Chemistry in Exoplanet Atmospheres

Julianne I. Moses
(Space Science Institute)

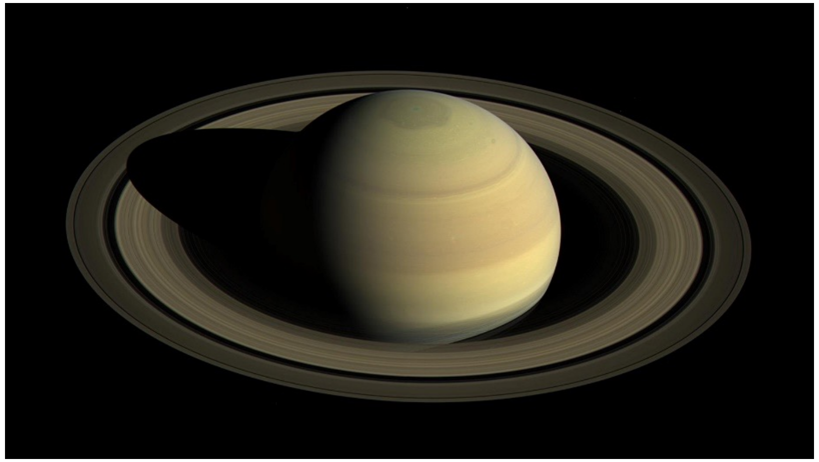
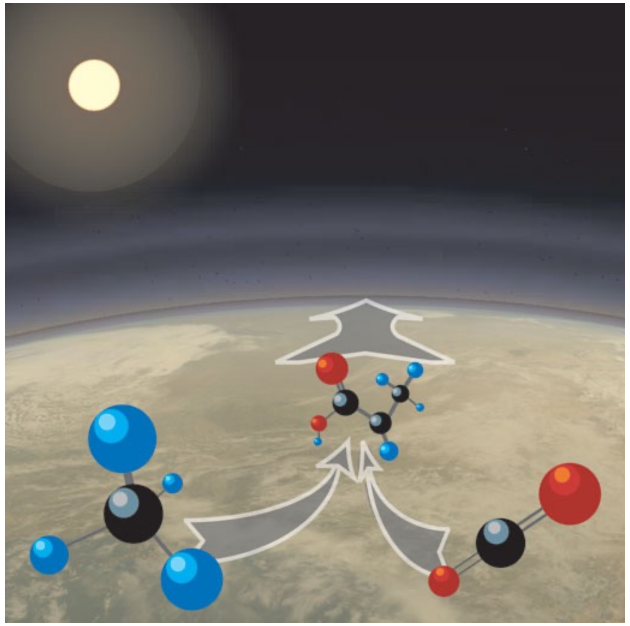


Image credit: Dana Berry



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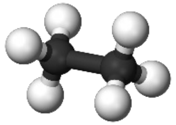
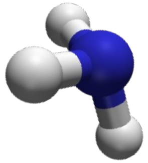
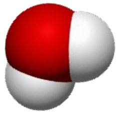
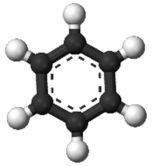




Why should you care?





Clues to planet formation/evolution

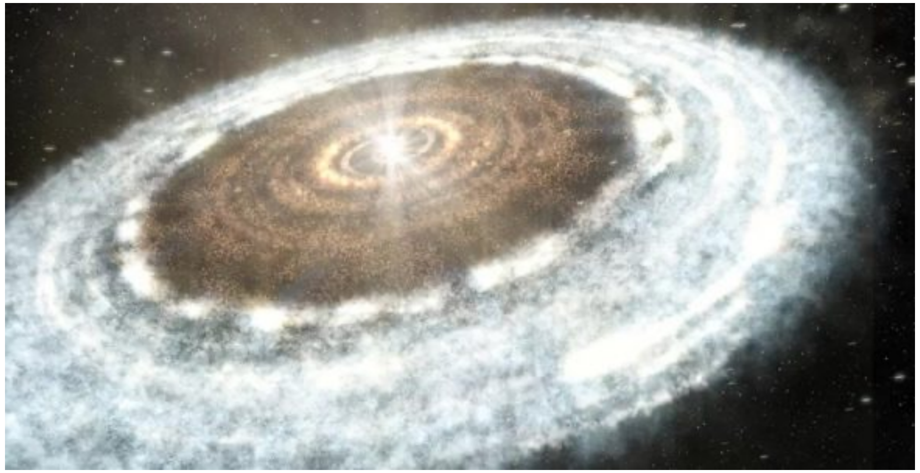
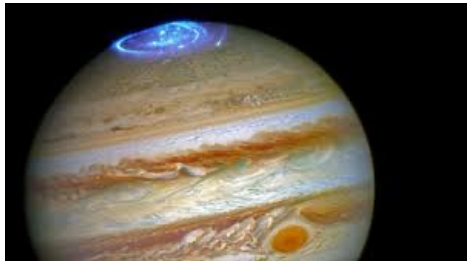


Image credit: Alexandra Angelich, NRAO/AUI/NSF

Clues to current processes



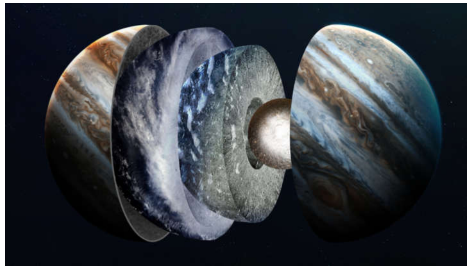
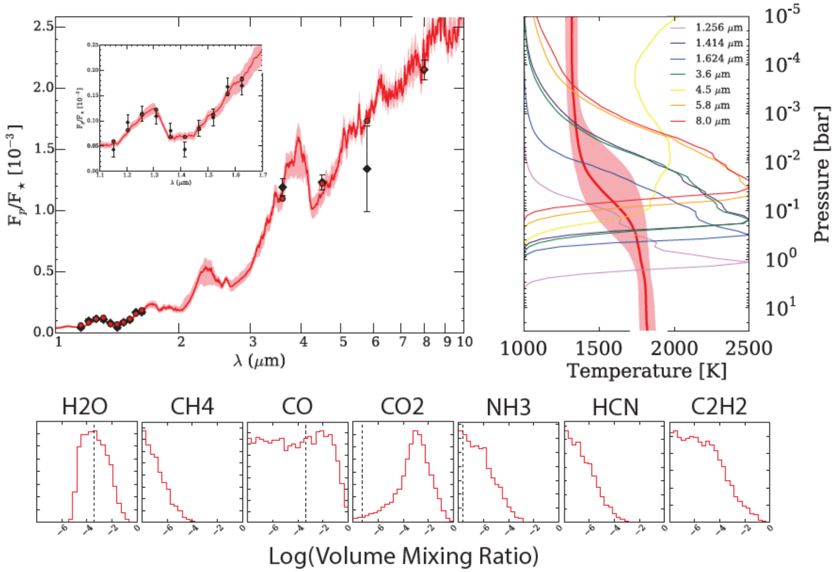


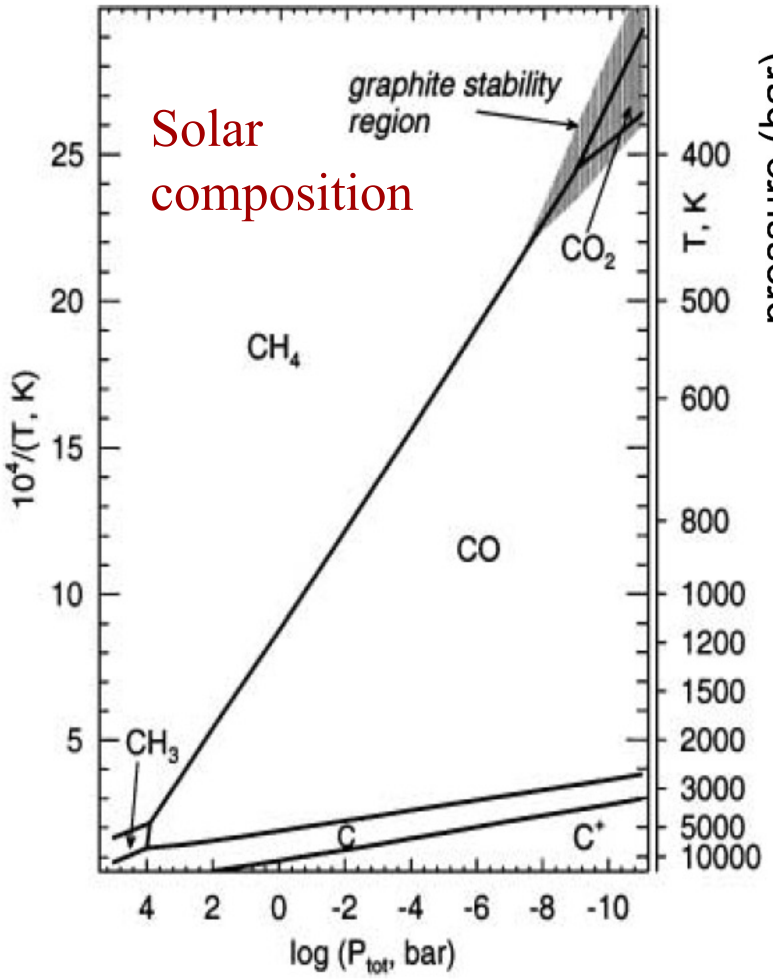
Image credit: IFLScience

Chemistry affects observations



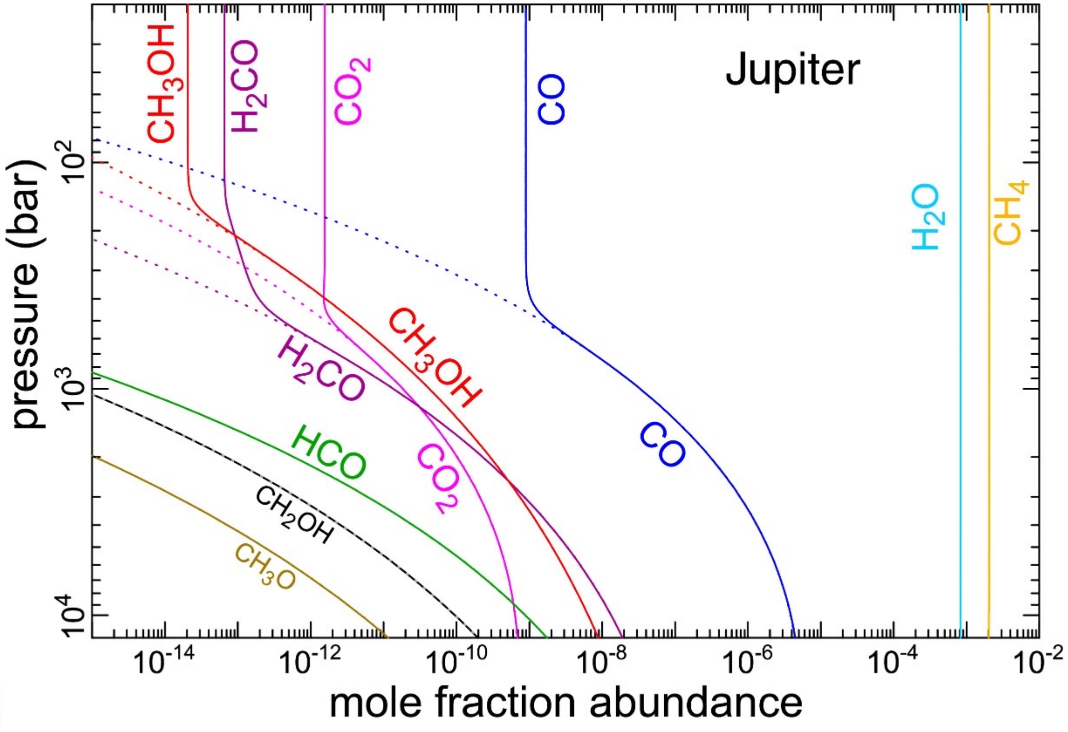
Line et al. (2013)

Thermochemical Equilibrium



Lodders & Fegley (2002)

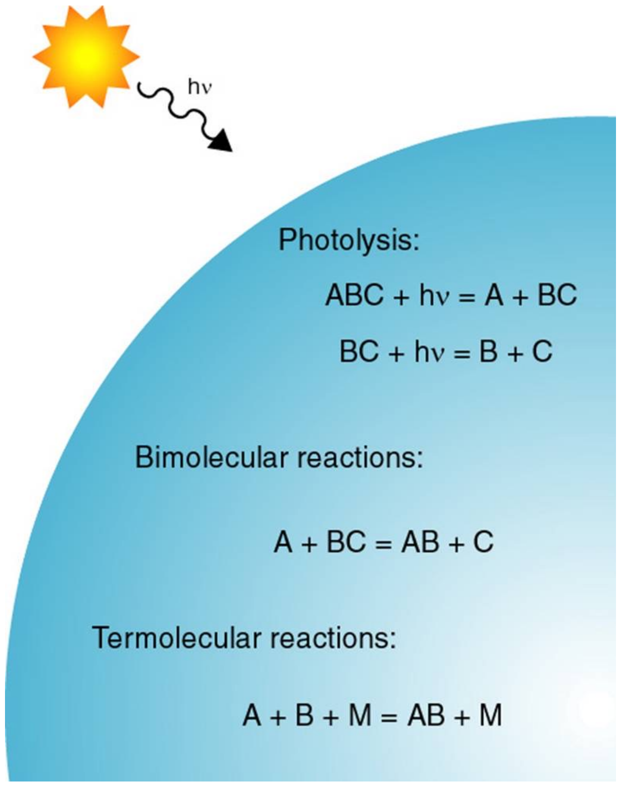
Transport-Induced Quenching



Visscher et al. (2010)

Three main chemical processes affect atmospheric composition on exoplanets. Each of these processes dominate in thermal regimes or atmospheric regions

Photochemistry



Photolysis:

ABC + hν = A + BC

BC + hν = B + C

Bimolecular reactions:

A + BC = AB + C

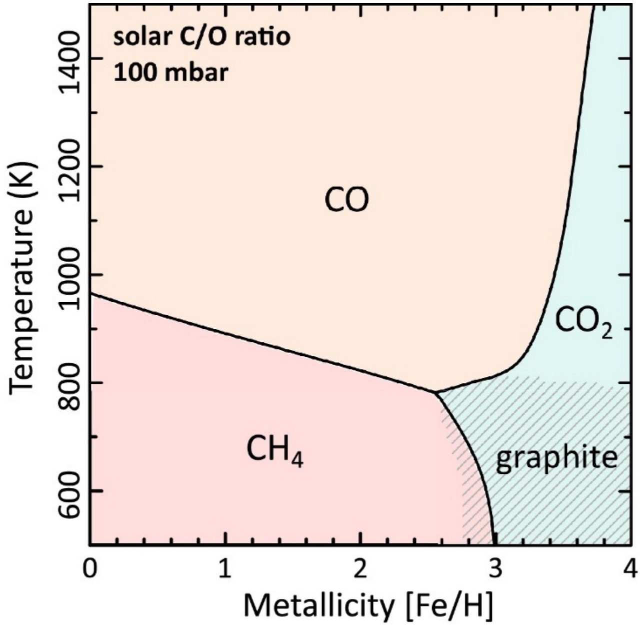
Termolecular reactions:

A + B + M = AB + M

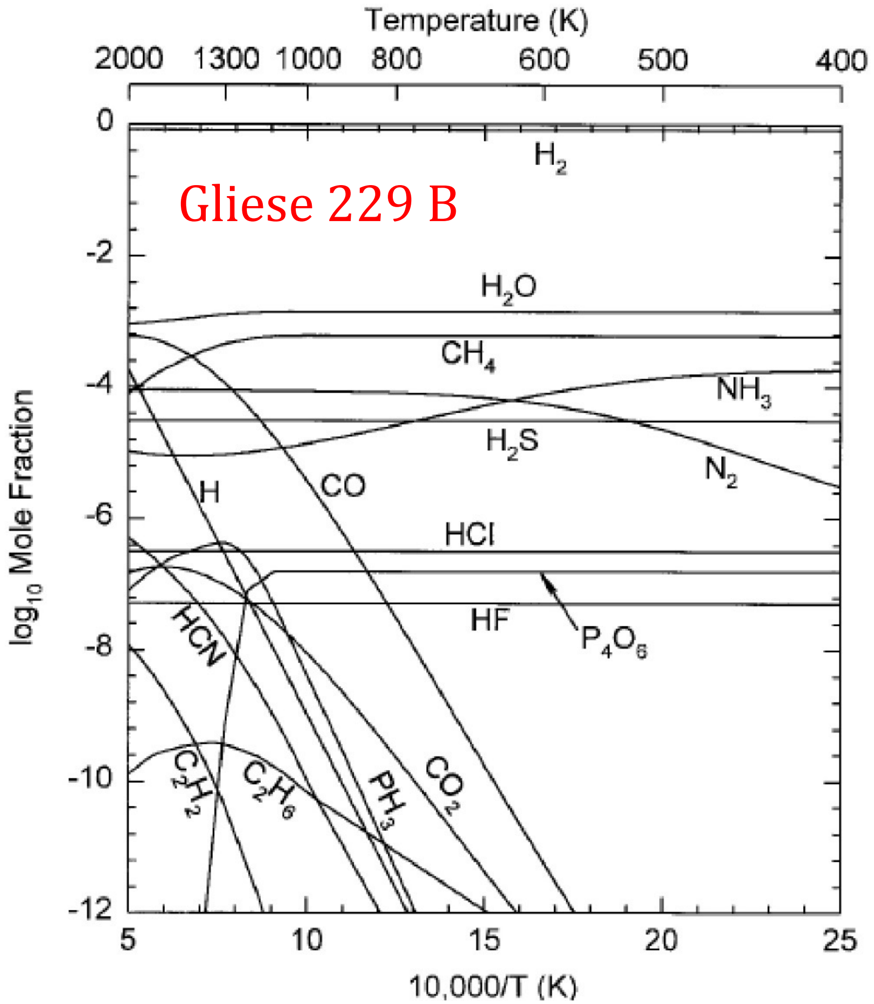
Thermochemical Equilibrium

- First-order prediction of composition, especially for hot planets
- Convenient: depends only on *T*, *P*, and relative elemental abundances. Some analytic solutions for simple cases available (e.g., Burrow & Sharp 1999, Heng et al. 2016, Woitke et al. 2021)
- *Several public-domain codes and databases available*

from Paul Mollière's ERS theory talk

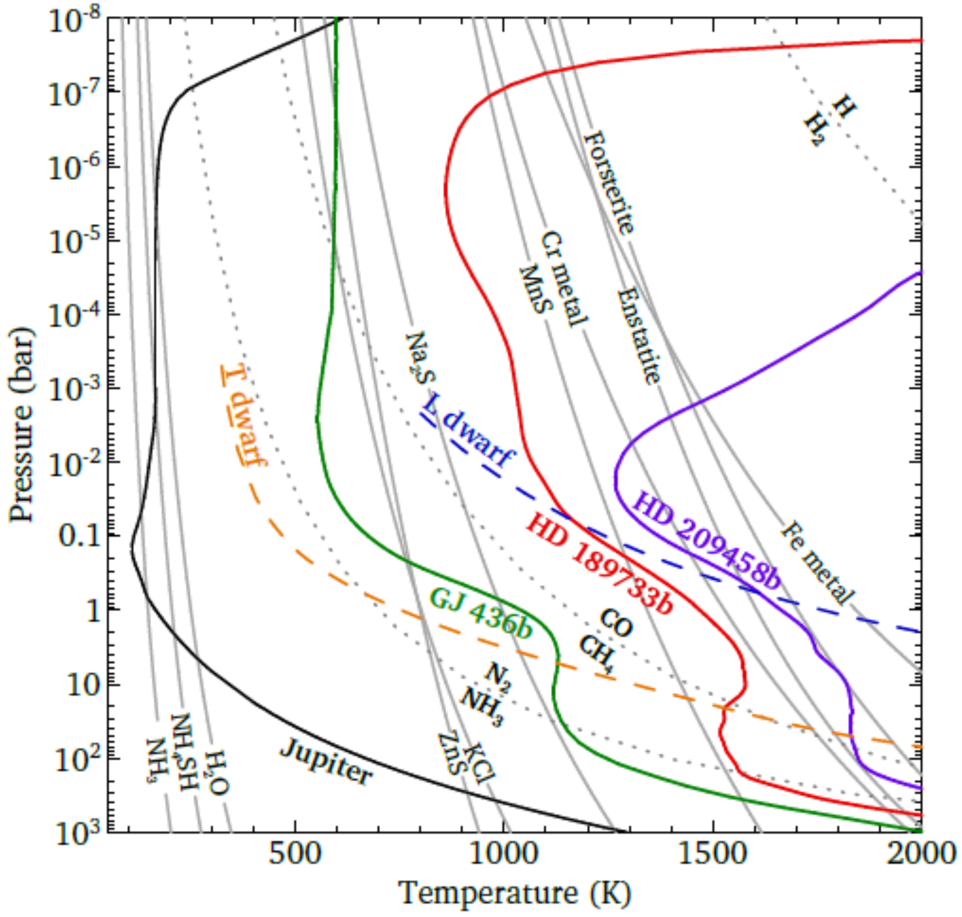


from Moses et al. (2013b)

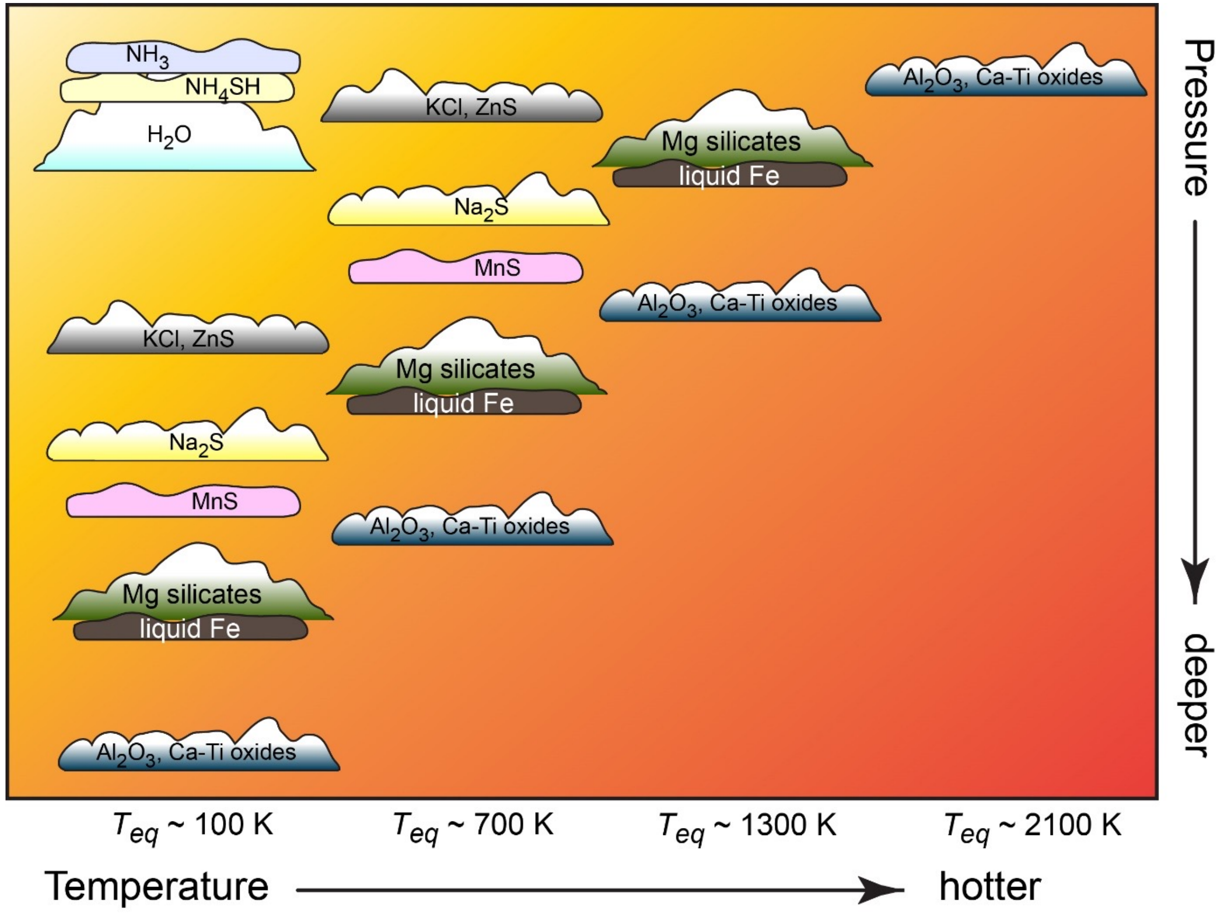


from Fegley & Lodders (1996)

Thermochemical Equilibrium: Clouds



from Channon Visscher

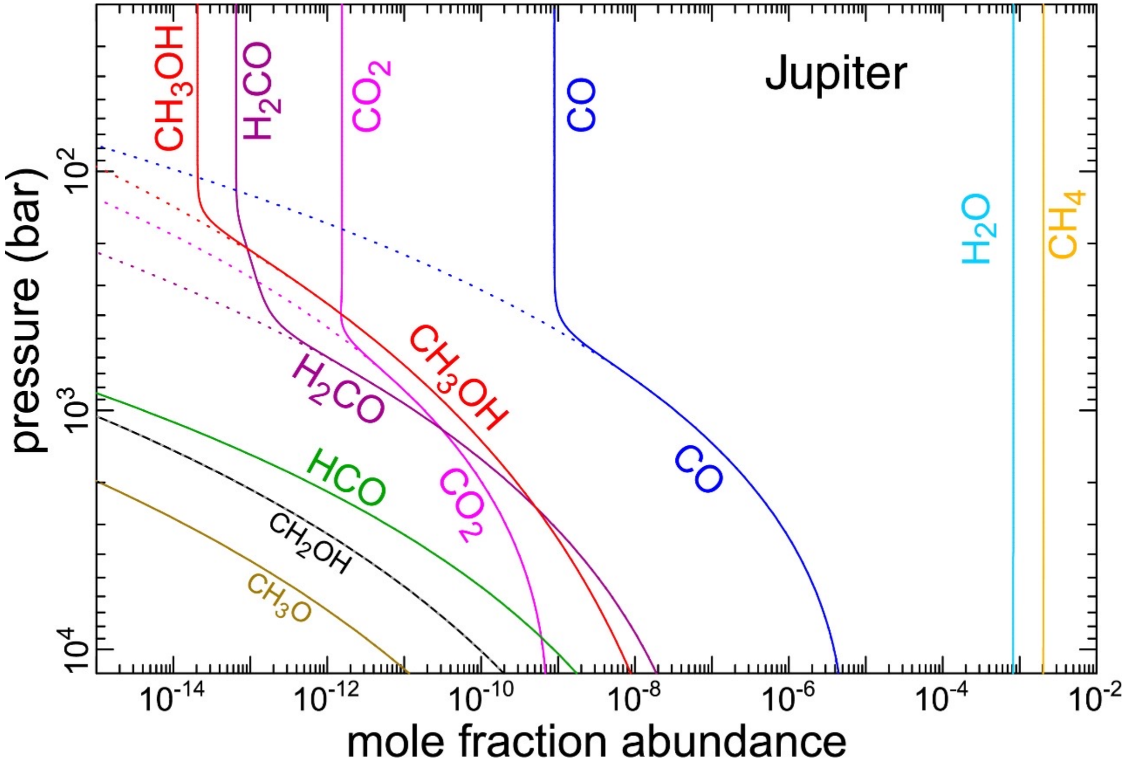


Moses et al. (2021), with original figure concept from Lodders & Fegley (2006)

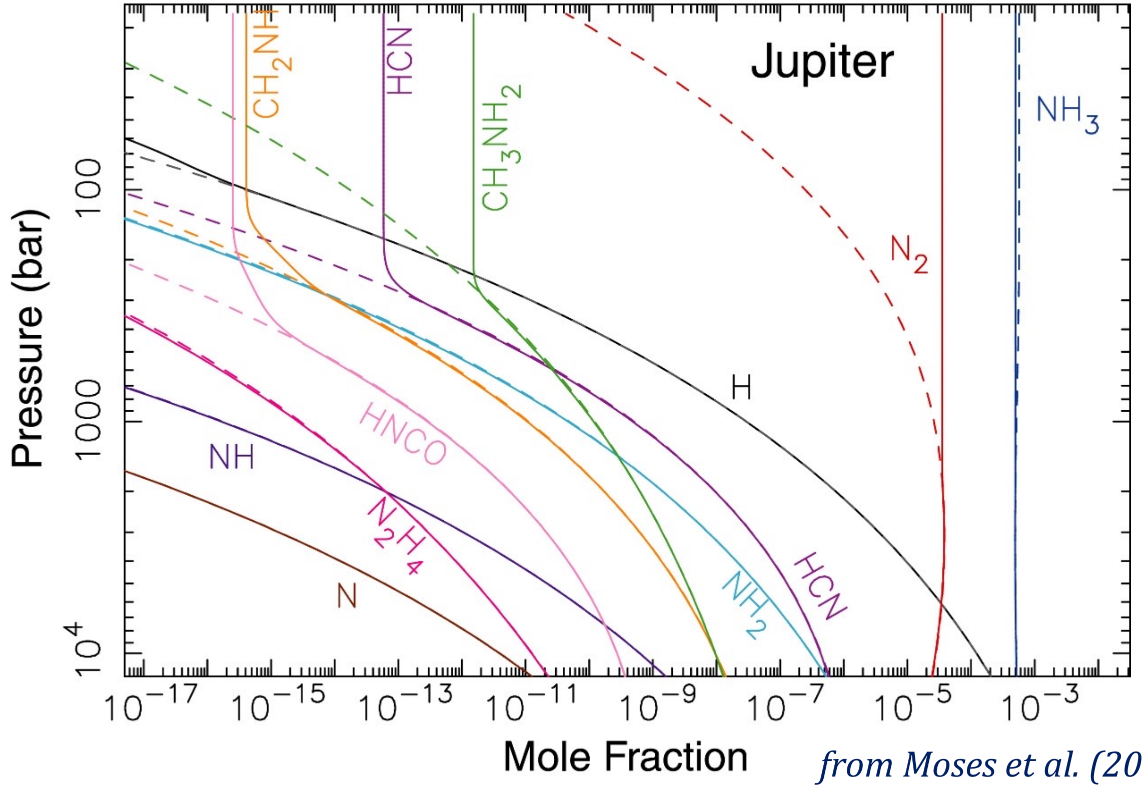
Thermochemical equilibrium also helps you predict where clouds should form (e.g., Morley et al. 2012); cloud formation can affect gas abundance ratios (e.g., Visscher et al. 2010, Helling et al. 2016, Woitke et al. 2021)

When the atmosphere doesn't have infinite time to reach equilibrium

Transport-Induced Quenching

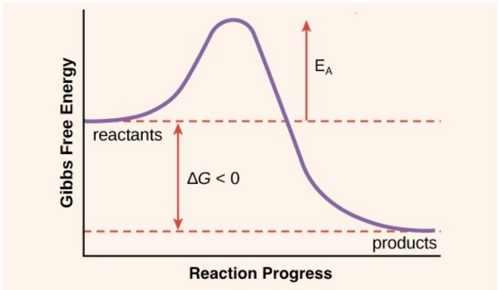


from Visscher et al. (2010)

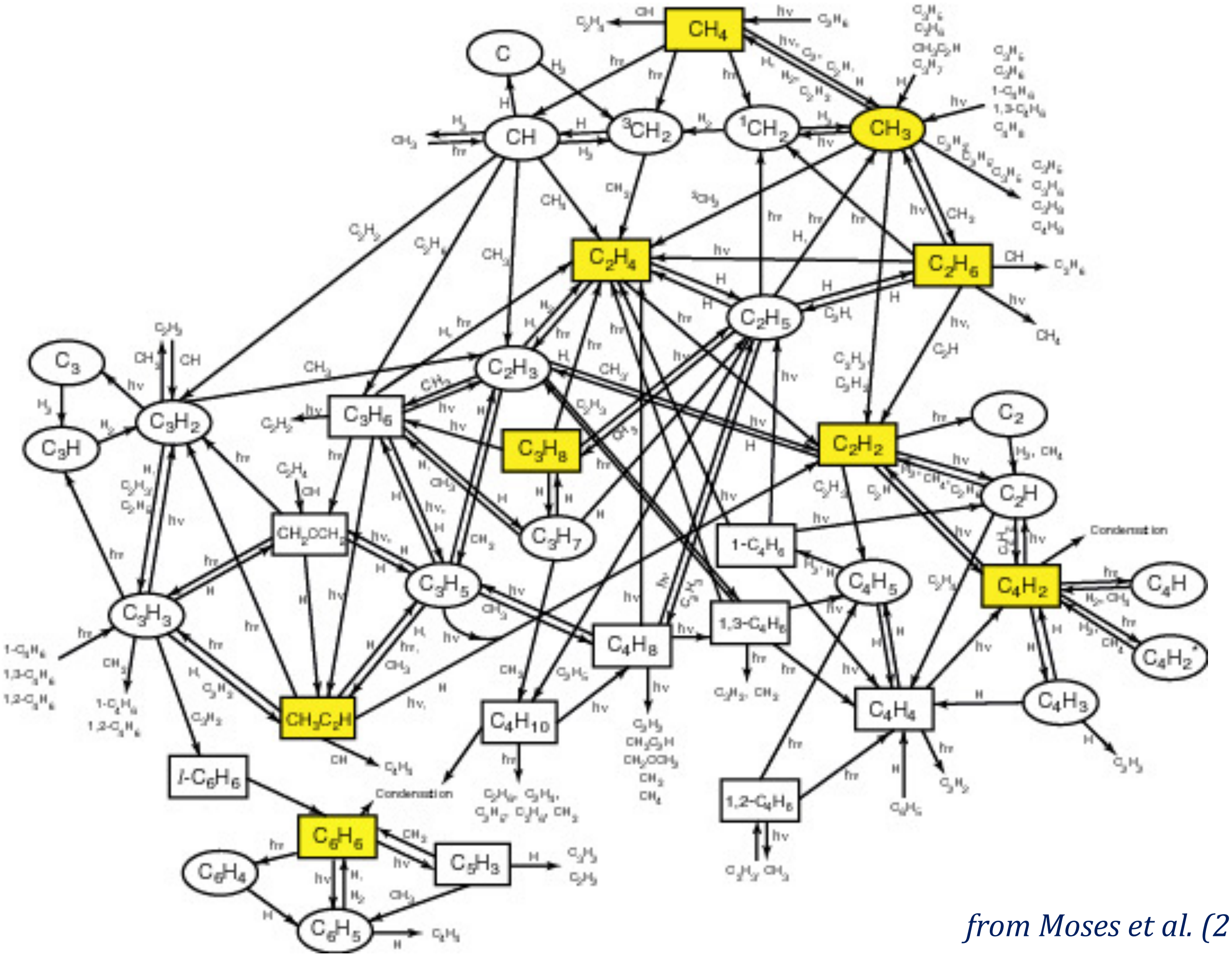


from Moses et al. (2010)

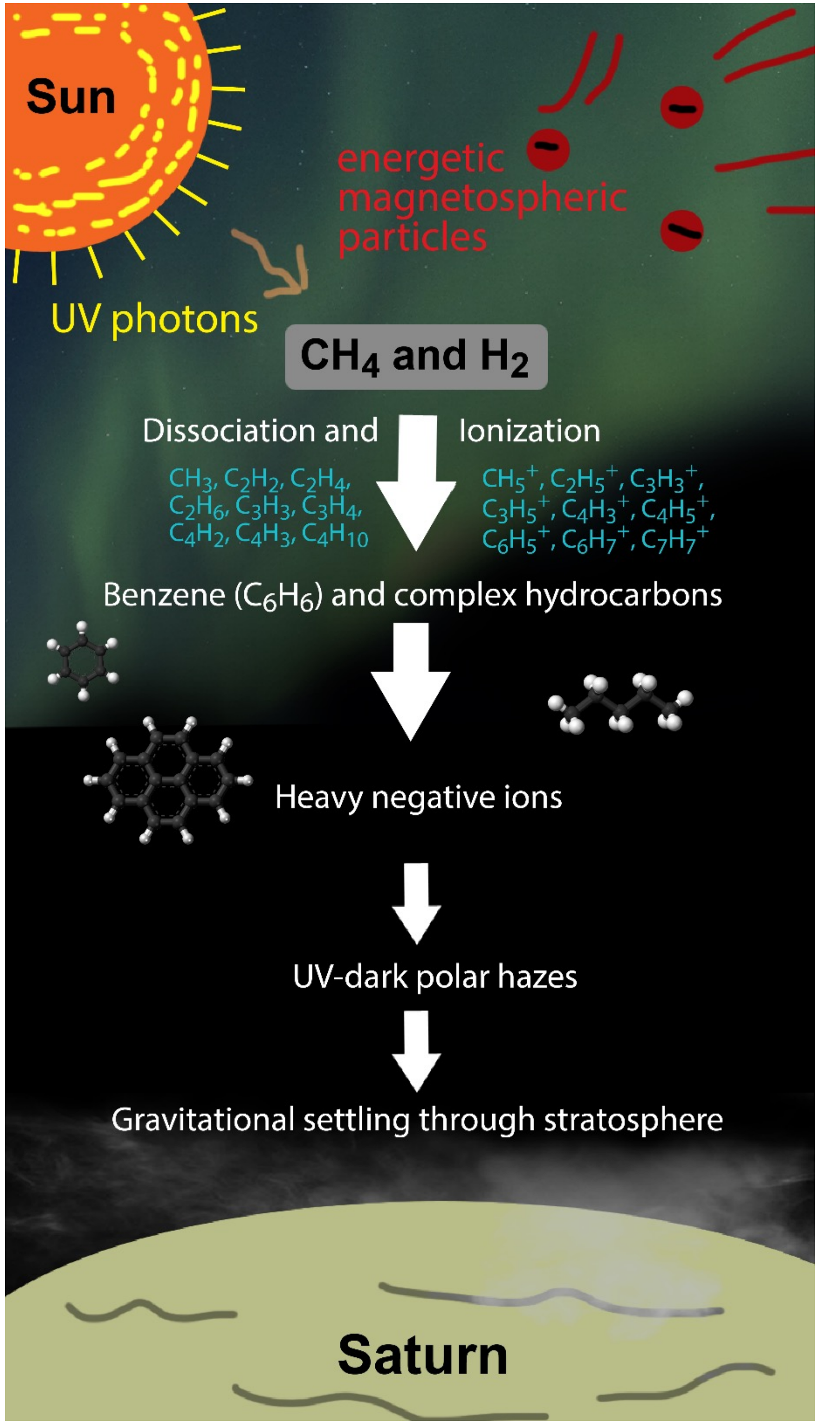
Transport-induced quenching will matter for any planet with temperature gradients whose atmosphere gets hot enough, e.g., T ≥ ~800-1000 K, somewhere (e.g., at depth or on the dayside)



Photochemistry



from Moses et al. (2000)



CH_4 and H_2

Dissociation and Ionization

CH_3, C_2H_2, C_2H_4, C_2H_6, C_3H_3, C_3H_4, C_4H_2, C_4H_3, C_4H_{10}

CH_5^+, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_4H_3^+$, $C_4H_5^+$, $C_6H_5^+$, $C_6H_7^+$, $C_7H_7^+$

Benzene (C_6H_6) and complex hydrocarbons

Heavy negative ions

UV-dark polar hazes

Gravitational settling through stratosphere

J. Moses, Sagan workshop, July 2023

Photochemical Models

Solve the continuity equations: (Conservation of mass)

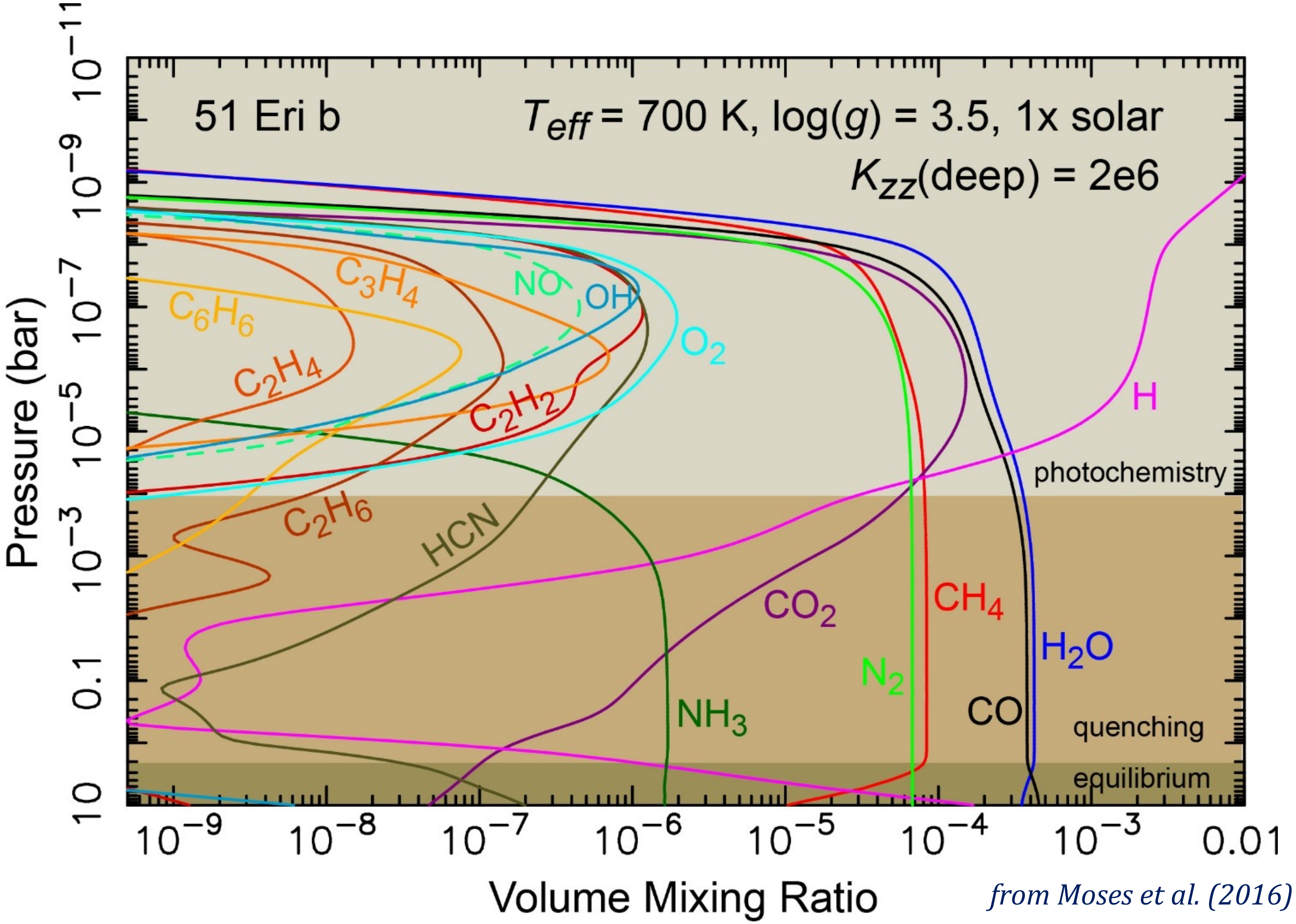
$$\frac{\partial n_i}{\partial t} + \vec{\nabla} \cdot (n_i \vec{v}_i) = P_i - L_i$$

Non-linear system of coupled partial differential equations. Solve using finite-difference techniques

In 1D, $n_i v_i = n_i w_i$ = vertical flux ϕ_{i} based on "eddy" and molecular diffusion

Inputs to photochemical models:
reactions and rate coefficients, thermodynamic parameters, UV cross sections and photodissociation/photoionization pathways, stellar flux, planetary and orbital parameters, atmospheric structure, wind fields and/or diffusion coefficients

Photochemical Models

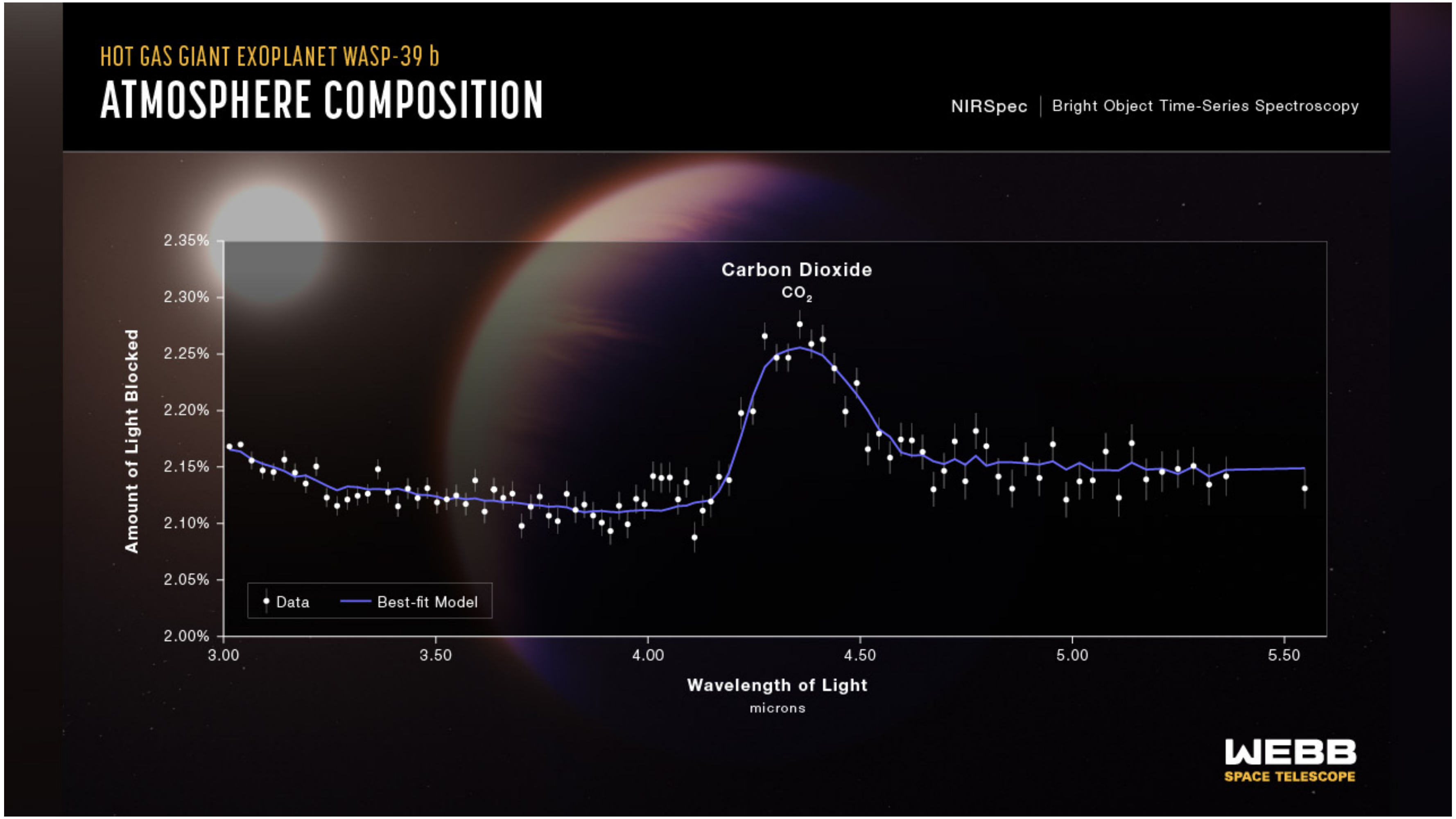


from Moses et al. (2016)

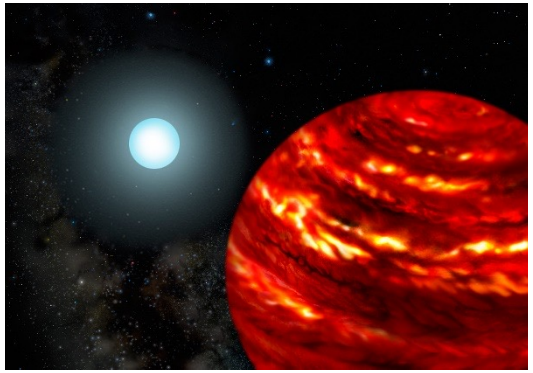
Photochemical models can give you results pertaining to all three main chemical regimes in exoplanet atmospheres

Infamous spaghetti plots!

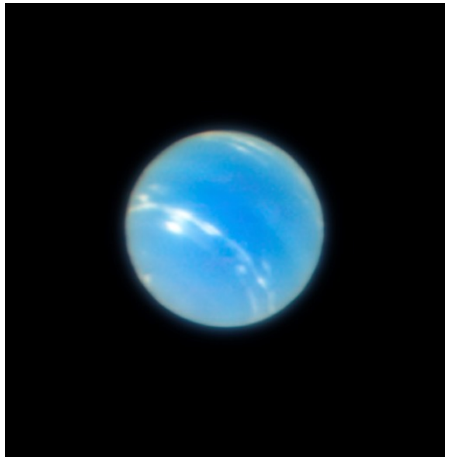
Giant Planets (including Neptunes)



Credit: NASA, ESA, CSA, Leah Hustak (STScI), Joseph Olmsted (STScI)

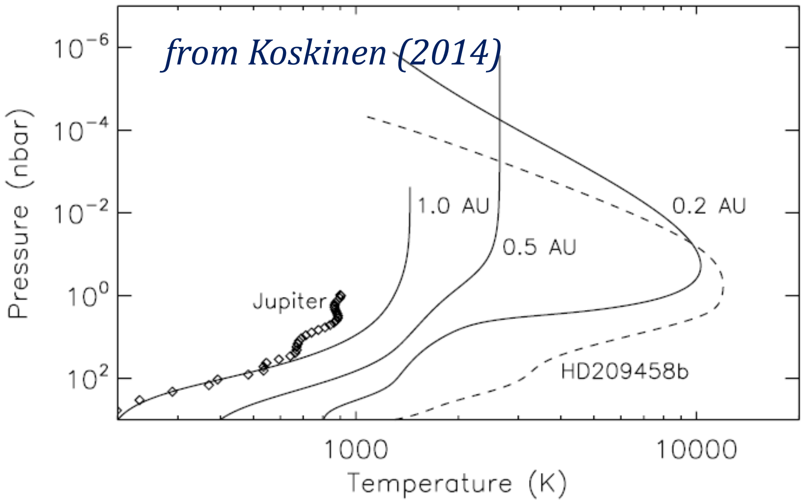


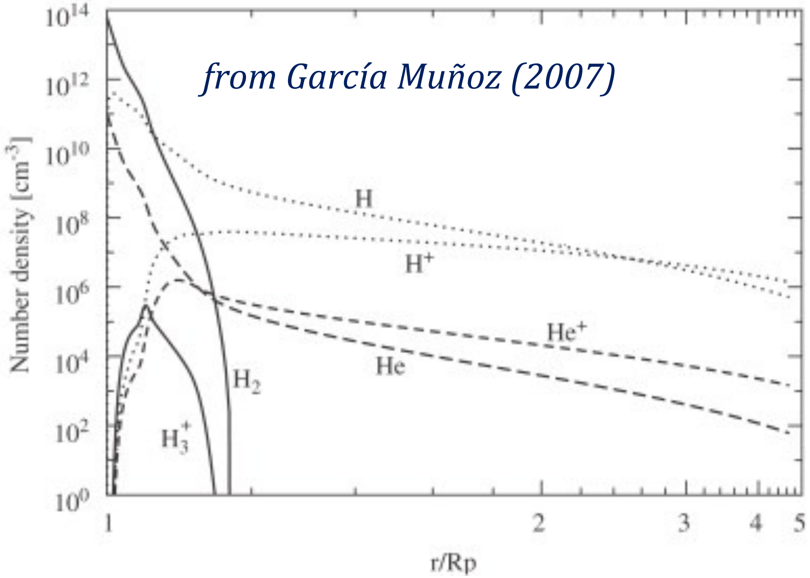
Credit: Gemini Observatory/AURA/ Lynette Cook

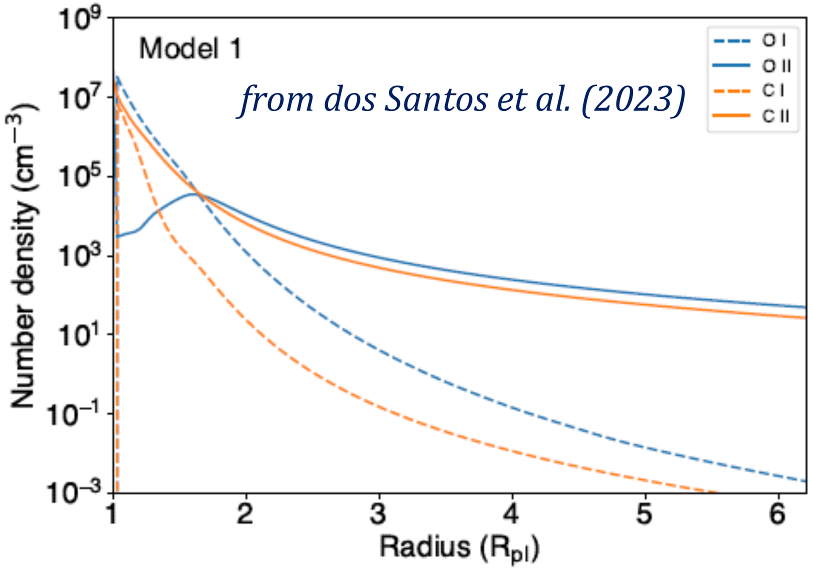


Credit: ESO VLT/P. Weilbacher (AIP)

Giant Planets: Thermospheres







Extended thermospheres

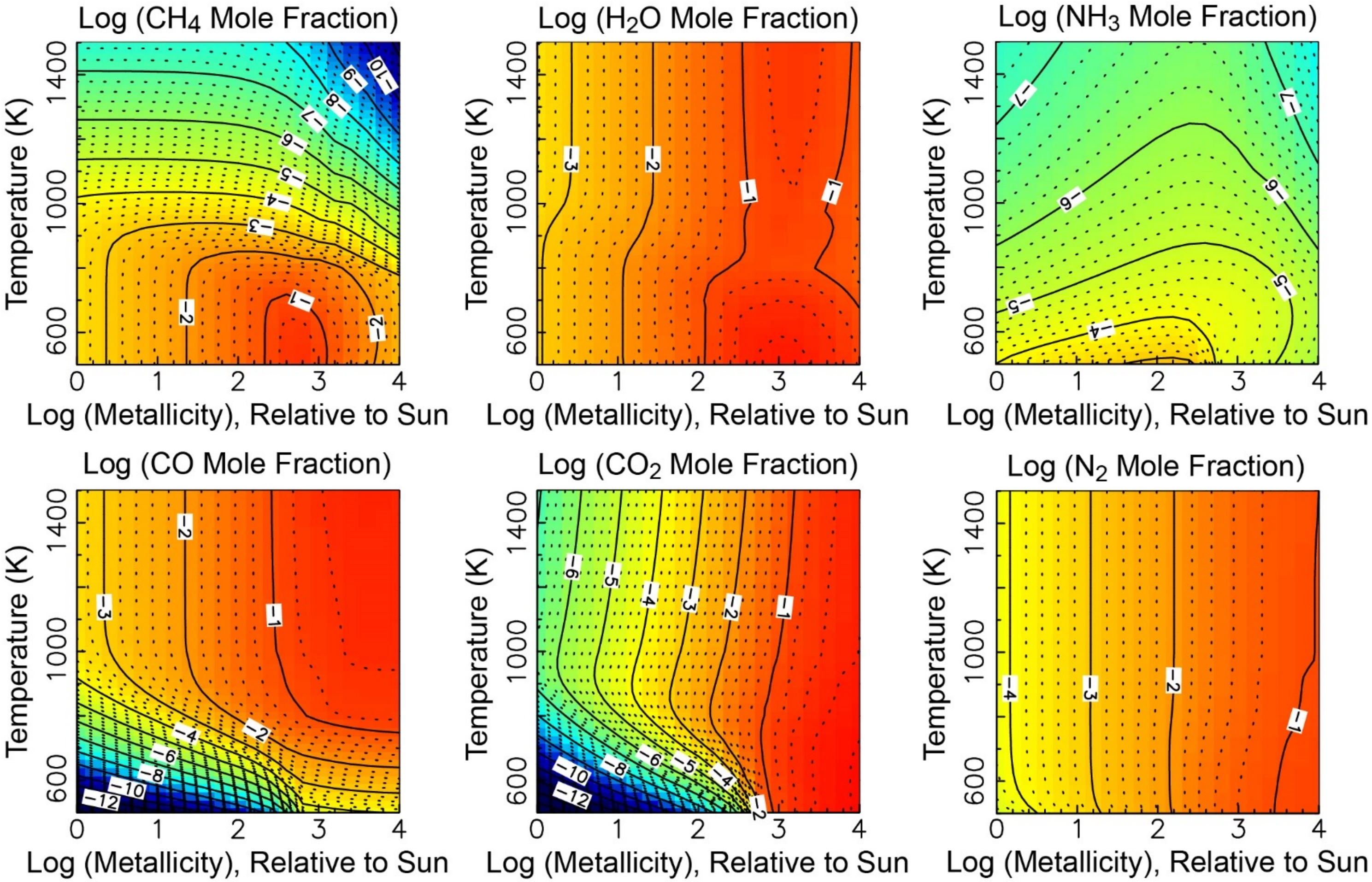
Powered by absorption of XUV radiation from the host star

Greatly increases the planet's cross section during transit in some UV/Vis spectral lines

Close-in giant exoplanets – and really any close-in planet with H-bearing molecules in the lower atmosphere – will have very hot, hydrodynamically escaping thermospheres dominated by H and H^+ that drag heavier species up along with the escaping hydrogen (e.g., Yelle et al., 2004; García-Muñoz, 2007; Koskinen et al., 2013; Shaikhislamov et al., 2018)

Ultra-hot Jupiters will have metal atoms and ions throughout atmosphere (e.g., Lothringer et al., 2020)

Giant Planets: thermochemical equilibrium in IR “photosphere”



at 100 mbar, solar C/O ratio

modified from Moses et al. (2013b)

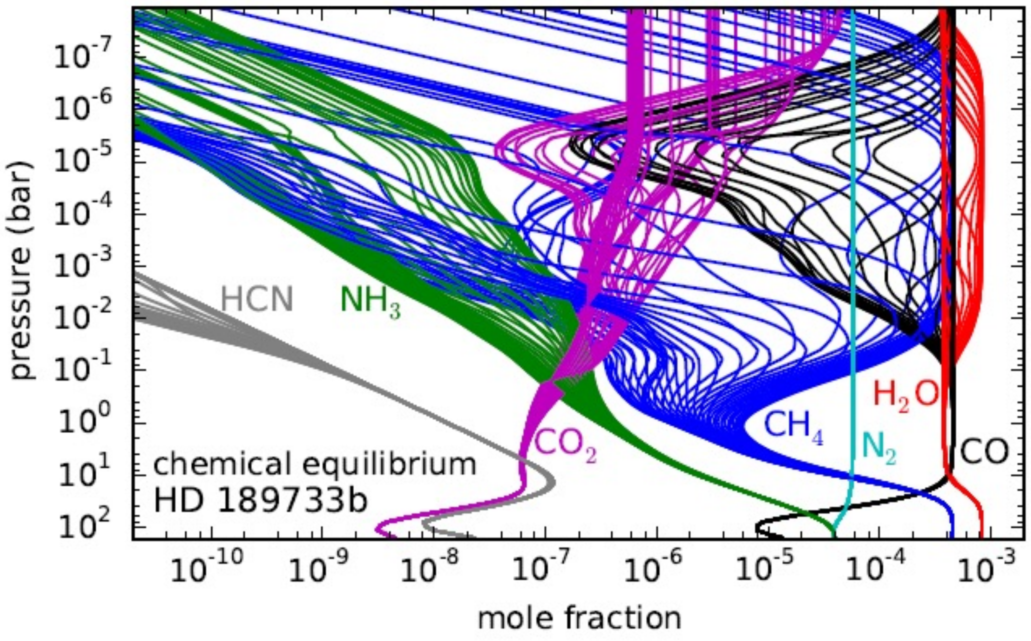
Giant planets are likely H_2-He rich

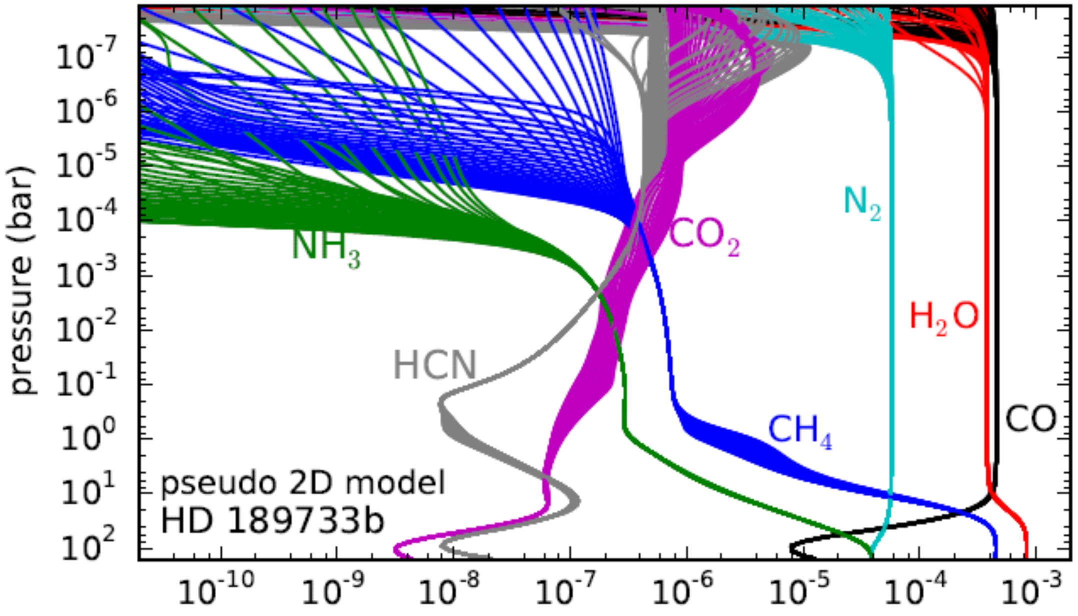
Thermochemical equilibrium predictions will depend on the relative abundance of the different elements, including **metallicity** (Fe/H).

Forward model grids are a useful tool and can provide a sanity check to supplement retrievals

Lower-mass giant planets may have higher-metallicity atmospheres (e.g., Fortney et al. 2013)

Giant Exoplanets: Quenching in IR “photospheres”



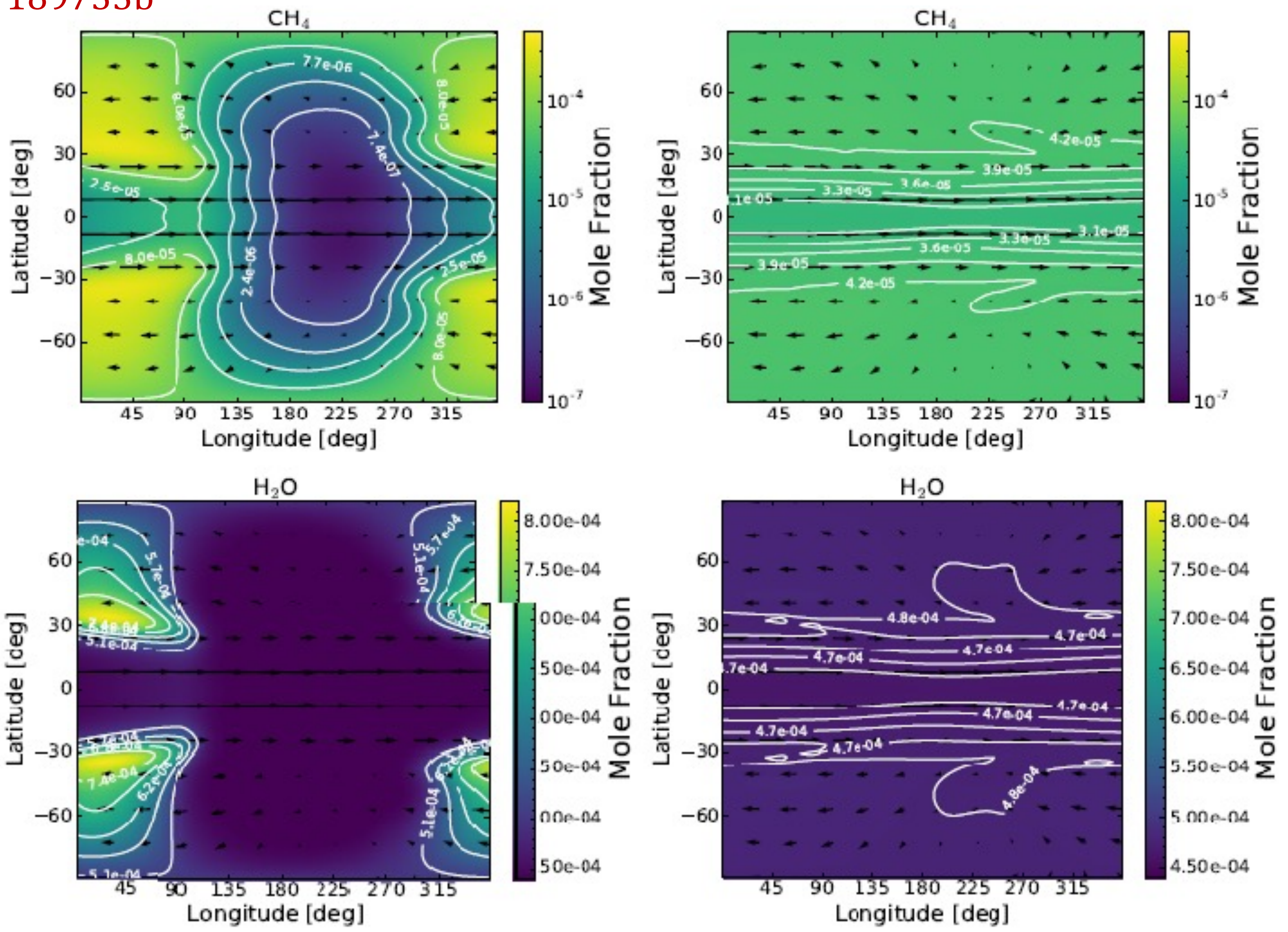


from Agúndez et al. (2014)

The composition can quench in the horizontal direction, as well as the vertical direction, if horizontal winds are faster than chemical conversion between different species (e.g., Cooper & Showman, 2006; Agúndez et al., 2012, 2014; Venot et al., 2020; Moses et al., 2021; Baeyens et al., 2021; Roth et al., 2021); see also 3D models (next slide). *Horizontal quenching can particularly affect phase curve observations*

Giant Exoplanets: 3D Quenching in IR "photospheres"

HD 189733b



Thermochemical equilibrium

Kinetics included (quenching)

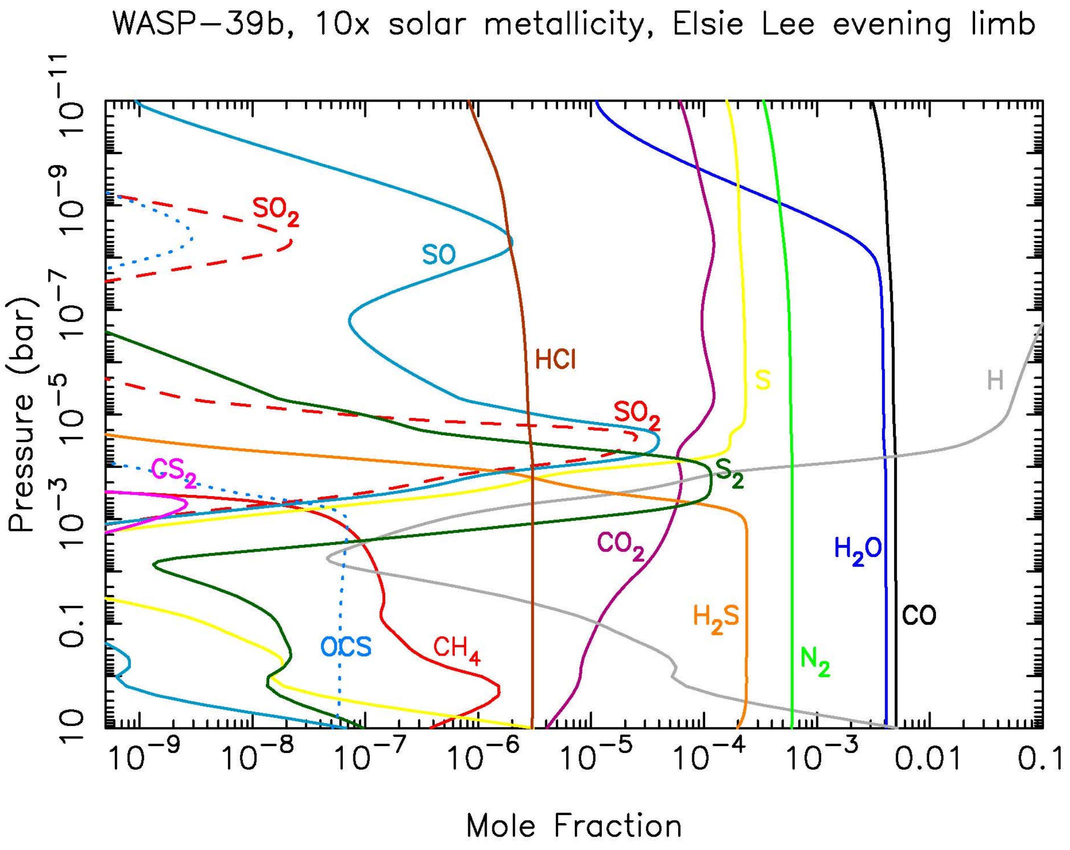
from Drummond et al. (2020)

3D-GCMs with chemical kinetics and/or quenching included via relaxation methods exhibit complicated behavior but typically show more homogenized atmospheres that would be predicted by thermochemical equilibrium. Horizontal quenching is very important for transiting giant exoplanets (e.g., Drummond et al., 2018a,b, 2020; Mendonça et al., 2018; Steinrueck et al. 2019; Zamyatina et al. 2023; Lee et al. 2023).

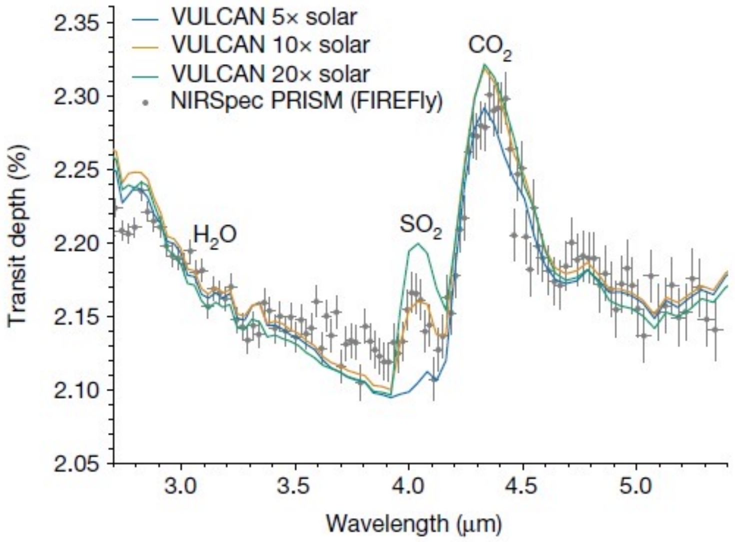
Evolving towards the ultimate goal of handling realistic chemistry in GCMs! … but photochemistry still missing, and if vertical quenching occurs deep, the deep adiabat must be prescribed realistically (see also Carone et al. 2020).

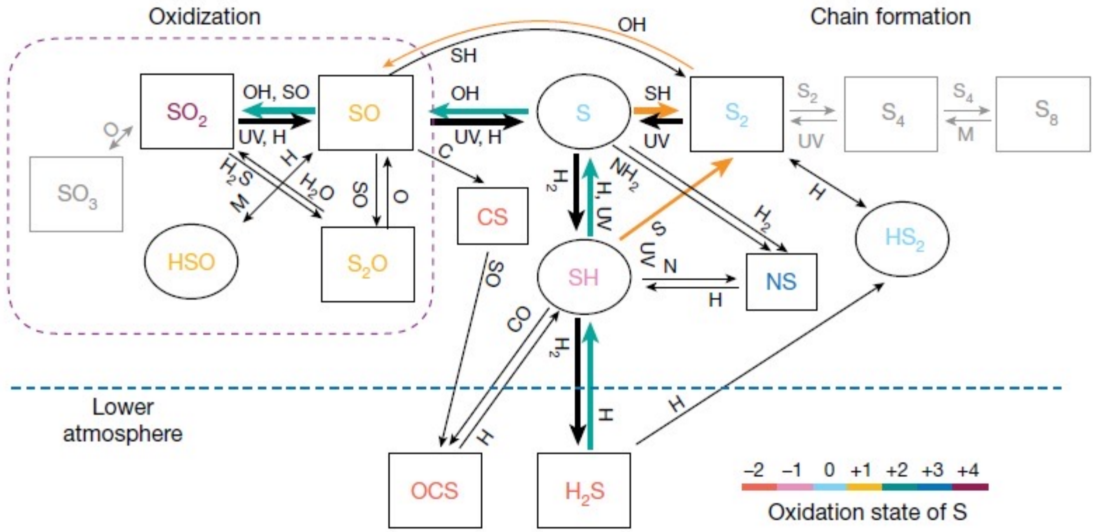
Giant Exoplanets: IR “photospheres” photochemistry

Sulfur!



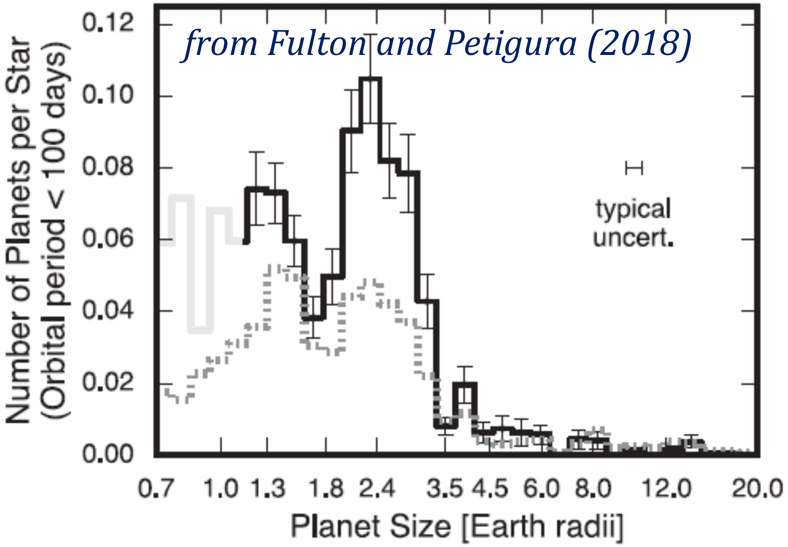
$$
\begin{aligned}
H_2O &\xrightarrow{h\nu} OH + H \\
H_2O + H &\longrightarrow OH + H_2 \\
H_2S + H &\longrightarrow SH + H_2 \\
SH + H &\longrightarrow S + H_2 \\
S + OH &\longrightarrow SO + H \\
SO + OH &\longrightarrow SO_2 + H \\
\hline
\text{net: } H_2S + 2H_2O &\longrightarrow SO_2 + 3H_2
\end{aligned}
$$



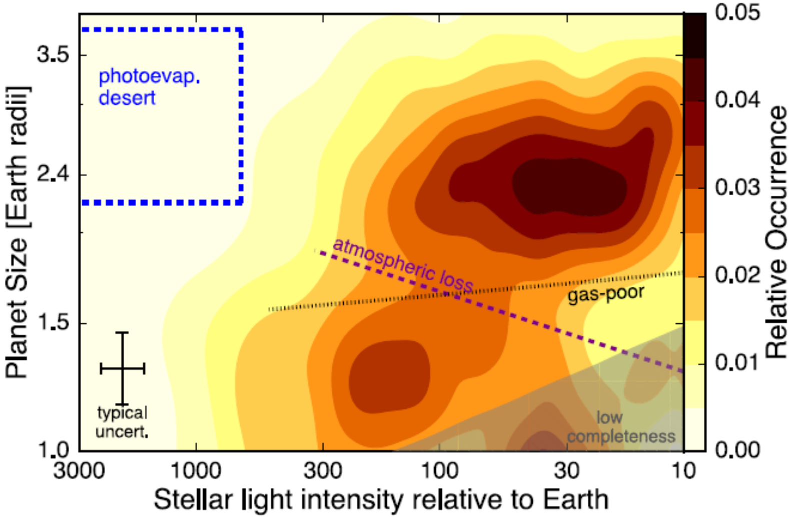


Figures and/or models from Tsai et al. (2023)

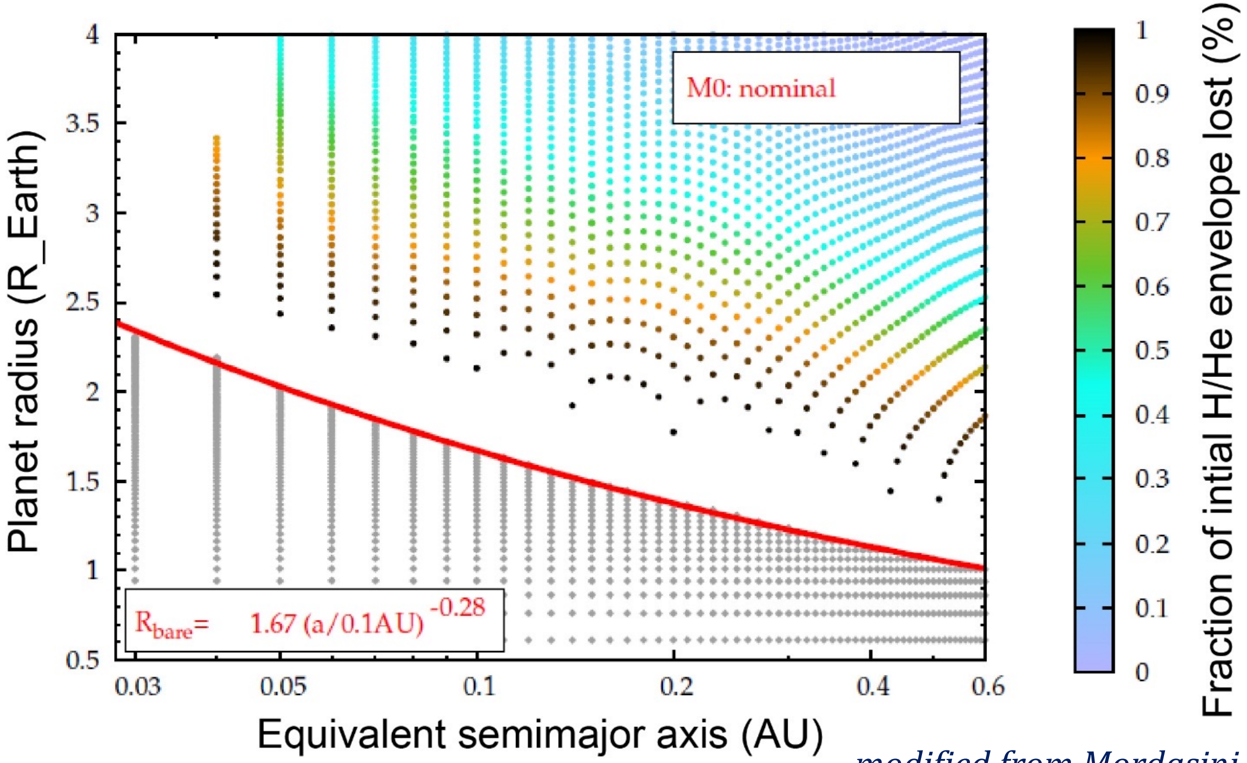
Intermediate-sized Planets



from Fulton and Petigura (2018)



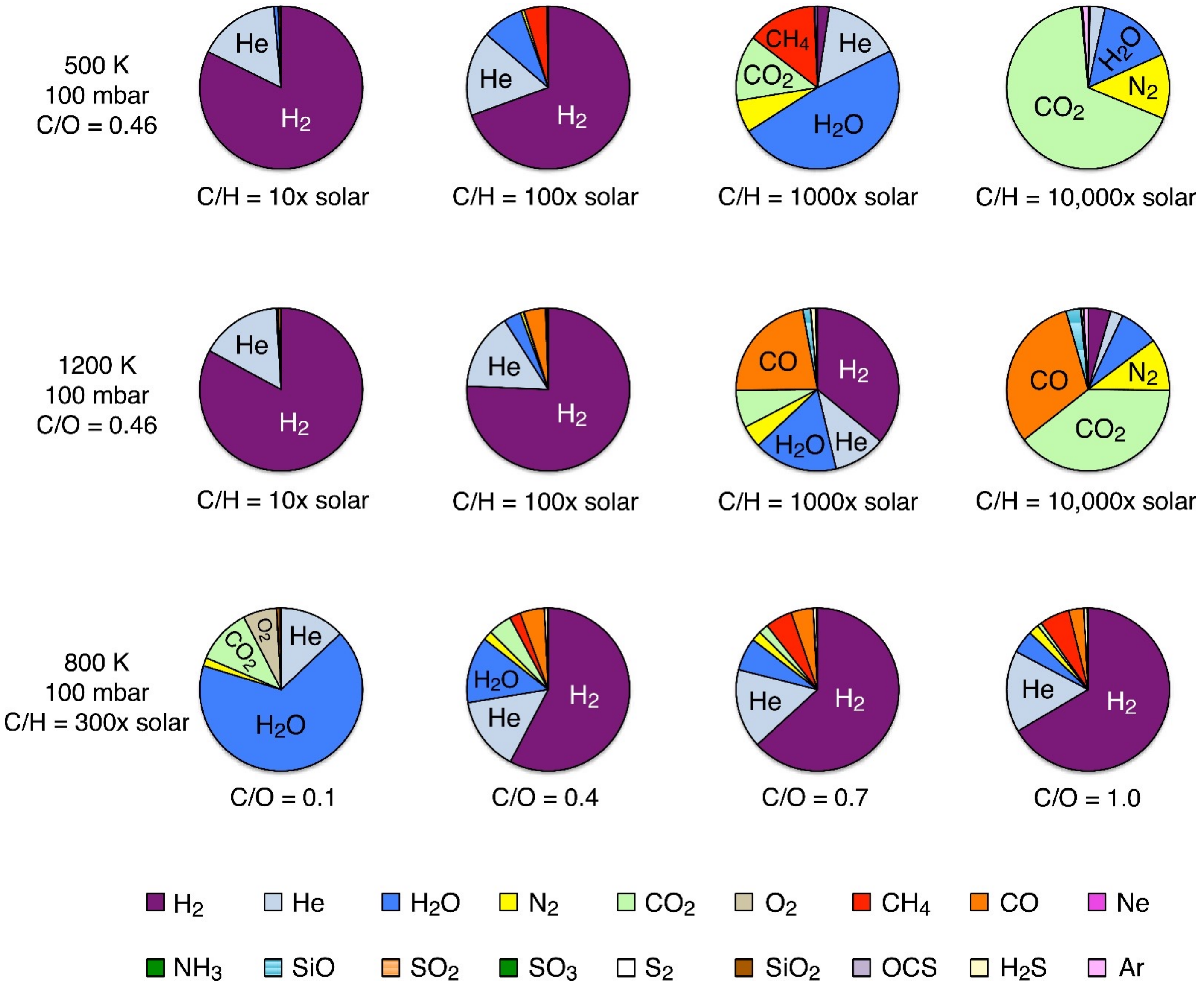
from Fulton et al. (2017)



modified from Mordasini (2020)

Sub-Neptunes transition into Super Earths due to the escape of H/He from "photoevaporation" or core-powered mass loss (or both)? e.g., Owen & Wu, 2013; Lopez & Fortney, 2014; Gupta & Schlichting, 2019; Mordasini, 2020

Thermochemical Equilibrium: Giants through Intermediate

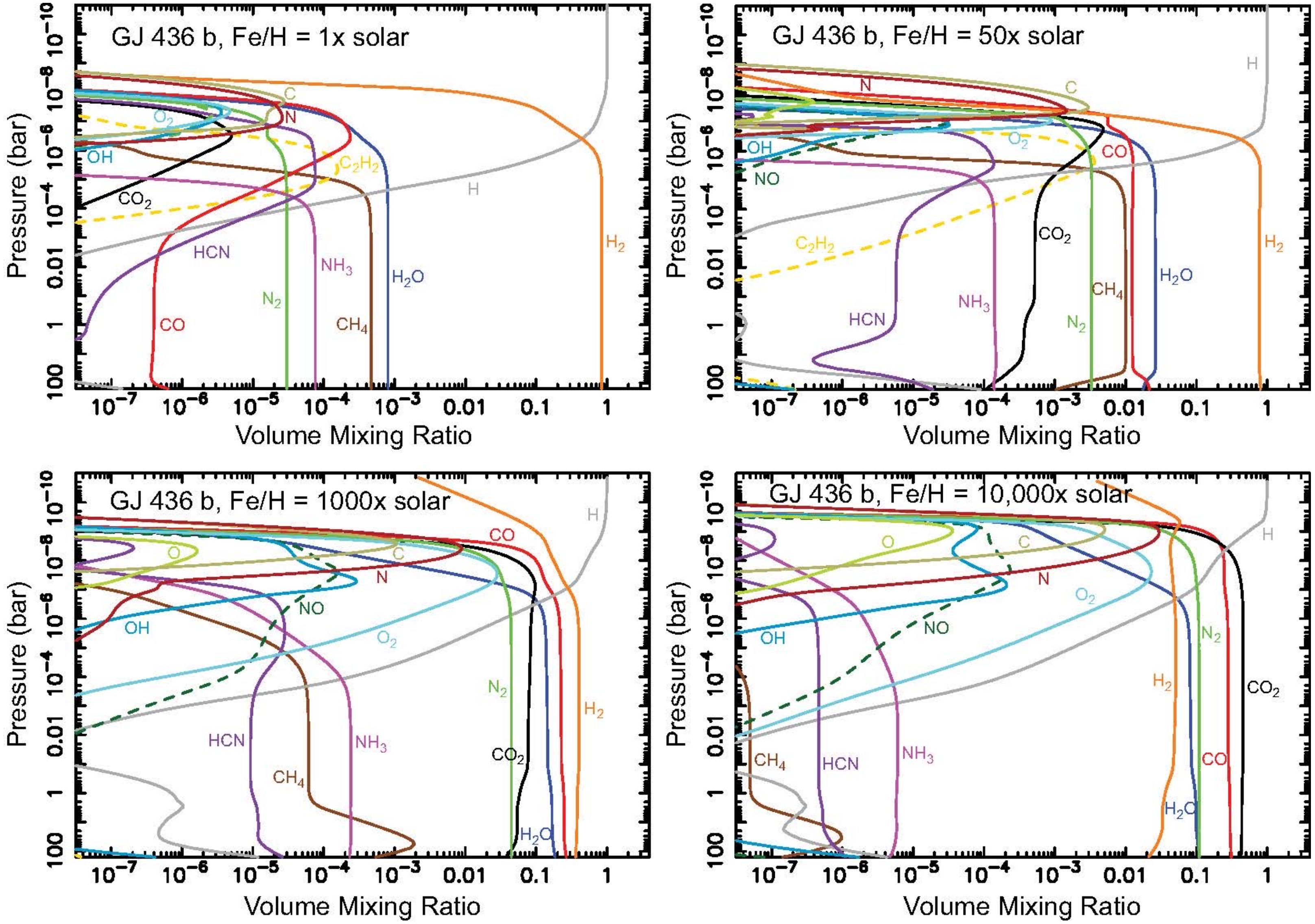


Neptune-class exoplanets, sub-Neptunes, and super-Earths are likely to have diverse atmospheric compositions. Even if different planets formed in a similar location or similar ways, their evolutionary history could differ (impacts, escape, outgassing, etc.)

Thermochemical equilibrium can help define the possible parameter space

from Moses et al. (2013); see also Guzmán-Mesa et al. (2022)

Photochemistry: Intermediate-sized Exoplanets



As H is lost from intermediate-sized planets, CO_2 and N_2 become more prominent and species such as CH_4 and NH_3 become less prominent, but H_2O is still important until atmosphere is severely depleted in hydrogen. There are probably lots of Venus-like super-Earths in known exoplanet population.

from Moses et al. (2013)

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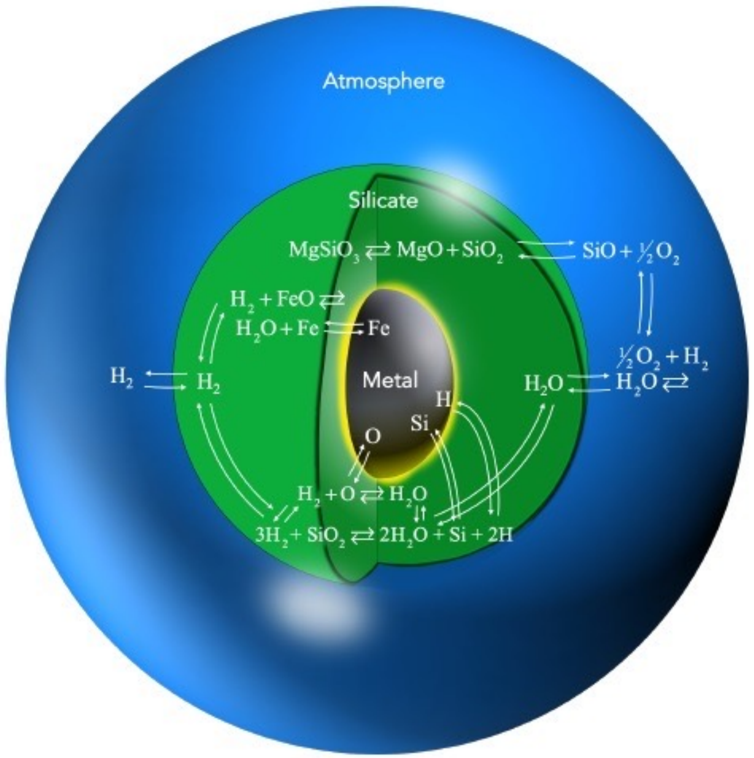
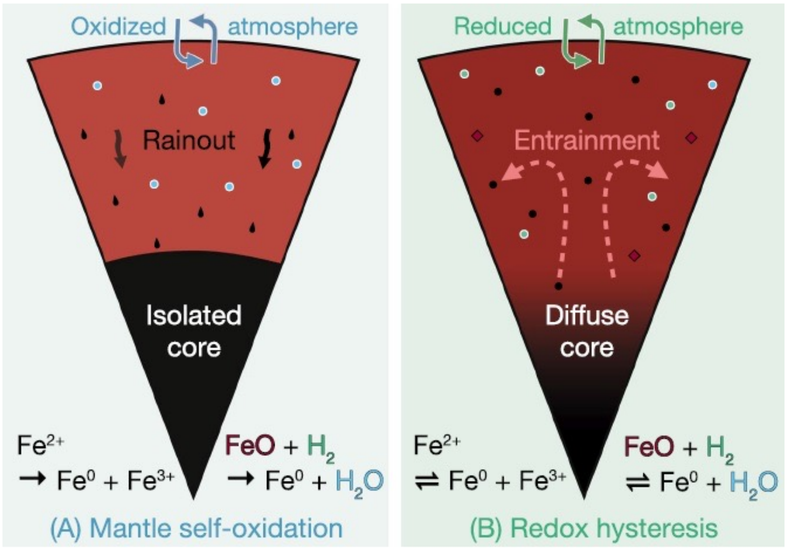
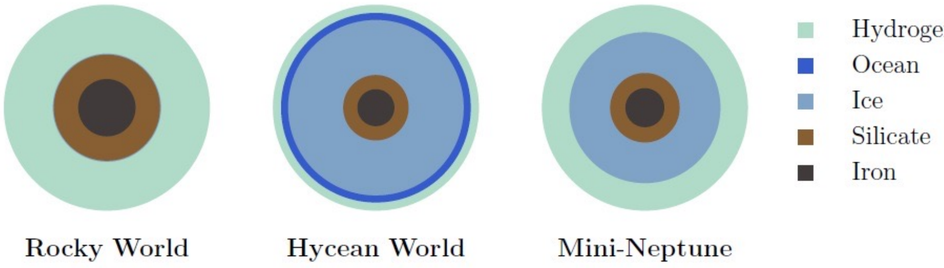
Thermochemical Equilibrium: Intermediate-sized Planets



from Schlichting & Young (2022)



from Lichtenberg (2021)

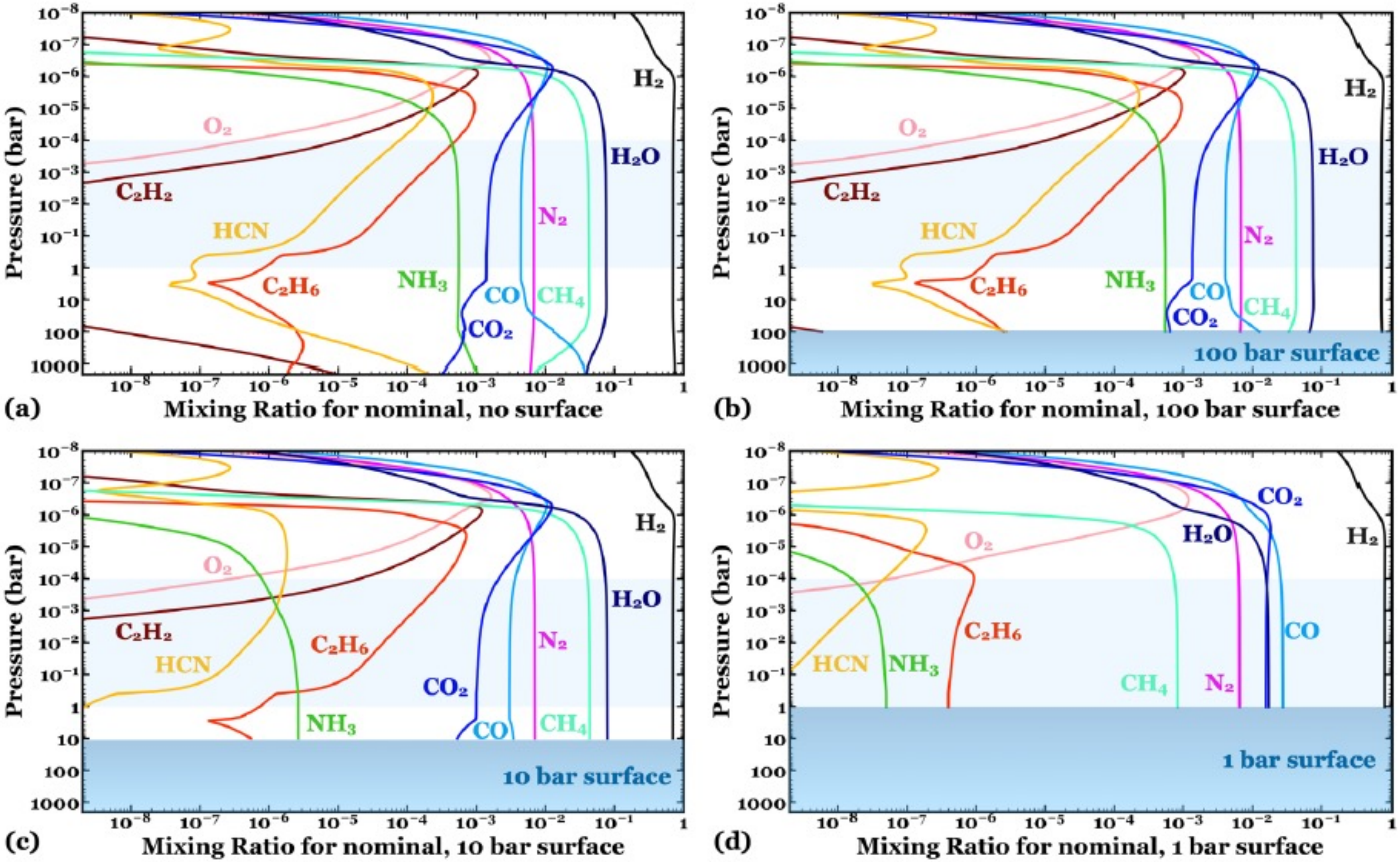


from Madhusudhan et al. (2023)

Radius valley: Neptunes and ***sub-Neptunes*** *are likely to have higher-metallicity atmospheres than hot Jupiters, assuming accretion of H/He occurs at all. If the H/He escapes, they can become* ***super-Earths****. While super-Earths don't have "primordial" H/He atmospheres, outgassing and retention of species is possible*

To estimate bulk atmospheric content, **consider the planet in context** with its radius, mass, interior models (e.g., Malsky & Rogers, 2020; Kite et al., 2021; Schlichting & Young 2022), evolutionary history (including EUV instellation, e.g., Owen & Wu; Lopez & Fortney; Mordasini; and dissolution/ outgassing, e.g., Kite et al., Schaefer et al., Misener & Schlichting)

Photochemistry: sub-Neptune with inert surface

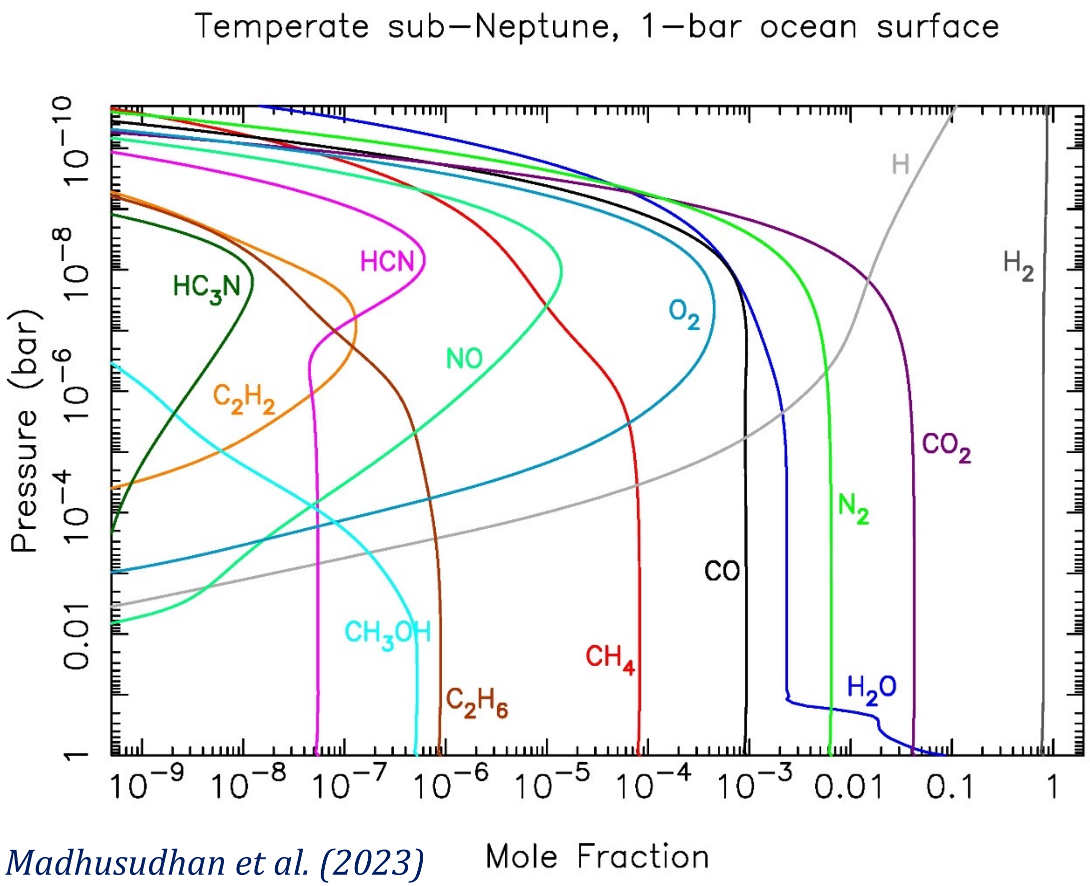


from Yu et al. (2021)

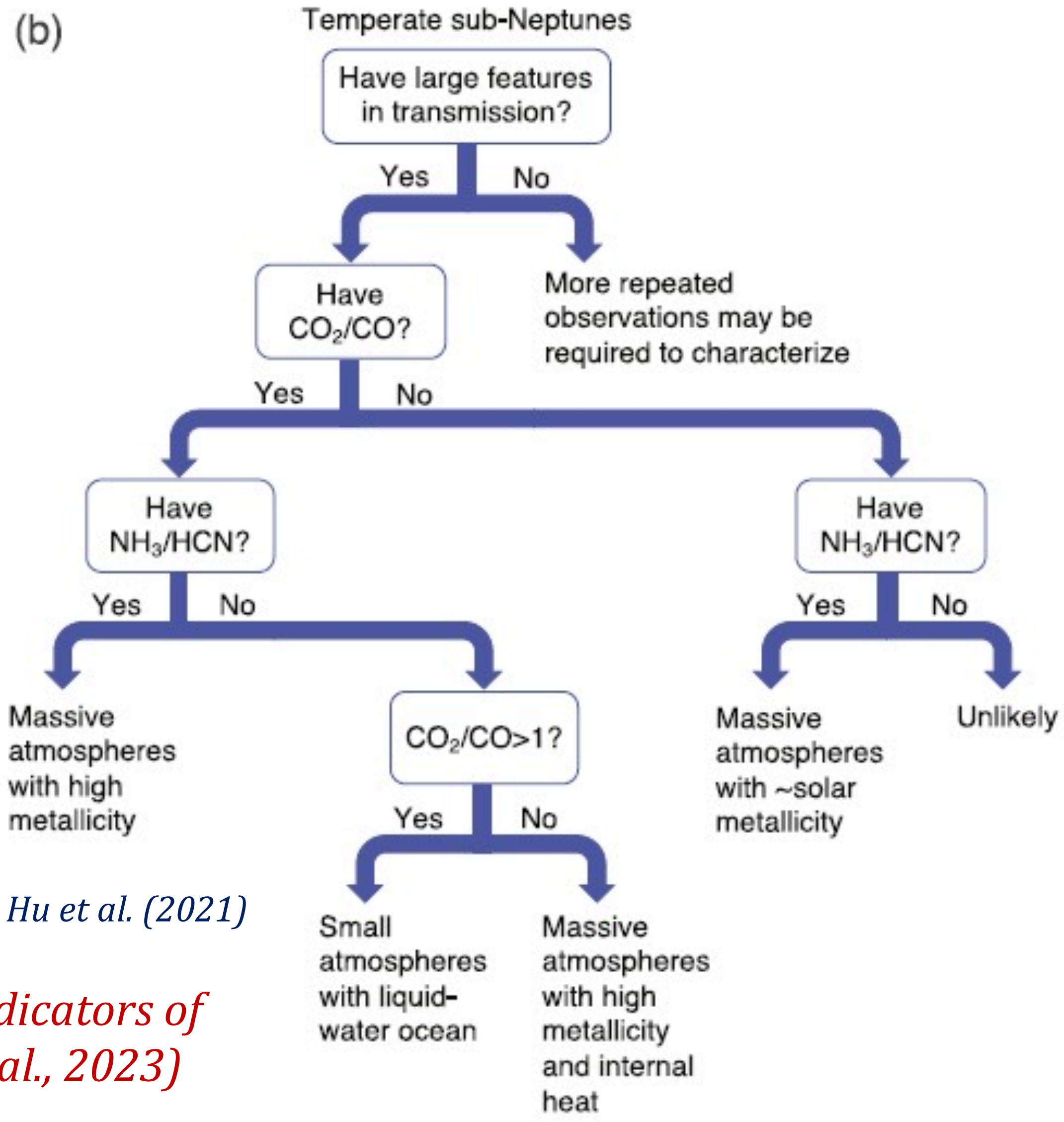
The presence of a surface can affect atmospheric chemistry, even if the atmosphere and surface do not interact, simply because the atmosphere may not reach high-enough temperatures at depth to recycle photochemical products (e.g., Yu et al., 2021; Tsai et al., 2021).

Of course, the surface may not be "inert" and surface-atmosphere exchange can also occur, altering the atmospheric composition, e.g., magma oceans, water oceans, active geology, biology, etc. (see Kite et al. papers, Schlichting & Young, 2021; Krissansen-Totton et al., 2021; Hu et al., 2021).

Photochemistry: Temperate sub-Neptune with ocean



from Madhusudhan et al. (2023)



from Hu et al. (2021)

Also, observations of CH_3OH and C_2H_6 might provide good indicators of the presence of a surface (Tsai et al., 2021; Madhusudhan et al., 2023)

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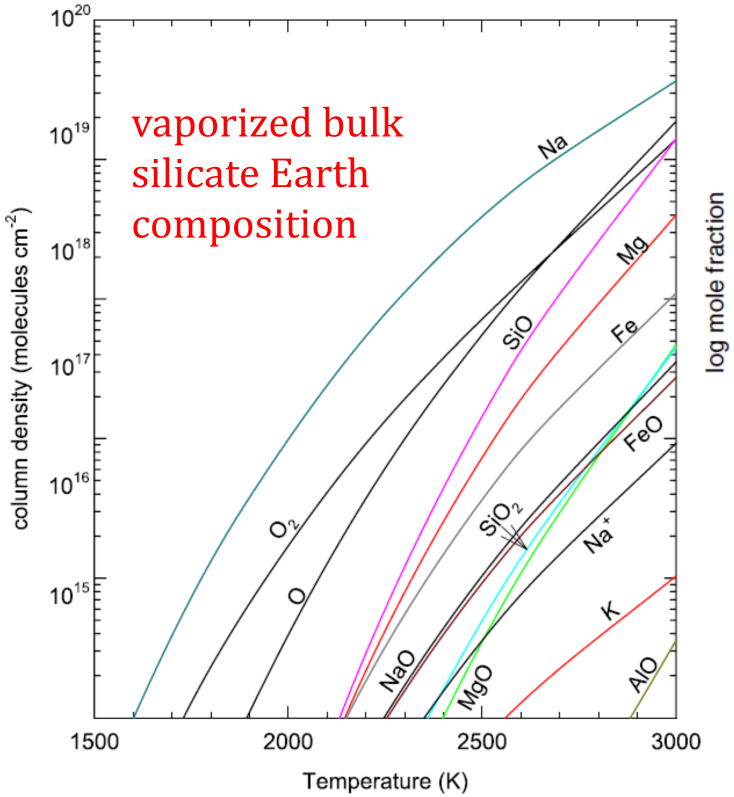
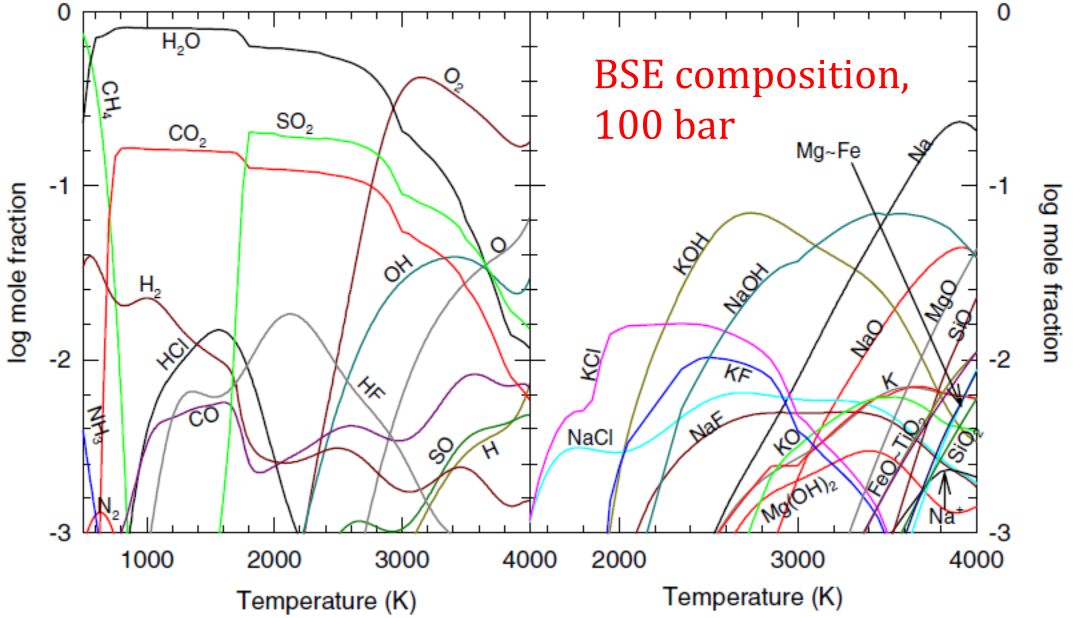
Thermochemical Equilibrium: Hot Rocky Planets



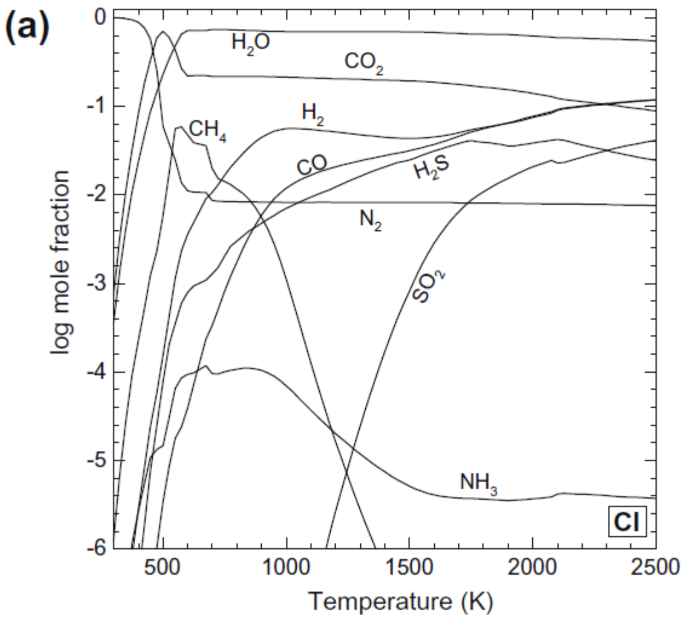
vaporized bulk silicate Earth composition

Atmospheric composition as a function of T for planet with g = 36.2, from Schaefer et al. (2009)

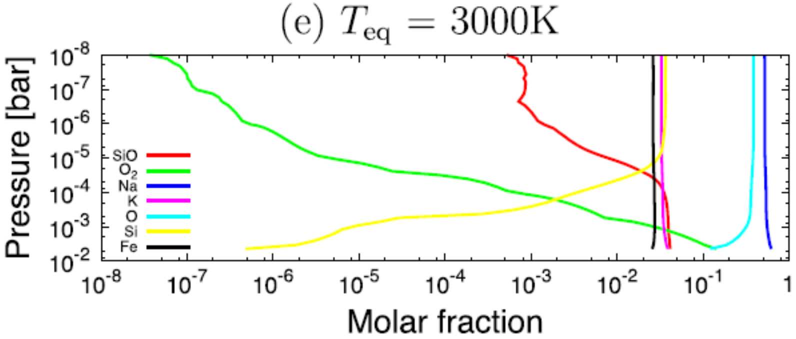


BSE composition, 100 bar

from Schaefer et al. (2012)



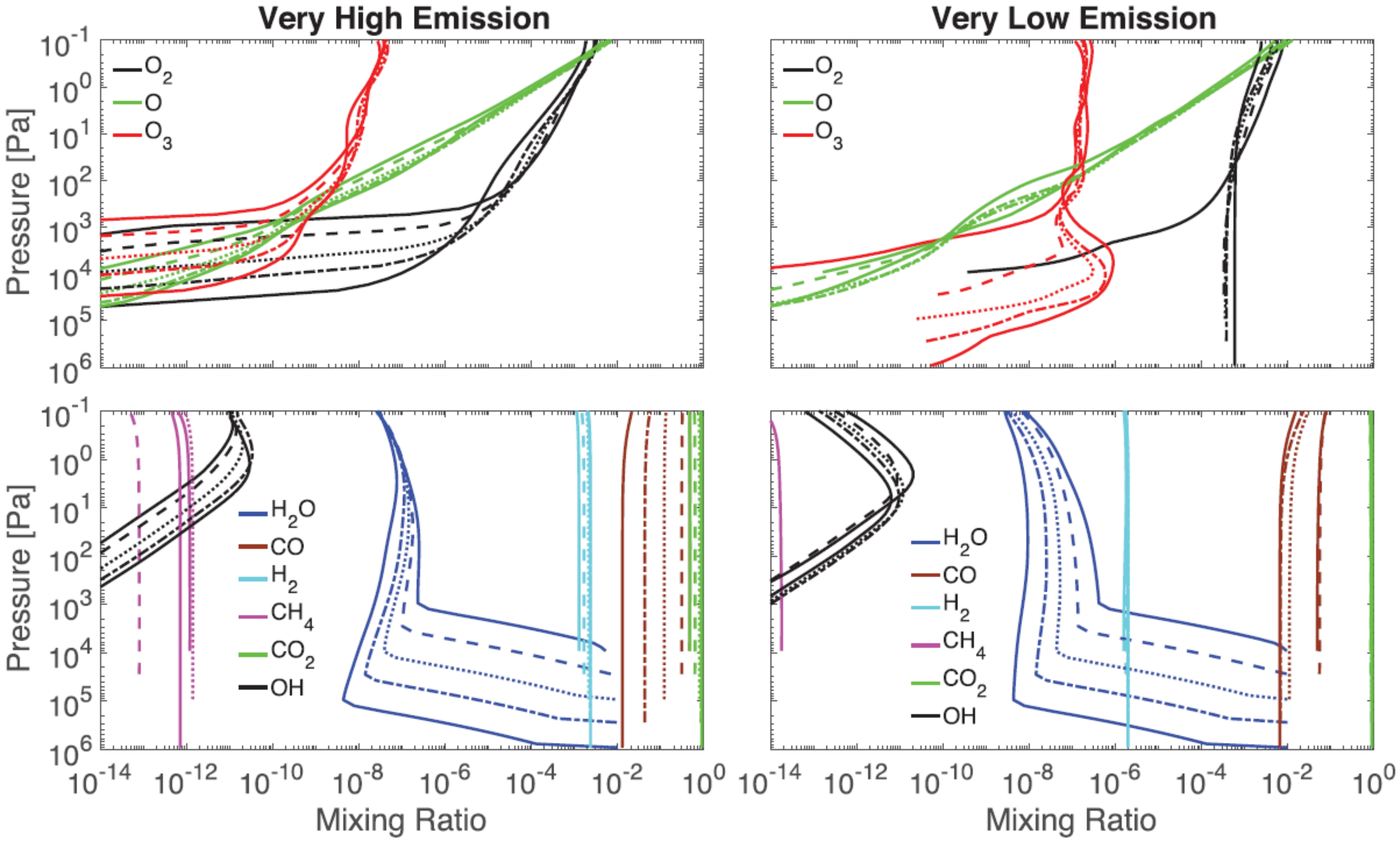
Outgassed atmospheric composition at 100 bar from rocky planet with assumed CI chondrite composition, from Schaefer et al. (2010)


(e) $T_{\rm eq} = 3000$K

Hot rocky super-Earth atmosphere, from Ito et al. (2015)

Secondary atmosphere affected by "geochemistry"

Photochemistry: Rocky Exoplanets



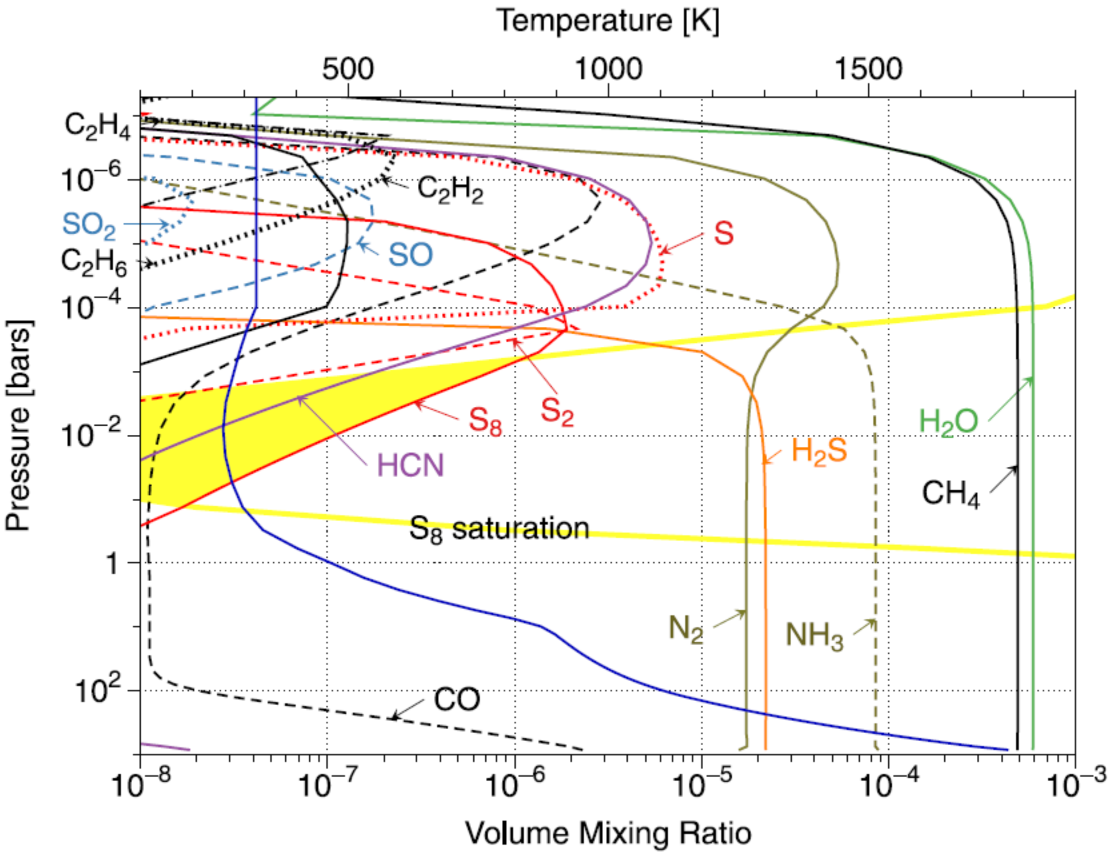
from James & Hu (2018)

For rocky terrestrial planets, boundary conditions and assumptions about background atmospheric composition control almost everything!

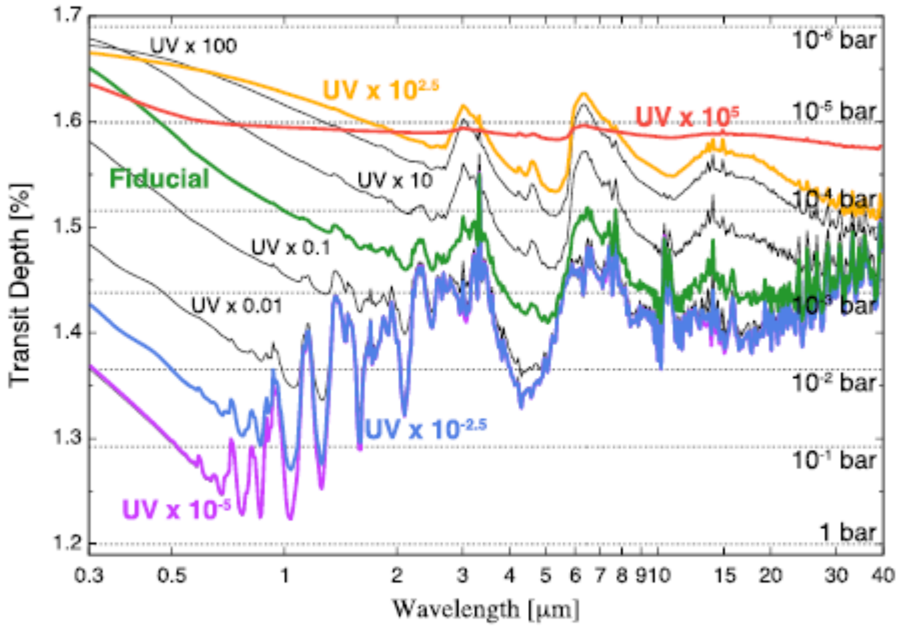
- *Outgassing flux matters*
- *Effect of ocean (magma & water)*
- *Potential biosignatures*
- *Effect of stellar type*
- *Different catalytic cycles*
- *Pre-biotic chemistry*

Is O_2 a biosignature on CO_2-dominant planets? e.g., James & Hu (2018), Hu et al. (2020), Harman et al. (2015, 2018), Ranjan et al. (2023) → atmospheric top boundary location matters

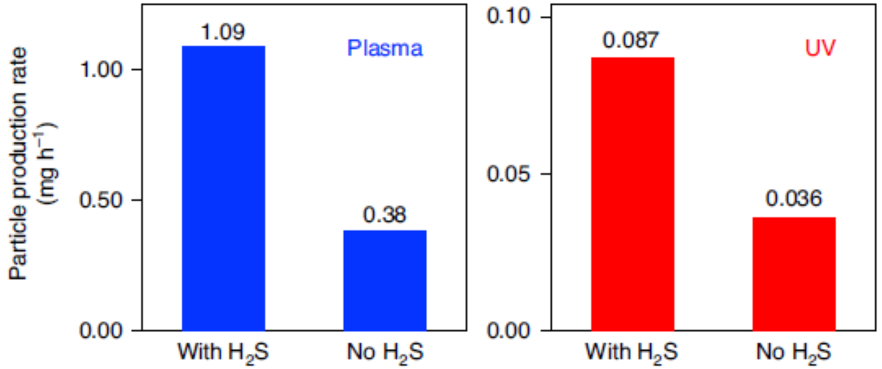
Photochemically produced hazes



from Gao et al. (2017), sulfur haze on a young Jupiter; see also Lavvas et al. (2017, 2019, 2021)



from Kawashima & Ikoma (2019), organic haze on warm sub-Neptunes



from He et al. (2020), laboratory simulations super Earth / sub-Neptune atmospheres

Conclusions

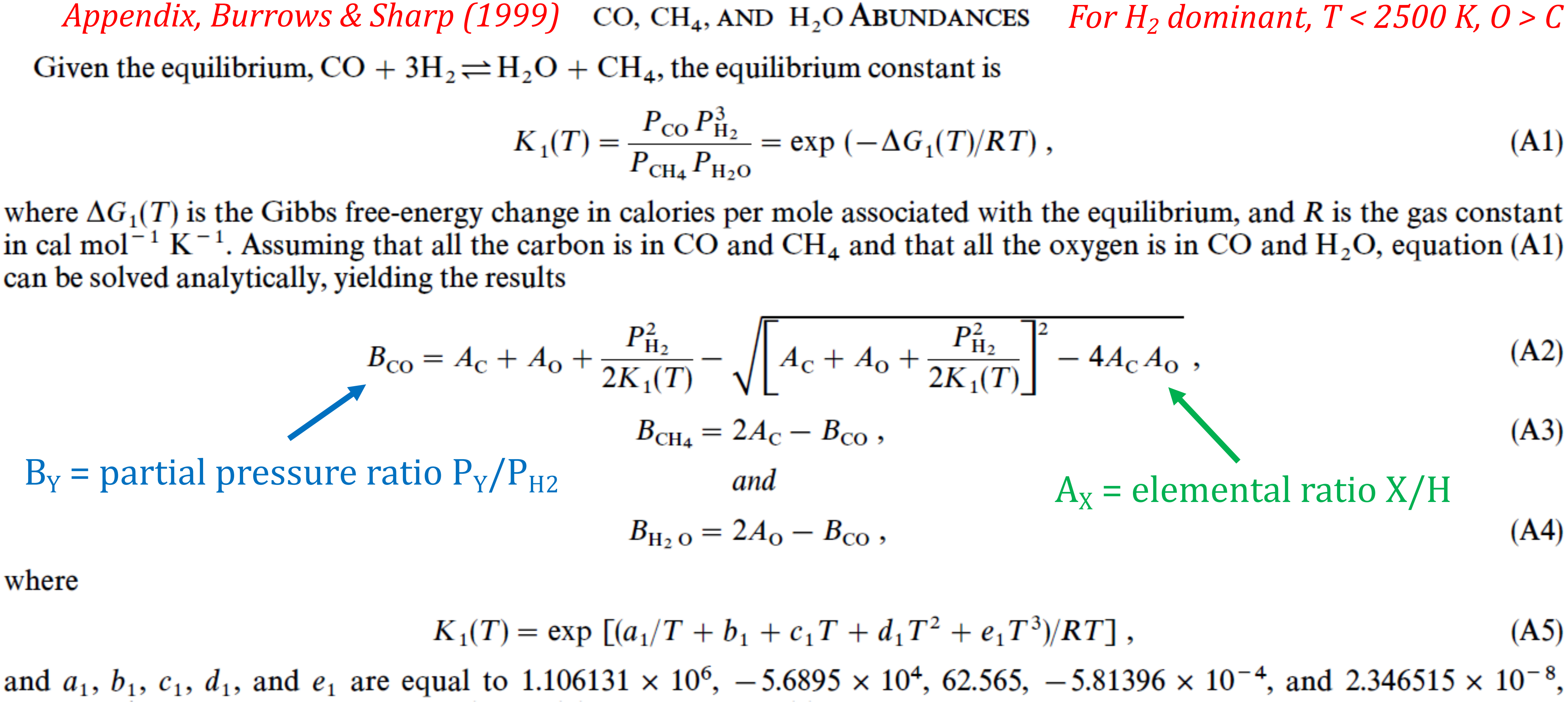
- Thermochemical equilibrium is a good starting point for predicting atmospheric composition, but disequilibrium processes like transport-induced quenching and photochemistry are likely affecting exoplanet atmospheres.
- Quenching is important if the planet has thermal gradients crossing from above to below ~1000 K. *Practical tip:* assume thermochemical equilibrium to some quench point (treat as free parameter) and then assume vertically constant mixing ratio above that point. Quenching likely affects observations on transiting planets.
- Photochemistry is more important for cooler planets. On hot ones, kinetics can drive composition back to equilibrium. Photochemically produced species have non-constant profiles (greater mixing ratio in peak production region). *Practical tip*: take a vertical profile from a chemical model and scale it, using the scaling factor as a free parameter. Key photochemical products on a variety of exoplanets include C_xH_y hydrocarbons, HCN, O_2, O_3, sometimes CO_2, depending on situation, and hazes
- Super-Earths/sub-Neptune atmospheres are probably widely diverse, potentially exotic, and chemically interesting; don't presume anything. Same with terrestrial exoplanets. "Free" retrievals may be better.
- 3D effects matter for the chemistry of tidally locked planets. Practical tip may be to consider vertically quenched dayside atmospheric composition as representative everywhere… situation dependent.
- Use chemical models as a sanity check for retrievals, to help break degeneracies in posterior distributions, and to better understand exactly what you're seeing and what that's telling you about big-picture things

Back-up slides

Thermochemical Equilibrium: Giant Planets

Appendix, Burrows & Sharp (1999)

For H_2 dominant, $T < 2500$ K, $O > C + Si$



CO, CH_4, AND H_2O ABUNDANCES

Given the equilibrium, $CO + 3H_2 \rightleftharpoons H_2O + CH_4$, the equilibrium constant is

$$K_1(T) = \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}} = \exp\left(-\Delta G_1(T)/RT\right) , \tag{A1}$$

where $\Delta G_1(T)$ is the Gibbs free-energy change in calories per mole associated with the equilibrium, and R is the gas constant in cal mol^{-1} K^{-1}. Assuming that all the carbon is in CO and CH_4 and that all the oxygen is in CO and H_2O, equation (A1) can be solved analytically, yielding the results

$$B_{CO} = A_C + A_O + \frac{P_{H_2}^2}{2K_1(T)} - \sqrt{\left[A_C + A_O + \frac{P_{H_2}^2}{2K_1(T)}\right]^2 - 4A_C A_O} , \tag{A2}$$

$$B_{CH_4} = 2A_C - B_{CO} , \tag{A3}$$

and

$$B_{H_2O} = 2A_O - B_{CO} , \tag{A4}$$

B_Y = partial pressure ratio P_Y/P_{H2}

A_X = elemental ratio X/H

where

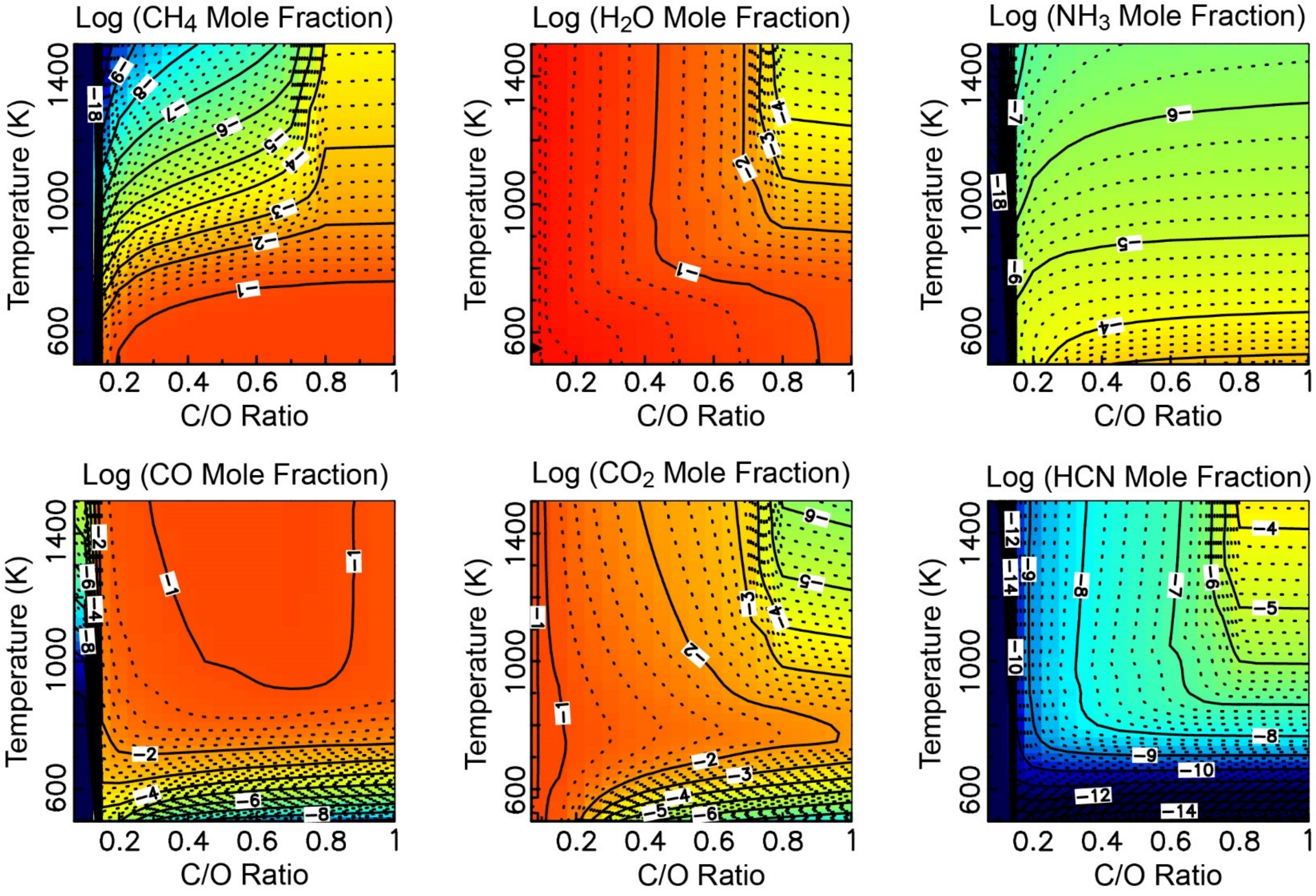
$$K_1(T) = \exp\left[(a_1/T + b_1 + c_1 T + d_1 T^2 + e_1 T^3)/RT\right] , \tag{A5}$$

and a_1, b_1, c_1, d_1, and e_1 are equal to 1.106131×10^6, -5.6895×10^4, 62.565, -5.81396×10^{-4}, and 2.346515×10^{-8},

Similar procedure for NH_3-N_2. Heng et al. (2016) add C_2H_2; see also Woitke et al. (2021) for H_2O, N_2, CO_2, CH_4

J. Moses, ERS Theory talk, Aug. 2021

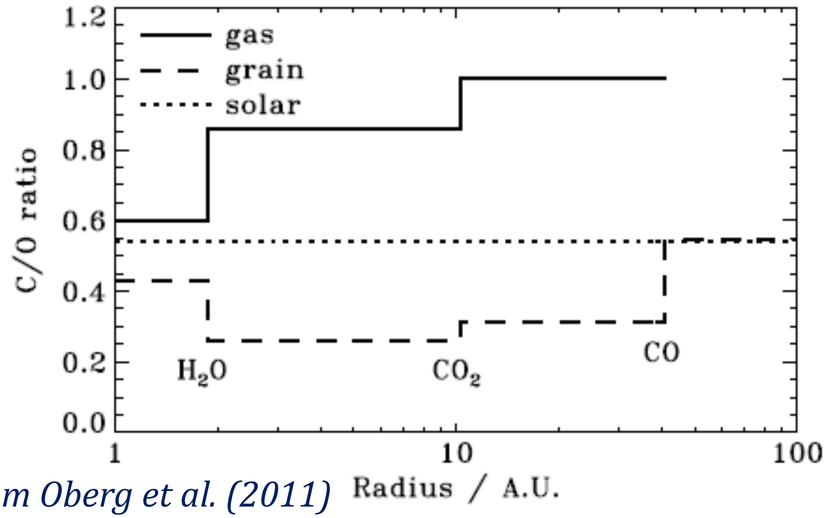
Giant Planets: thermochemical equilibrium in IR "photosphere"



at 100 mbar, 300x solar metallicity *modified from Moses et al. (2013b)*

Thermochemical equilibrium predictions will depend on the relative abundance of the different elements, including metallicity (Fe/H) and **C/O ratio**

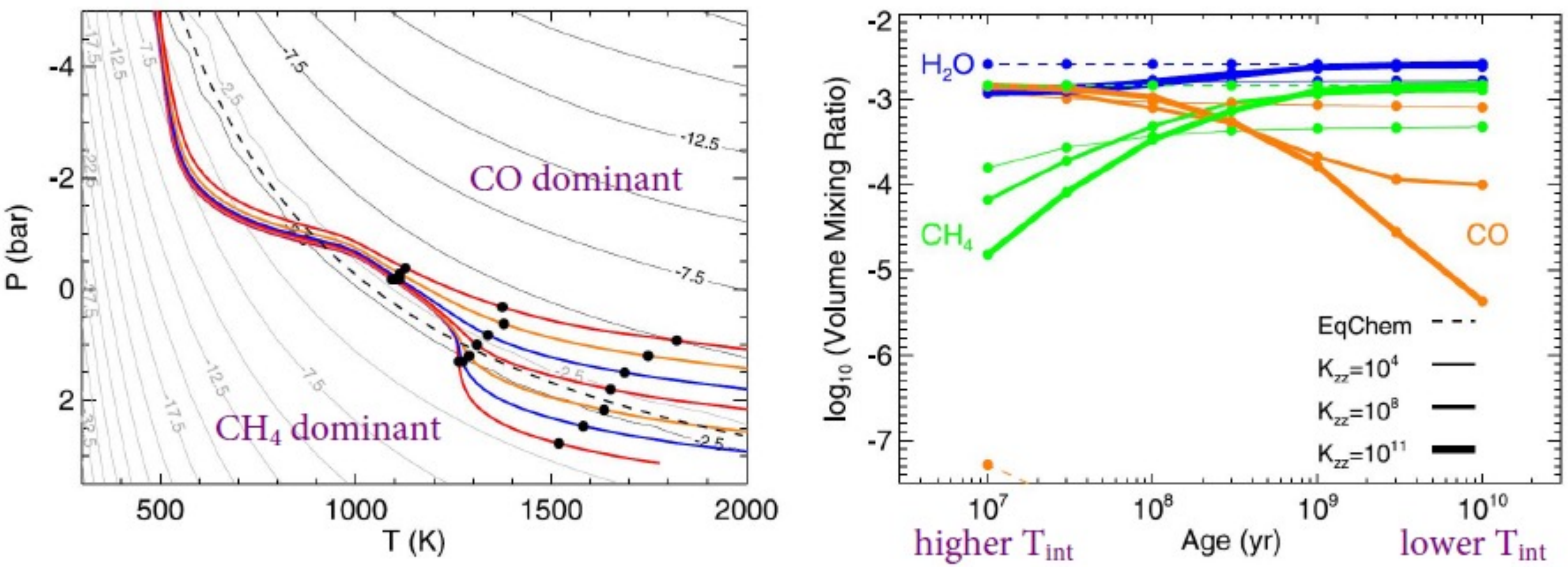
see also Hu & Seager (2014), Woitke et al. (2021)



from Oberg et al. (2011)

Transport-Induced Quenching

Quench point depends on internal heat flux and dynamics



from Fortney et al. (2020)

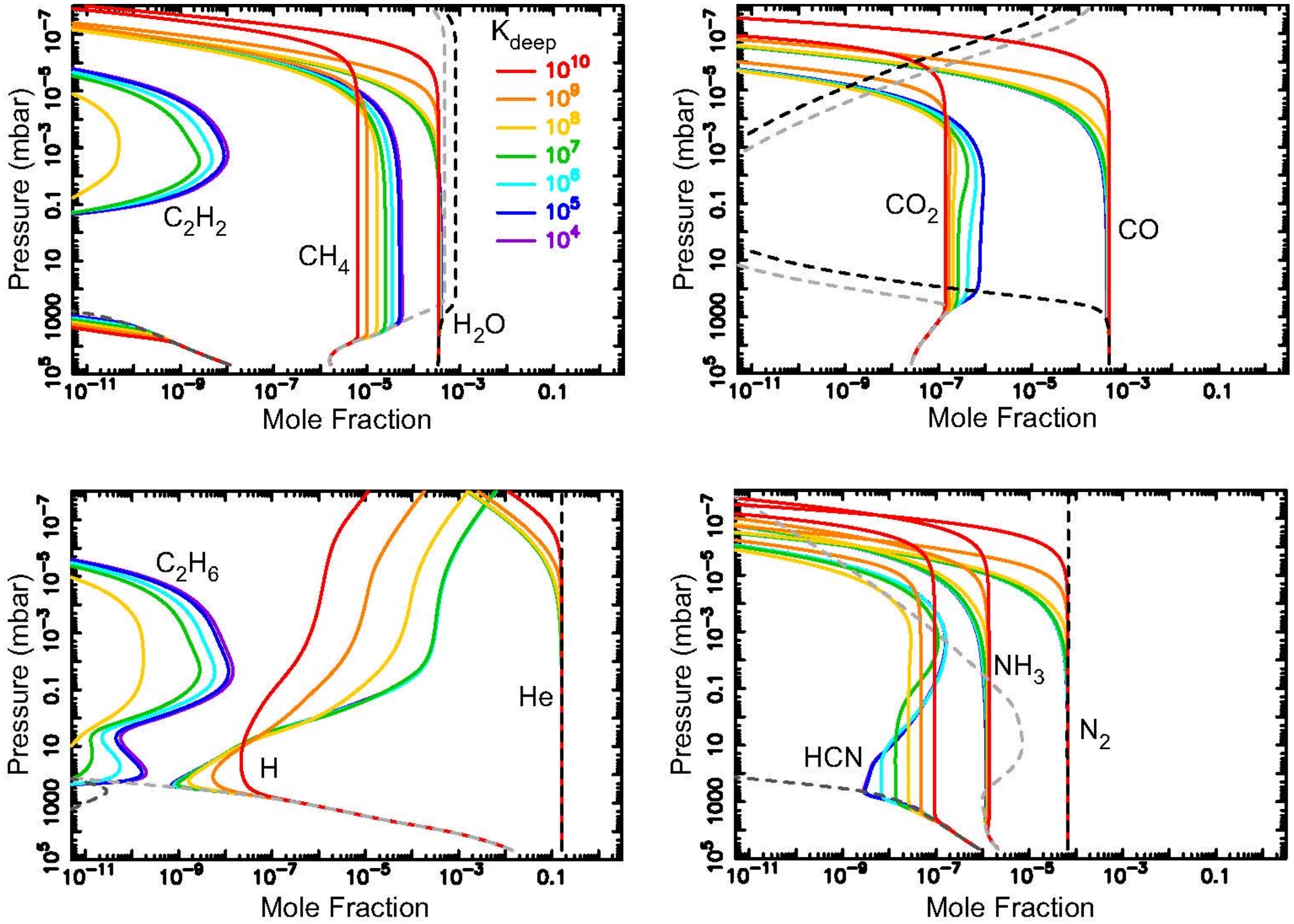
Quenching happens when $\tau_{dyn} \le \tau_{chem}$ (e.g., Prinn and Barshay, 1977)

So, you just need to figure out what pressure that occurs at, and quenched abundances equal equilibrium abundances at that point.

BUT… both τ_{dyn} and τ_{chem} are model-dependent

Practical tips for predicting quench points: Visscher & Moses, 2011; Venot et al., 2012; Moses, 2014; Zahnle & Marley, 2014; Tsai et al., 2018).

Transport-Induced Quenching



Quench point depends on dynamics

Quenching happens when $\tau_{dyn} \leq \tau_{chem}$ (e.g., Prinn and Barshay, 1977)

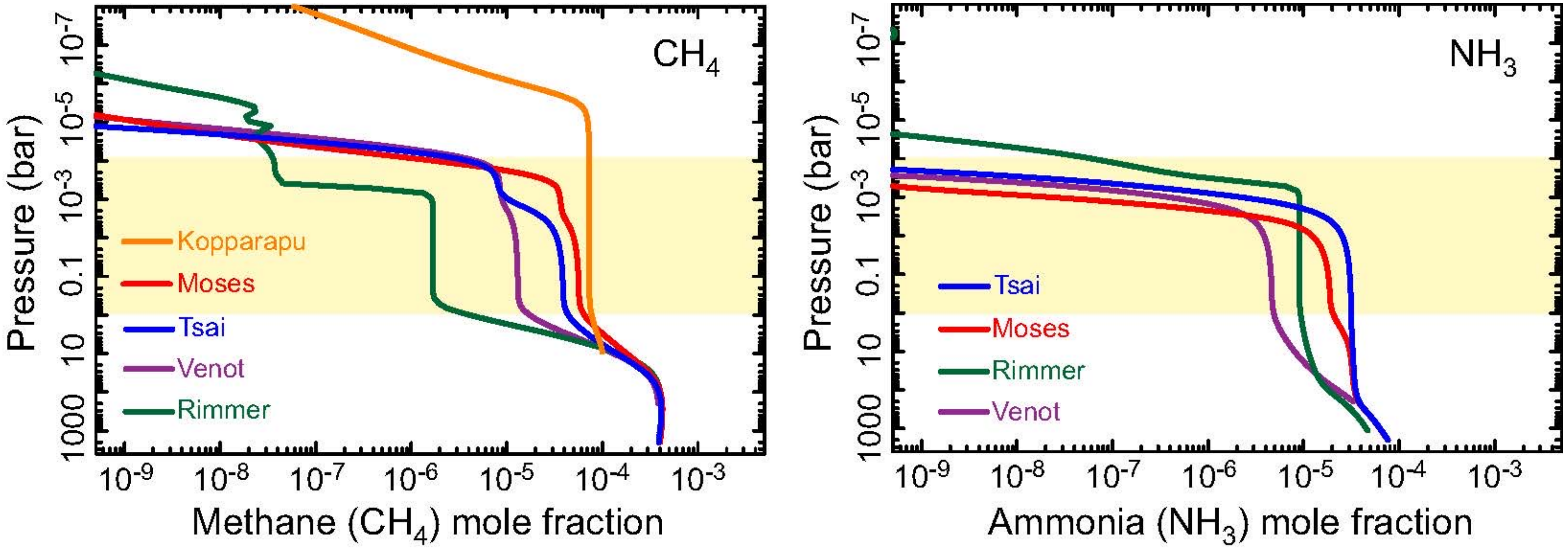
So, you just need to figure out what pressure that occurs at, and quenched abundances equal equilibrium abundances at that point.

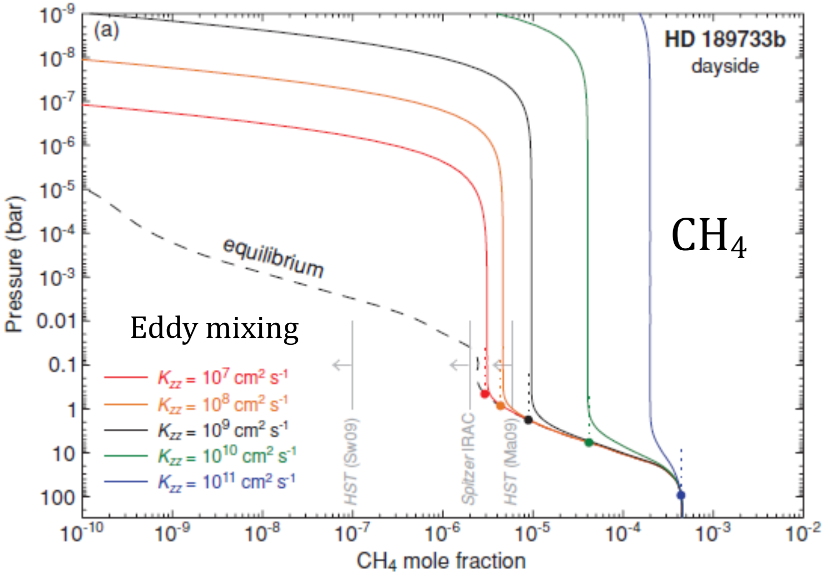
BUT… both τ_{dyn} and τ_{chem} are model-dependent, so quench points can be complicated to predict in practice (e.g., Visscher & Moses, 2011; Venot et al., 2012; Moses, 2014; Zahnle & Marley, 2014; Tsai et al., 2018). The method in the Z&M is probably the easiest to use, but it still depends on an uncertain reaction mechanism and K_{zz} profile

J. Moses, ERS Theory talk, Aug. 2021

Transport-Induced Quenching

Hypothetical hot Jupiter benchmark tests, Ben Drummond's ISSI team meeting

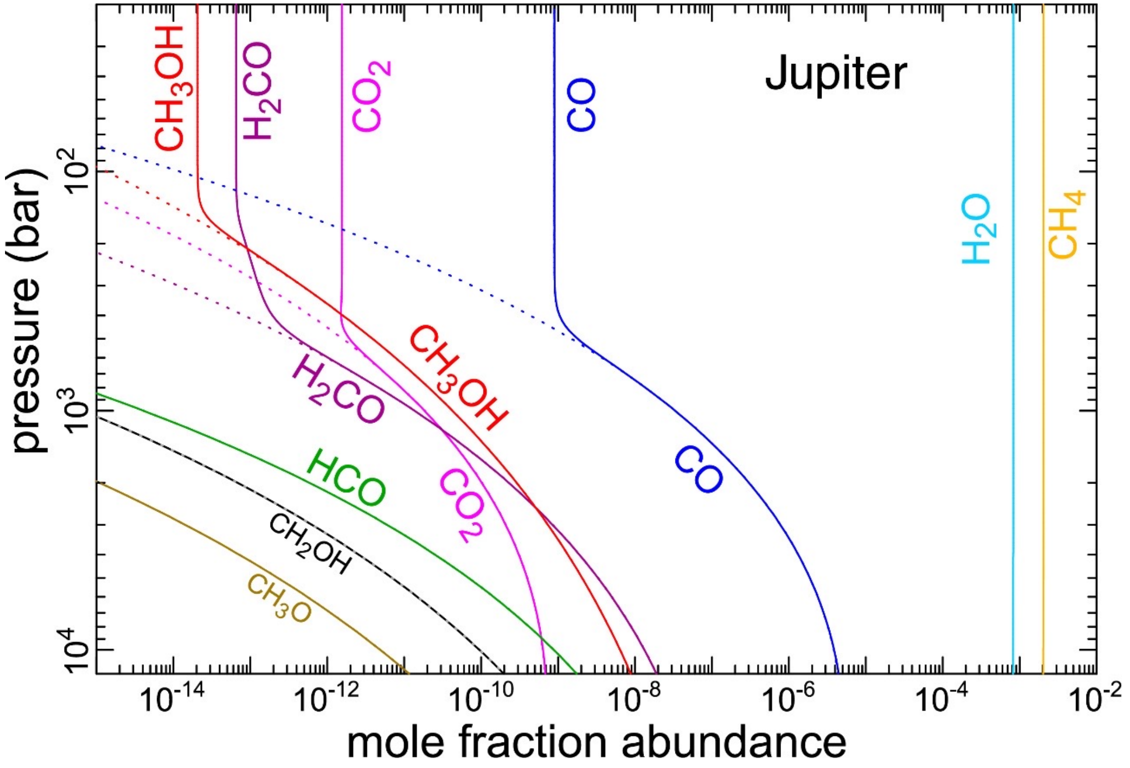




from Visscher & Moses (2011)

The predicted quenched abundances depend on the assumed chemistry as well as the assumed transport rates. Different modelers use different reaction mechanisms.

Transport-Induced Quenching: What should you do?



Lots of uncertainties revolving around quenching, so how should you handle it for your own application?

(1) Just pick someone's method (e.g., Visscher & Moses, 2011; Zahnle & Marley; 2015; Tsai et al., 2018) and consider a range of possible parameter space, especially in K_{zz}

(2) Run your own kinetics-transport model to more accurately predict things yourself

(3) Most practical solution: Consider the CH_4-CO-H_2O and NH_3-N_2 quench points as (separate) free parameters in your retrievals/forward spectra models… following equilibrium at depth and using (1) to define a reasonable range of possible quench points. Assume constant mixing ratio above quench point

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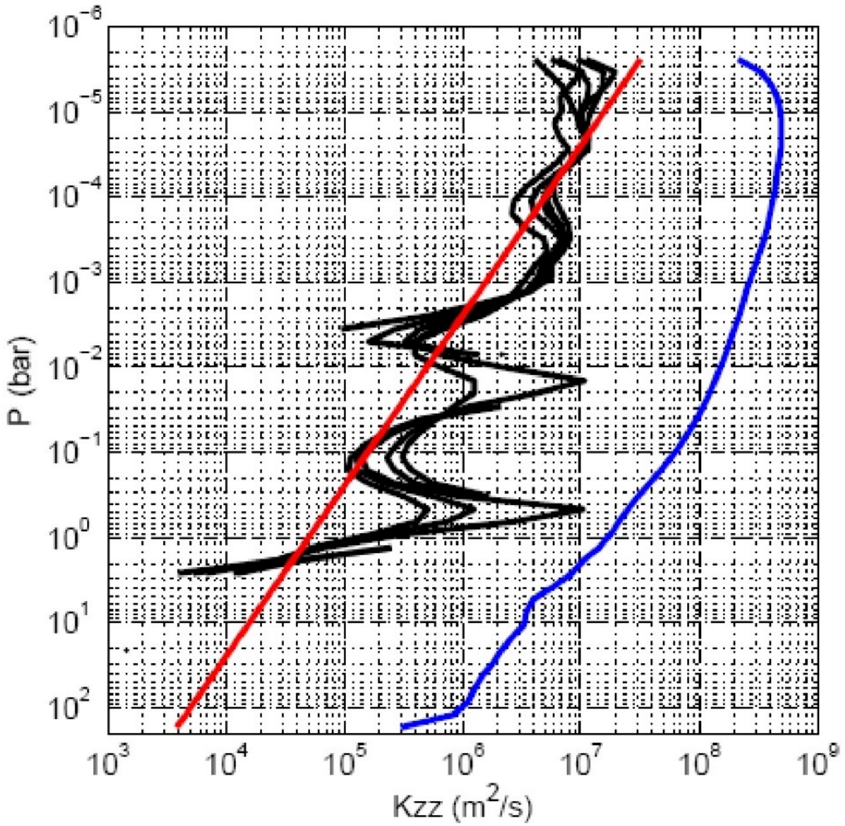
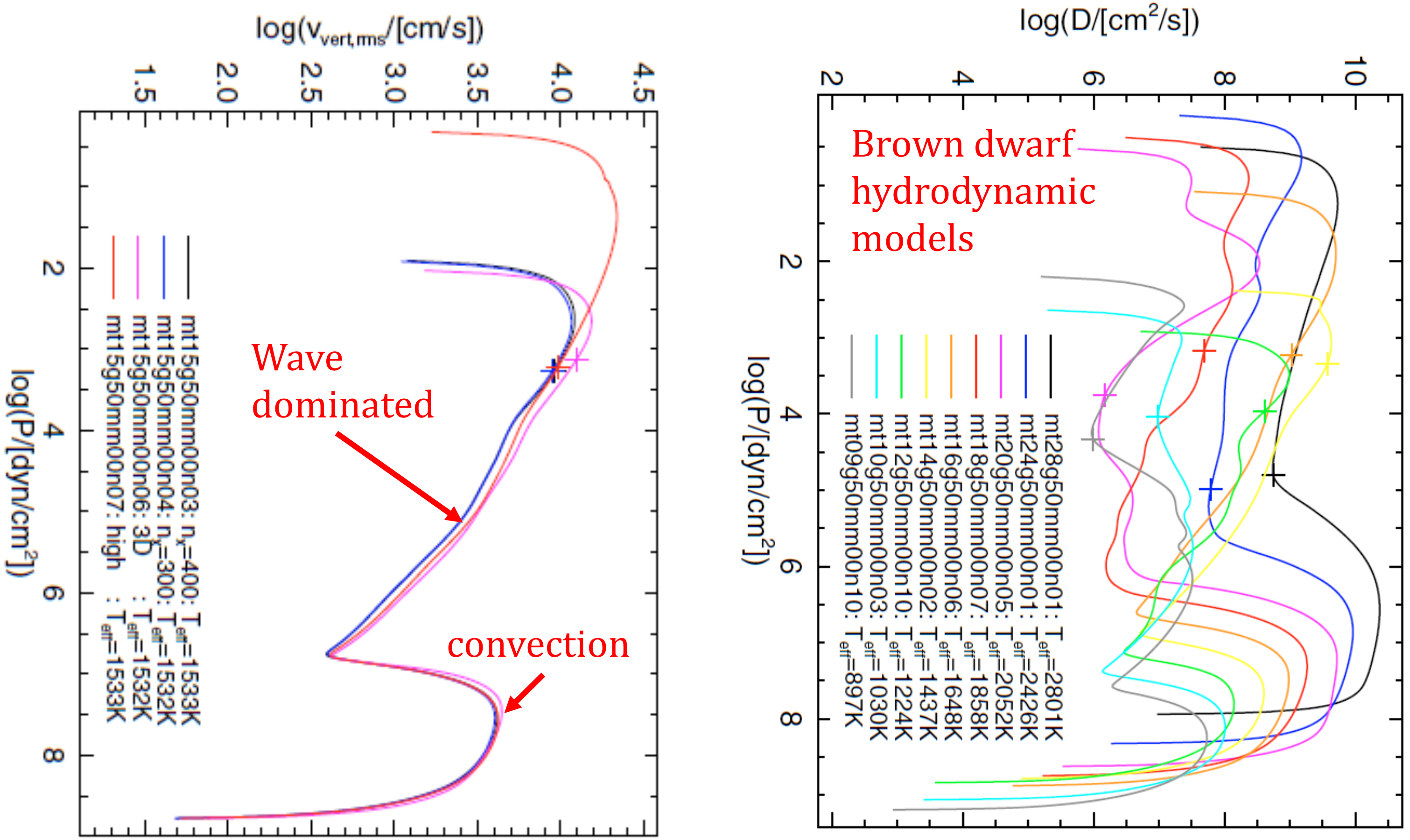
Photochemistry: What to do about K_{zz}



from Parmentier et al. (2013)



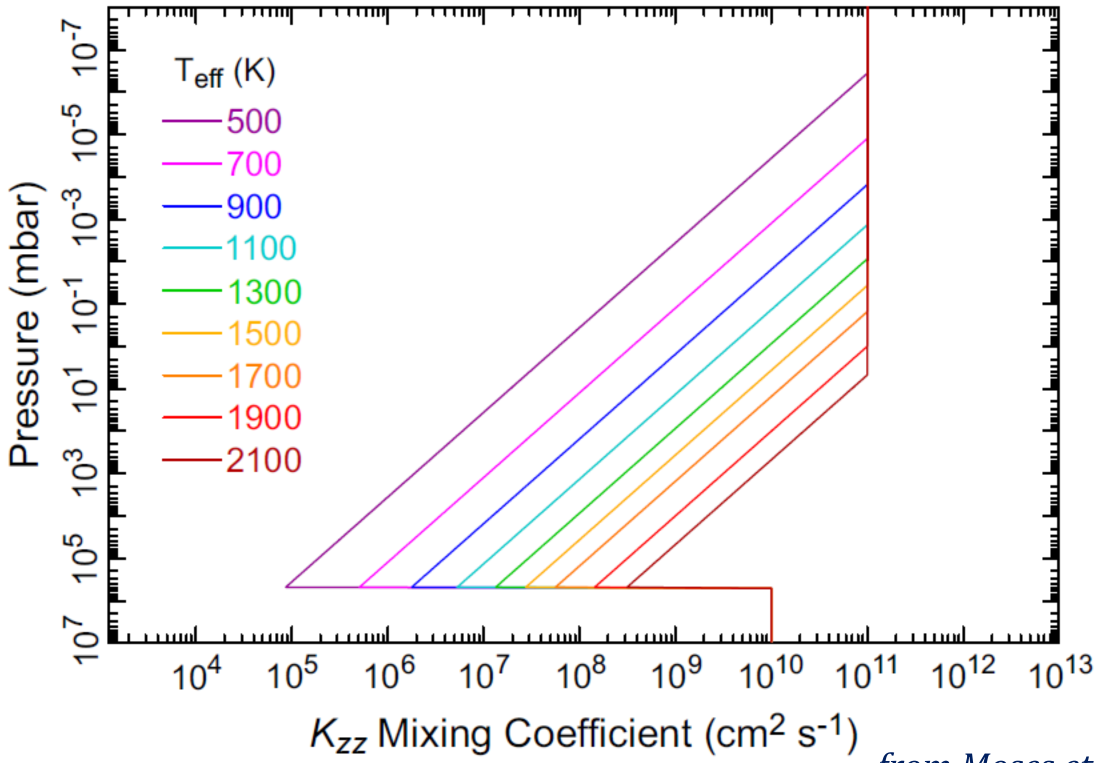
from Freytag et al. (2010)

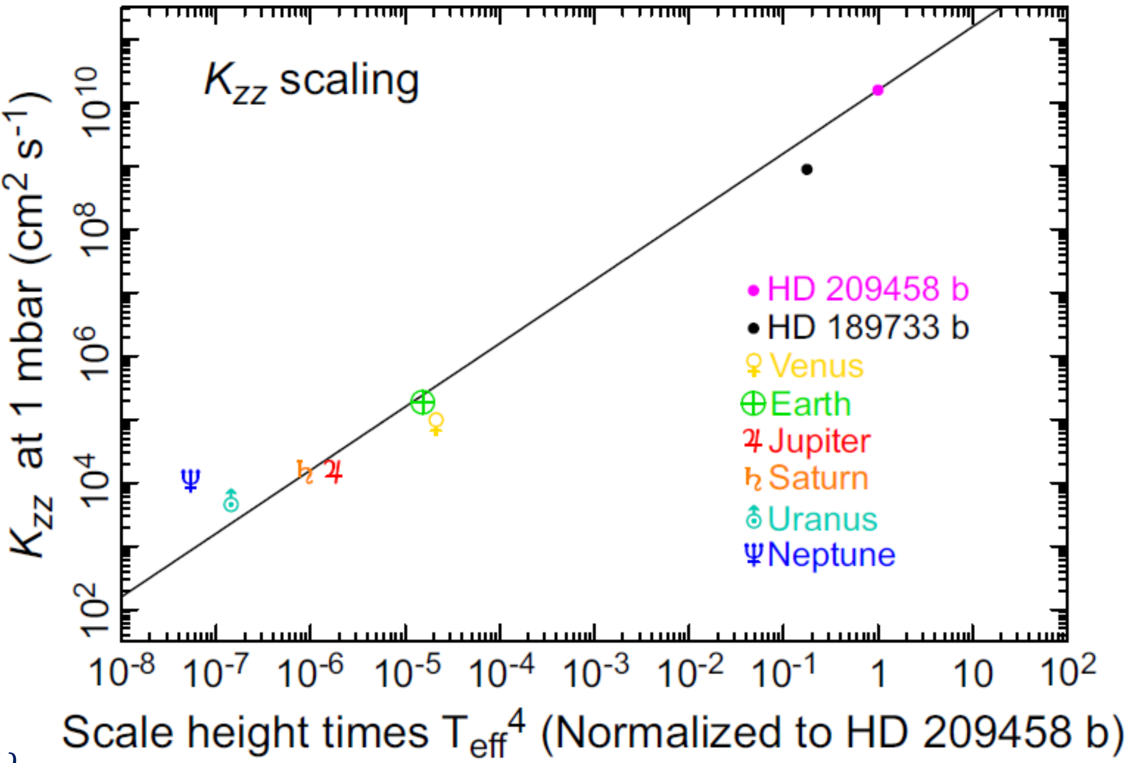
Radiative region: $K_{zz} \propto P^{-0.5}$, dominated by waves, e.g., gravity wave breaking; Lindzen, 1981

$$K_{zz} \approx wH \approx \left(\frac{F k_B}{\rho m c_p}\right)^{1/3} H,$$

Convective region: Use free-convection, mixing-length theory, e.g., Gierasch & Conrath (1985), or get fancier with rotation rate & latitude dependence (Visscher et al. 2010, **Wang et al. 2015**)

Photochemistry: What to do about K_{zz}





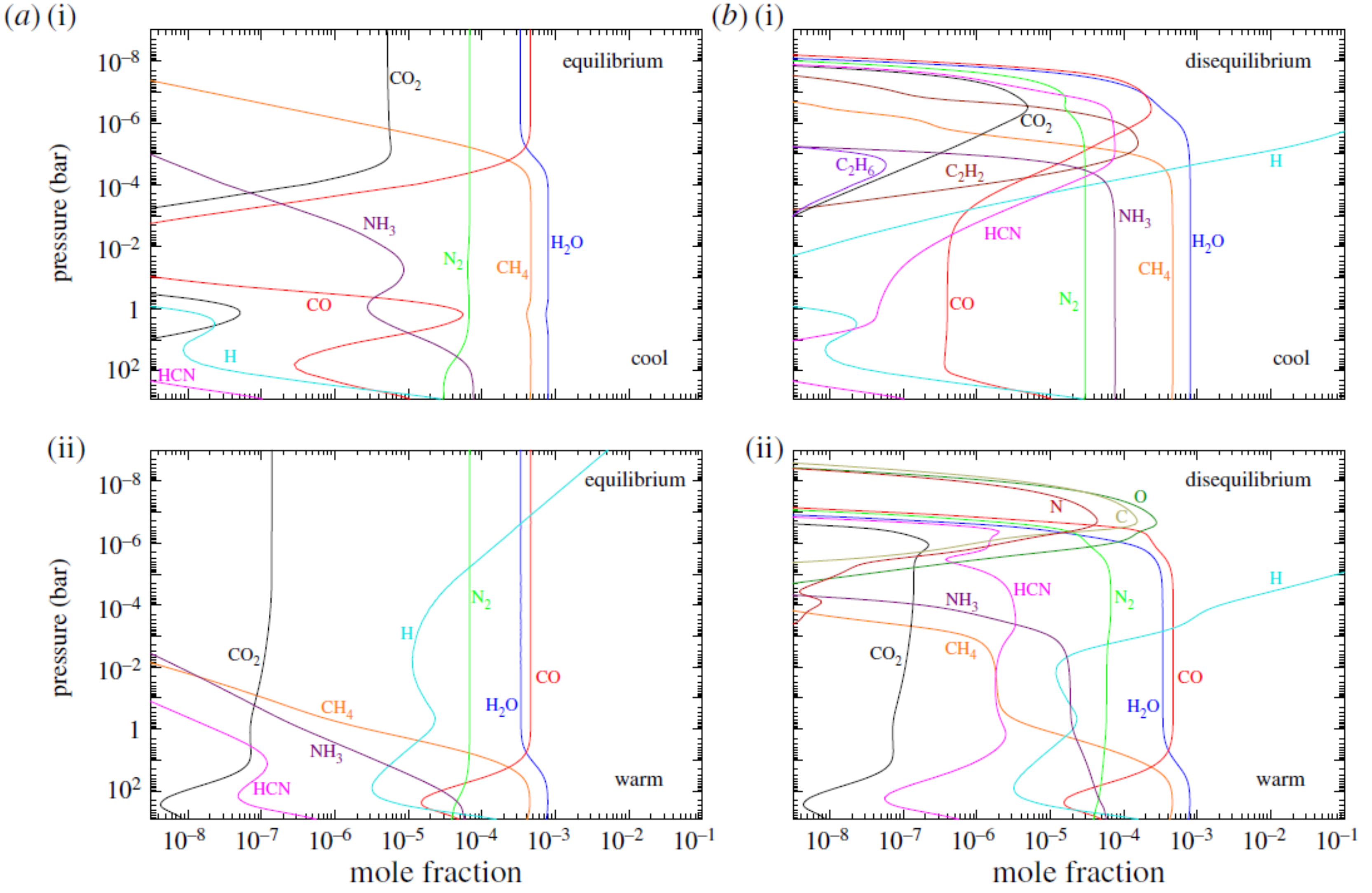
from Moses et al. (2021)

The magnitude of K_{zz} in the radiative region depends on various properties of the planet and its atmosphere, such as T_{eq}, H, a, g (Zhang & Showman, 2018a,b; Komacek et al., 2019). I tried their exact scaling expressions, and they didn't quite work for all the solar-system planets, so I've used this simple scaling:

$$K_{zz} = 5 \times 10^8 \, [P(\text{bar})]^{-0.5} \left(\frac{H_{1\text{mbar}}}{620\text{ km}}\right) \left(\frac{T_{\text{eff}}}{1450\text{ K}}\right)^4 ,$$

where K_{zz} is in units of cm^2 s^{-1}, P is the atmospheric pressure (in bar),

Giant Exoplanets: Quenching in IR "photospheres"



from Moses (2014)

Both transport-induced quenching and photochemistry affect composition of cool-to-warm giant exoplanets, whereas thermochemical equilibrium dominates on the hotter exoplanets

Reactions should be fully reversed for close-in exoplanets

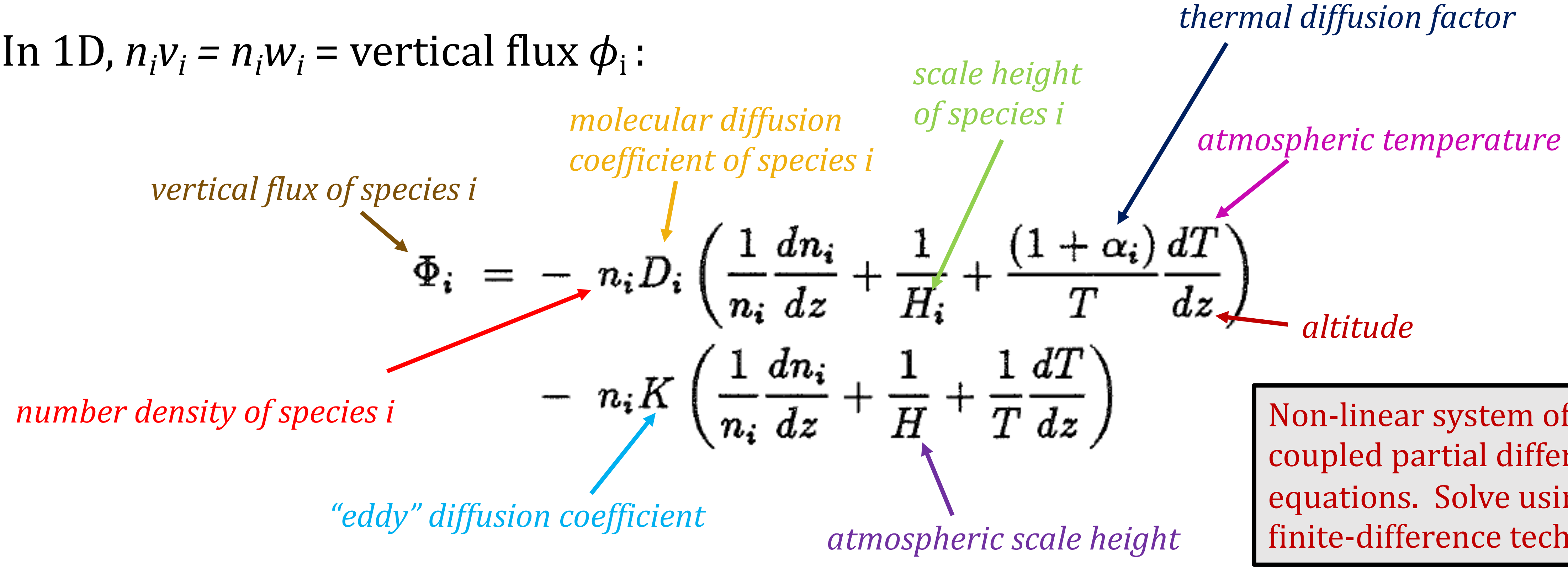
J. Moses, Sagan workshop, July 2023

Photochemistry

Solve the continuity equations: (Conservation of mass)

$$\frac{\partial n_i}{\partial t} + \vec{\nabla}\cdot(n_i\vec{v}_i) = P_i - L_i$$

In 1D, $n_i v_i = n_i w_i$ = vertical flux ϕ_i :



thermal diffusion factor

scale height of species i

atmospheric temperature

molecular diffusion coefficient of species i

vertical flux of species i

$$\Phi_i = -n_i D_i\left(\frac{1}{n_i}\frac{dn_i}{dz} + \frac{1}{H_i} + \frac{(1+\alpha_i)}{T}\frac{dT}{dz}\right) - n_i K\left(\frac{1}{n_i}\frac{dn_i}{dz} + \frac{1}{H} + \frac{1}{T}\frac{dT}{dz}\right)$$

altitude

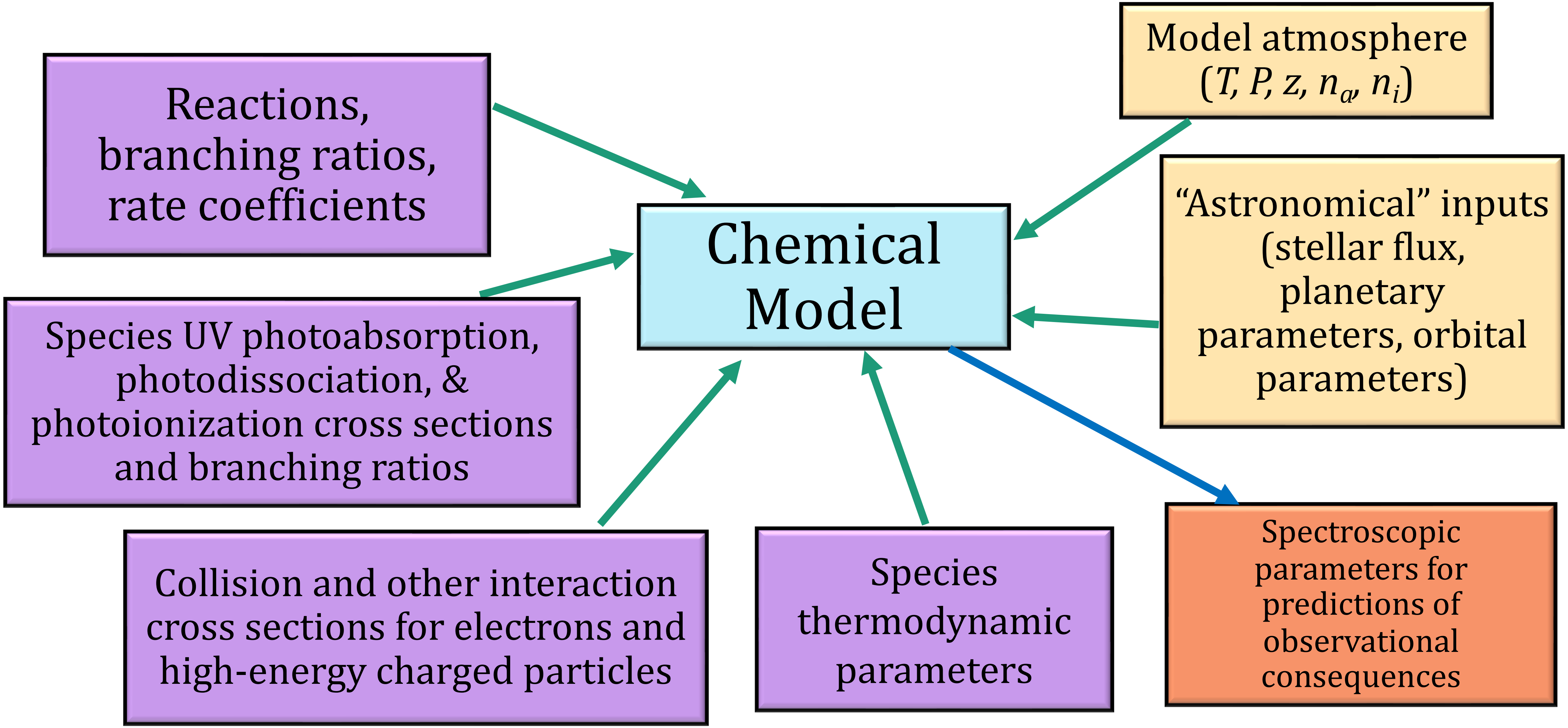
number density of species i

"eddy" diffusion coefficient

atmospheric scale height

Non-linear system of coupled partial differential equations. Solve using finite-difference techniques

Photochemistry



Reactions, branching ratios, rate coefficients

Species UV photoabsorption, photodissociation, & photoionization cross sections and branching ratios

Collision and other interaction cross sections for electrons and high-energy charged particles

Species thermodynamic parameters

Chemical Model

Model atmosphere (T, P, z, n_a, n_i)

“Astronomical” inputs (stellar flux, planetary parameters, orbital parameters)

Spectroscopic parameters for predictions of observational consequences

J. Moses, ERS Theory talk, Aug. 2021

Chemical Kinetics 101

Photolysis rate: depends on molecular cross sections and local UV flux

Photolysis reaction:	$AB + h\nu \rightarrow A + B$	J_1 (s^{-1})
Unimolecular reaction:	$AB \rightarrow A + B$	k_2 (s^{-1})
Bimolecular reaction:	$AB + C \rightarrow AC + B$	k_3 ($cm^3\ s^{-1}$)
Termolecular reaction:	$A + B + M \rightarrow AB + M$	k_4 ($cm^6\ s^{-1}$)

The k's are reaction rate coefficients

M stands for any third body (constituent) in the atmosphere

Production rate P ($cm^{-3}\ s^{-1}$) for species AB: $k_4[A][B][M]$

Loss rate L ($cm^{-3}\ s^{-1}$) for species AB: $J_1[AB] + k_2[AB] + k_3[AB][C]$

where square brackets mean number density (cm^{-3})

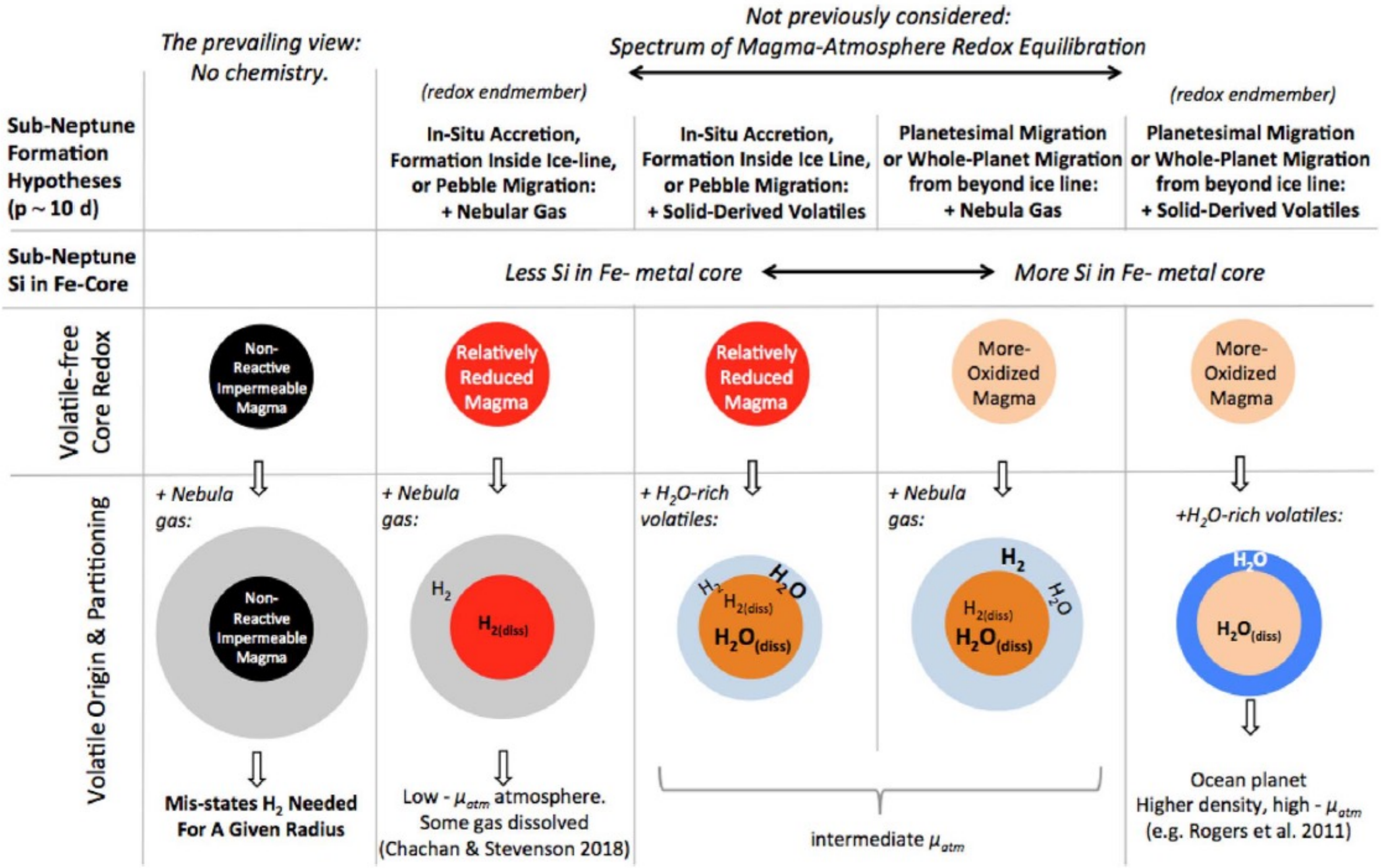
In *photochemical equilibrium* $d[AB]/dt = P - L = 0$, so

$$k_4[A][B][M] = J_1[AB] + k_2[AB] + k_3[AB][C]$$

Rearrange algebraically to get

$$[AB] = k_4[A][B][M]/(J_1 + k_2 + k_3[C])$$

Thermochemical Equilibrium: Intermediate-sized Planets



from Kite et al. (2020)

Sub-Neptunes and Super-Earths: Need to consider atmosphere-interior interactions, core formation, magma dissolution and outgassing, and other "geochemical" considerations.

Dissolution of H in magma ocean and allows H to survive longer (Kite et al. 2020).

Core formation and mantle chemistry matter for subsequent outgassed atmosphere