion

Condensation

Reservoir effects:

No reservoir effect:

- -infinite, well-mixed gas reservoir
- -kinetic fractionation

$$\delta_{\mathrm{Cond}} = \delta_{\mathrm{o,Vapor}} + 10^3 \ln\left(\alpha_{\mathrm{COND}}\right)$$

Condensation

Reservoir effects:

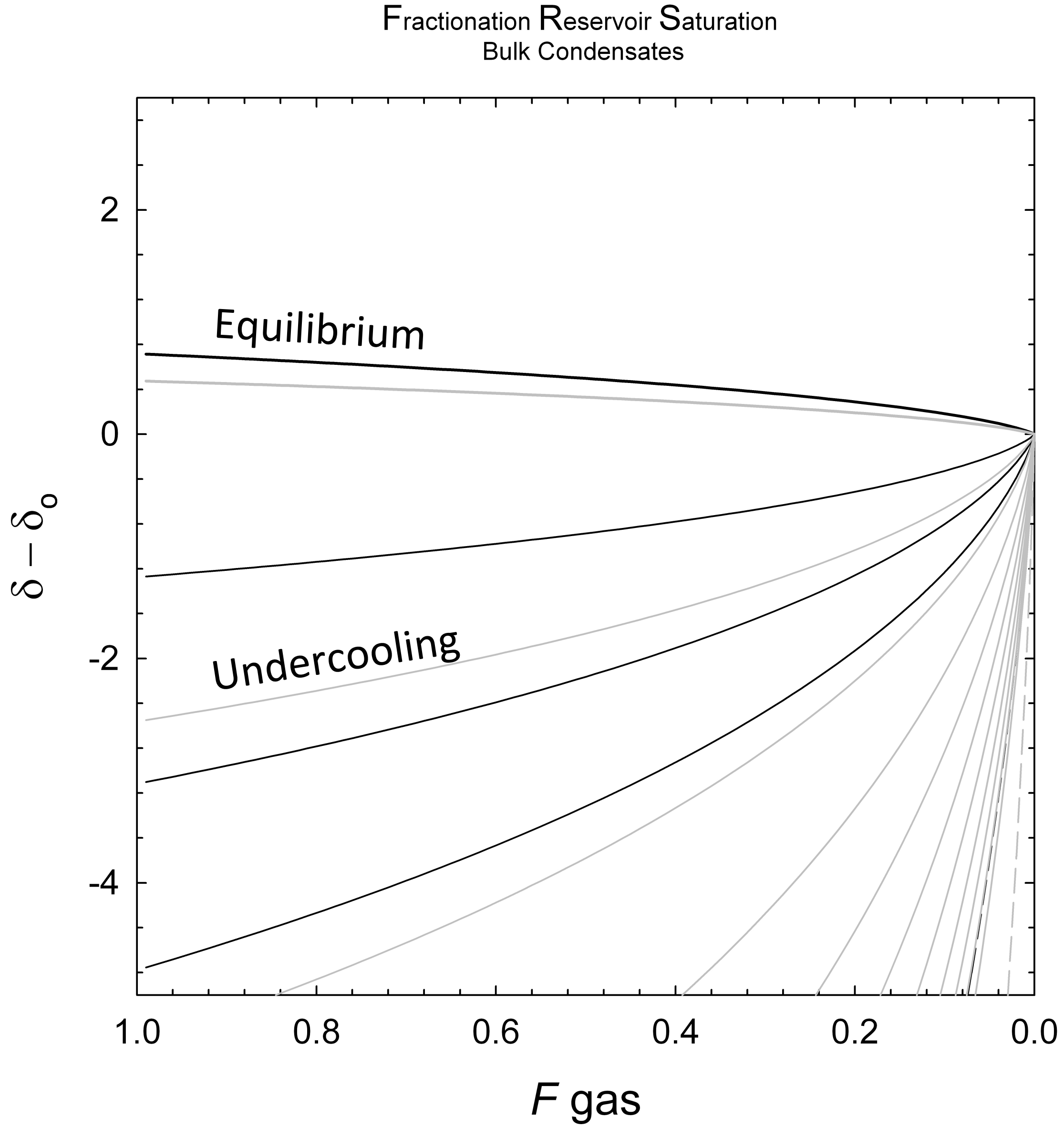
Rainout:

- well-mixed parcel of gas "rains" out condensate
- cumulative compositions

$$\bar{\delta}_{\mathrm{Cond}} = (\delta_{\mathrm{o,Vapor}} + 10^3)\left(\frac{1 - f^{\alpha_{\mathrm{COND}}}}{1 - f}\right) - 10^3$$

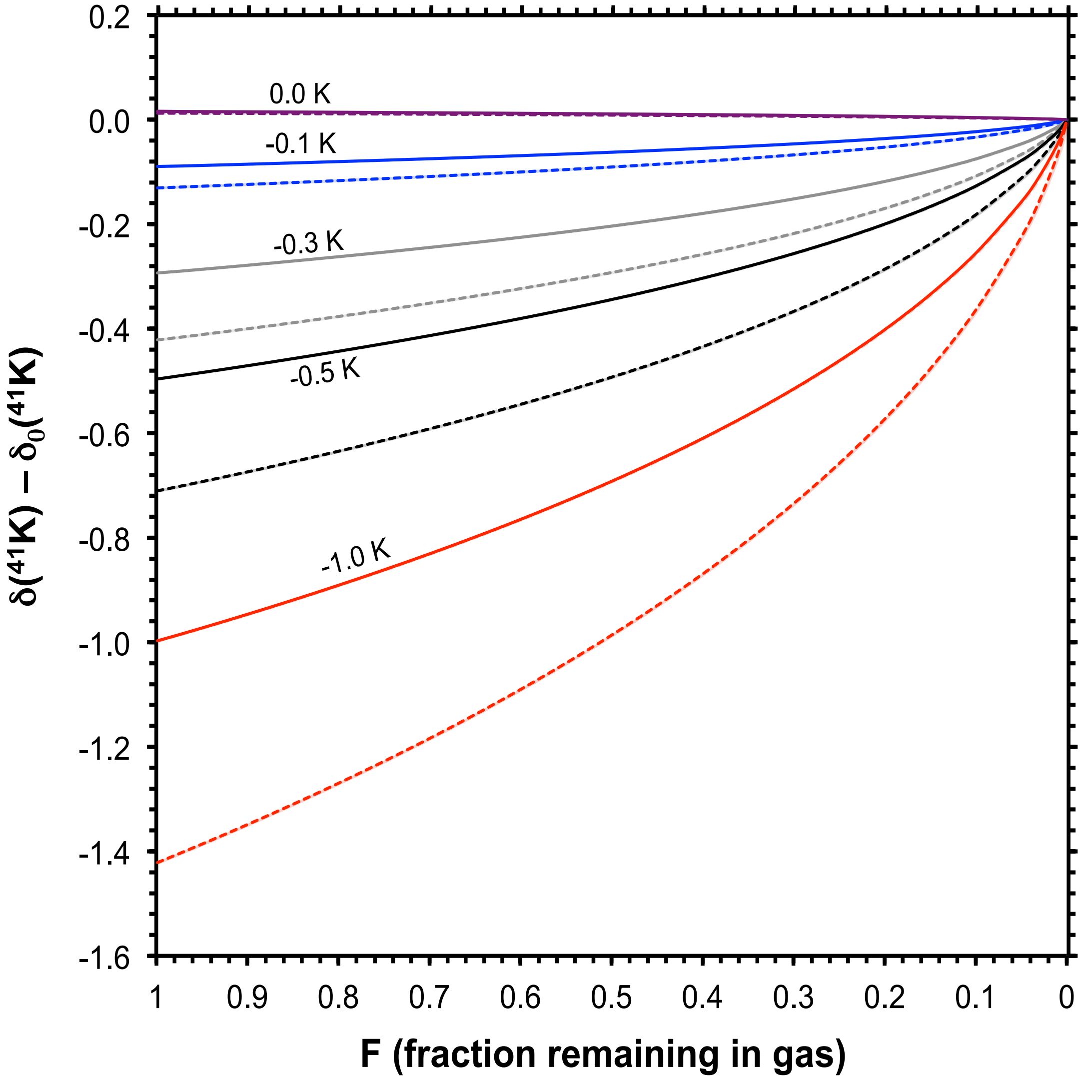
f = fraction remaining in source

Condensation



$$\ln(S)=\frac{\Delta\hat{H}_{rxn}}{R}\left(\frac{1}{T}-\frac{1}{T_{EQ}}\right)$$

Condensation



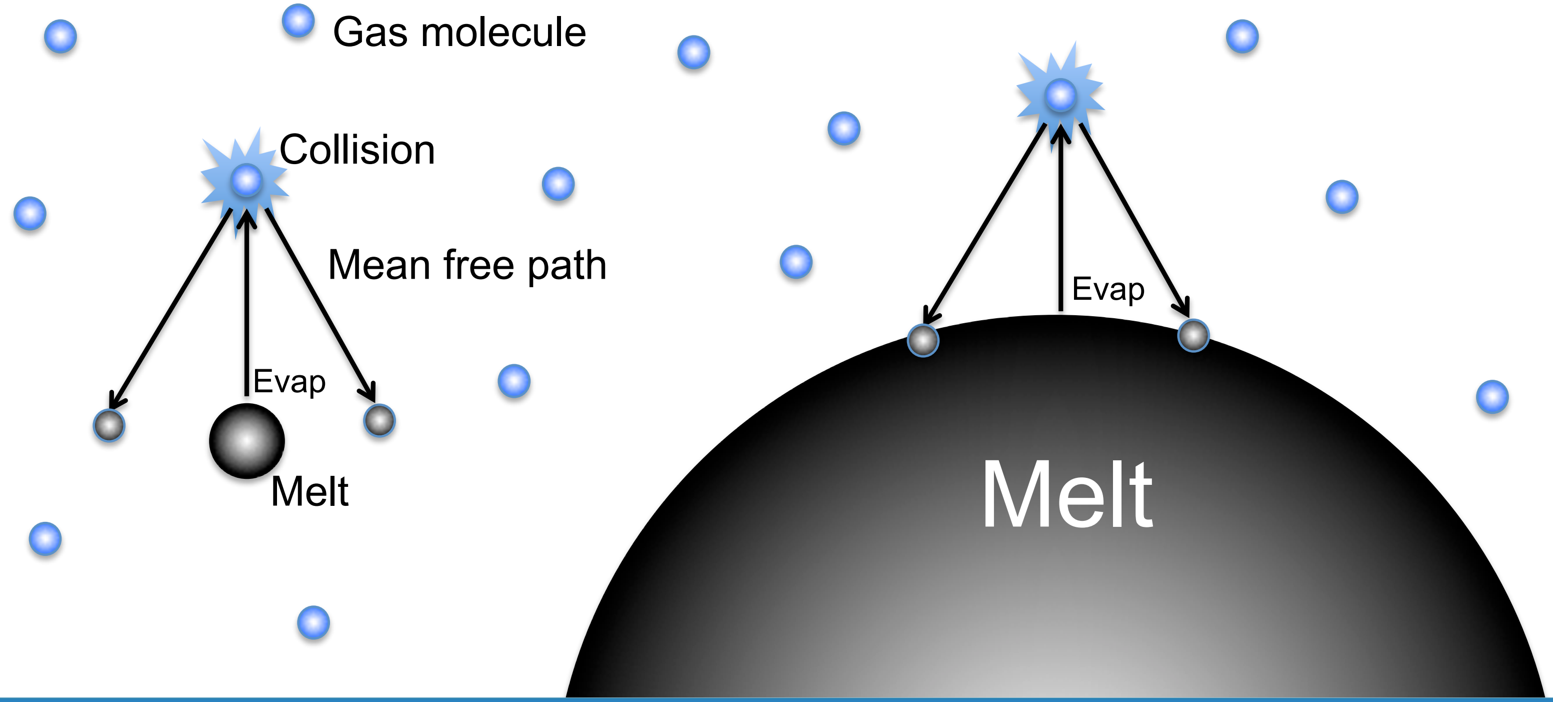
Bulk condensate ^{41}K/^{39}K
3500 and 3000 K

$$\ln(S) = \frac{\Delta\hat{H}_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_{EQ}}\right)$$

Evaporation

$S_i < 1$

$$J_{i,\mathrm{net}} = \frac{\gamma_i \left(P_{i,\mathrm{sat}} - P_i \right)}{\sqrt{2\pi m_i RT}}$$



Evaporation

$$S_i < 1$$

Pressure build up at surface:

$$P_i(r_+ = s, t) = RT\frac{s}{D_i}J_{i,\mathrm{net}}\left[1 - e^{\xi}\,\mathrm{erfc}\left(\sqrt{\xi}\right)\right]$$

Evaporation

$S_i < 1$

Pressure build up at surface:

Radius of body

$$P_i(r_+ = s, t) = RT \frac{\overset{\swarrow}{s}}{D_i} J_{i,\mathrm{net}} \left[1 - e^{\xi} \operatorname{erfc}\left(\sqrt{\xi} \right) \right]$$

$$\xi = \frac{tD_i}{s^2}$$

Evaporation

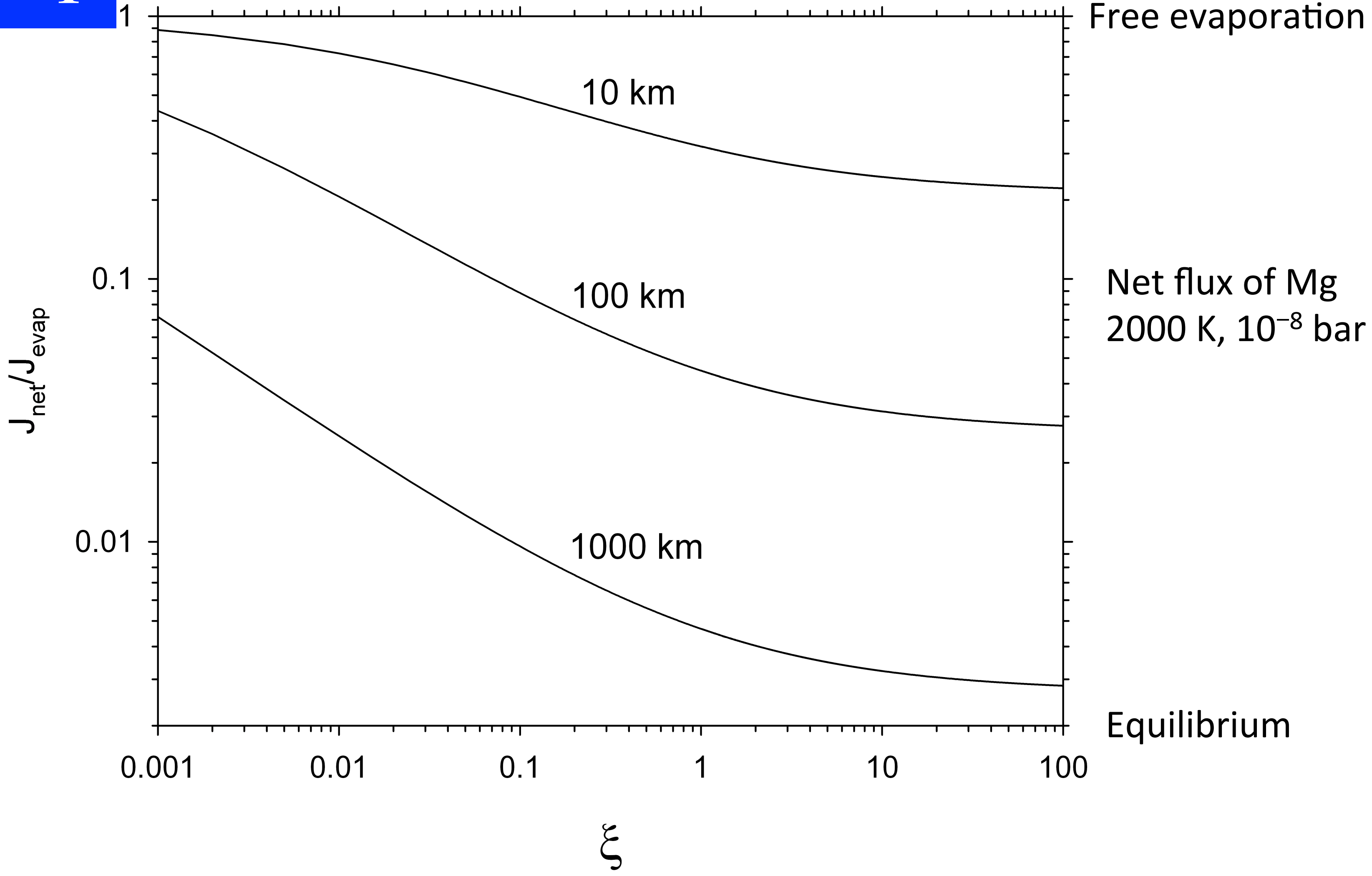
$S_i < 1$

$$J_{i,\mathrm{net}}/J_{i,\mathrm{evap}} = 1/(1+J_{i,\mathrm{return}}/J_{i,\mathrm{net}}).$$

$$J_{i,\,\mathrm{net}} = \frac{J_{i,\,\mathrm{evap}}}{1+\dfrac{\gamma_i RT}{\sqrt{2\pi m_i RT}}\dfrac{s}{D_i}\left[1-e^{\xi}\,\mathrm{erfc}\left(\sqrt{\xi}\right)\right]}$$

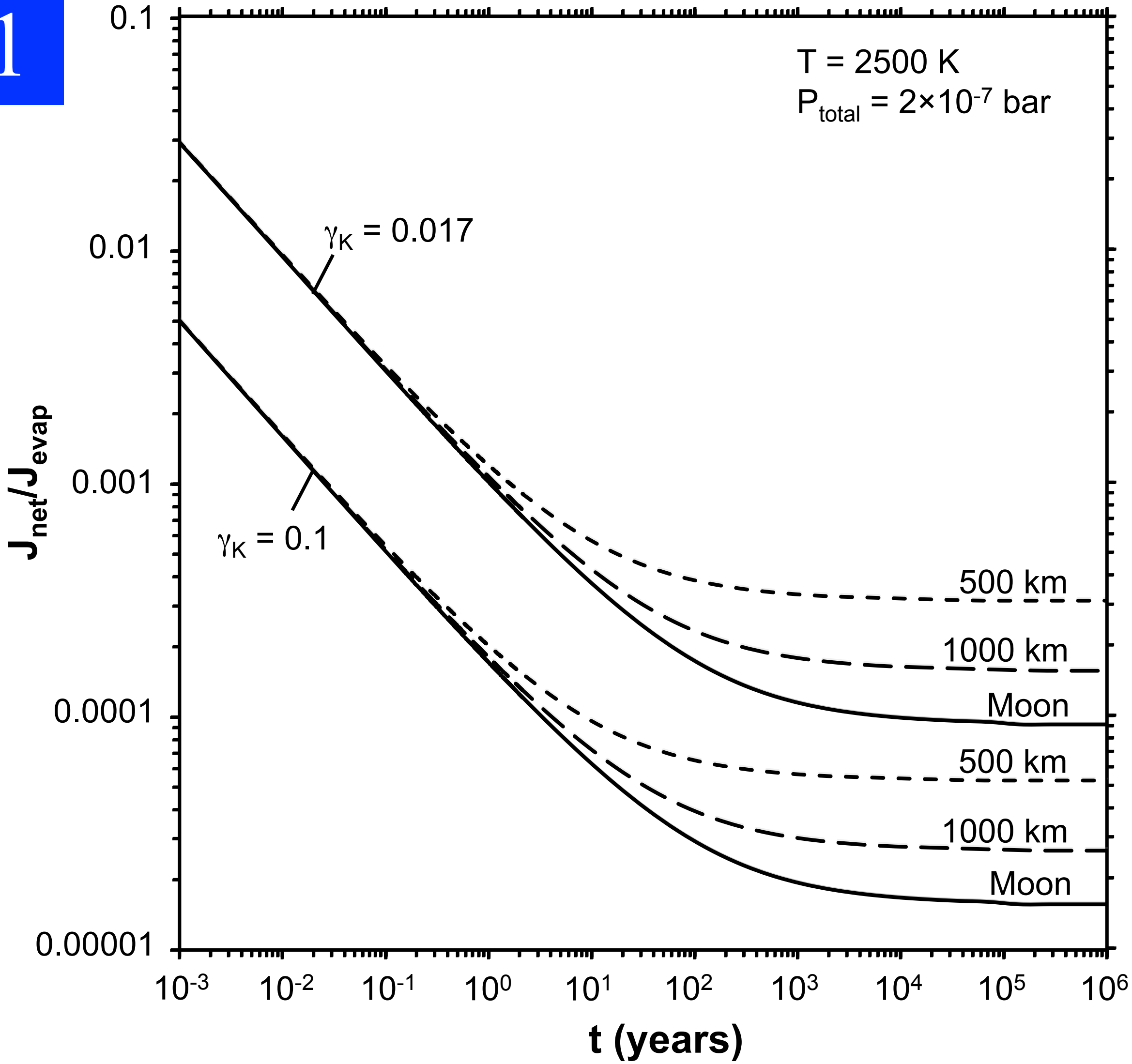
Evaporation

$S_i < 1$



Evaporation

$S_i < 1$



Net flux of K

Evaporation

$S_i < 1$

Net flux for the heavy isotope, including insertion:

$$\frac{J^{*\prime}_{i,\,\mathrm{net}}}{J_{i,\,\mathrm{evap}}} = \frac{1}{\left(1 + \alpha_{\mathrm{EQ}}\alpha_{\mathrm{EVAP}} J'_{i,\,\mathrm{return}} \,/\, J'_{i,\,\mathrm{net}}\right)}$$

Evaporation

$$S_i < 1$$

$$\alpha_{\text{net, evap}} = \frac{\left(\dfrac{J^{*\prime}_{i,\,\text{net}}}{J_{i,\,\text{net}}}\right)}{\left(\dfrac{n'_{i,\,\text{melt}}}{n_{i,\,\text{melt}}}\right)} = \alpha_{\text{EVAP}} \frac{1 + \dfrac{\gamma_i RT}{\sqrt{2\pi m_i RT}} \dfrac{s}{D_i}\left[1 - e^{\xi}\,\text{erfc}\left(\sqrt{\xi}\right)\right]}{1 + \dfrac{\alpha_{\text{EQ}}\alpha_{\text{EVAP}}\gamma_i RT}{\sqrt{2\pi m_i{}' RT}} \dfrac{s}{D_i{}'}\left[1 - e^{\xi'}\,\text{erfc}\left(\sqrt{\xi'}\right)\right]}$$

Evaporation

$S_i < 1$

In the limit of a high return flux, $J^{*\prime}_{i,\text{net}}/J_{i,\text{net}}$:

$$\alpha_{\text{net, evap}} = (n'_{i,\,\text{melt}} / n_{i,\,\text{melt}})\alpha_{\text{EVAP}}\sqrt{\mu' / \mu}\sqrt{\mu / \mu'} / (\alpha_{\text{EQ}}\alpha_{\text{EVAP}})$$

$$= (n'_{i,\,\text{melt}} / n_{i,\,\text{melt}}) / \alpha_{\text{EQ}}$$

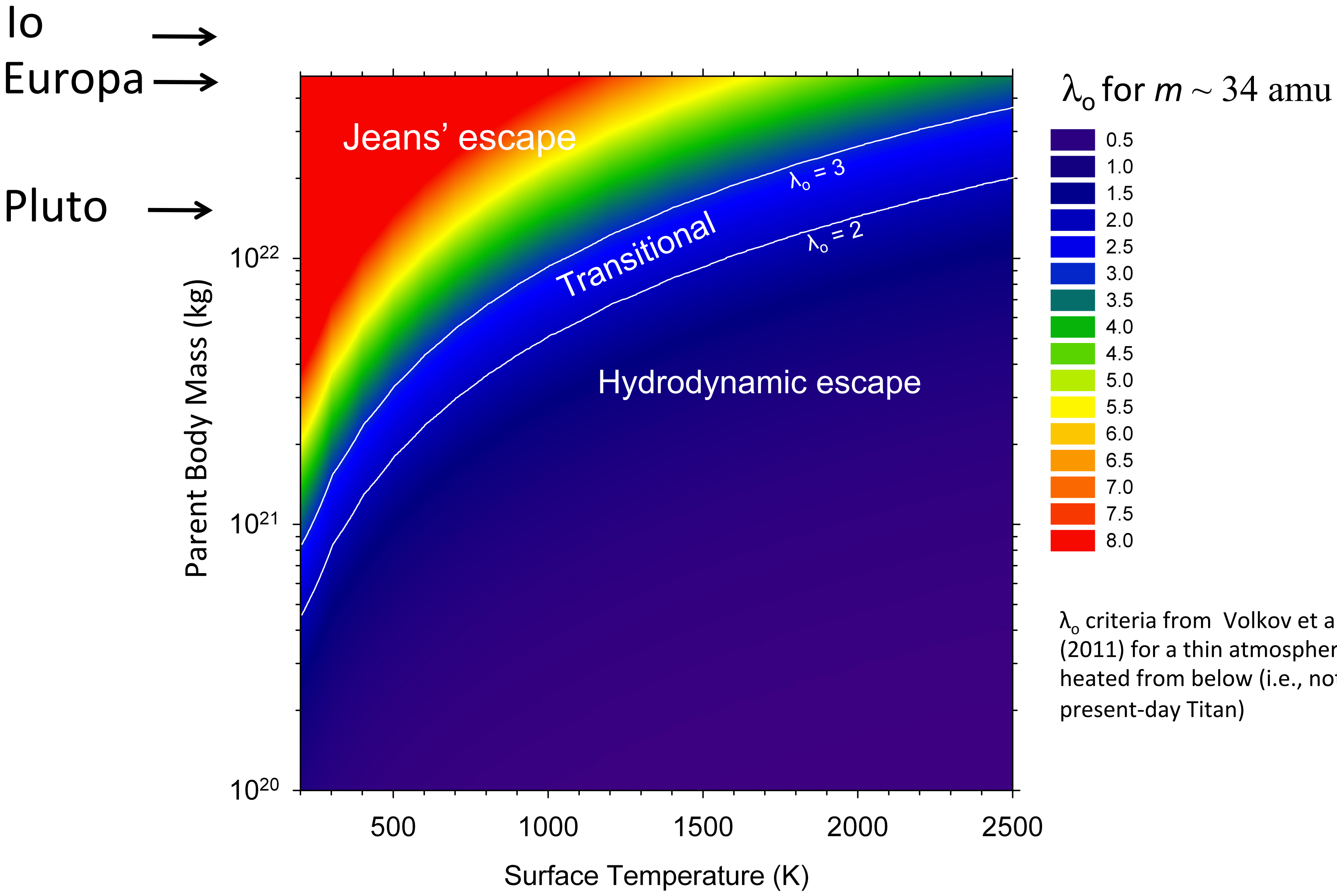
Escape

Escape mechanisms:

Escape parameter:
Gravitational energy/thermal energy

$$\lambda = \frac{G\,M\,m_{\mathrm{gas}}\,/\,r}{k_{\mathrm{b}}T(r)}$$

Escape



λ_o criteria from Volkov et al. (2011) for a thin atmosphere heated from below (i.e., not present-day Titan)

Escape

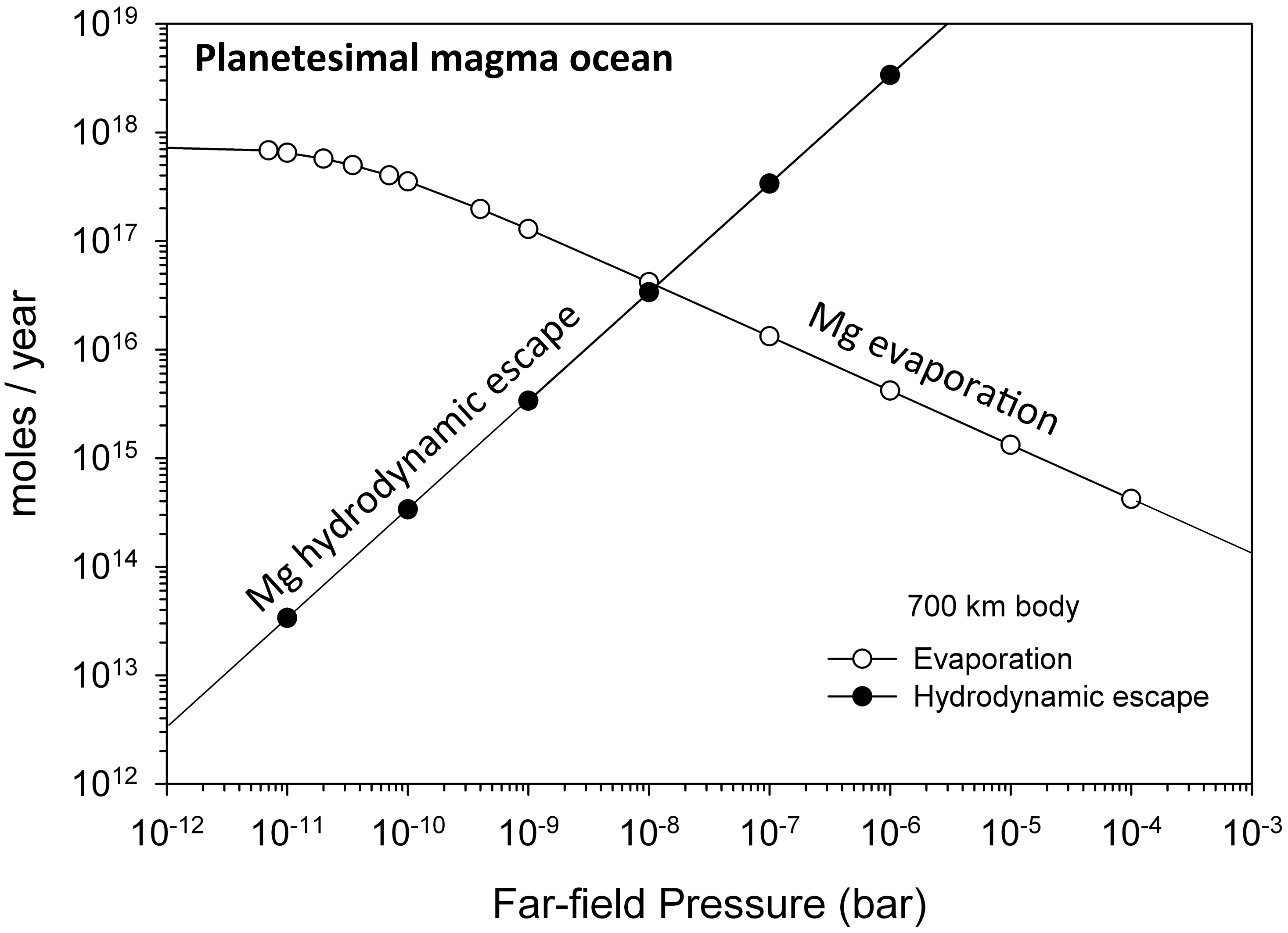
Steady-state atmospheres: surface-integrated fluxes

$$\theta_{\mathrm{hydro}} = 4\pi r_{\mathrm{B}}^{2} C_{\mathrm{S}}(r_{\mathrm{B}}) \left(\frac{P(r_{\mathrm{B}})}{k_{\mathrm{b}} T} \right)$$

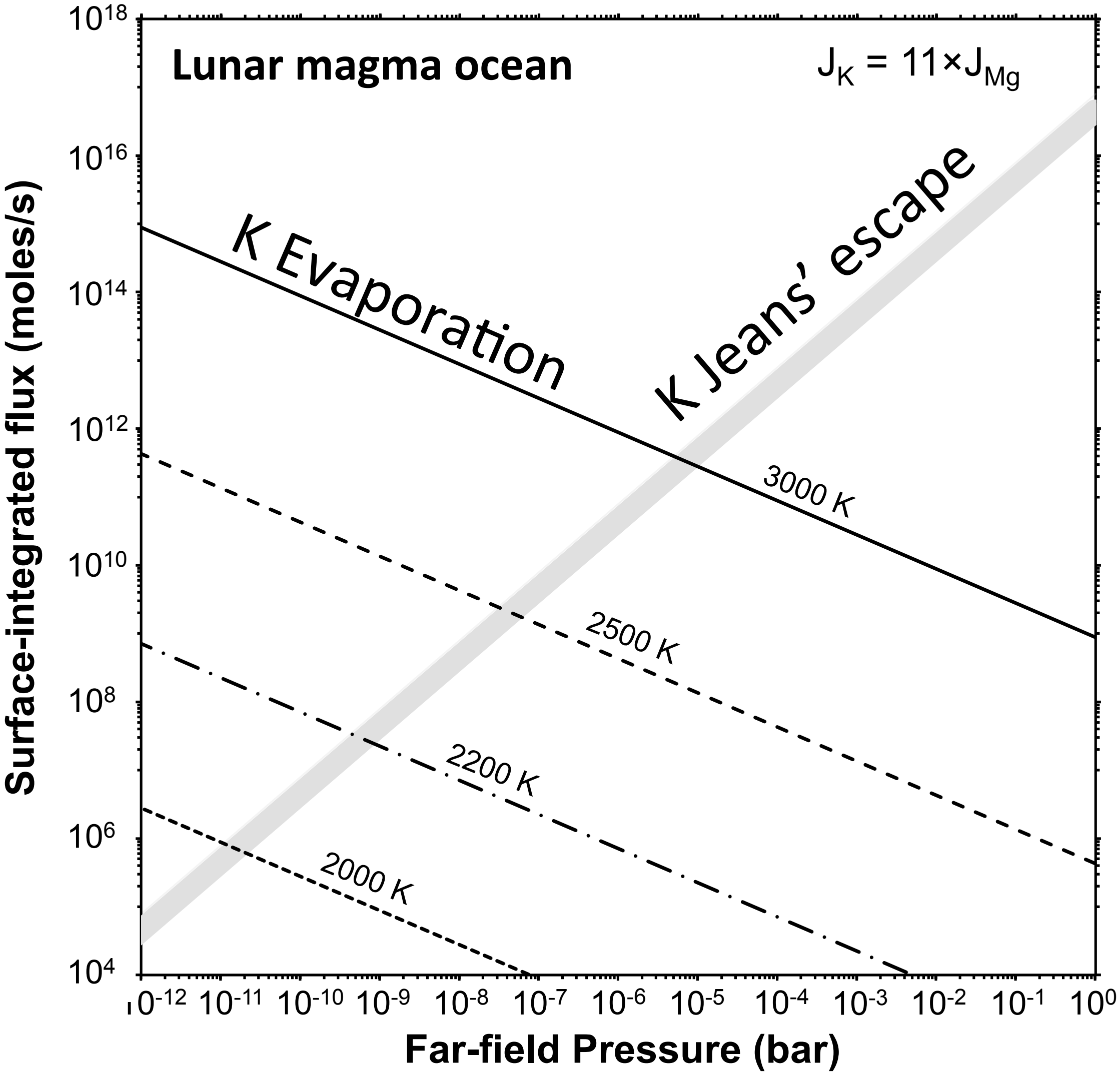
$$\theta_{\mathrm{Jeans'}} = 4\pi r_{\mathrm{Ex}}^{2} \omega_{J} n_{\mathrm{Ex}}$$

$$\omega_{J} = \frac{1}{2\sqrt{\pi}} (1 + \lambda(r_{\mathrm{Ex}}))\ \exp\left(-\lambda(r_{\mathrm{Ex}})\right) \sqrt{\frac{2 k_{\mathrm{b}} T_{\mathrm{Ex}}}{m_{\mathrm{gas}}}}$$

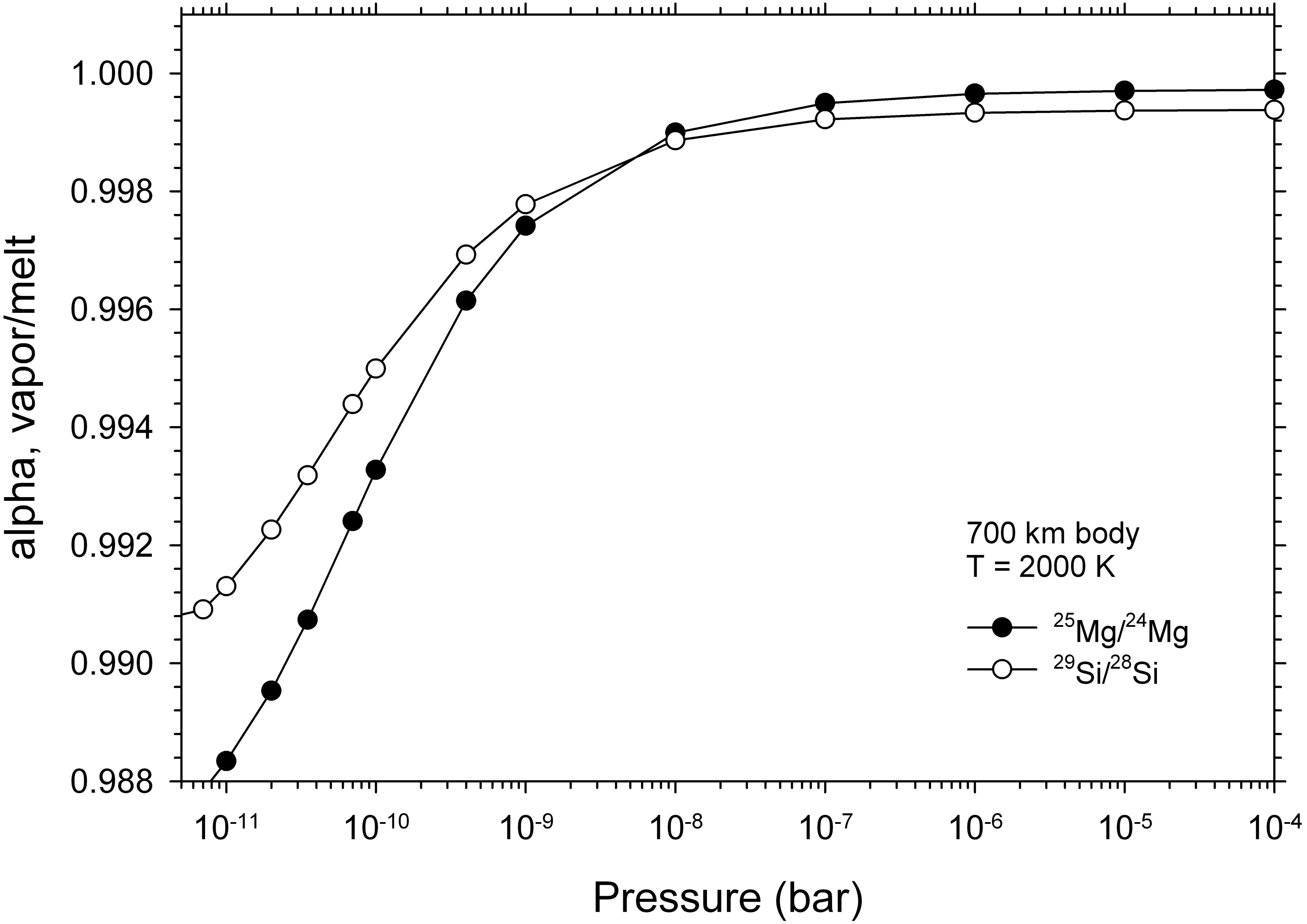
Steady-state



Steady-state

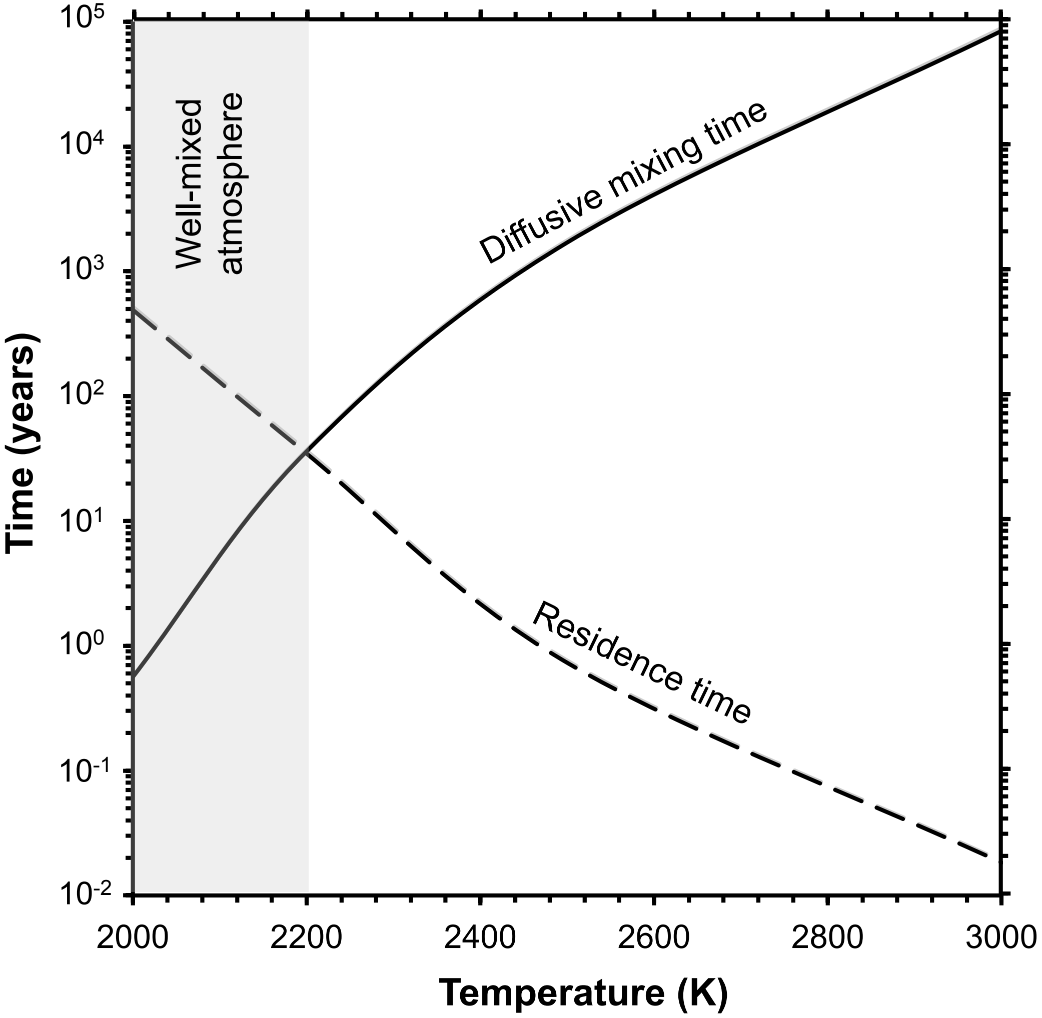


Steady-state



Exchange with atmosphere

Example: K isotopes, proto-Moon



Exchange with atmosphere

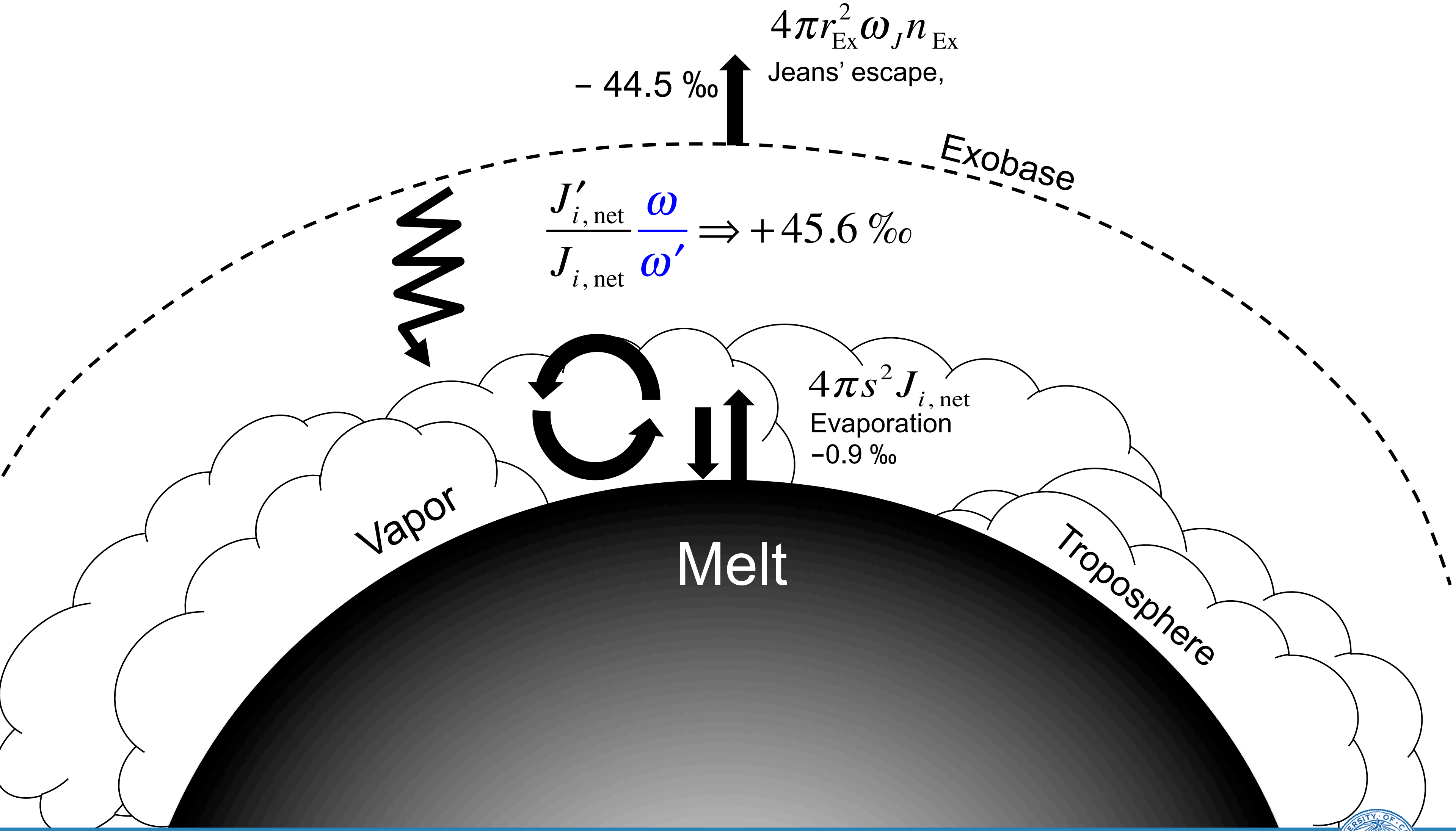
Steady-state atmosphere isotopic composition: Jeans' escape

$$\frac{dN_{i,\,\mathrm{gas}}}{dt} = 4\pi s^2 J_{i,\,\mathrm{net}} - 4\pi r_{\mathrm{Ex}}^2 \omega_J n_{\ i,\,\mathrm{Ex}} = 0$$

$$\left(\frac{n'_{i,\,\mathrm{gas}}}{n_{i,\,\mathrm{gas}}}\right)_{t=\infty} = \frac{J'_{i,\,\mathrm{net}}}{J_{i,\,\mathrm{net}}}\,\frac{\omega}{\omega'}$$

Exchange with atmosphere

Example: Mg isotopes, evaporating planetesimal



$4\pi r_{\mathrm{Ex}}^2 \omega_J n_{\mathrm{Ex}}$

Jeans' escape,

– 44.5 ‰

Exobase

$$\frac{J'_{i,\mathrm{net}}}{J_{i,\mathrm{net}}} \frac{\omega}{\omega'} \Rightarrow +45.6 \text{‰}$$

$4\pi s^2 J_{i,\mathrm{net}}$

Evaporation

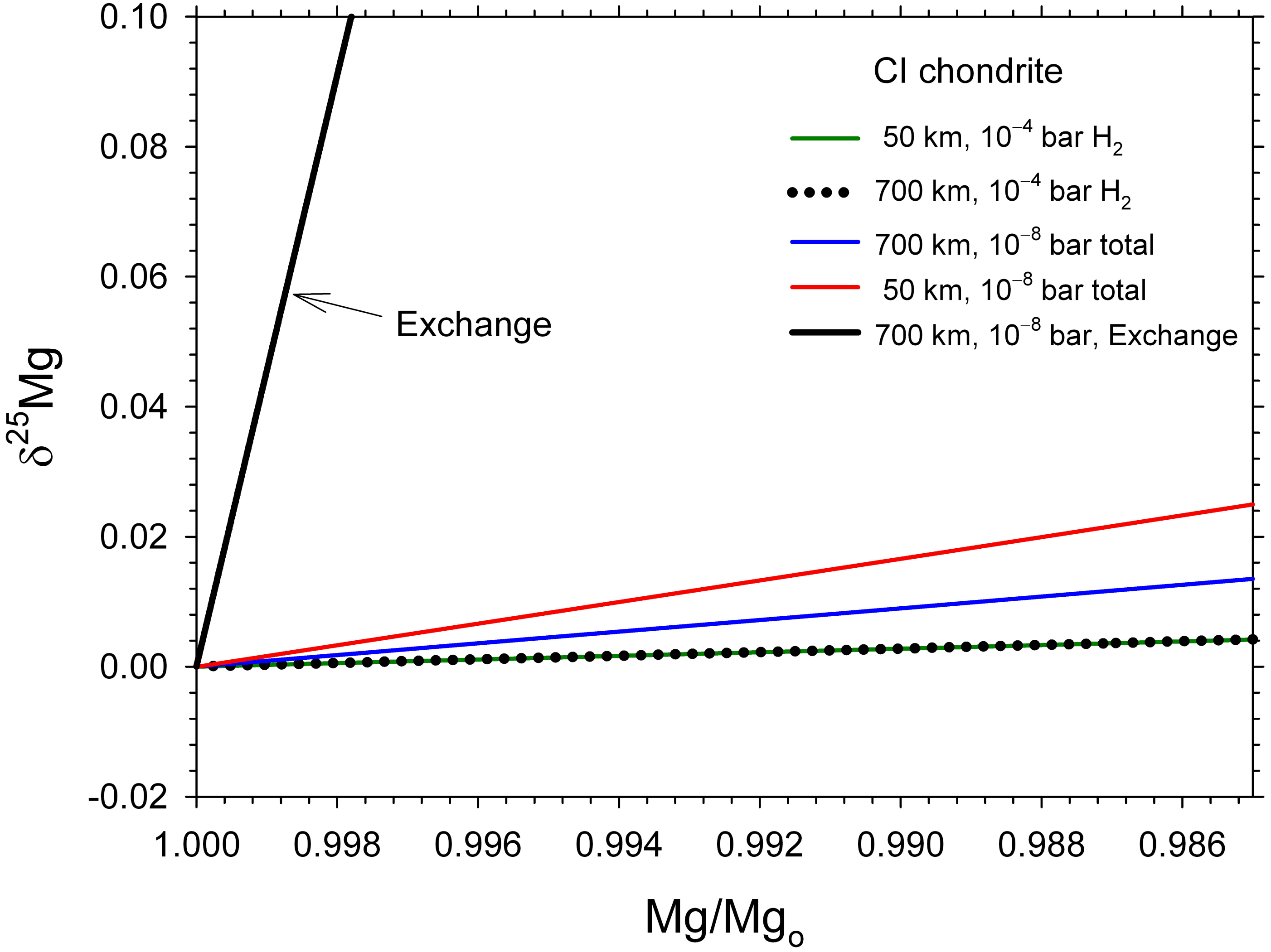
−0.9 ‰

Vapor

Melt

Troposphere

Exchange with atmosphere



Exchange with atmosphere

Hydrodynamic escape for ½ M_{Pluto} body: Bondi radius, $C_s = V_{esc}$

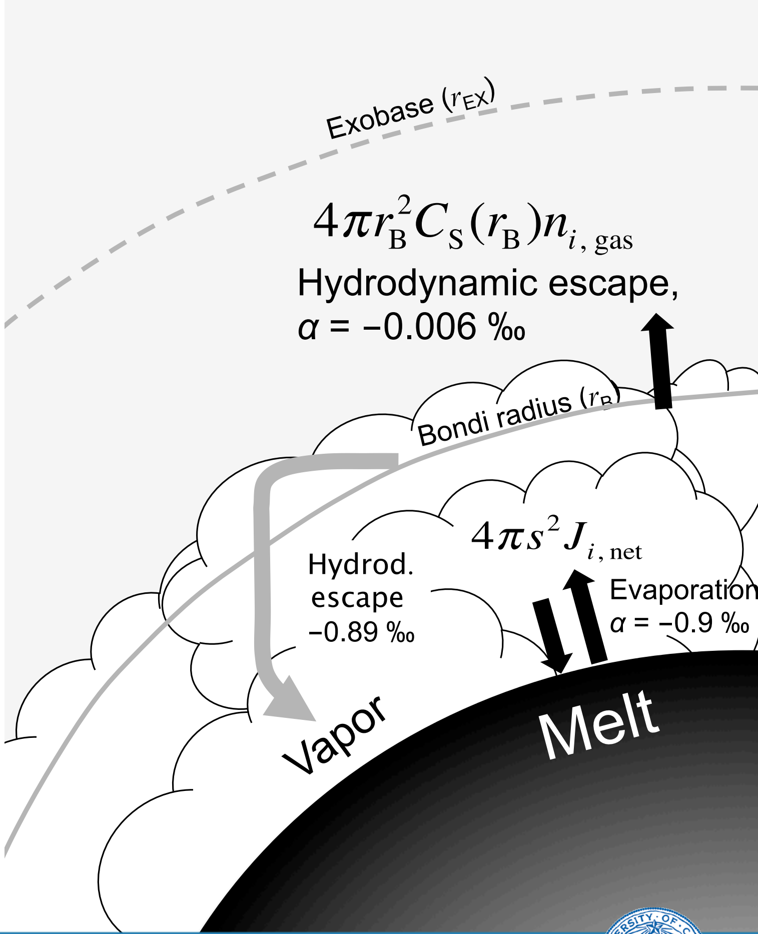
$$\frac{dN_{i,\text{gas}}}{dt} = 4\pi s^2 J_{i,\text{net}} - 4\pi r_B^2 C_S(r_B) n_{i,\text{gas}} = 0$$

$$\left(\frac{n'_{i,\text{gas}}}{n_{i,\text{gas}}}\right)_{t=\infty} = \frac{J'_{i,\text{net}}}{J_{i,\text{net}}} \frac{C_S(r_B)}{C'_S(r_B)}$$

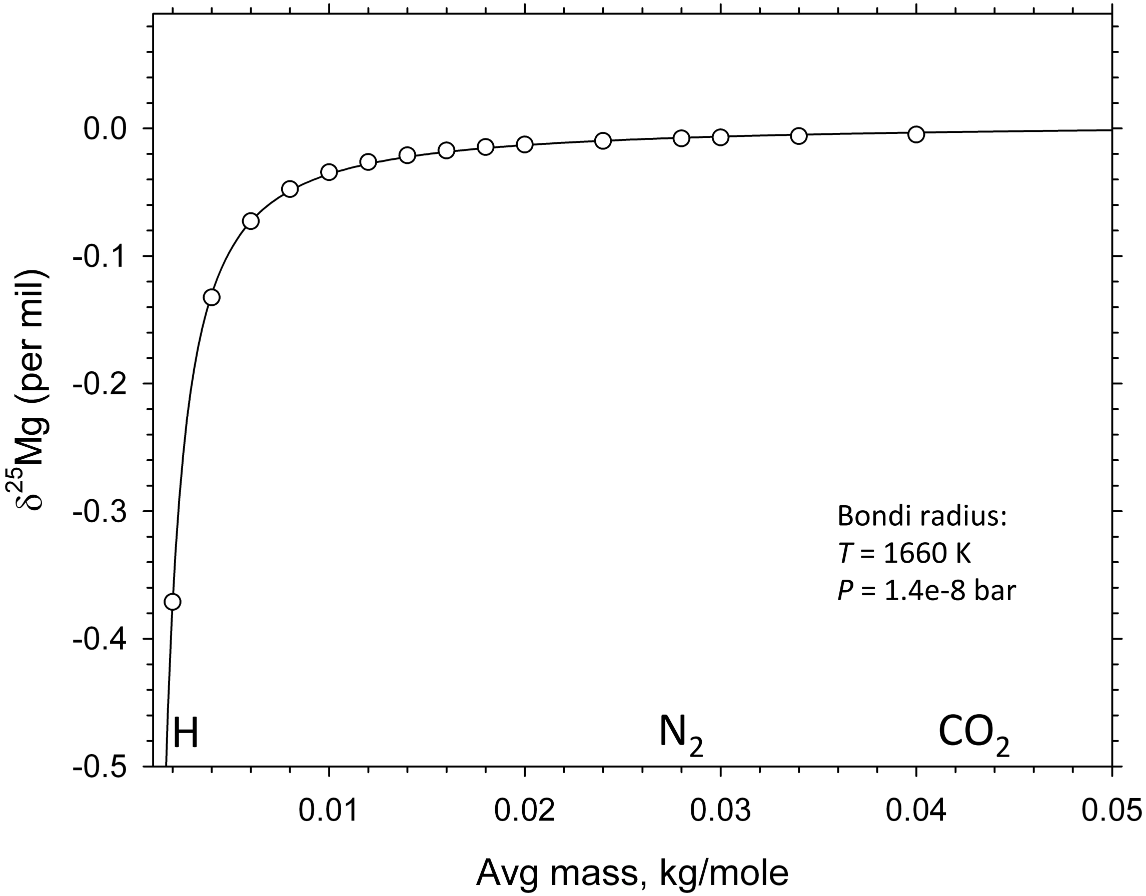
Fractionation factor relative to average mass, e.g. Zahnle and Kasting (1986):

$$\alpha_{\text{hydro}} \sim 1 - \frac{GM(m_i - m_{\text{Avg}})D_i n_{\text{Gas}}}{(C_S(r_B)n_{\text{Gas}})r_B{}^2 k_b T}$$

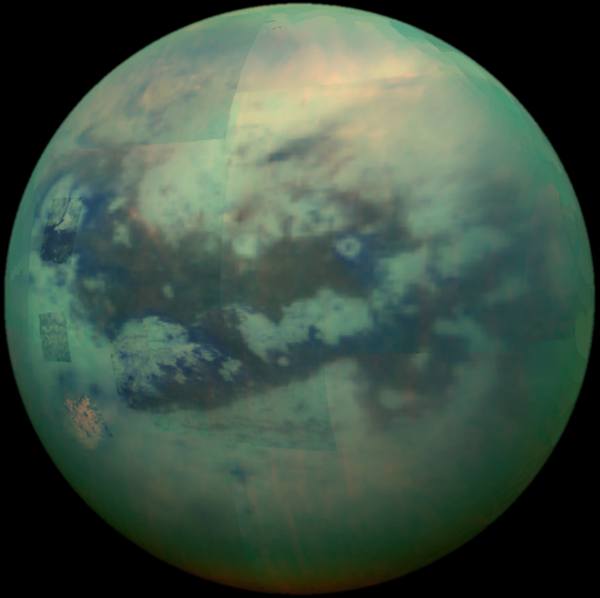
$\sim$ −0.006 ‰ for ^{25}Mg/^{24}Mg in a rock-vapor atmosphere

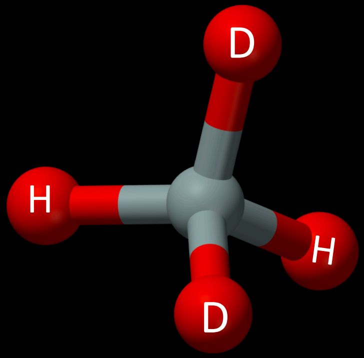


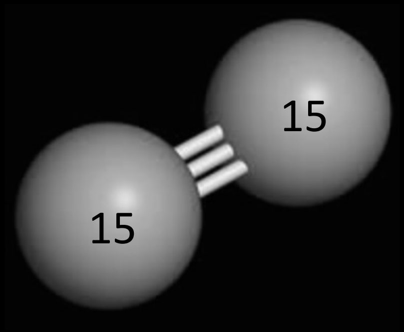
Hydrodynamic escape for ½ M_{Pluto} body: Bondi radius, C_s = V_{esc}

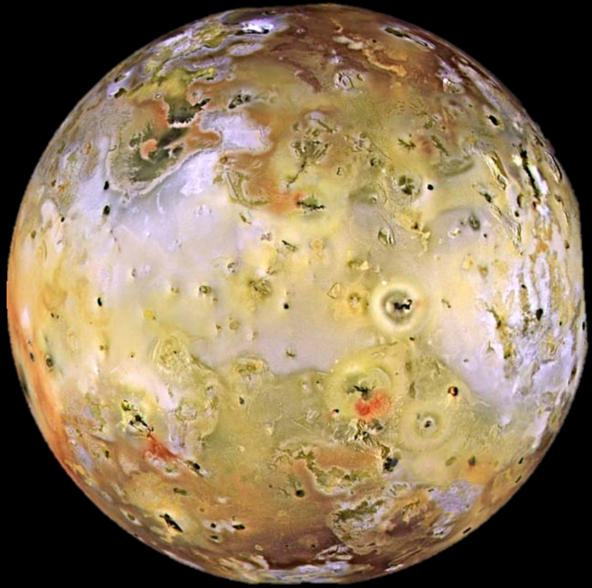


Multiply-substituted isotopologues



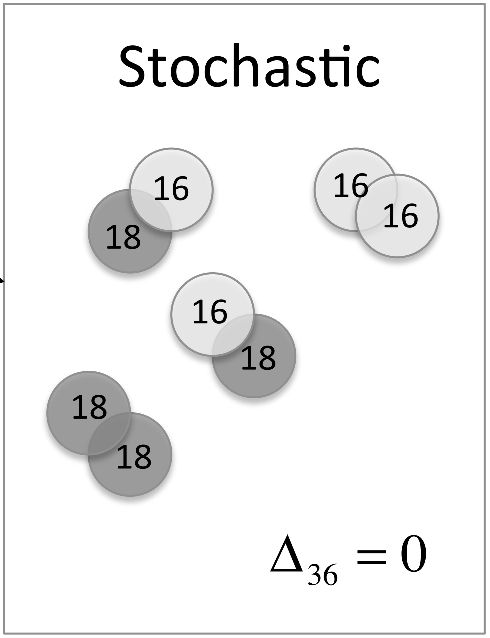






Multiply-substituted isotopologue abundances

4 ^{16}O atoms,
4 ^{18}O atoms



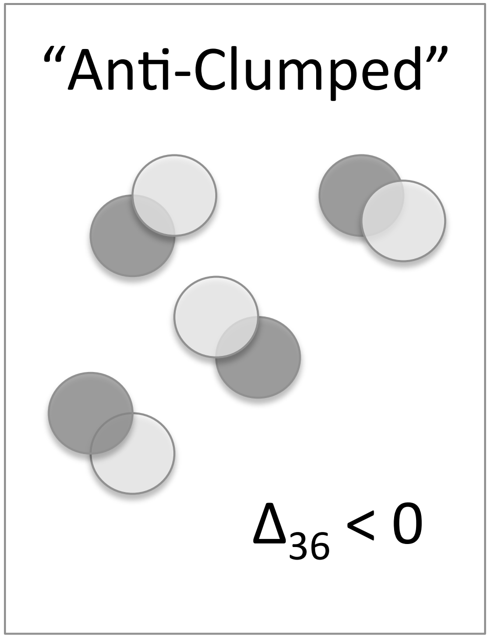
$$\Delta_{36} = 0$$

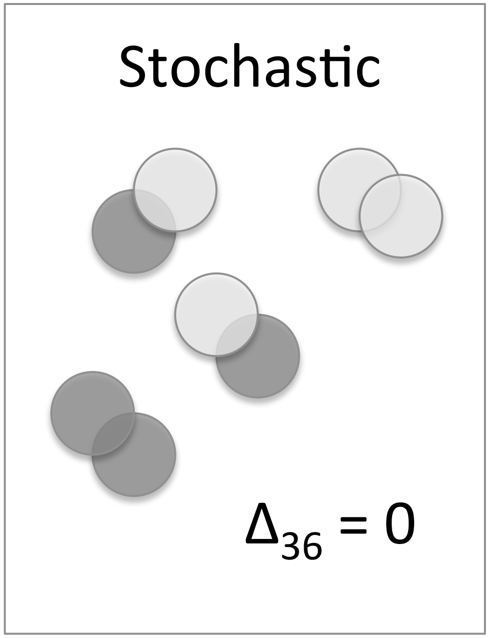
Fractional number of ^{18}O-^{18}O bonds

$$\Delta_{36} = 10^3\left(\frac{1/4 - 1/4}{1/4}\right) = 0$$

$$\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$$

Multiply-substituted isotopologue abundances



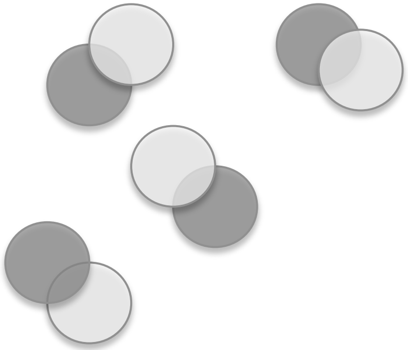


$$\Delta_{36} = 10^3\left(\frac{0 - 1/4}{1/4}\right) = -1{,}000$$

$$\Delta_{36} = 10^3\left(\frac{1/4 - 1/4}{1/4}\right) = 0$$

Multiply-substituted isotopologue abundances

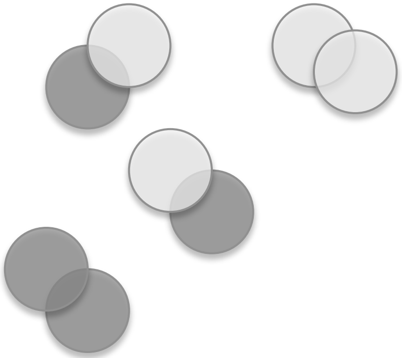
“Anti-Clumped”



$\Delta_{36} < 0$

$$\Delta_{36} = 10^3\left(\frac{0 - 1/4}{1/4}\right) = -1{,}000$$

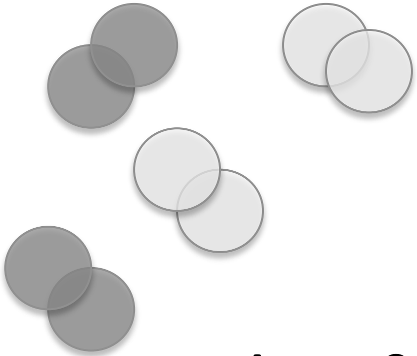
Stochastic



$\Delta_{36} = 0$

$$\Delta_{36} = 10^3\left(\frac{1/4 - 1/4}{1/4}\right) = 0$$

“Clumped”

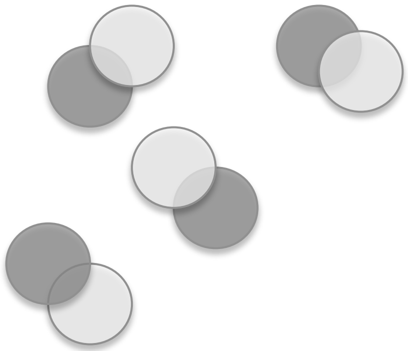


$\Delta_{36} > 0$

$$\Delta_{36} = 10^3\left(\frac{1/2 - 1/4}{1/4}\right) = +1{,}000$$

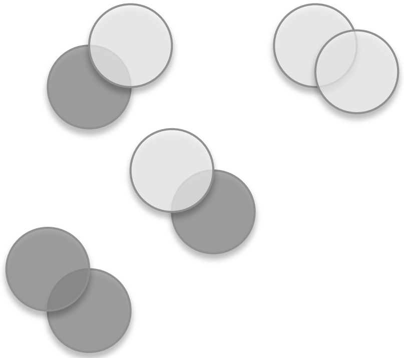
Multiply-substituted isotopologue abundances

“Anti-Clumped”



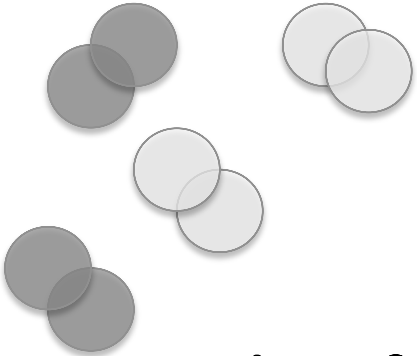
$\Delta_{36} < 0$

Stochastic



$\Delta_{36} = 0$

“Clumped”



$\Delta_{36} > 0$

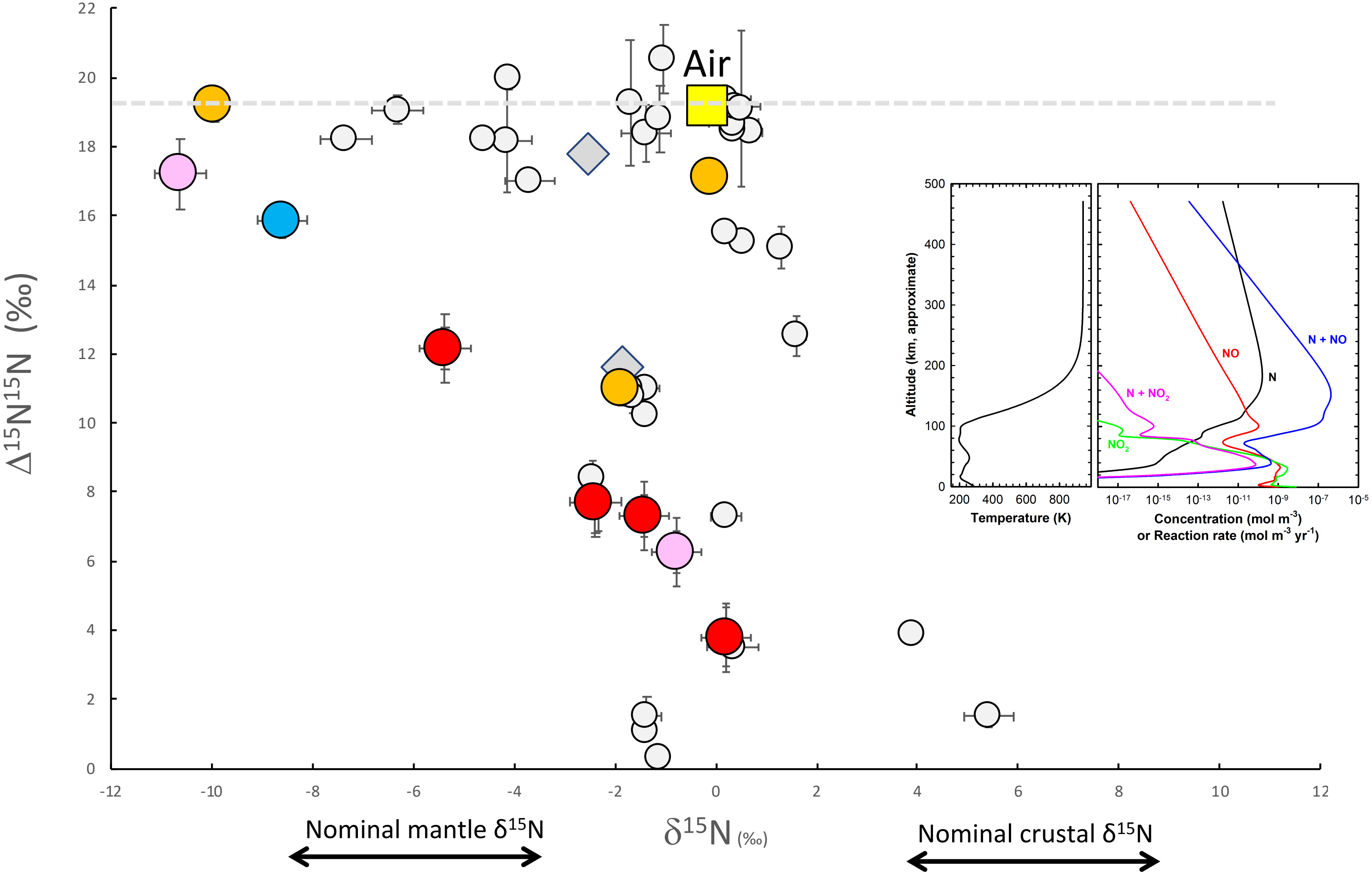
$$\Delta_{36} = 10^3\left(\frac{0 - 1/4}{1/4}\right) = -1{,}000$$

$$\Delta_{36} = 10^3\left(\frac{1/4 - 1/4}{1/4}\right) = 0$$

$$\Delta_{36} = 10^3\left(\frac{1/2 - 1/4}{1/4}\right) = +1{,}000$$

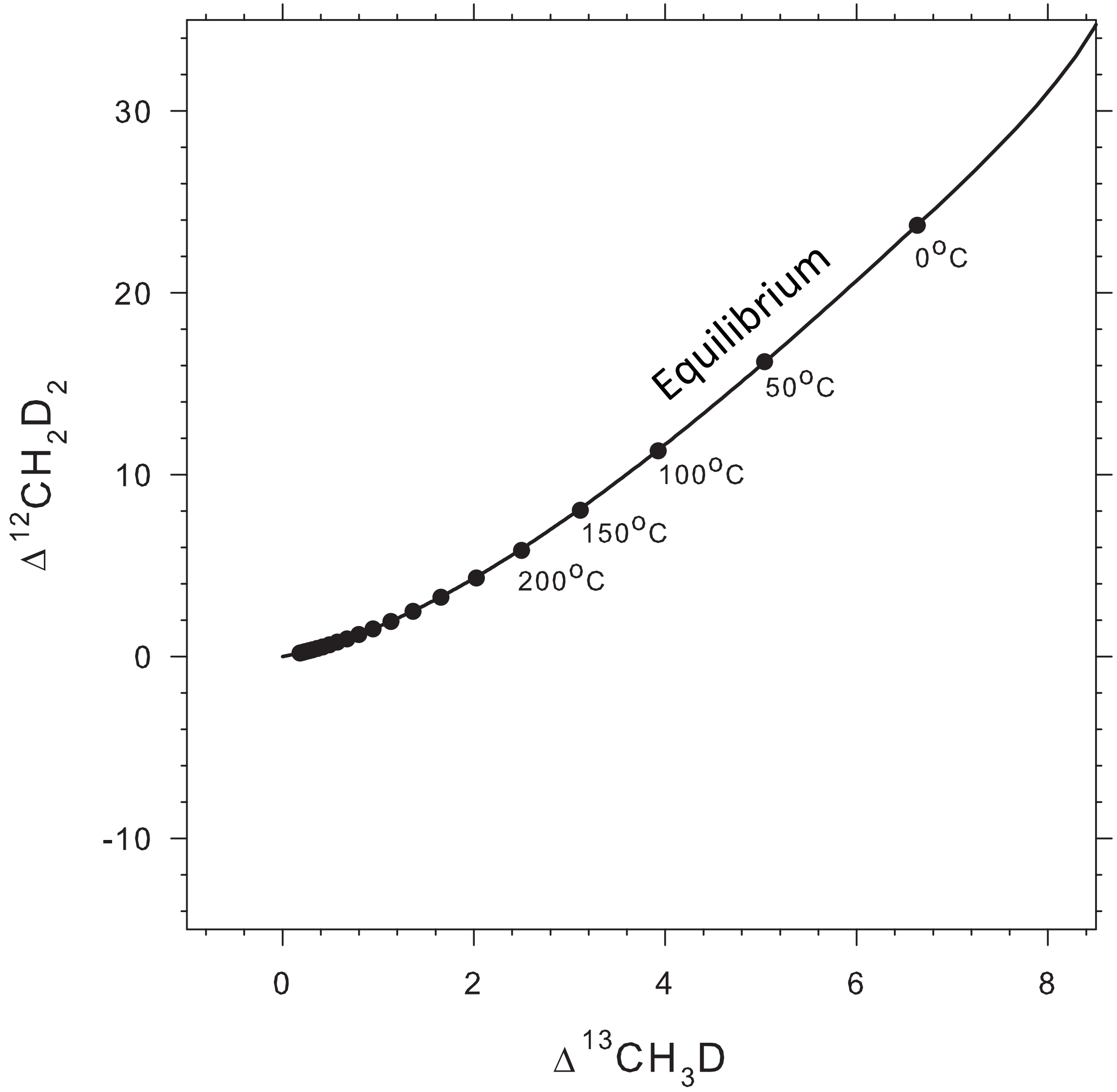
Multiply-substituted isotopologue abundances

$^{15}N^{15}N$



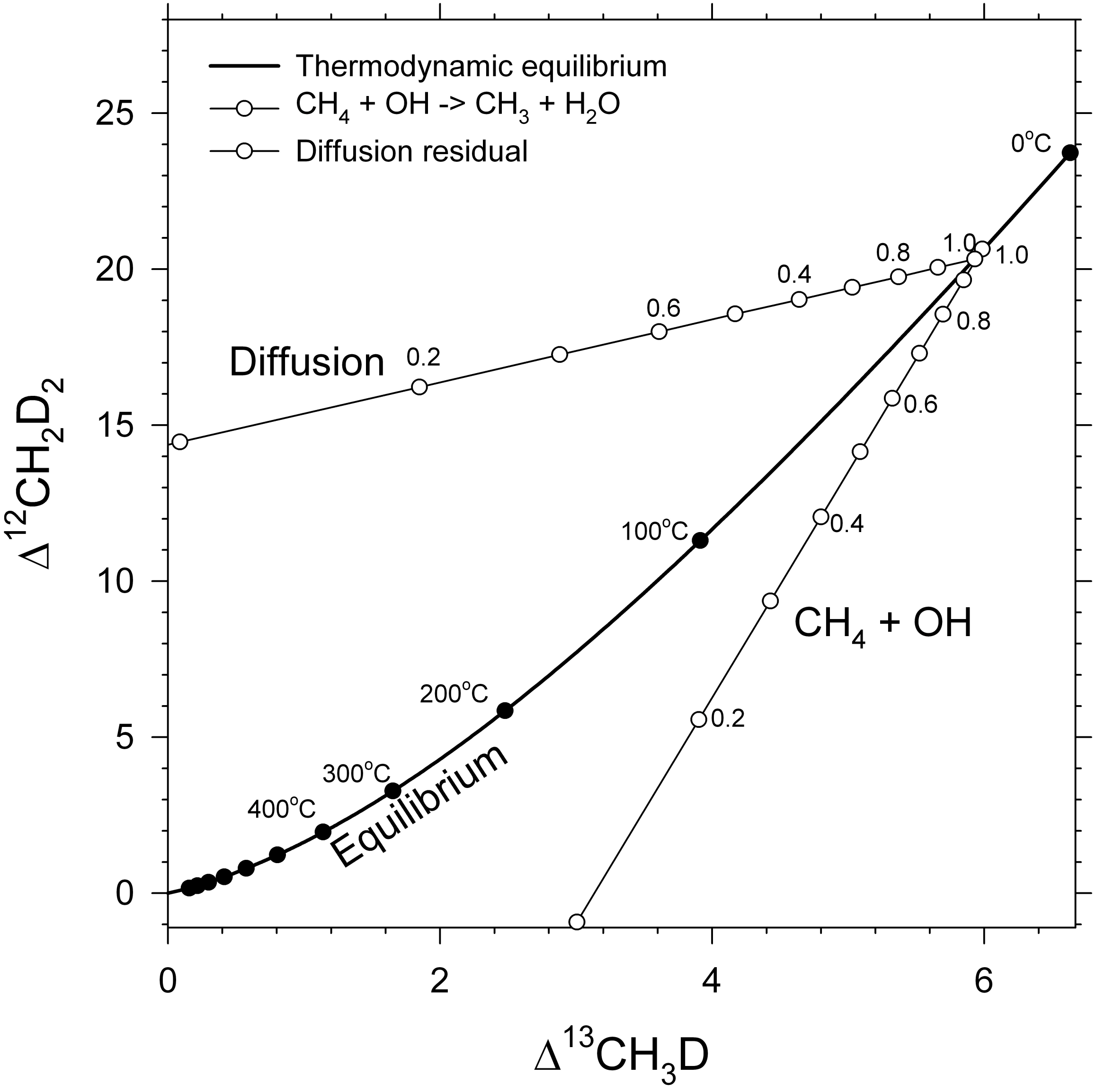
Multiply-substituted isotopologue abundances

CH_4



Multiply-substituted isotopologue abundances

CH_4

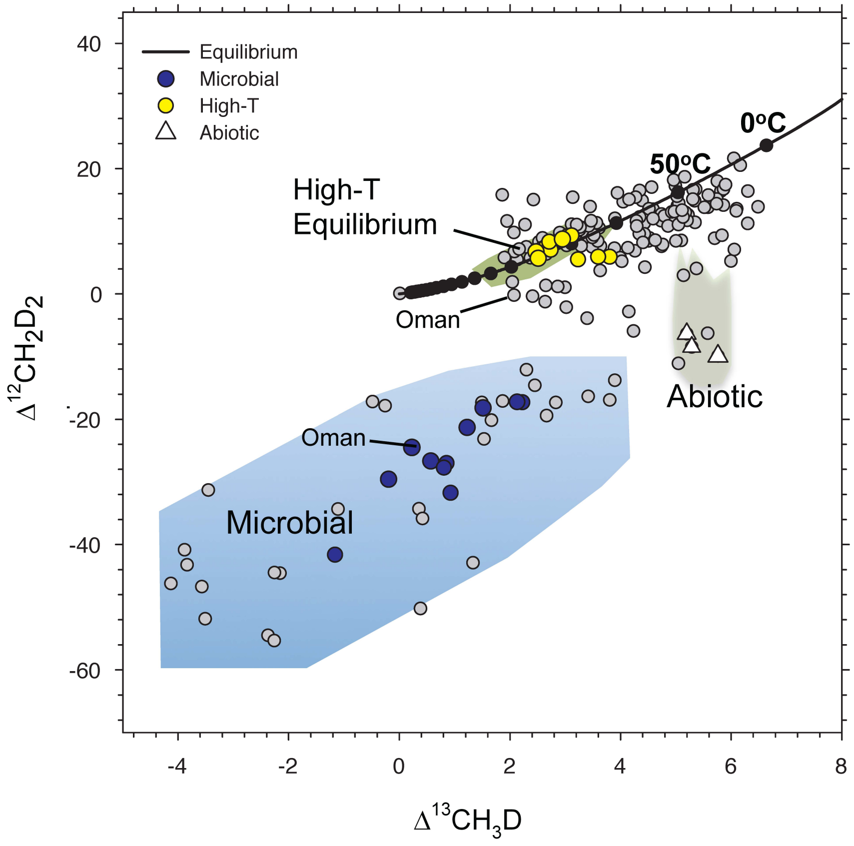


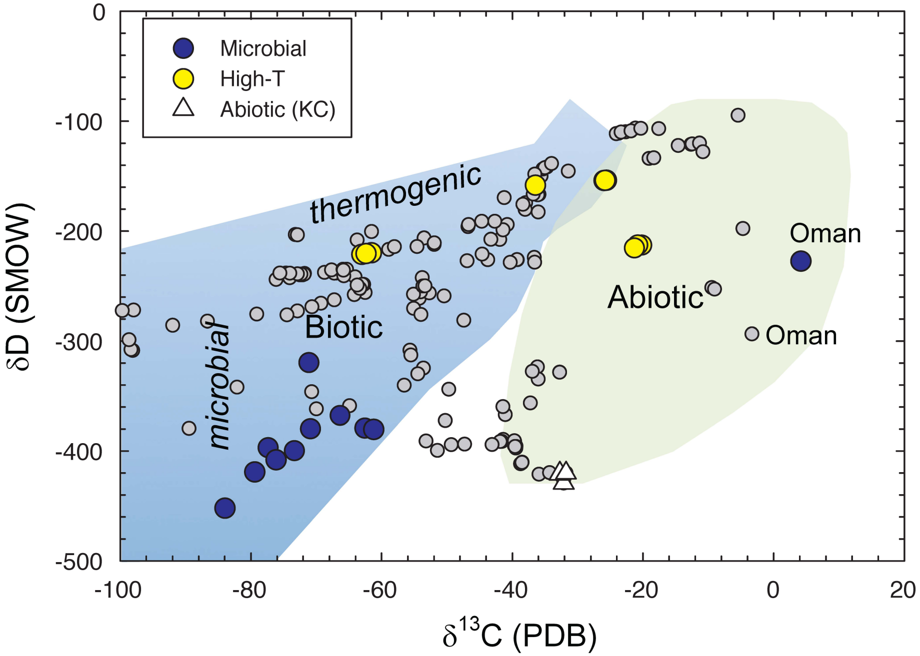
Multiply-substituted isotopologue abundances

CH_4

Process

Source + Process





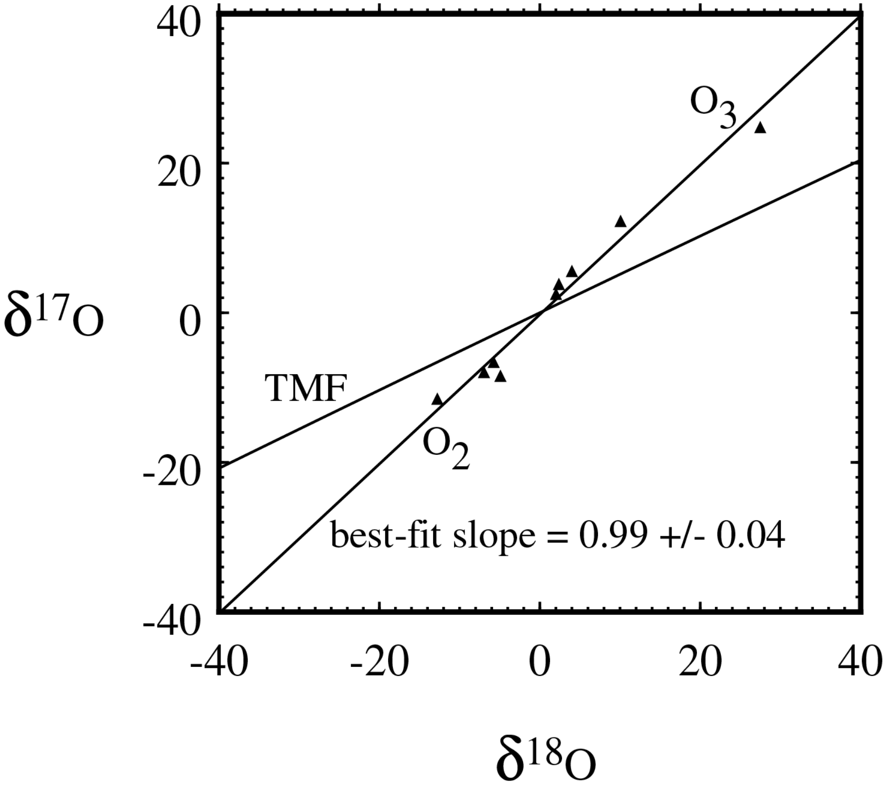
Photochemistry

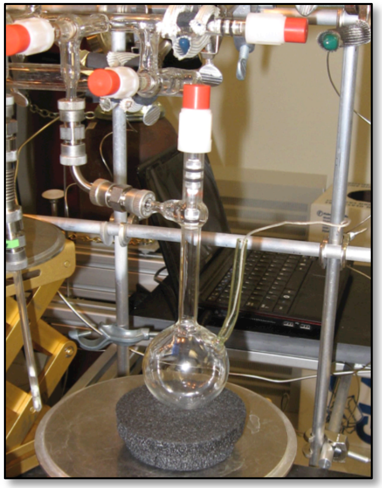
Intramolecular disequilibrium (Non-RRKM) effects

MIF Mass-independent fractionation (MIF)

Thiemens and others, since 1983

$O + O_2 = O_3$ (electrical discharge)





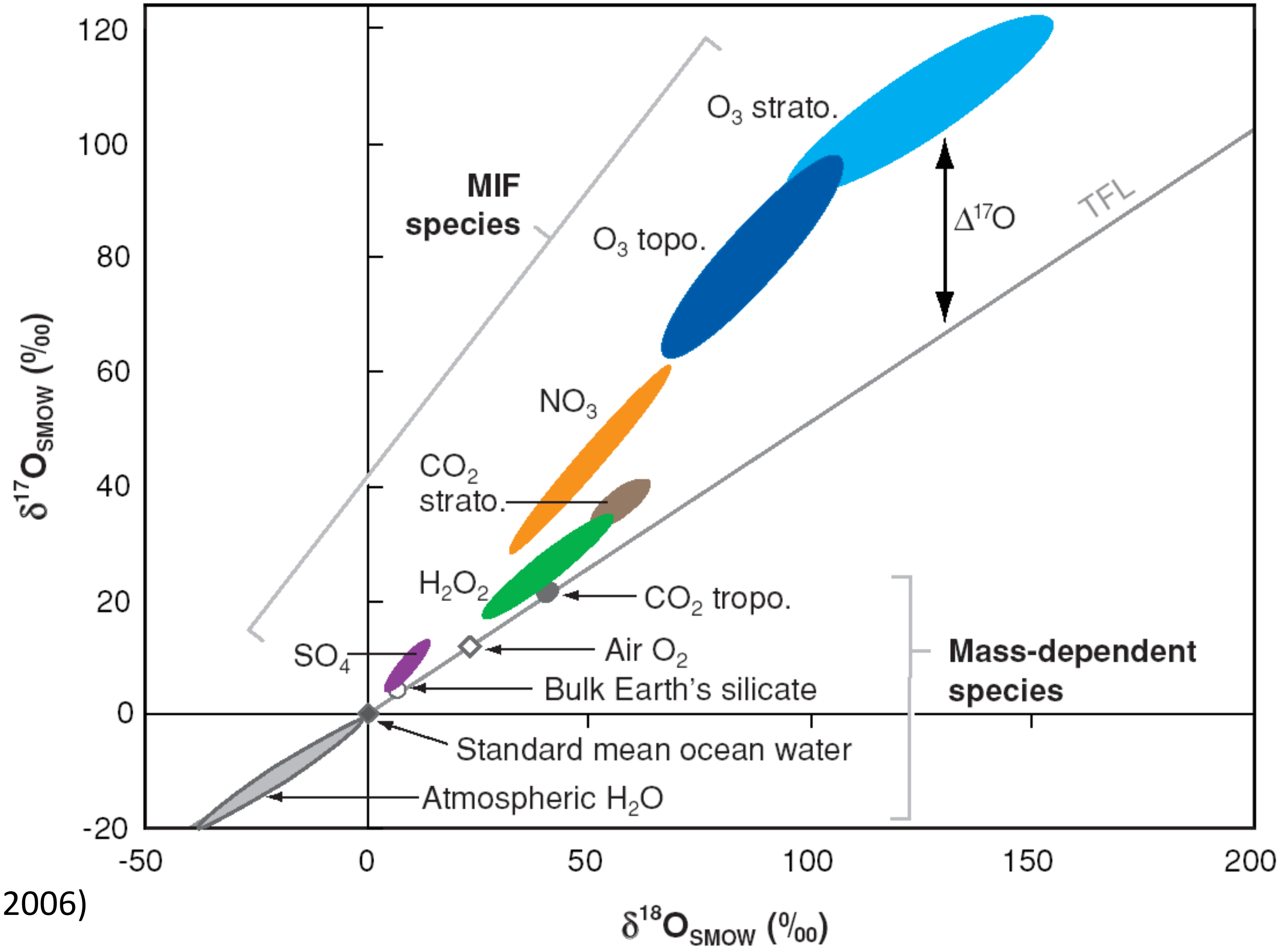
(Young and Hoering, unpub. data 1993)

P^O= 44-101 torr

Intramolecular disequilibrium (Non-RRKM) effects

MIF

Mass-independent fractionation (MIF)



Thiemens (2006)

Intramolecular disequilibrium (Non-RRKM) effects

MIF

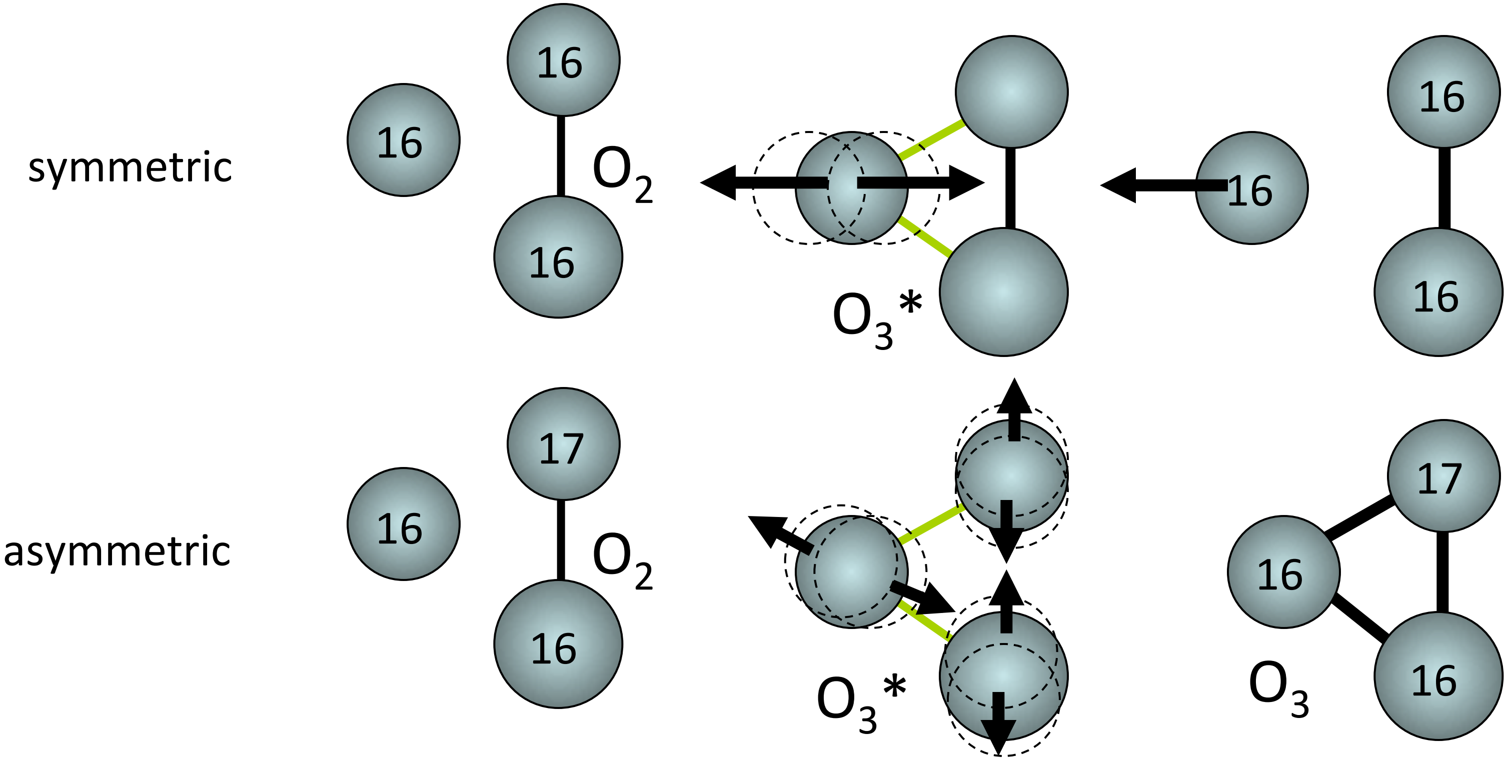
Mass-independent fractionation (MIF)

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)



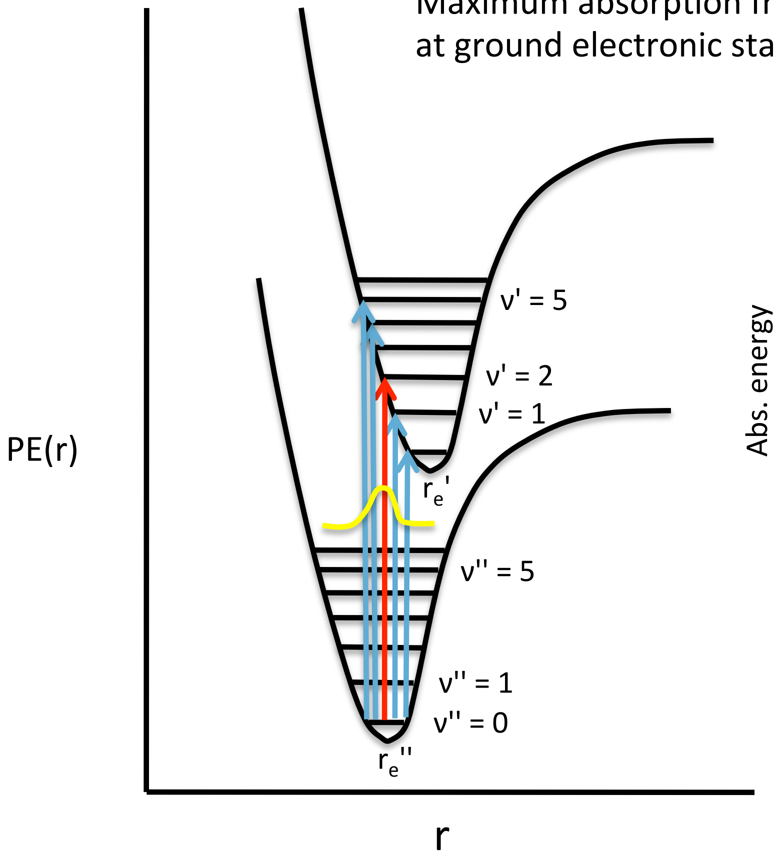
Photochemistry

Absorption

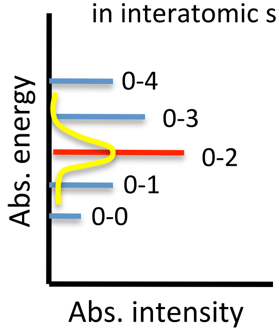
$$E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$$

Frank-Condon Principle for Vibronic Transitions

Electronic transition faster than vibrational motion

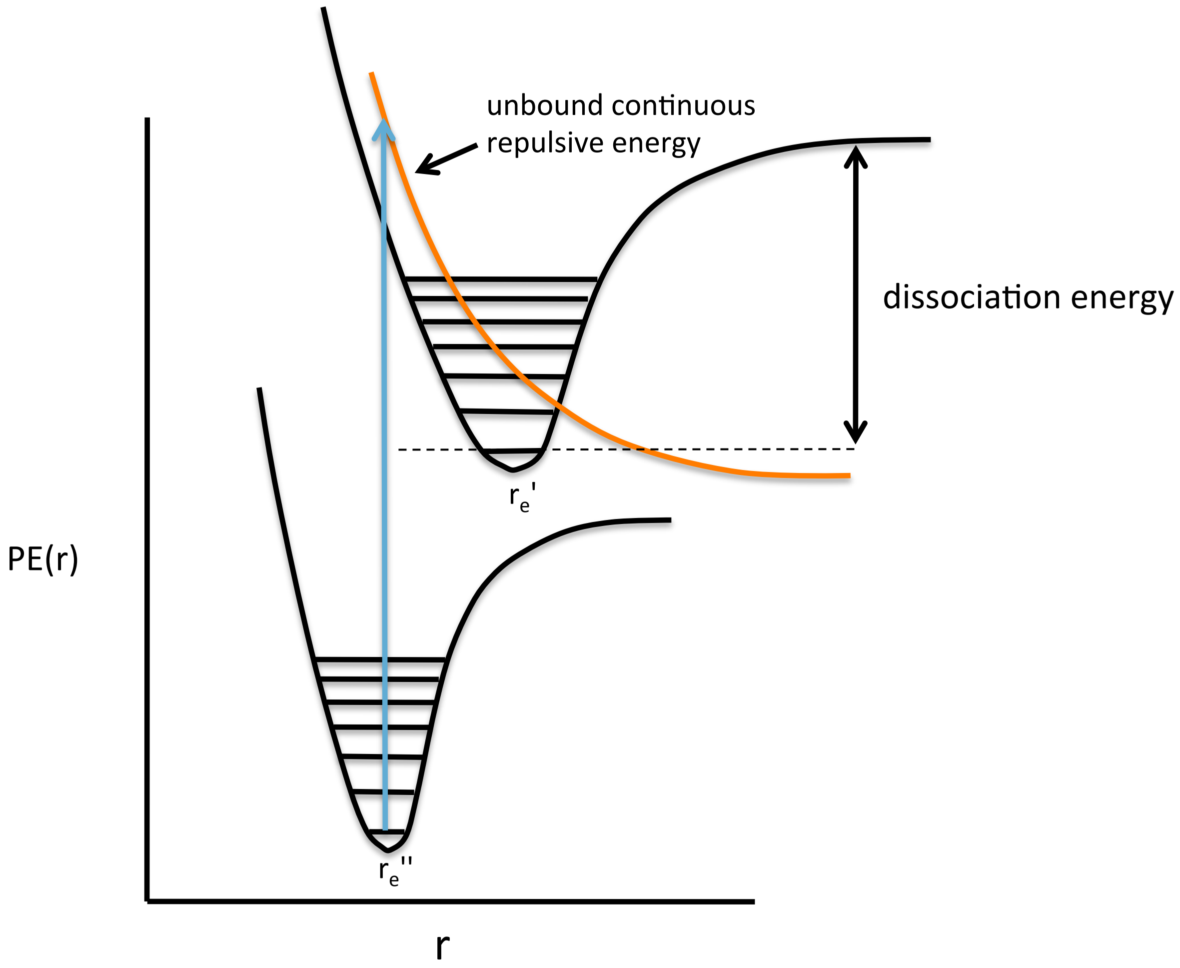


Maximum absorption from bottom of energy well at ground electronic state



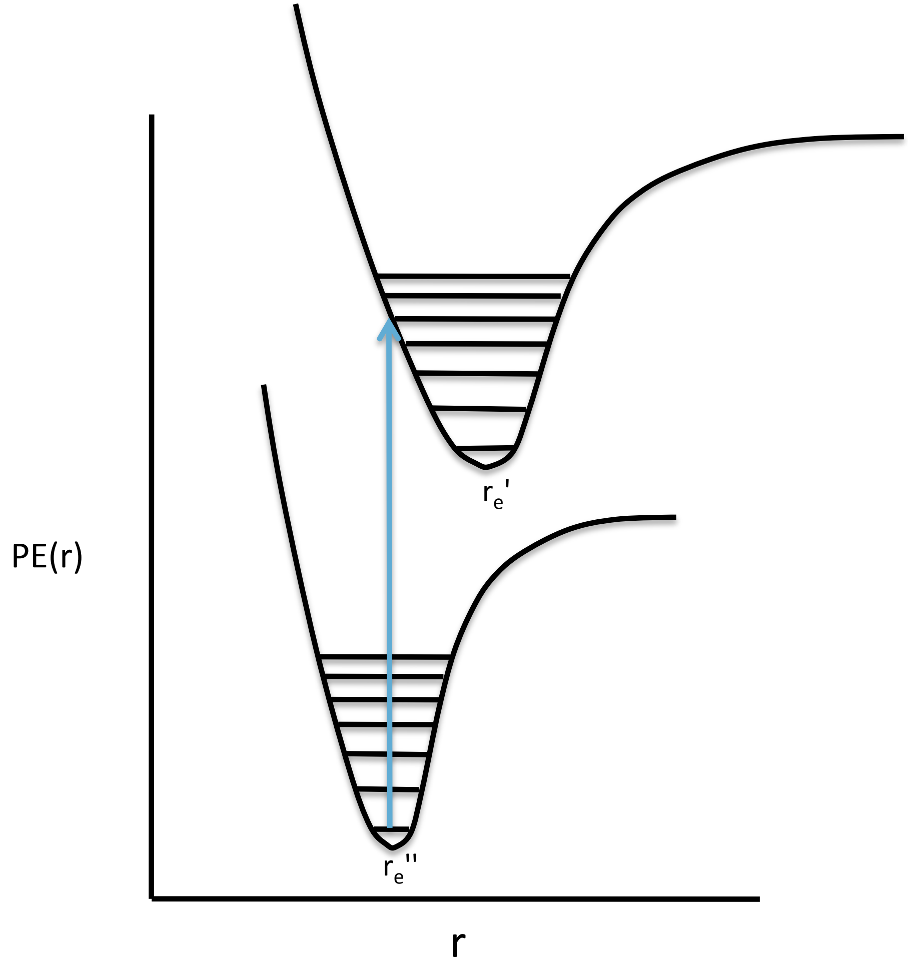
Peak in absorption depends on change in interatomic spacing r_e

Direct Photodissociation – excitation to unbound state



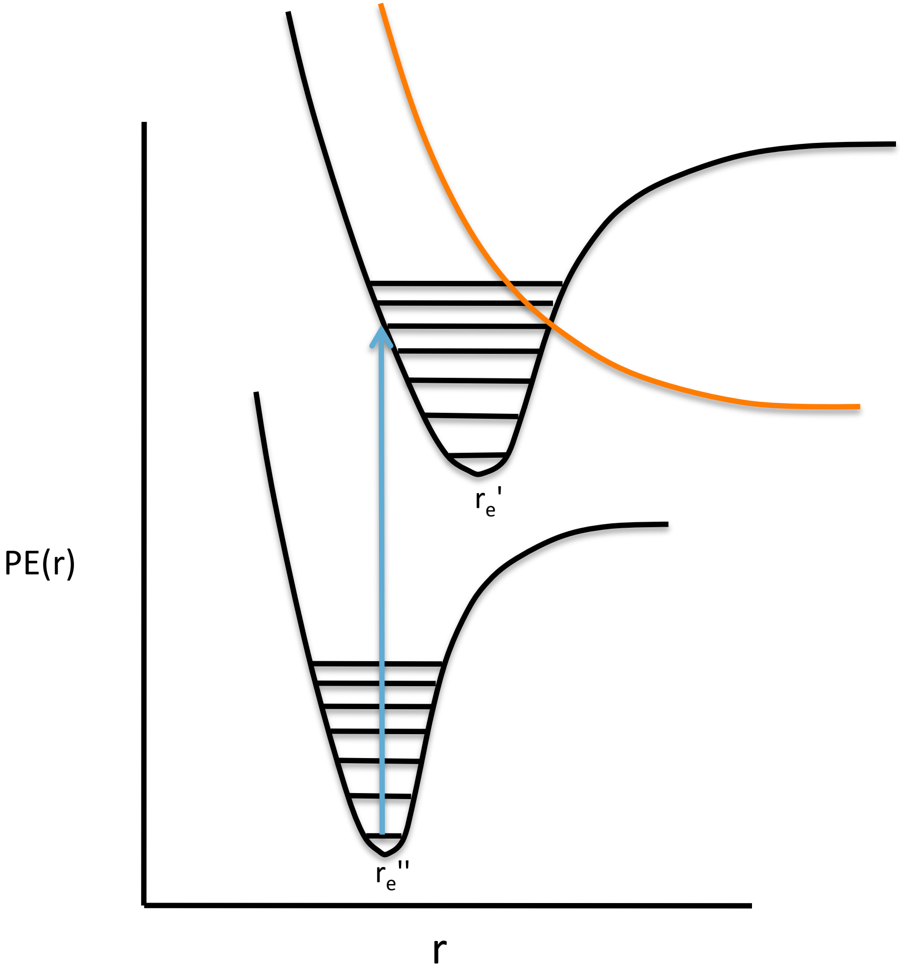
Photochemistry

Predissociation– excitation to bound state



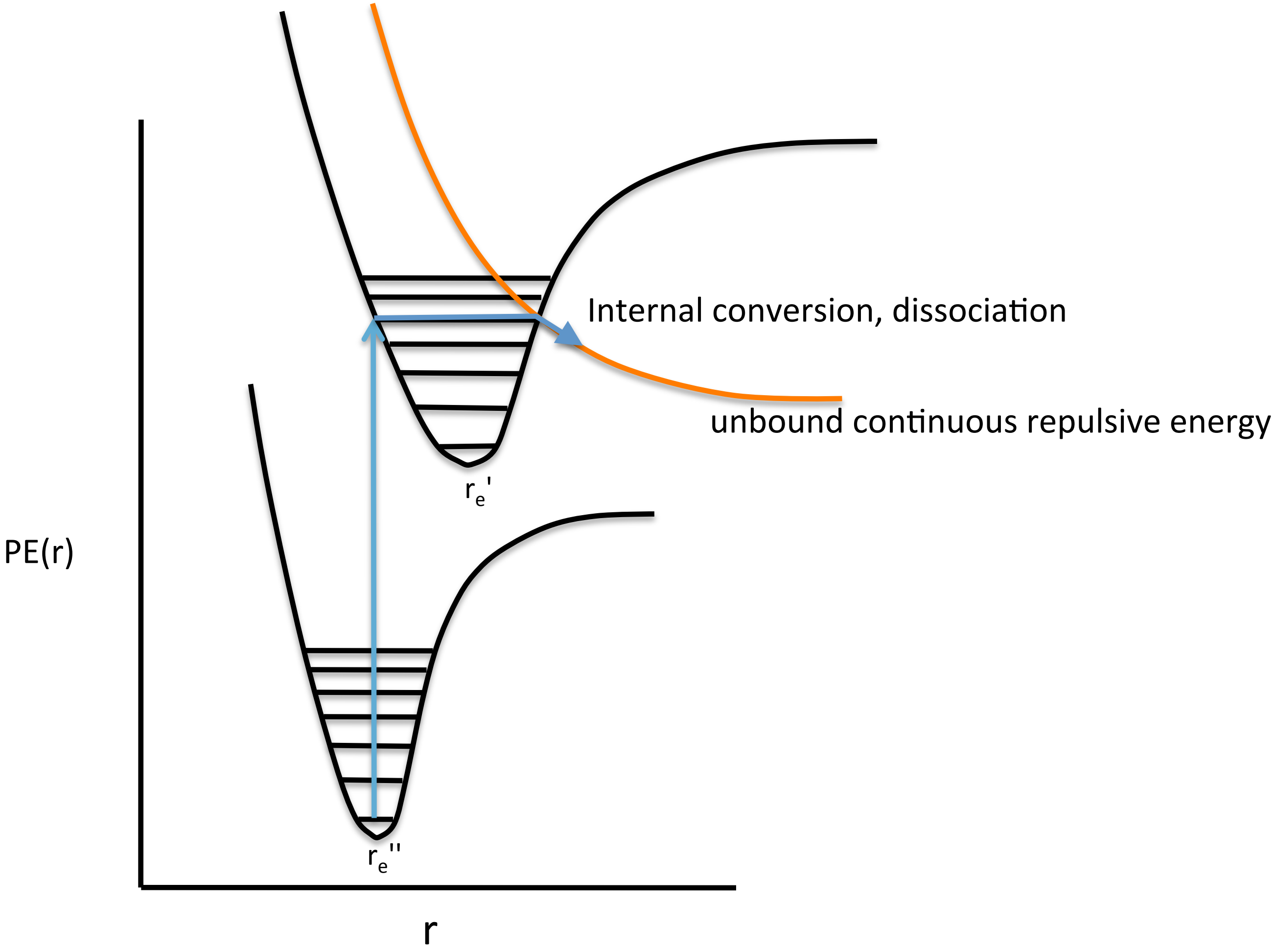
Photochemistry

Predissociation– excitation to bound state



Photochemistry

Predissociation– excitation to bound state



Photochemistry

Optical Depth Effects

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

Optical Depth Effects

Isotope fractionation due to abundance:

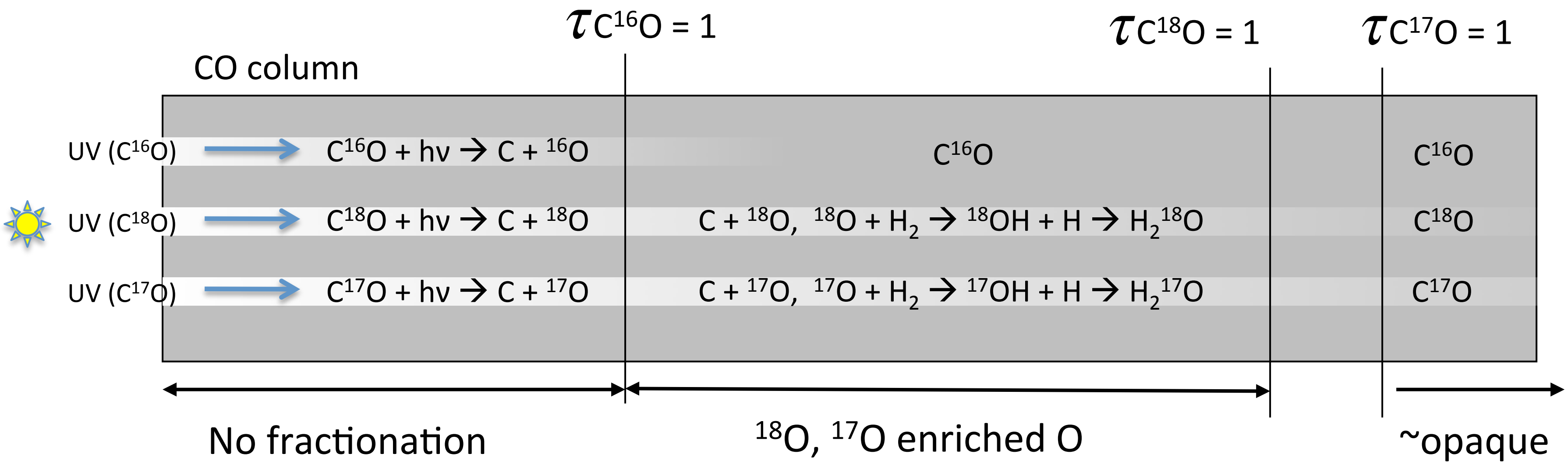
$$k = J^{\circ} \prod_i \exp(-\tau_i)$$

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

Photochemistry

CO Photodissociation self-shielding

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



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

$\tau C^{18}O = 1$

$\tau C^{17}O = 1$

CO column

UV ($C^{16}O$) → $C^{16}O + h\nu \rightarrow C + {}^{16}O$ | $C^{16}O$ | $C^{16}O$

UV ($C^{18}O$) → $C^{18}O + h\nu \rightarrow C + {}^{18}O$ | $C + {}^{18}O$, ${}^{18}O + H_2 \rightarrow {}^{18}OH + H \rightarrow H_2{}^{18}O$ | $C^{18}O$

UV ($C^{17}O$) → $C^{17}O + h\nu \rightarrow C + {}^{17}O$ | $C + {}^{17}O$, ${}^{17}O + H_2 \rightarrow {}^{17}OH + H \rightarrow H_2{}^{17}O$ | $C^{17}O$

No fractionation

${}^{18}O$, ${}^{17}O$ enriched O

~opaque

Photochemistry

New Focus on Cross Sections

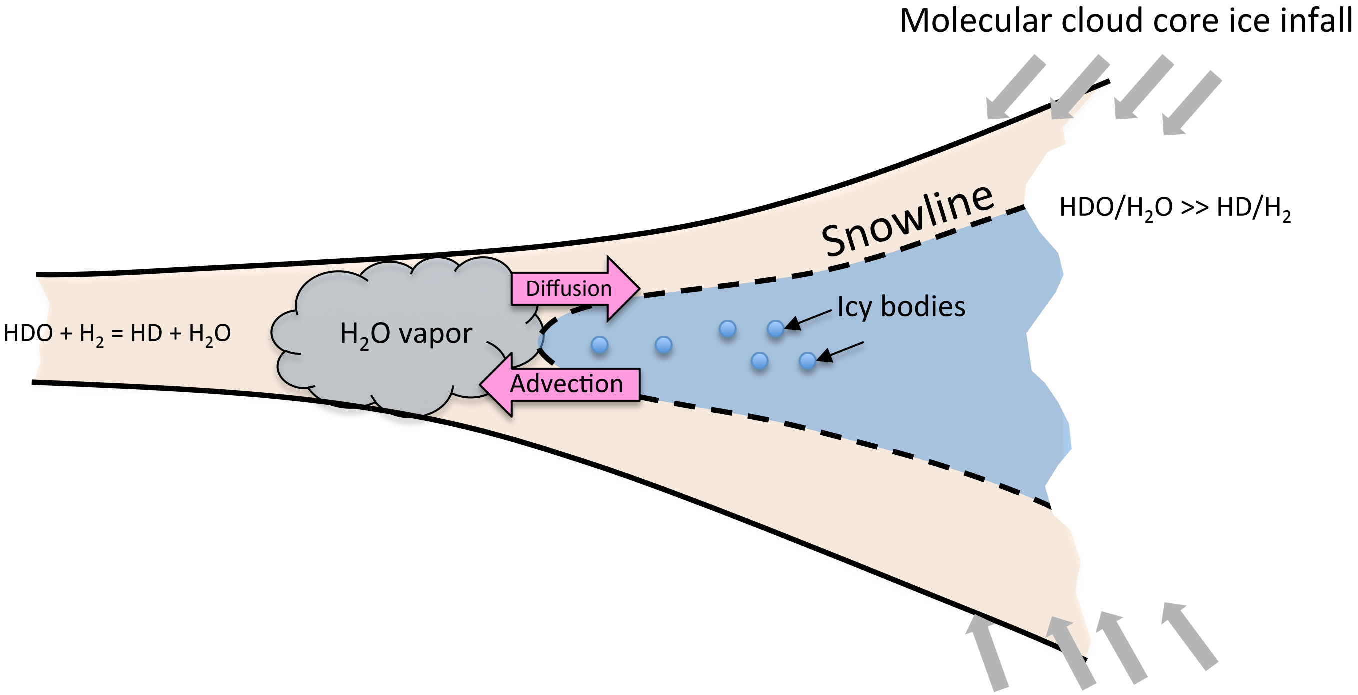
Deviation From Purely Abundance-Dependent Fractionation

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

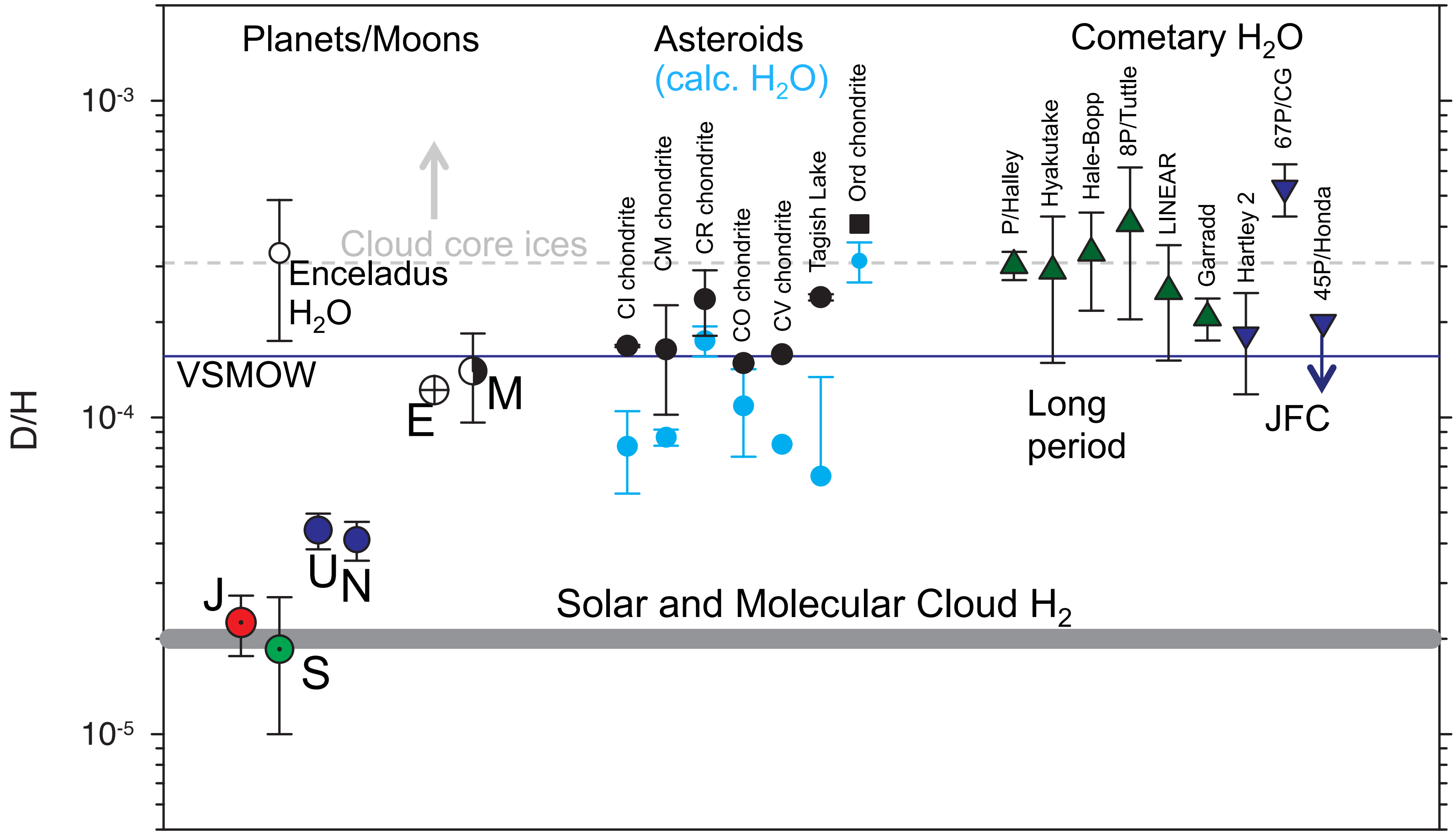
$$\alpha = \frac{k'}{k} = \frac{\prod_i \exp(-\boxed{\sigma_i} N'_i)}{\prod_i \exp(-\boxed{\sigma_i} N_i)}$$

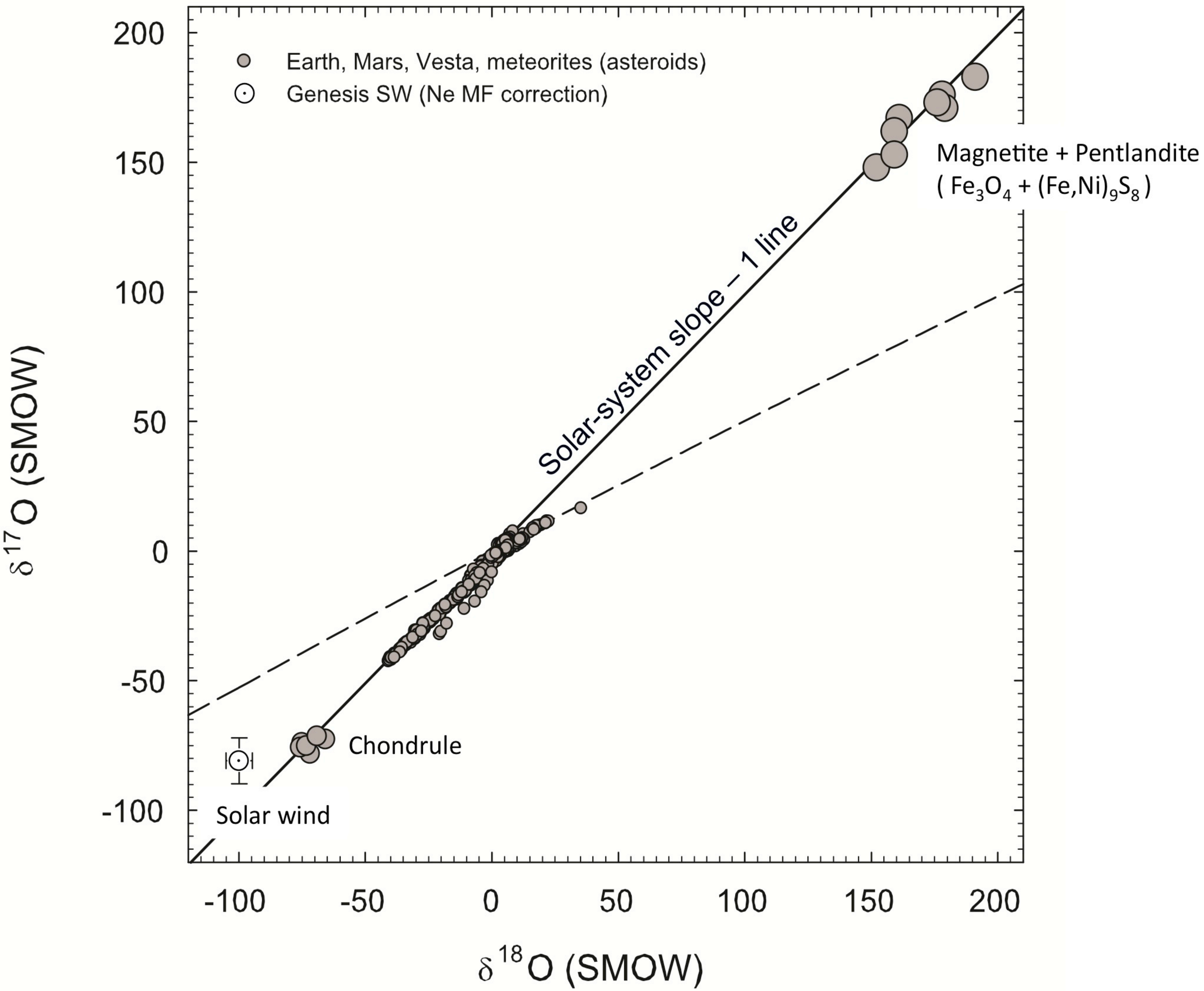
Cross-sections can’t be assumed to be equal for all isotopologues

Water D/H


Molecular cloud core ice infall
Snowline
$HDO/H_2O >> HD/H_2$
Diffusion
Icy bodies
$HDO + H_2 = HD + H_2O$
H_2O vapor
Advection

Water D/H


Planets/Moons
Asteroids
(calc. H_2O)
Cometary H_2O
10^{-3}
10^{-4}
10^{-5}
D/H
Cloud core ices
Enceladus
H_2O
VSMOW
E
M
U
N
J
S
CI chondrite
CM chondrite
CR chondrite
CO chondrite
CV chondrite
Tagish Lake
Ord chondrite
P/Halley
Hyakutake
Hale-Bopp
8P/Tuttle
LINEAR
Garradd
Hartley 2
67P/CG
45P/Honda
Long period
JFC
Solar and Molecular Cloud H_2

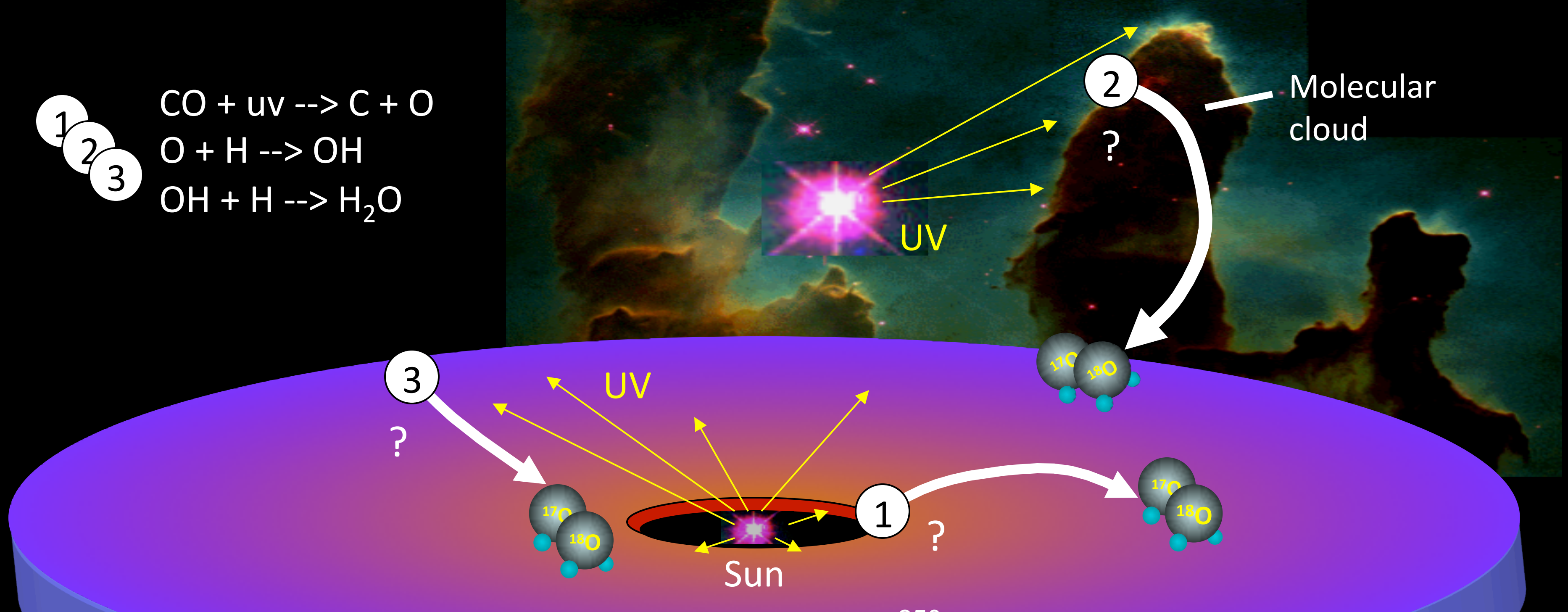


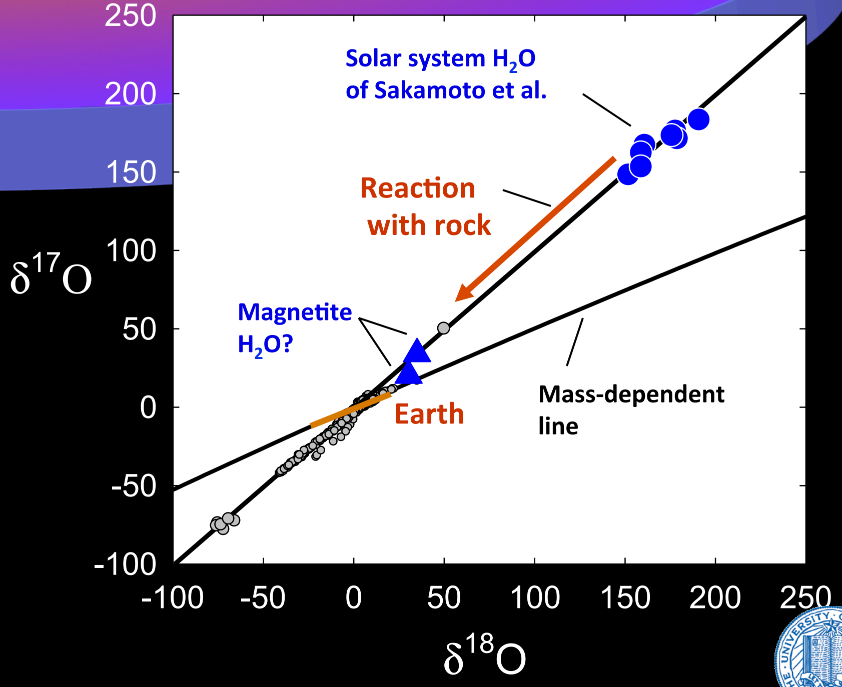
200
150
100
50
0
-50
-100
-100
-50
0
50
100
150
200
● Earth, Mars, Vesta, meteorites (asteroids)
⊙ Genesis SW (Ne MF correction)
Solar-system slope – 1 line
Magnetite + Pentlandite
(Fe_3O_4 + $(Fe,Ni)_9S_8$)
Chondrule
Solar wind
$\delta^{17}O$ (SMOW)
$\delta^{18}O$ (SMOW)

1 CO + uv --> C + O

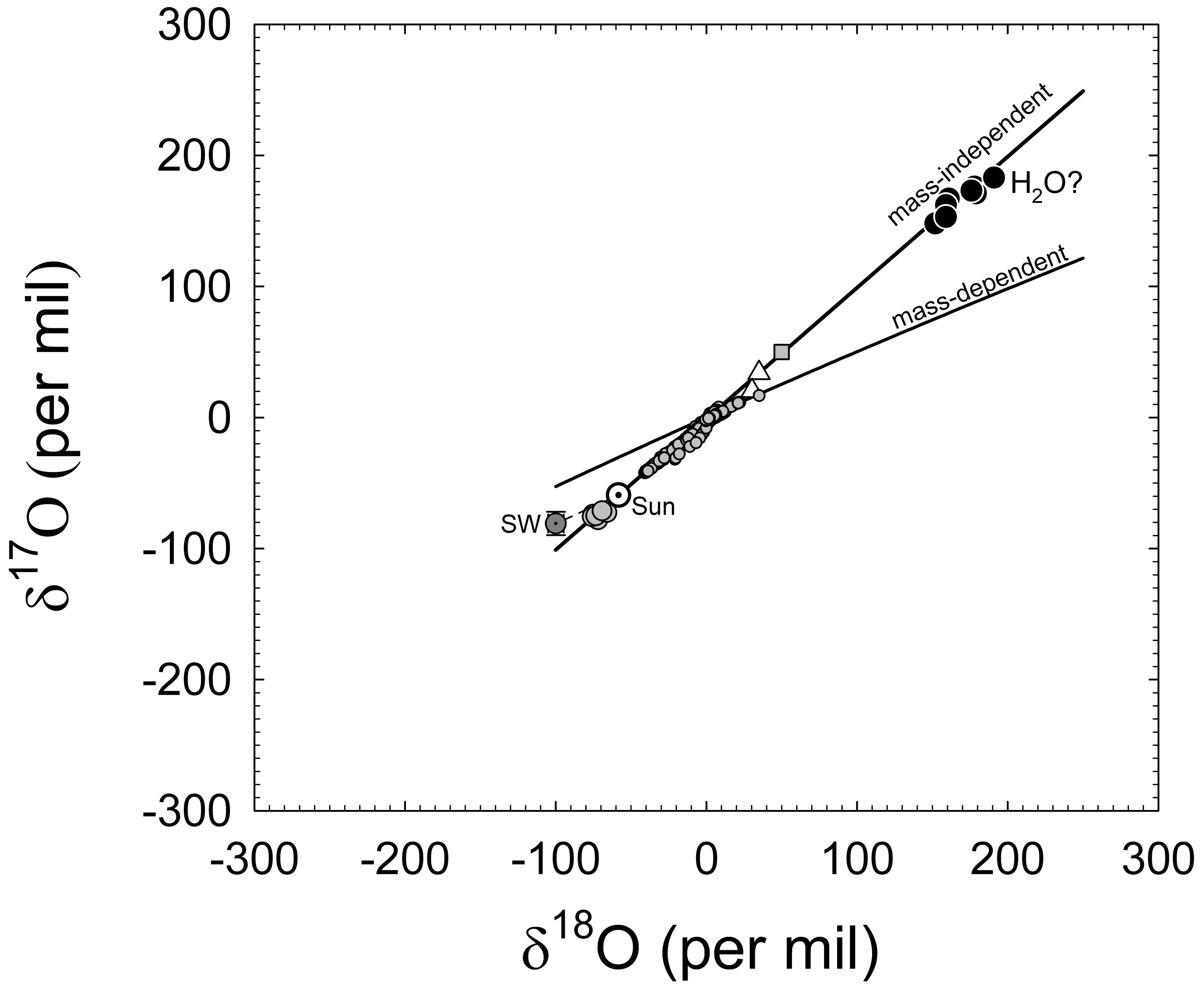
2 O + H --> OH

3 OH + H --> H_2O





Water Oxygen



Equilibrium

$$S_i = 1$$

$$\beta = \prod_i \frac{h\nu_i' / (k_b T)}{h\nu_i / (k_b T)} \frac{e^{-(h\nu_i'/(k_b T))/2}}{1 - e^{-h\nu_i'/(k_b T)}} \frac{1 - e^{-h\nu_i/(k_b T)}}{e^{-(h\nu_i/(k_b T))/2}}$$

Equilibrium

$$S_i = 1$$

Because $\operatorname{csch}(x) = 2/(e^x - e^{-x})$ and $\sinh(x) = (e^x - e^{-x})/2$ we rewrite

$$\beta = \prod_i \frac{u_i'}{u_i} \frac{\operatorname{csch}(u_i'/2)}{2} 2\sinh(u_i/2) \ .$$

Substitution of the Taylor series approximations for the hyperbolic functions truncated after two terms, $\operatorname{csch}(x) \sim 1/x - x/6$ and $\sinh(x) \sim x + x^3/3!$, results in

$$\beta = 1 + \frac{1}{24}\sum_i \left(u_i^2 - u_i'^2\right)$$

Exchange with atmosphere

Example: Mg isotopes, evaporating magma-ocean planetesimal

½ M_{Pluto}

$M = 4.7 \times 10^{21}$ kg