

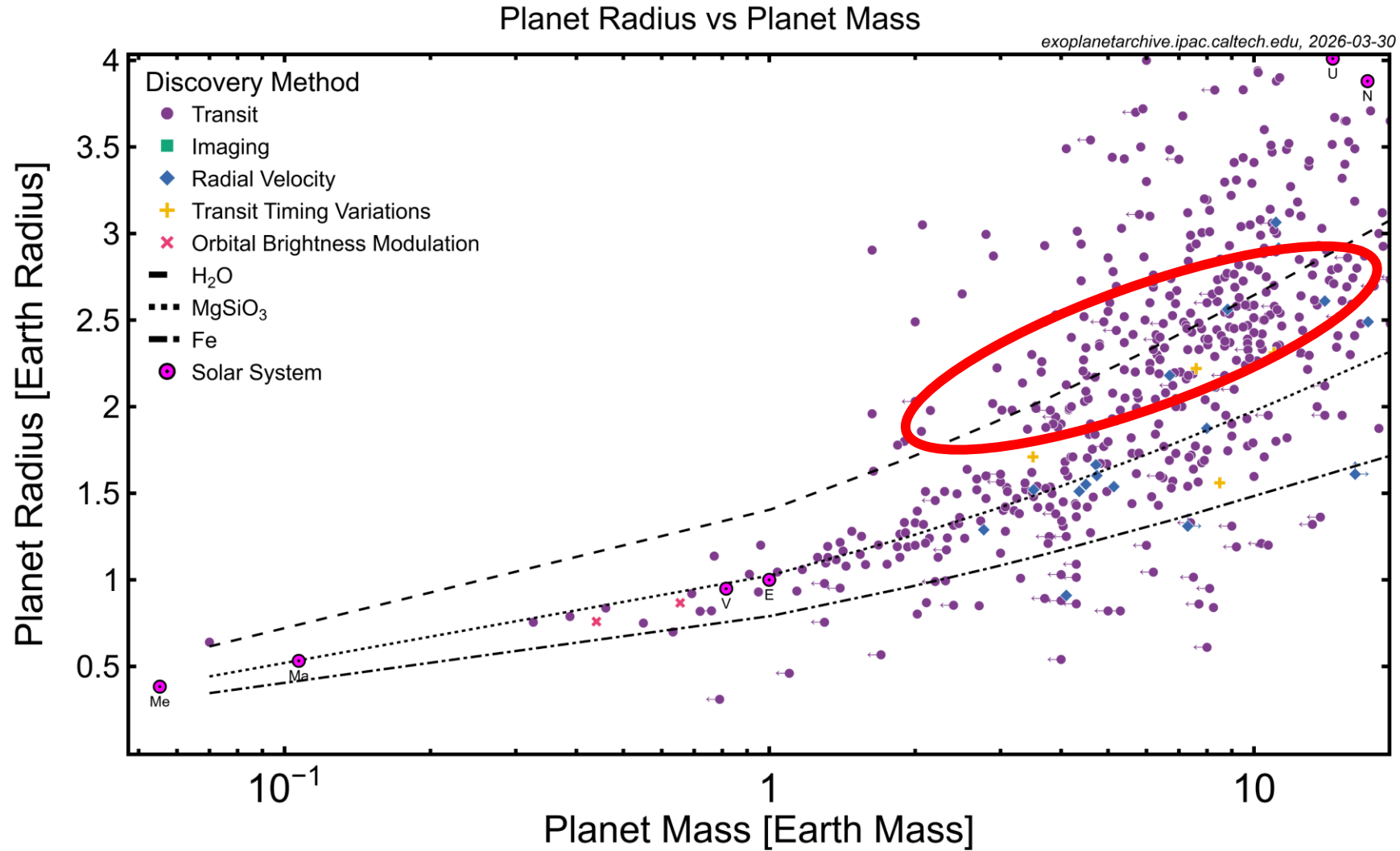
Thermodynamics of mixing in sub-Neptunes

Paolo A. Sossi

Department of Earth and Planetary Sciences, ETH Zürich

Exosystèmes V / 01.04.2026

Exoplanet statistics



Sub Neptunes

Density of sub-Neptunes ~ H₂O

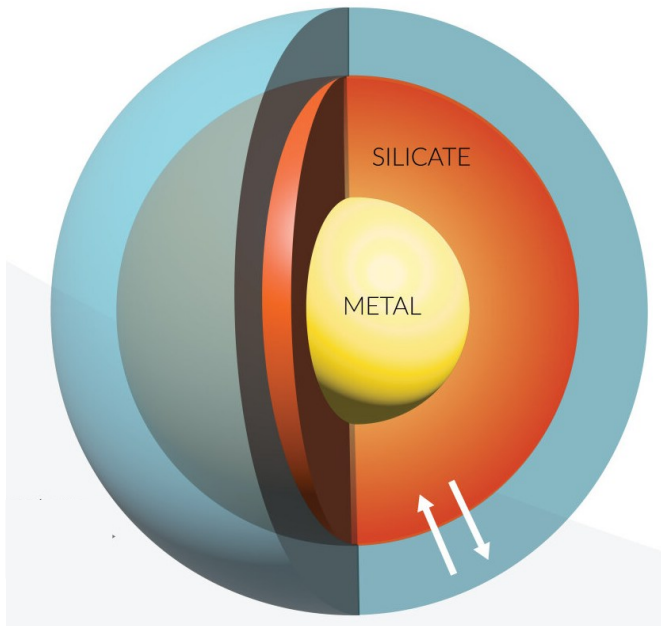
What are sub-Neptunes made of?

Radius as a proxy for composition

Sub-Neptunes as a combination of a **Earth-like rocky core** + **gas envelope** (Lopez and Fortney, 2014)

“...theoretical mass–radius curves are remarkably flat; that is, planets with a given H/He abundance have very similar sizes regardless of their mass.”

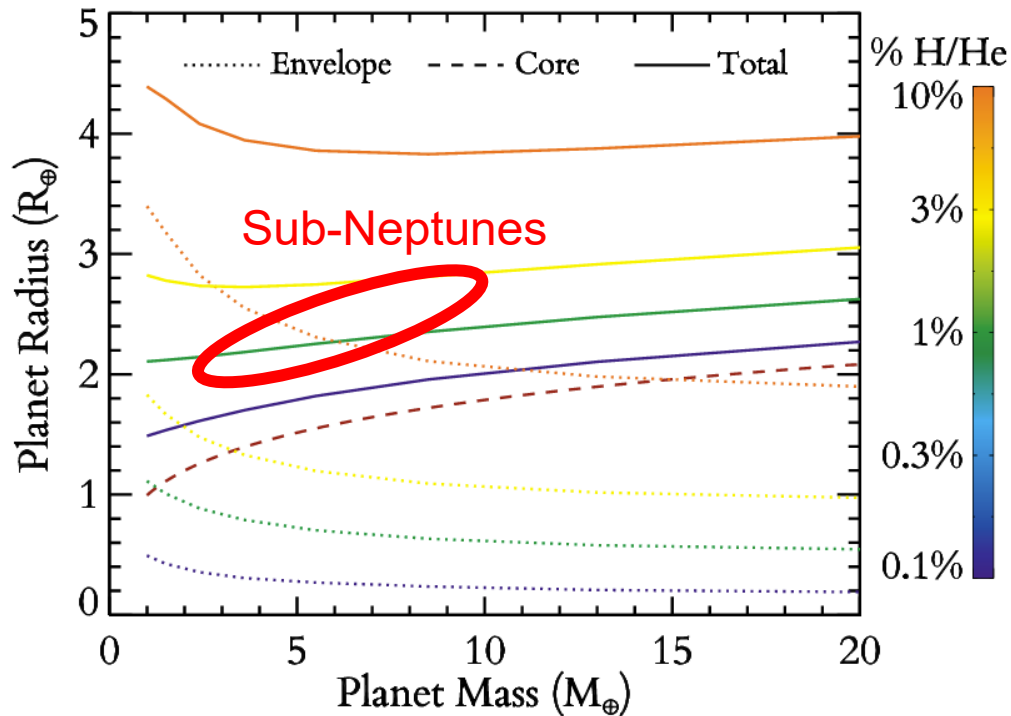
PLANETARY EMBRYO &
H₂ ATMOSPHERE



Radius as a proxy for composition

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“...theoretical mass–radius curves are remarkably flat; that is, planets with a given H/He abundance have very similar sizes regardless of their mass.”



Radius is proportional to H/He envelope fraction, independent of planet mass.

Assuming a “solar” H/He ratio, envelope is ~0.5 – 3 % of total mass

What if sub-Neptunes are not solar?

Radius as a proxy for composition

Sub-Neptunes as a combination of a **Earth-like rocky core + gas envelope** (Lopez and Fortney, 2014)

1. Assume isothermal atmosphere to calculate scale height:

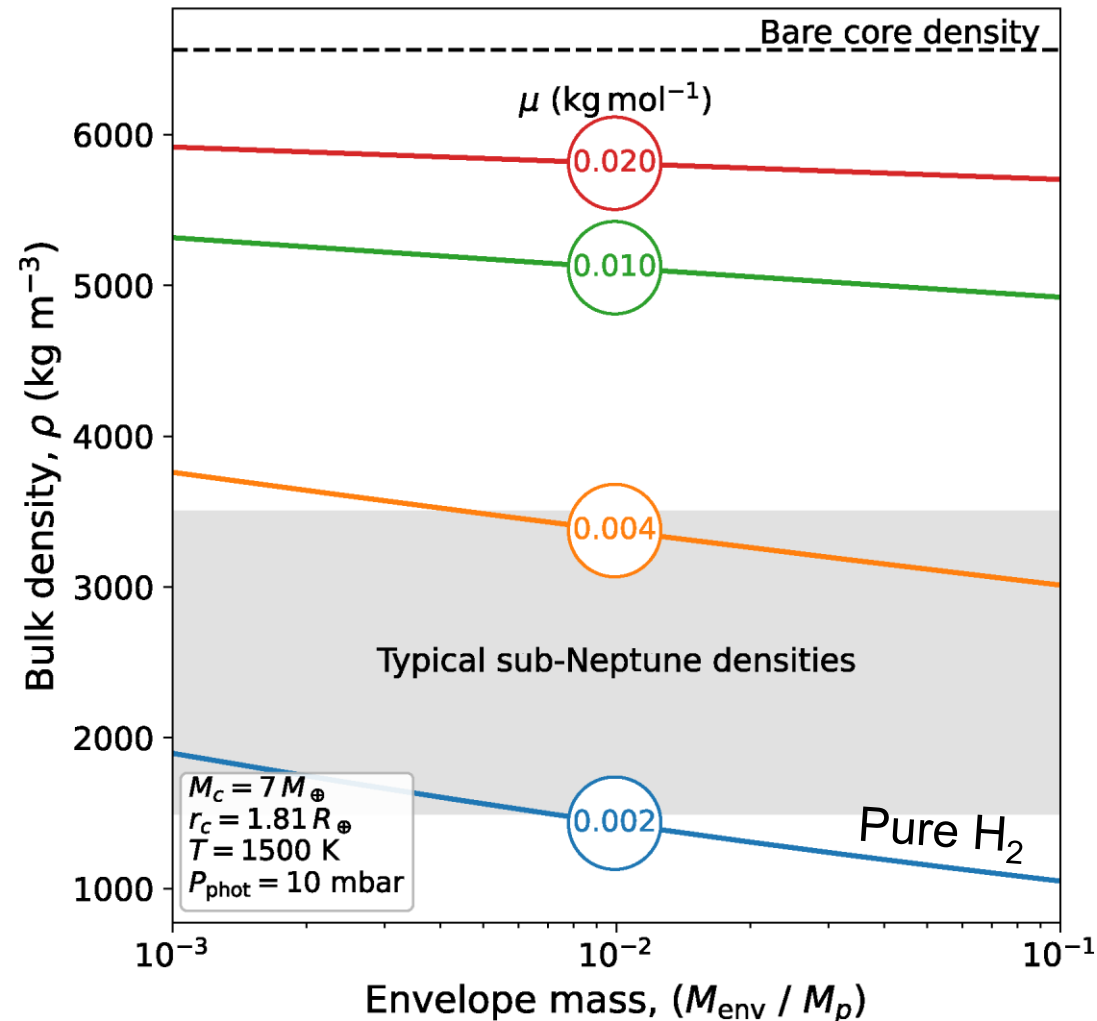
$$H = \frac{RT}{\mu g}$$

2. Approximate pressure at which optical depth ~ 1 (photosphere):

$$P_{\text{phot}} \approx \frac{g}{\kappa} \approx 10 \text{ mbar}$$

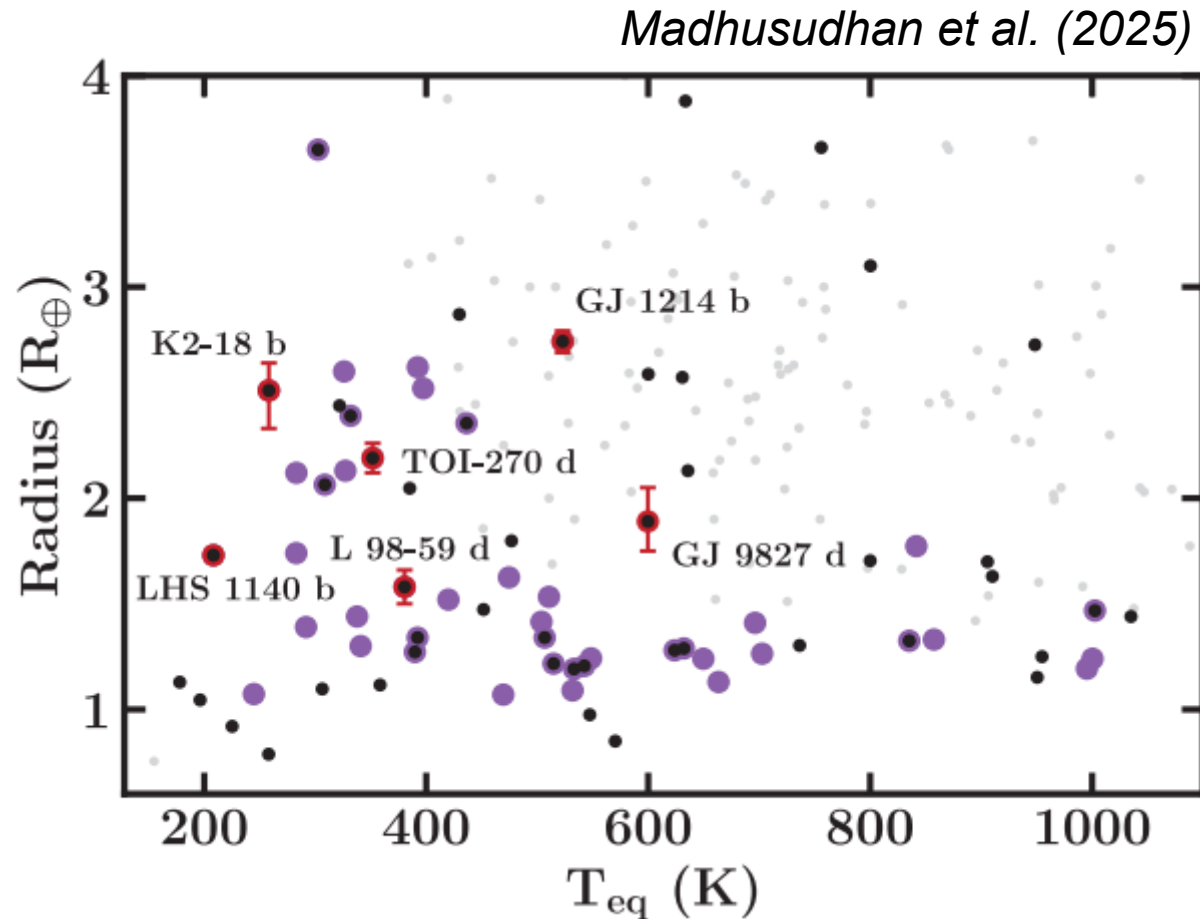
3. Calculate transit radius at photosphere with thin atmosphere:

$$r_{\text{transit}} = r_c + H \left(\frac{P_0}{P_{\text{phot}}} \right)$$



Mixing ratio
>80% H₂/He
to explain
bulk density

Equilibrium temperatures of sub-Neptunes

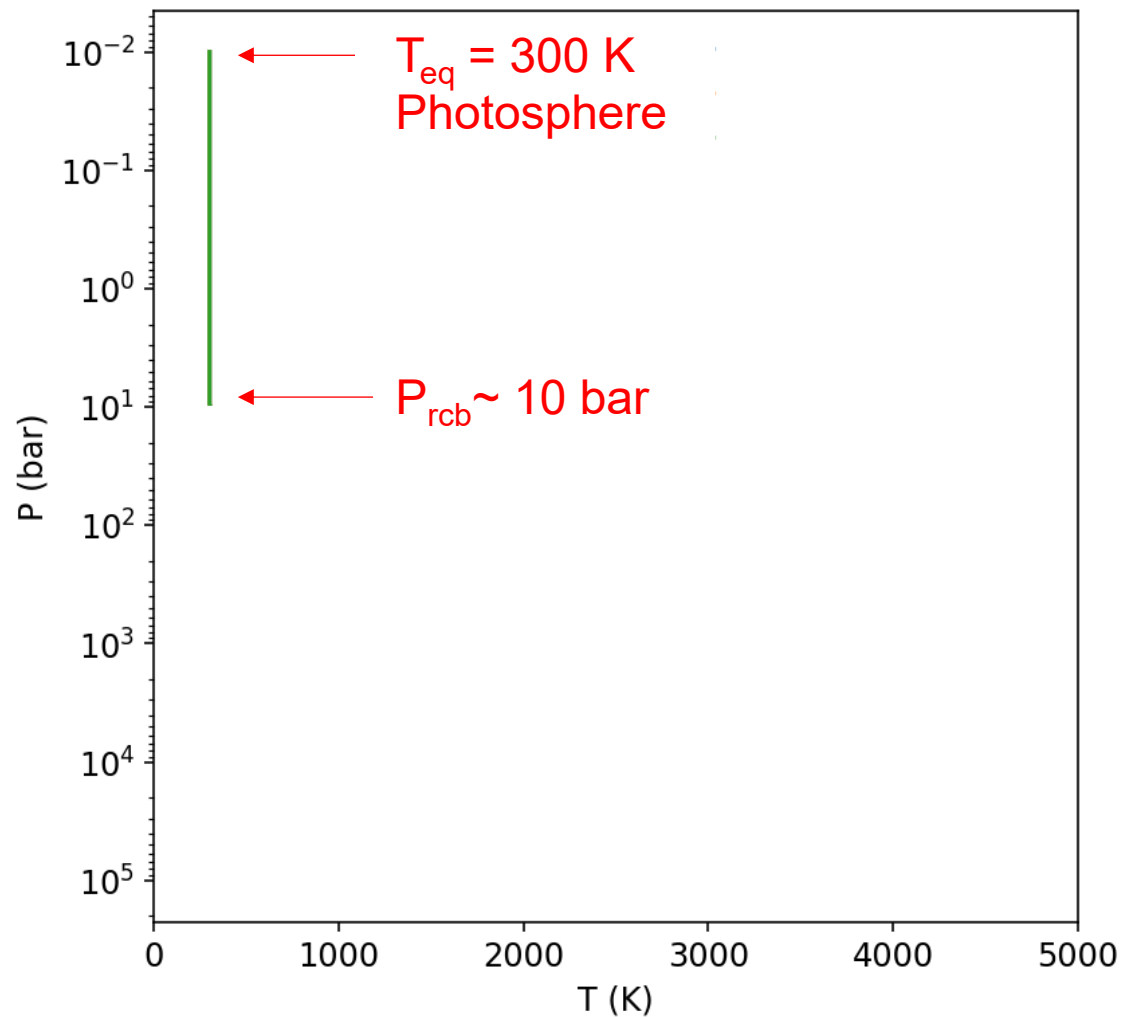


Most are temperate sub-Neptunes
with $280 < T_{\text{eq}} [\text{K}] < 600$

This is the temperature at the
photosphere (optical depth = 1) or
 $\sim 1 - 100$ mbar

**To what extent is the
photosphere representative of
the deeper envelopes of sub-
Neptunes?**

Simplified structures of sub-Neptune envelopes

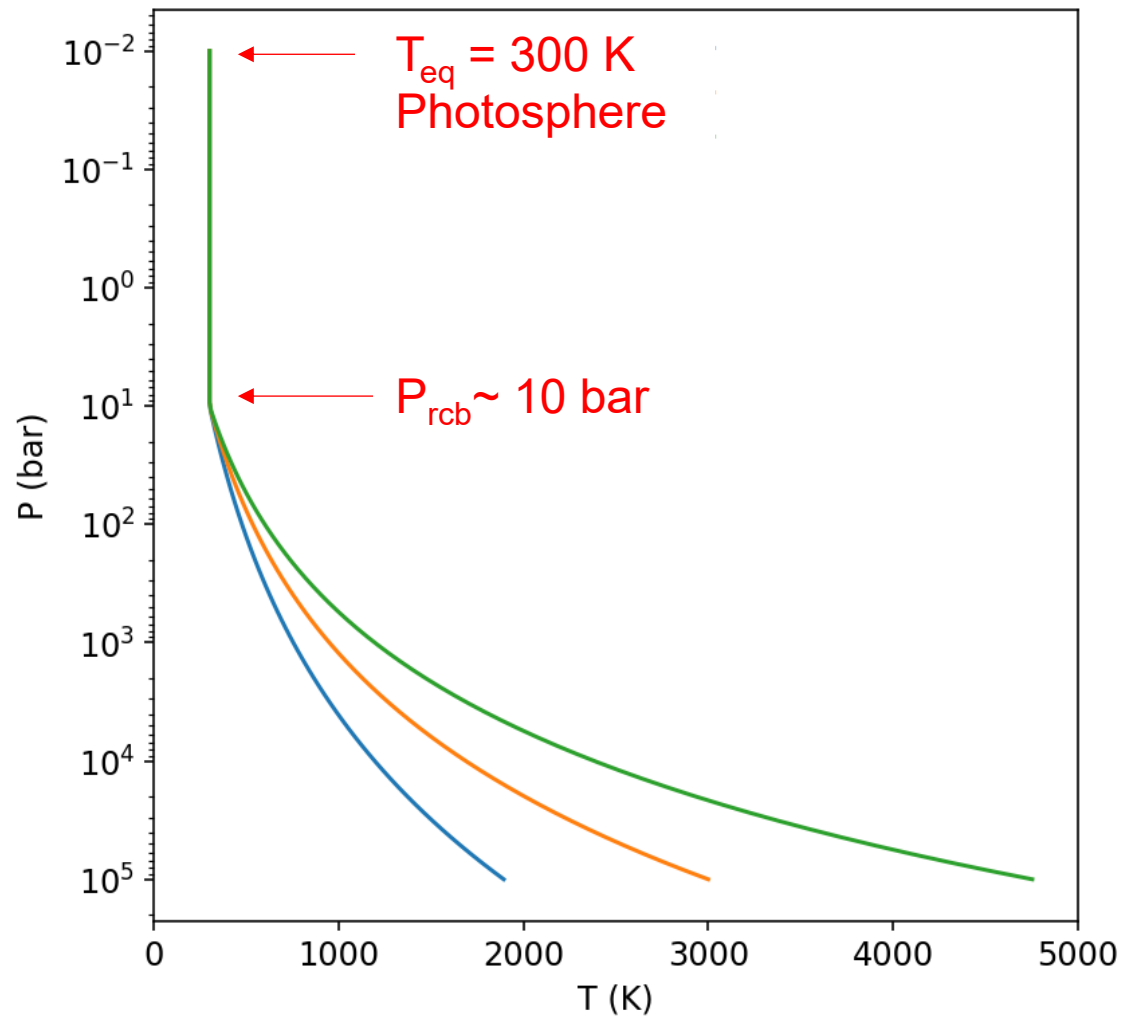


- In upper atmosphere, heat transport is **radiative**, P-T profile is roughly **isothermal**
- Where radiation \approx convection, i.e.,

$$\left(\frac{\partial \ln T}{\partial \ln P}\right)_{rad} = \left(\frac{\partial \ln T}{\partial \ln P}\right)_S$$

denotes the pressure at the radiative-convective boundary

Simplified structures of sub-Neptune envelopes



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$$\left(\frac{\partial \ln T}{\partial \ln P}\right)_{rad} = \left(\frac{\partial \ln T}{\partial \ln P}\right)_s$$

denotes the pressure at the radiative-convective boundary

- P-T profile set by adiabatic index (γ) –

$$\left(\frac{\partial \ln T}{\partial \ln P}\right)_s = \frac{\gamma - 1}{\gamma}$$

...**poorly known!**

See also Tang et al. 2024

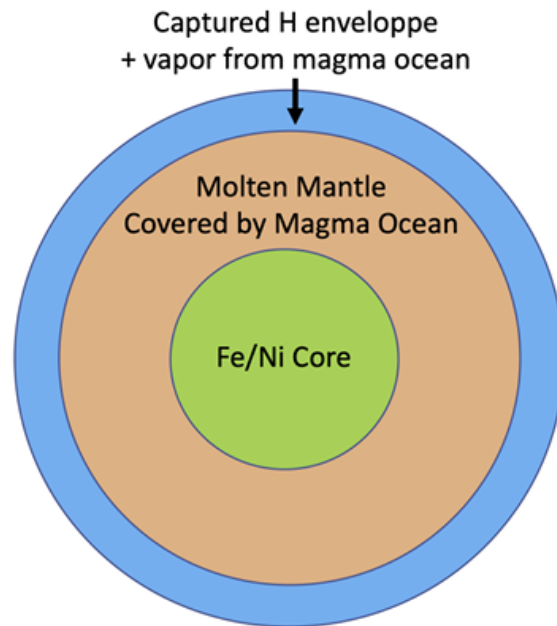
At $P = 1 - 10 \text{ GPa}$, $T = 2000 - 4000 \text{ K}$

Compositions of sub-Neptune envelopes

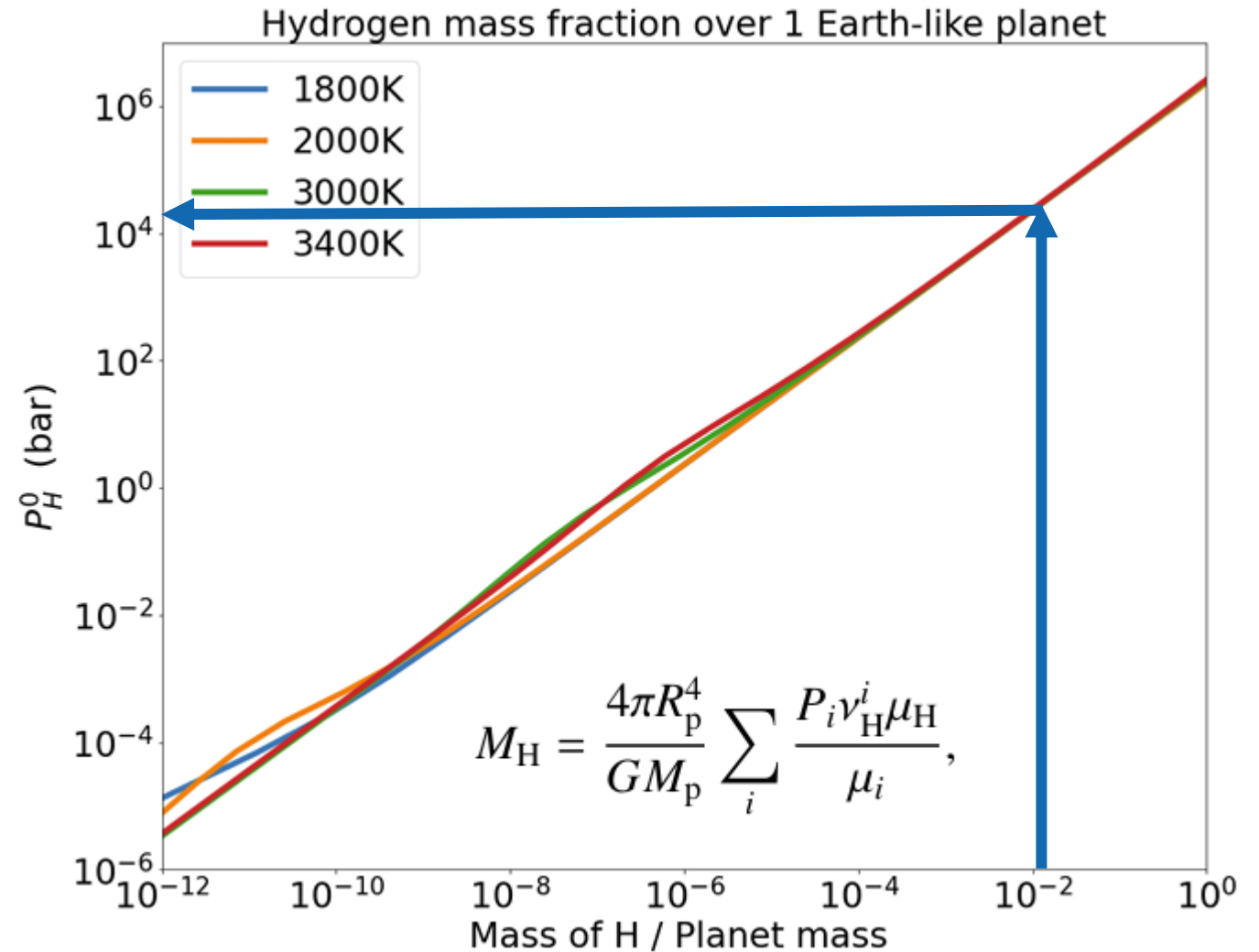
1) Earth-like rocky interior

2) H₂-rich envelope, 0.5 – 3 % M_{planet}

3) 2000 – 4000 K surface temperature



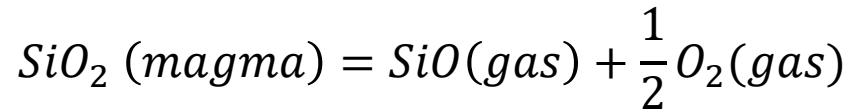
Charnoz, Sossi et al. (2023)



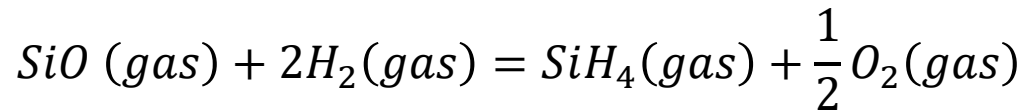
Compositions of sub-Neptune envelopes

Sub-Neptune range

Silicate evaporation is significant above ~2000 K



Because atmosphere contains hydrogen, other reactions occur:



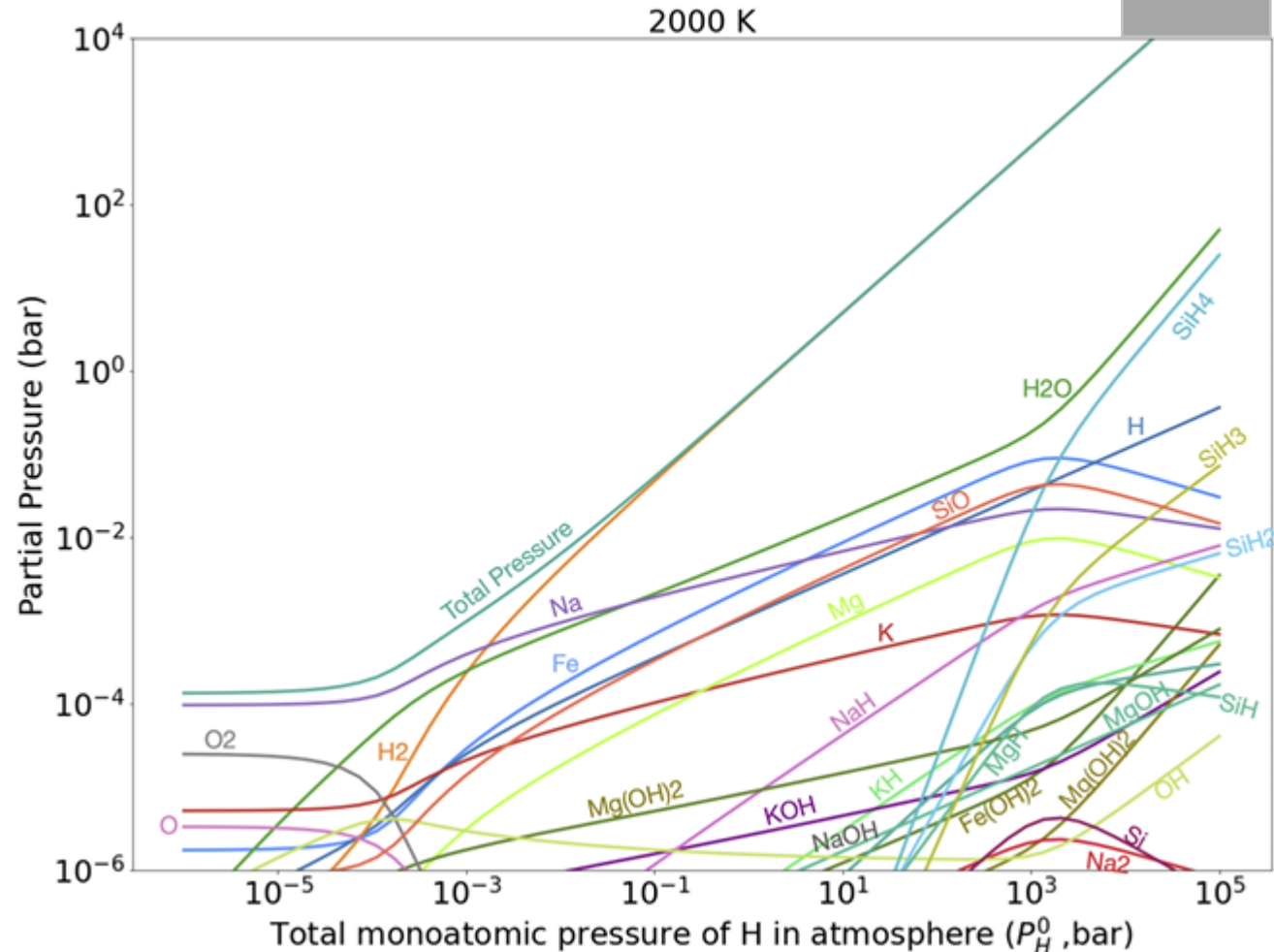
Addition of Hydrogen

- 1) Lowers $fO_2 \rightarrow$ favours evaporation of $SiO(g)$
- 2) Higher total pressure \rightarrow favours $SiH_4(g)$

Increasing T

- 1) Entropy of evaporation \rightarrow favours $SiO(g)$

Charnoz, Sossi et al. (2023)

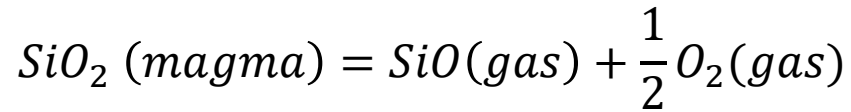


Something is missing...

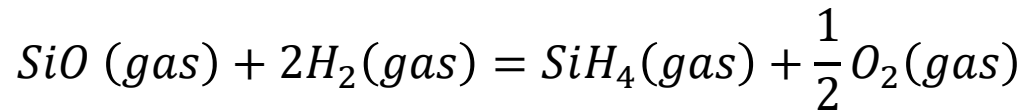
Compositions of sub-Neptune envelopes

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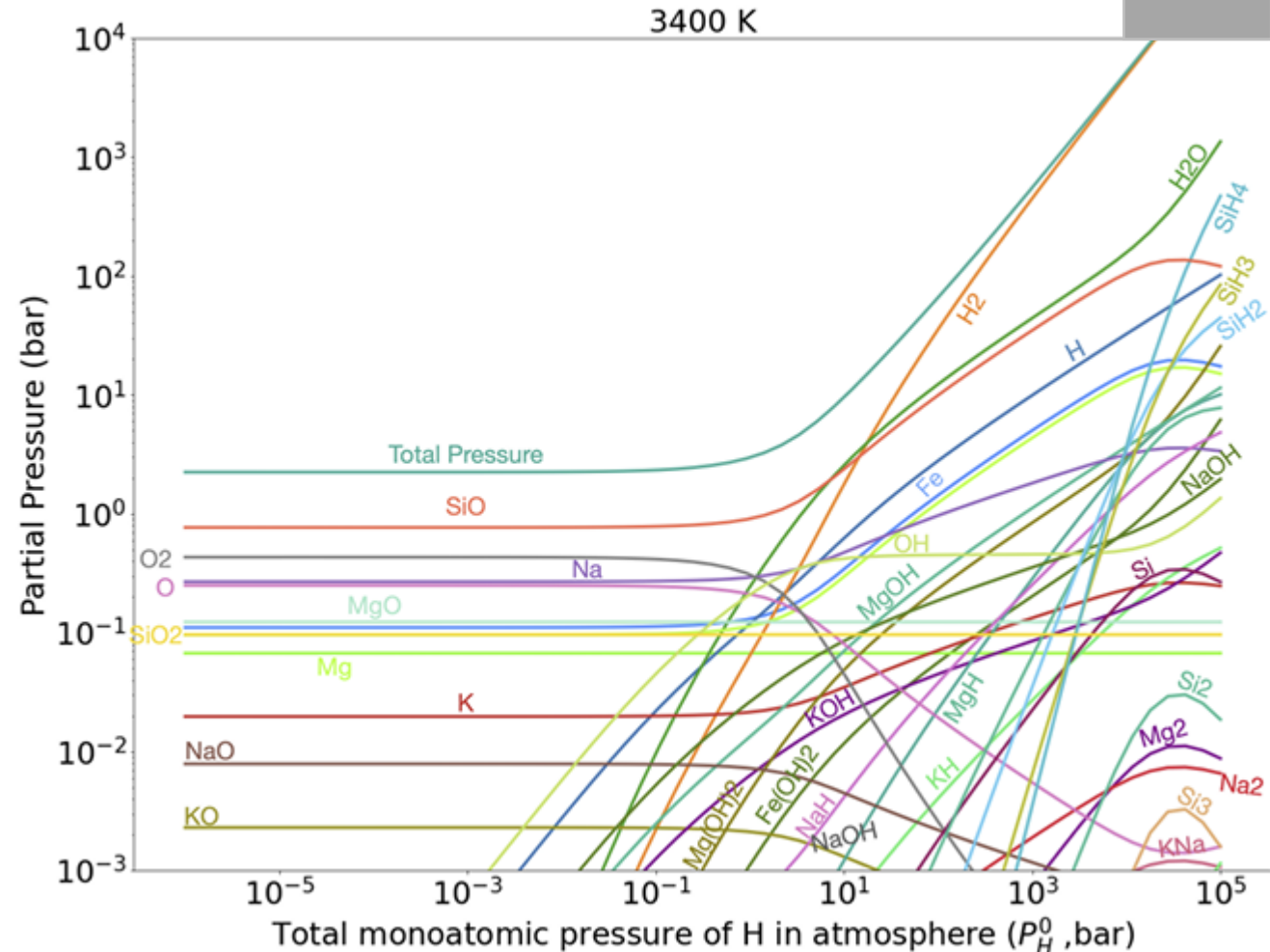
Addition of Hydrogen

- 1) Lowers $f\text{O}_2 \rightarrow$ favours evaporation of $\text{SiO}(\text{g})$
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Increasing T

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Charnoz, Sossi et al. (2023)

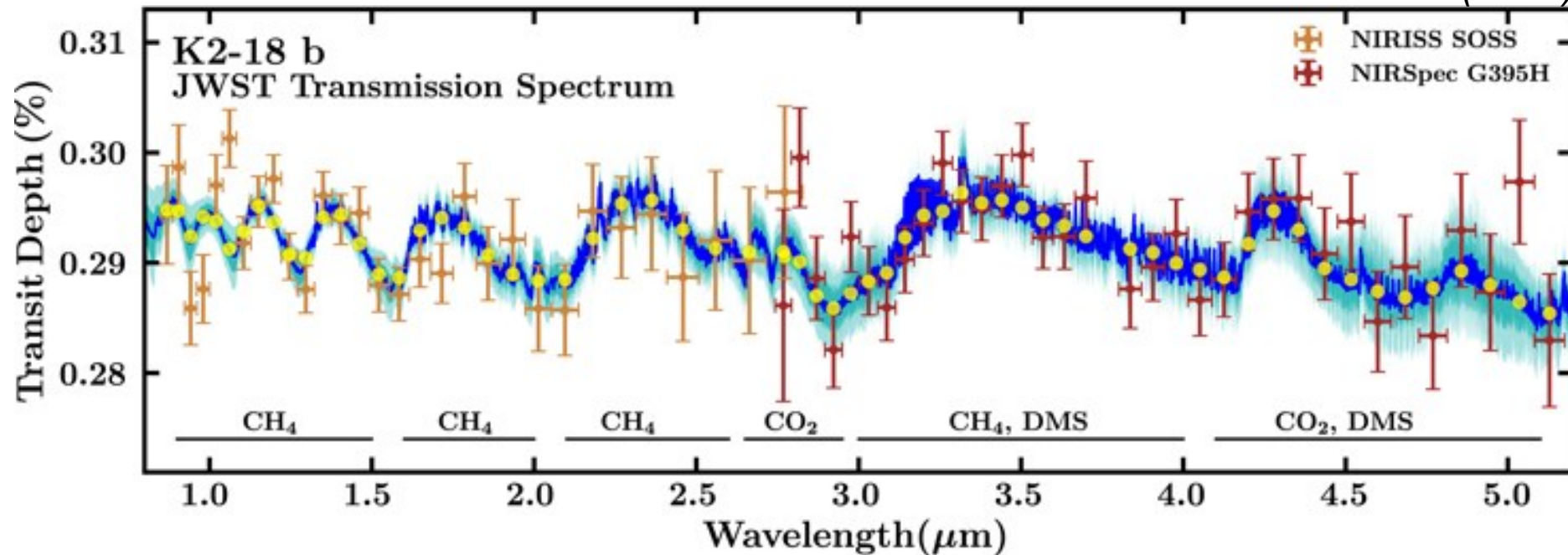


Something is missing...

First sub-Neptune observations

Atmospheric composition by JWST

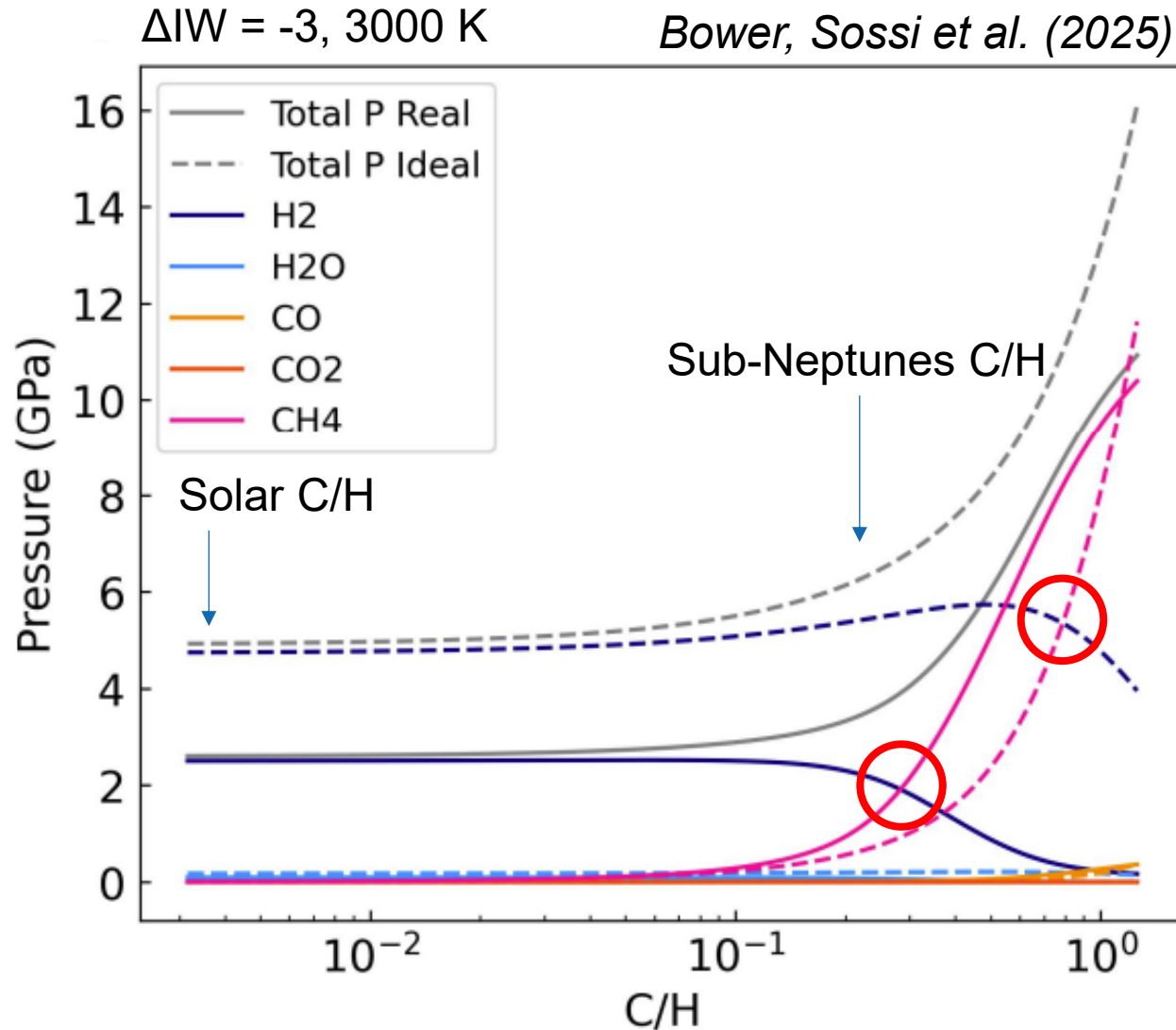
Madhusudhan et al. (2023)



‘Temperate’ sub-Neptunes ($T_{\text{eq}} \sim 250 - 400$ K; K2-18b, TOI-270d) have $\sim 1\text{-}5$ mol. % CH₄, CO₂ \pm H₂O ([Madhusudhan et al. 2023](#); [Benneke et al. 2024](#)), remainder is H₂/He

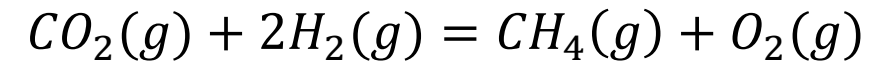
Metallicity $\sim 100 \times$ solar

The effect of carbon



Speciation at super-solar metallicity

- In **ideal gas**, H₂ dominant up to C/H = 0.8
- In **real gas**, H₂ dominant up to C/H = 0.3
- Methane present at high mixing ratios for sub-Neptune-like metallicities (Z ~ 100)



at equilibrium

$$K = \frac{f_{\text{CH}_4} \cdot f_{\text{O}_2}}{f_{\text{CO}_2} \cdot (f_{\text{H}_2})^2} = \frac{\varphi_{\text{CH}_4} \cdot \varphi_{\text{O}_2}}{\varphi_{\text{CO}_2} \cdot (\varphi_{\text{H}_2})^2} \cdot \frac{p_{\text{CH}_4} \cdot p_{\text{O}_2}}{p_{\text{CO}_2} \cdot (p_{\text{H}_2})^2}$$

Calculated
(equations of
state)

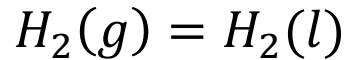
Measured
(atmospheric
spectra)

The effect of non-ideality

Fugacity, not partial pressure, determines phase stability and activity

Heterogeneous equilibria

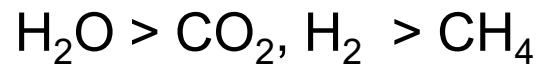
Solubility



$$K = \frac{a_{H_2}}{f_{H_2}} = \frac{a_{H_2}}{\phi_{H_2} p_{H_2}}$$

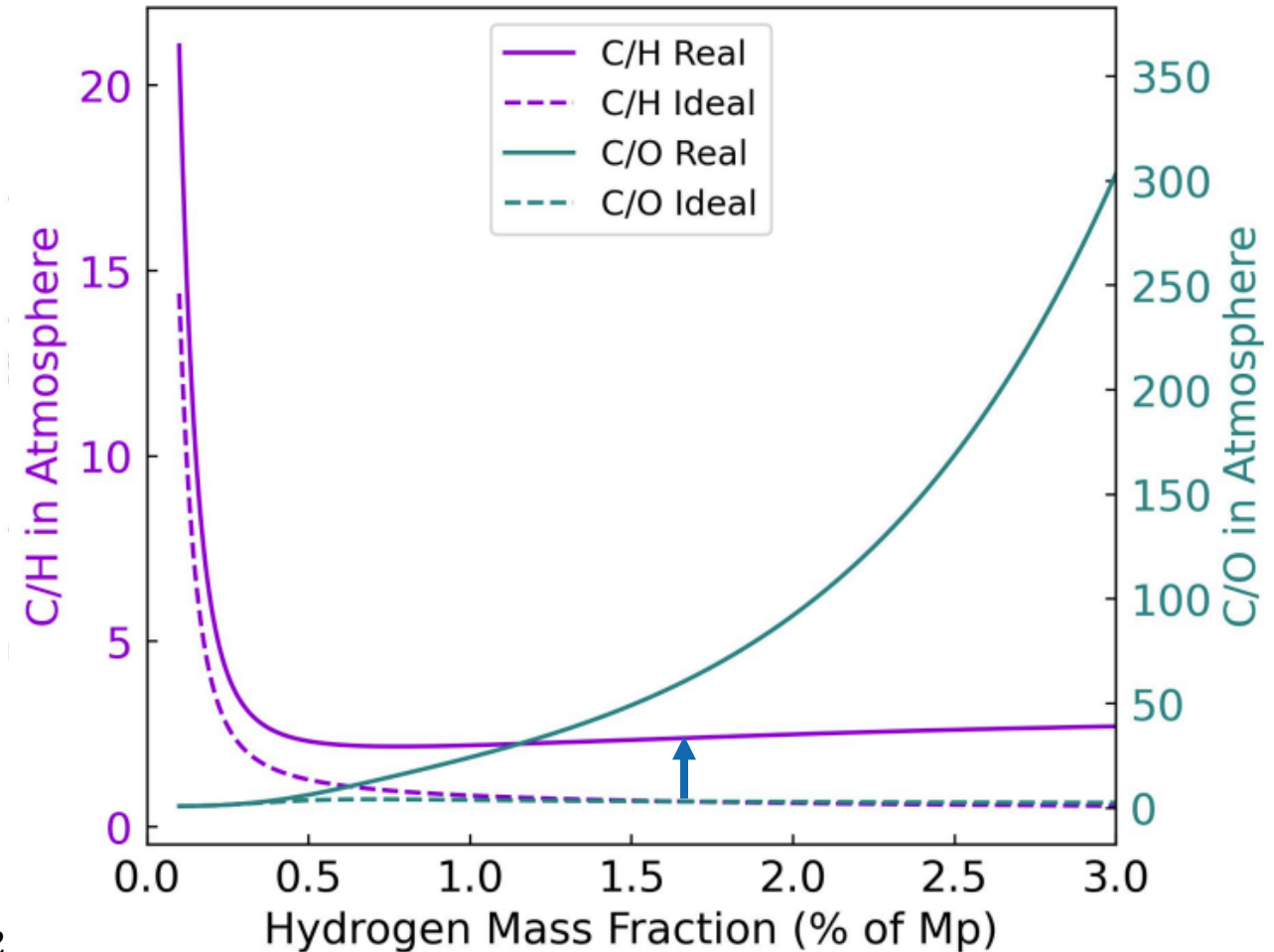
>1 at high pressure

Gases dissolve in silicate magma ocean in order:



Increasing ϕ_{H_2} causes dissolved hydrogen (a_{H_2}) to increase \rightarrow C/H of atmosphere increases

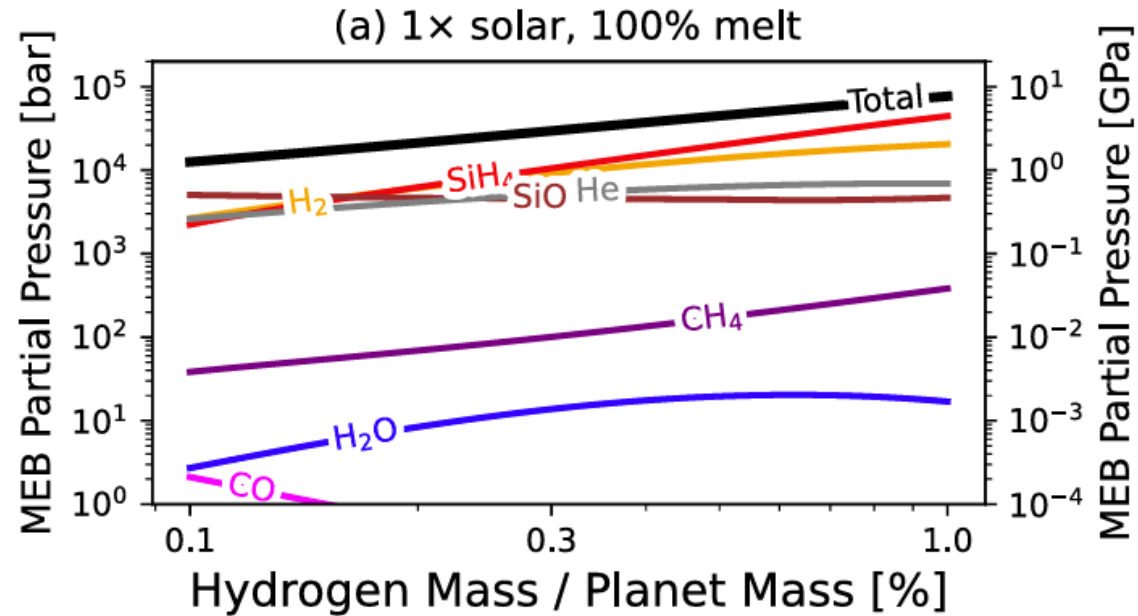
C/H = 0.3, 3000 K *Bower, Sossi et al. (2025)*



Silane-methane competition

Equations of state for both CH_4 and SiH_4 (Hakim, Sossi et al. 2026)

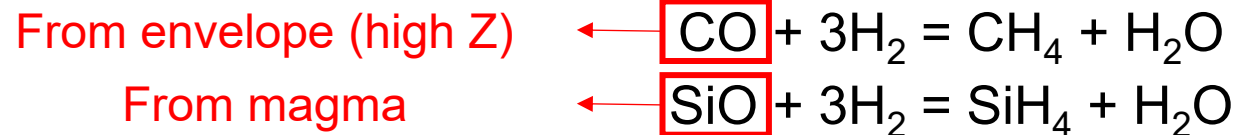
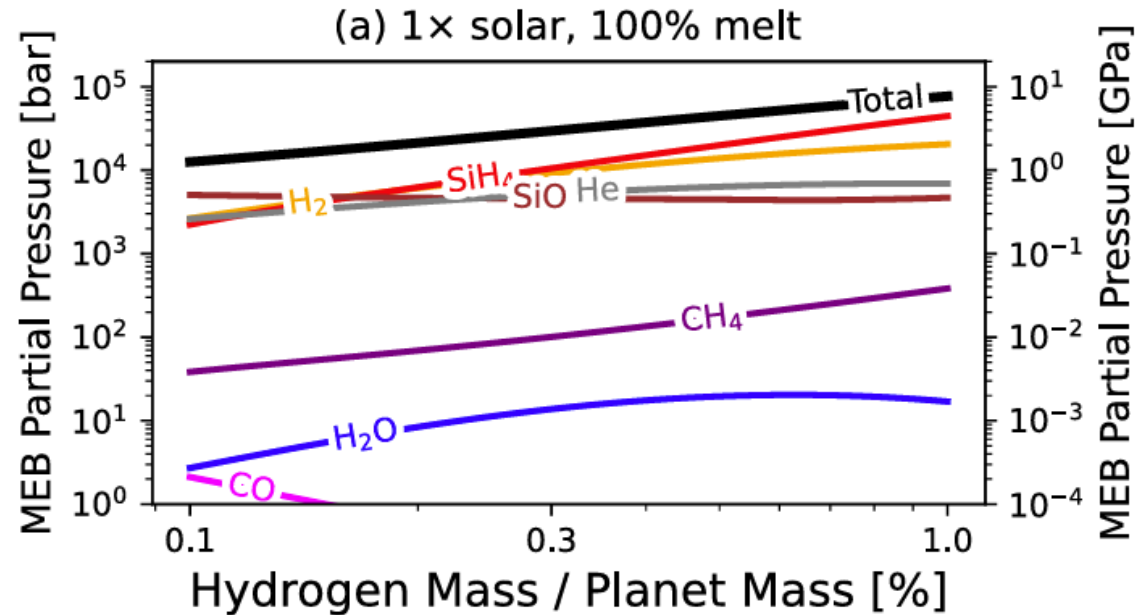
Envelope Composition at MEB (H–He–C–N–O–Si system)



Silane-methane competition

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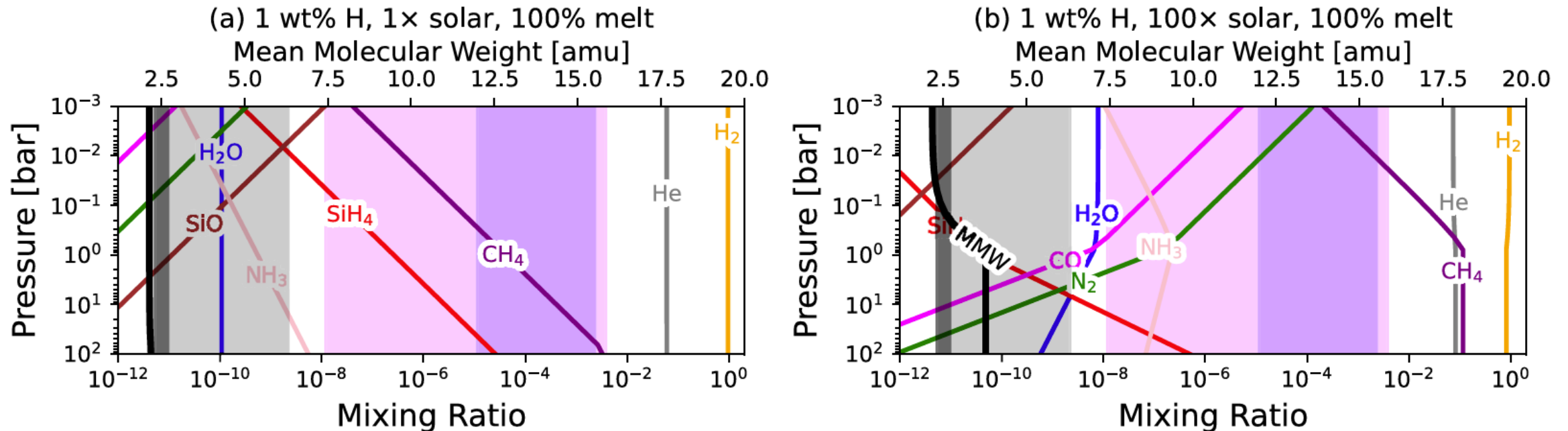


Presence of SiH₄ is diagnostic of magma oceans

Silane-methane competition

Equations of state for both CH_4 and SiH_4 (Hakim, Sossi et al. 2026)

Equilibrium Atmospheric Composition with Condensation

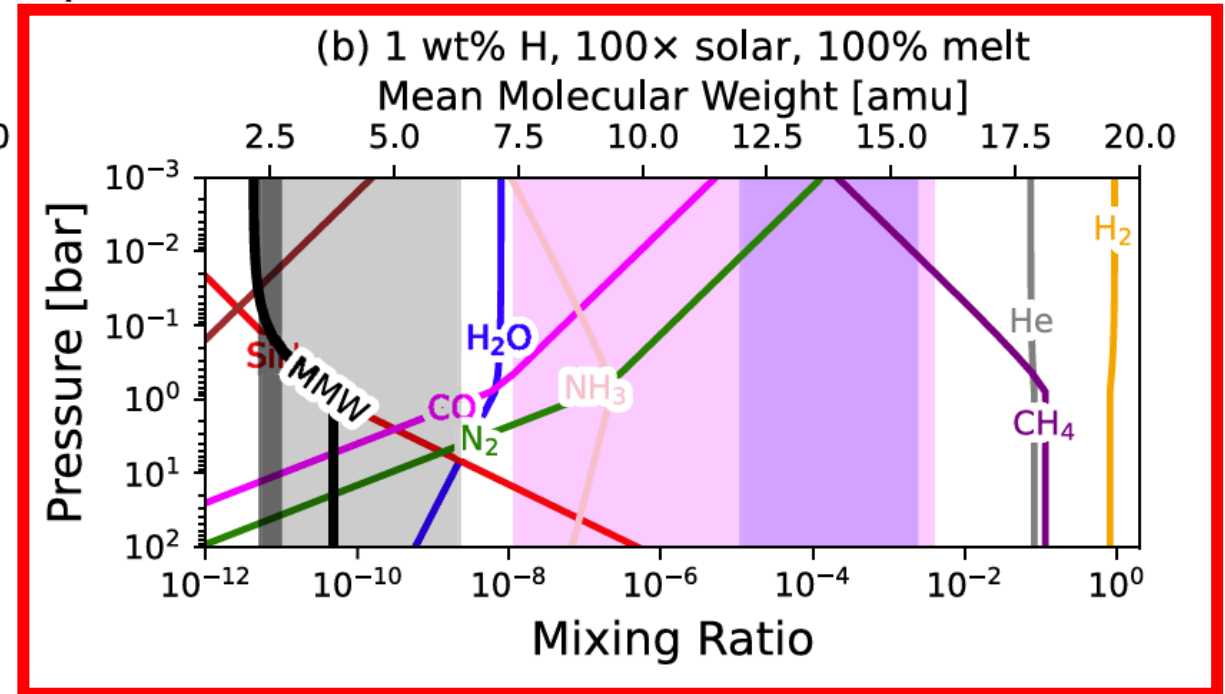
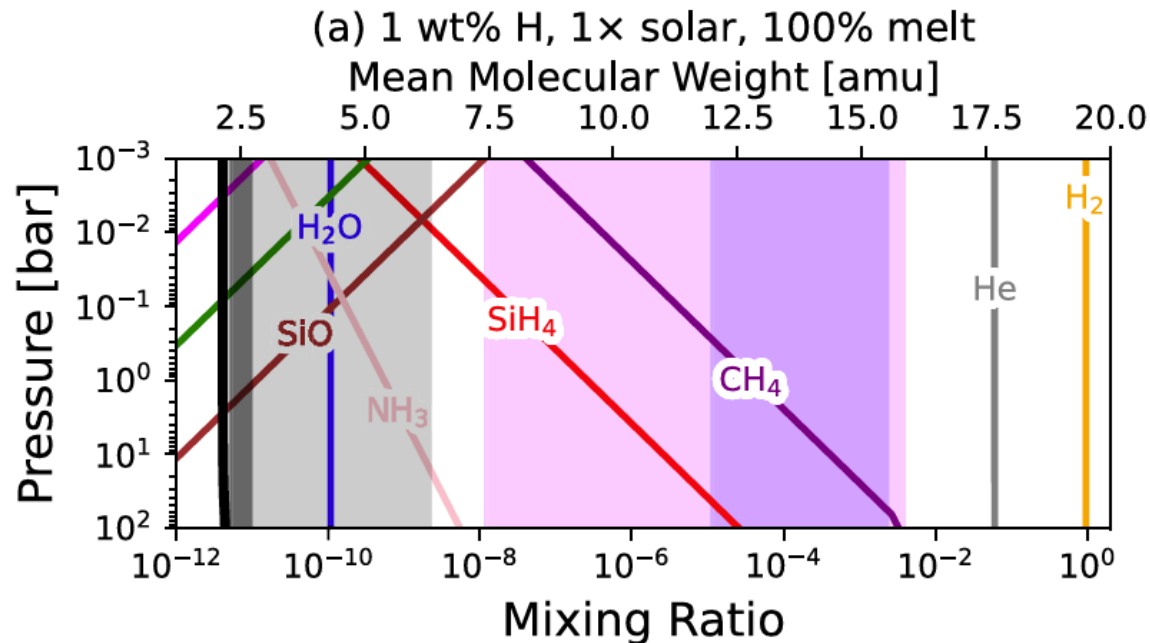


- SiH_4 condensation as SiC , Si and SiO_2 → not visible in upper atmosphere

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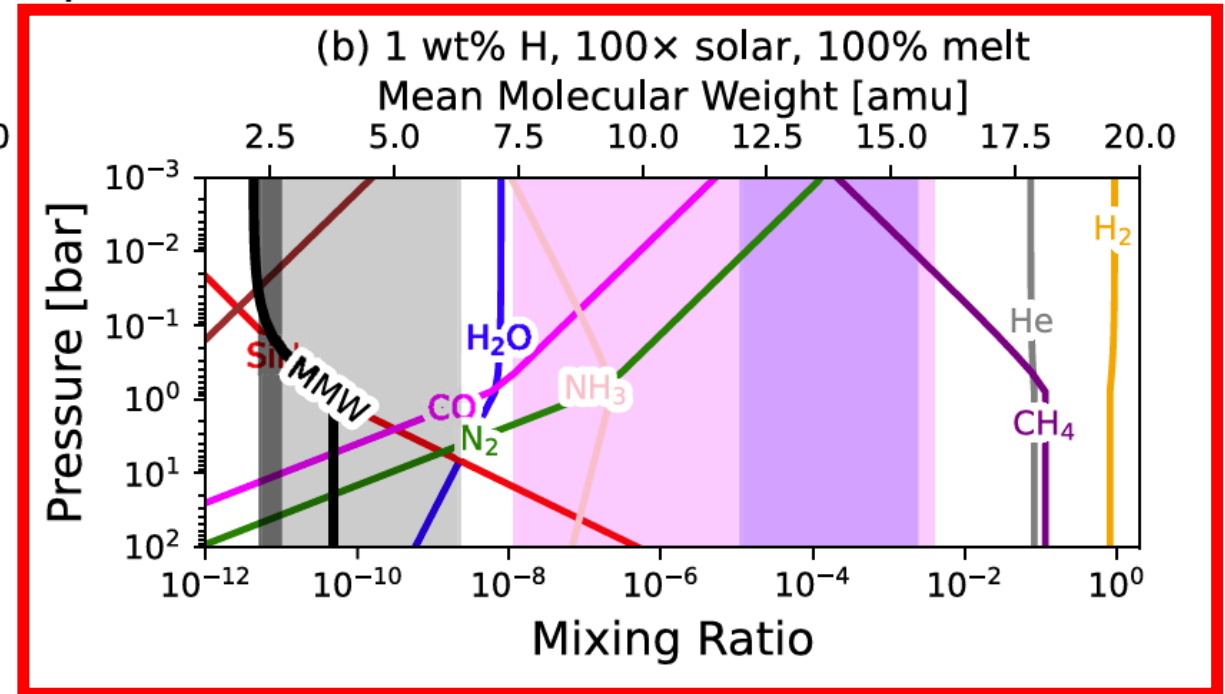
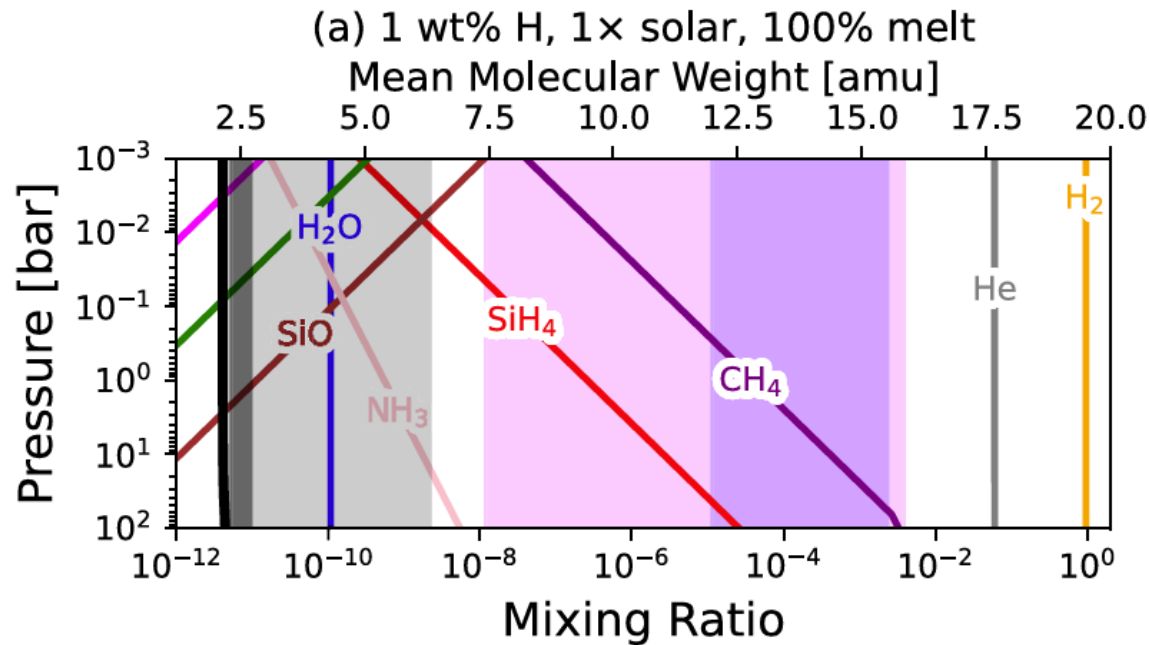


- SiH_4 condensation as SiC , Si and SiO_2 → not visible in upper atmosphere
- 100 × solar cases predict **correct** $x\text{CH}_4$ and mean molecular weight (**MMW**), but **CO_2 not observed**

Silane-methane competition

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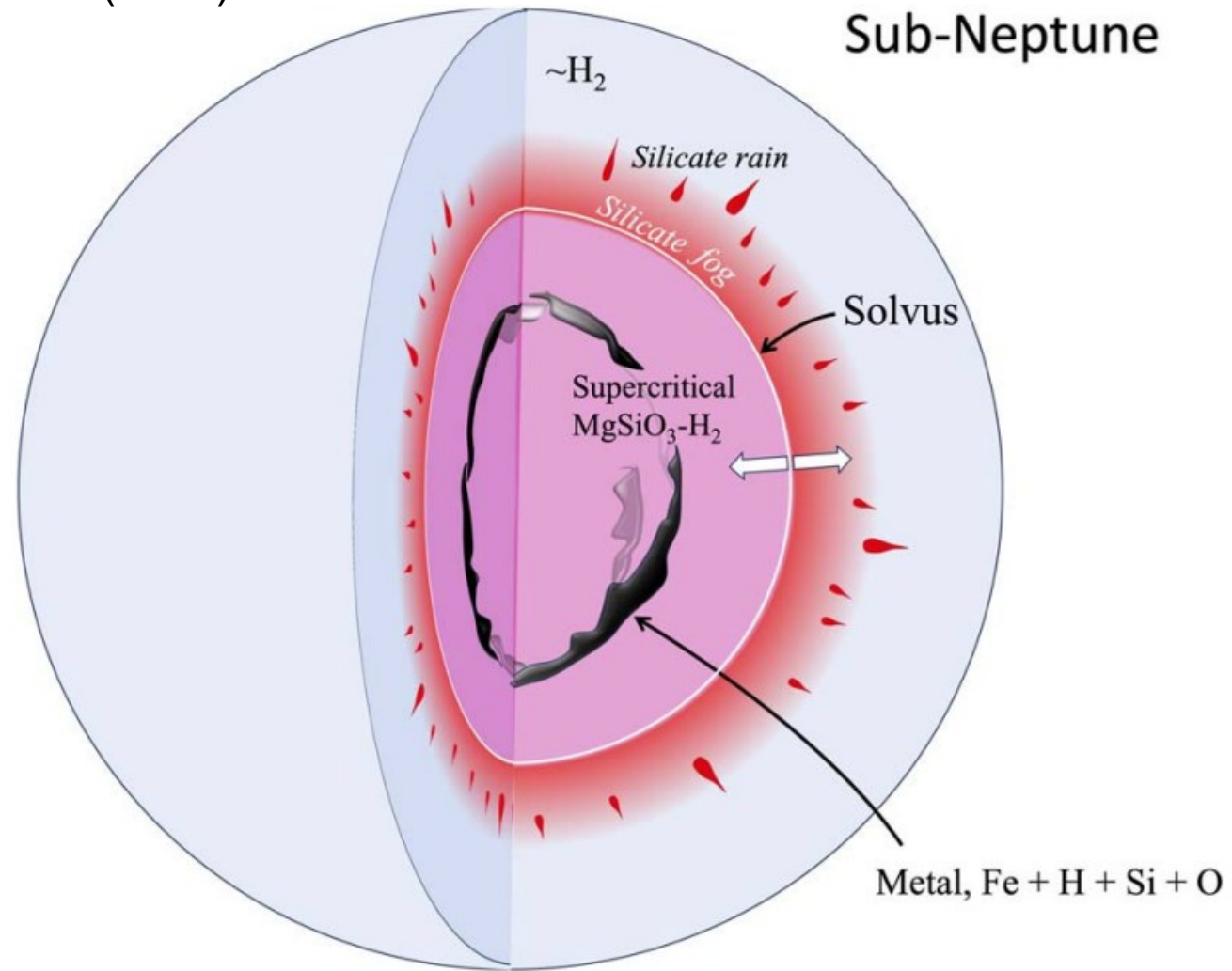
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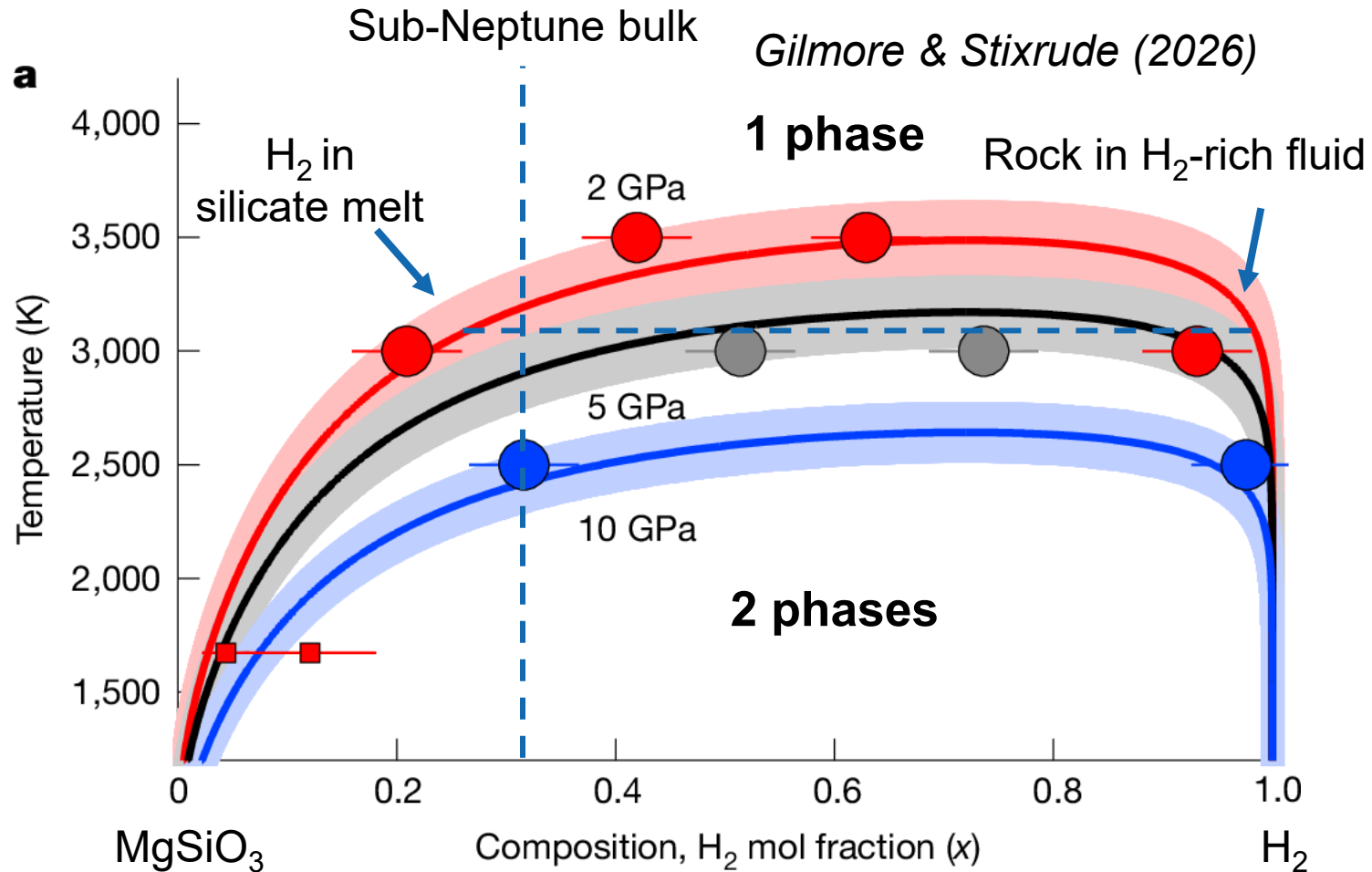
- SiH_4 condensation as SiC , Si and SiO_2 → not visible in upper atmosphere
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Needs additional oxygen...

Young et al. (2024)



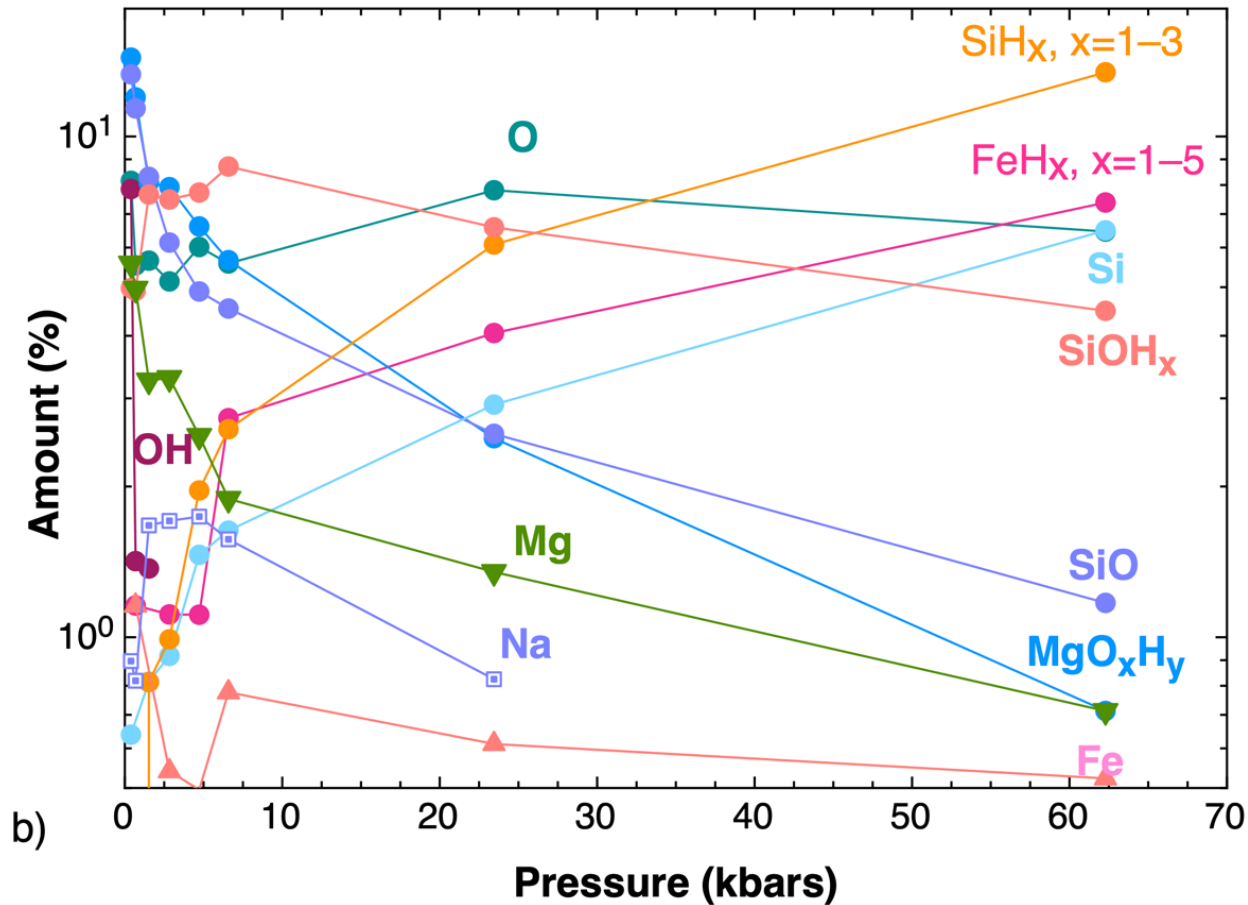
Towards miscibility



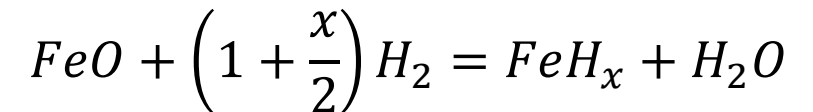
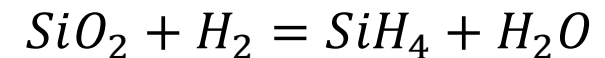
- Ab-initio simulations of system H_2 - $MgSiO_3$
- Closure of two-phase field $>$ 3500 K, 2 GPa
- Sub-Neptunes may have no surface
- Implicit is the stoichiometry of species in simplified system...

Towards miscibility

Caracas et al. (submitted)



- Ab-initio simulations of system H₂-peridotite
- Species including SiH₄ and FeH_x are stable > 2 GPa
- Presence of these species stabilises the fluid phase
- Cannot be considered as a simple binary



Experiments on stability of silane and iron hydrides sorely needed!

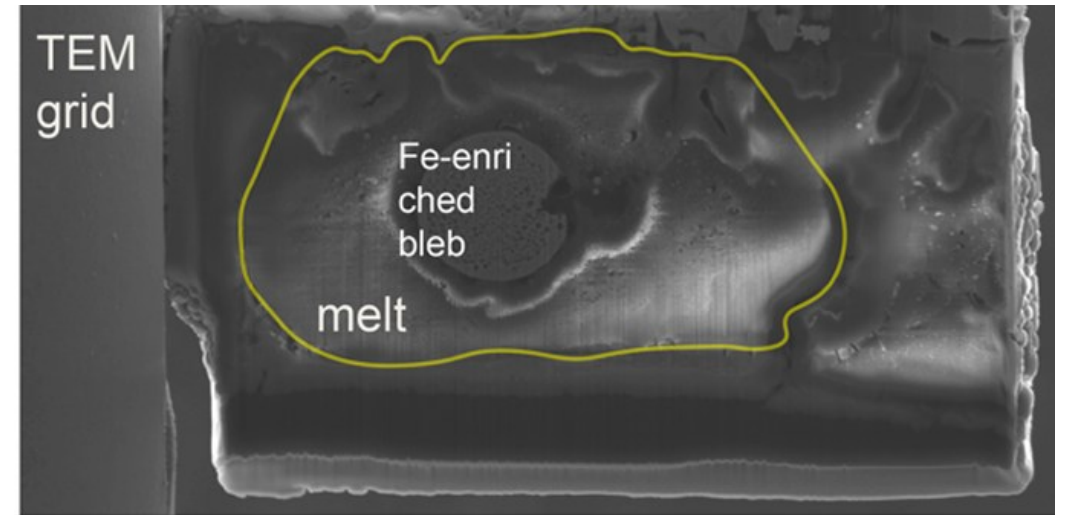
Towards miscibility

- Diamond-anvil cell experiments up to **~72 GPa** and **4700 K** on **peridotite**
- Loaded in 75Ar-25H₂ pressure medium to generate high fH_2
- Two phases clearly observed
- Silicate phase contains 6 wt. % H as H₂, but **speciation not determined**

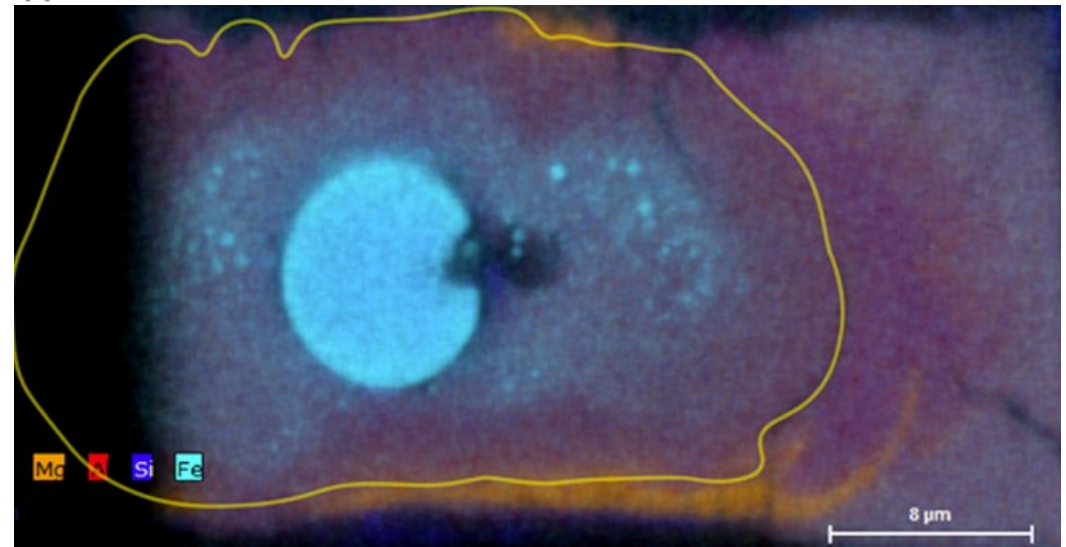
Phase relations in sub-Neptune envelopes and interiors are uncertain

30.7 GPa, 4100-4200 K

Miozzi et al. (2025)



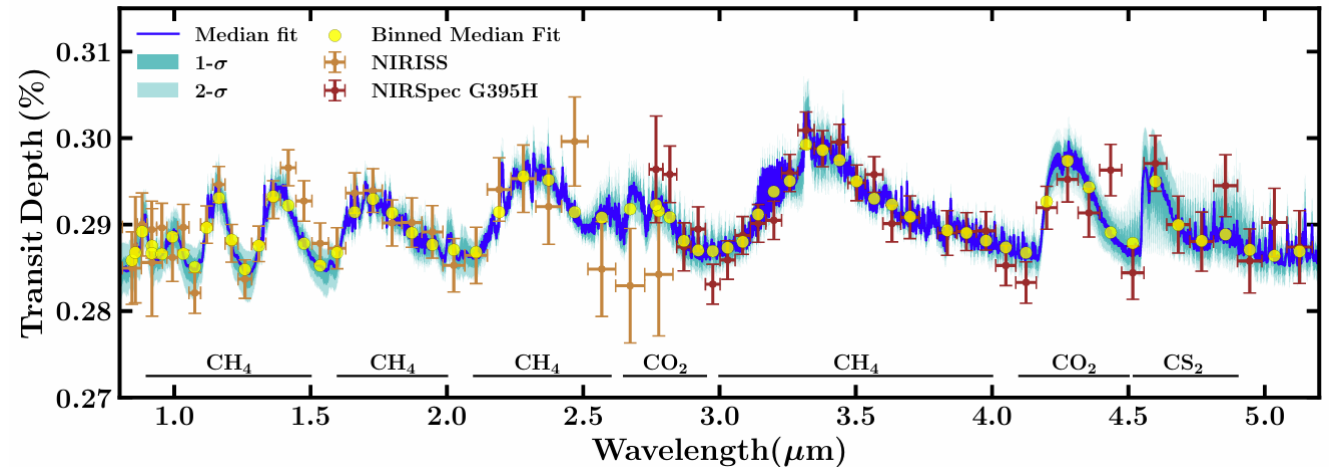
1 μ m
H EHT = 10.00 kV Detector = SESI Mag = 2.09 KX WD = 5.1 mm



Population studies of sub-Neptune envelopes

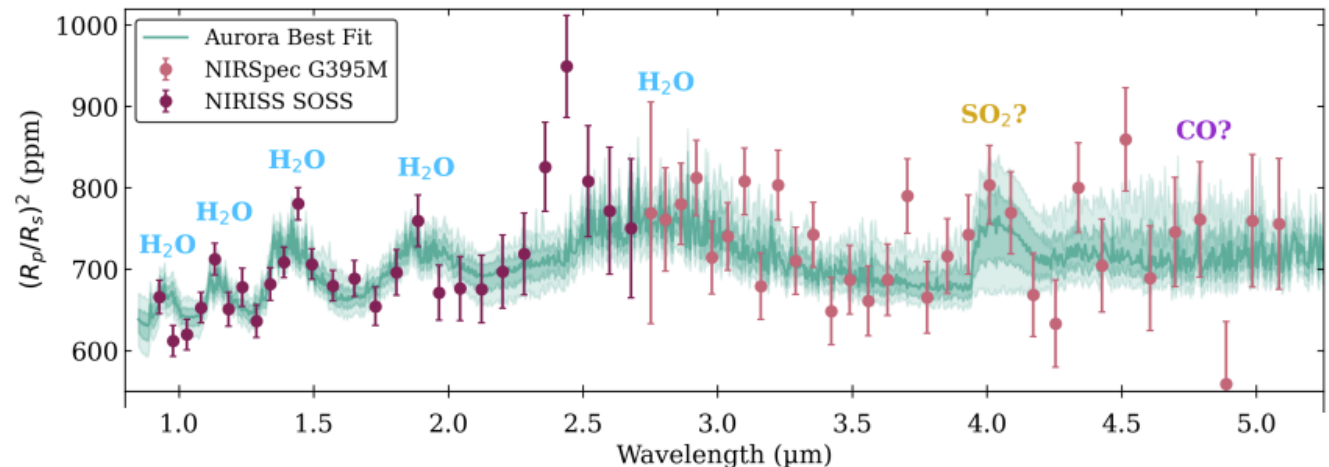
- Temperate sub-Neptunes $T_{\text{eq}} < 400$ K (K2-18b, TOI-270d) have either CH_4 and/or CO_2 in their atmospheres

TOI-270 d, $T_{\text{eq}} = 350$ K (Constantinou et al. 2026)

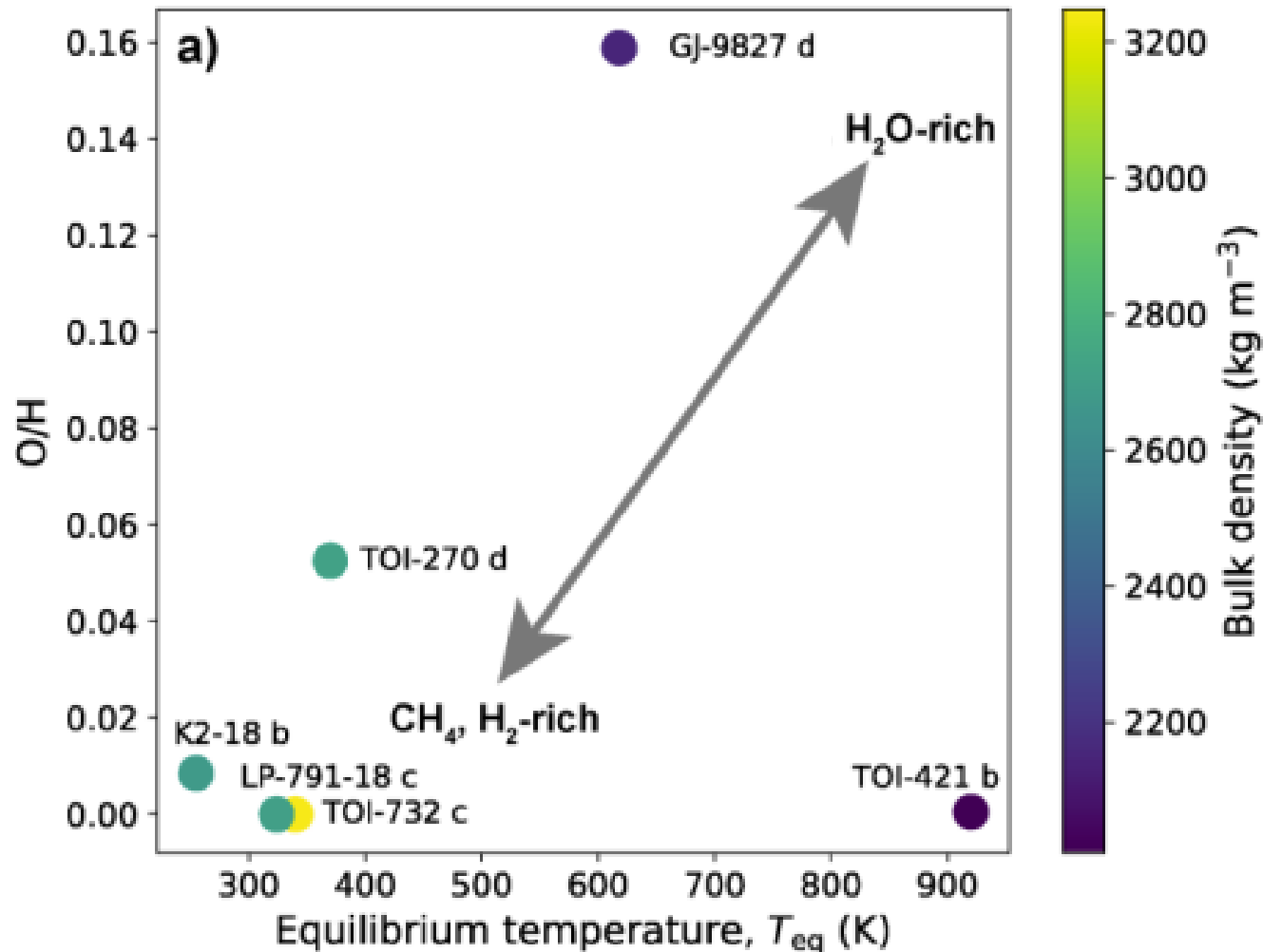


- Warmer sub-Neptunes $T_{\text{eq}} > 600$ K (GJ 9827-d, TOI-421 b) have H_2O in their atmospheres

TOI-421 b, $T_{\text{eq}} = 920$ K (Davenport et al. 2025)



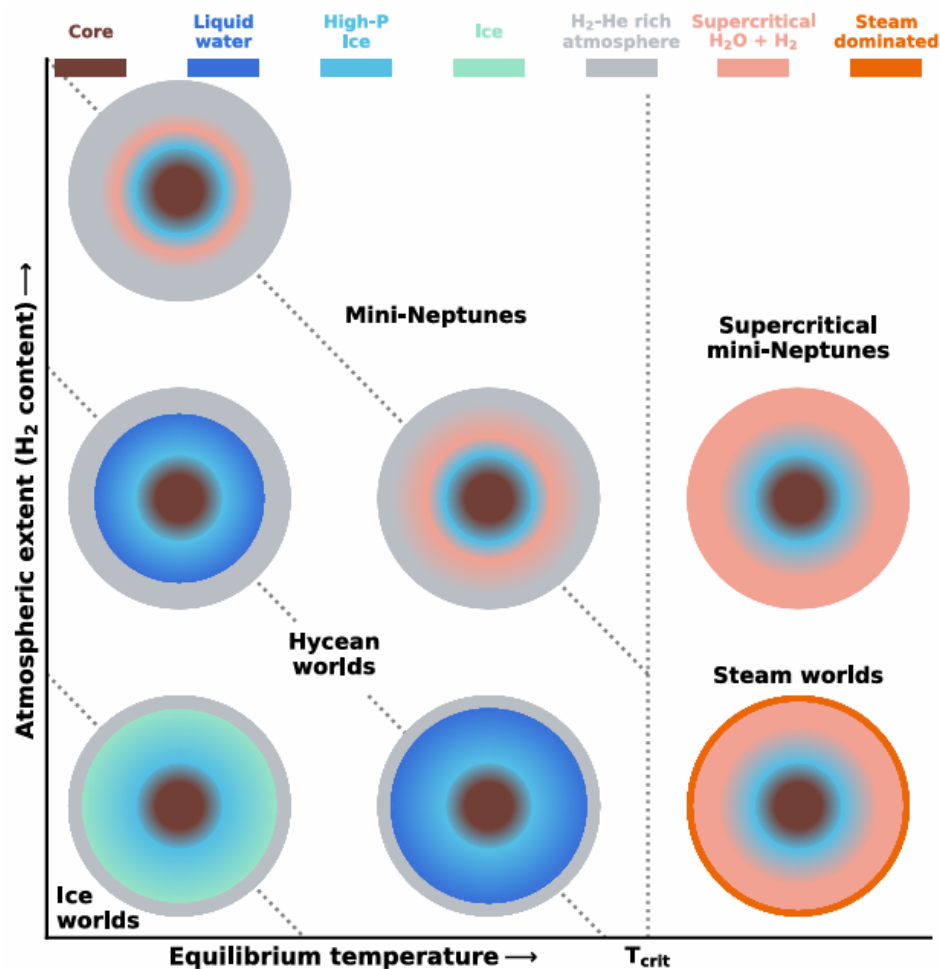
Population studies of sub-Neptune envelopes



- Temperate sub-Neptunes have **elevated densities ($>2800 \text{ kg/m}^3$)** compared to warmer sub-Neptunes ($<2400 \text{ kg/m}^3$)
- Higher O/H implies release of H_2O , either
 - Evaporation of an ocean layer (i.e., post-Hycean)
 - Higher oxygen release from interior
- Could these planets form a continuum governed by T_{eq} and the **mass of H_2/He accreted?**

Population studies of sub-Neptune envelopes

Madhusudhan et al. (2025)

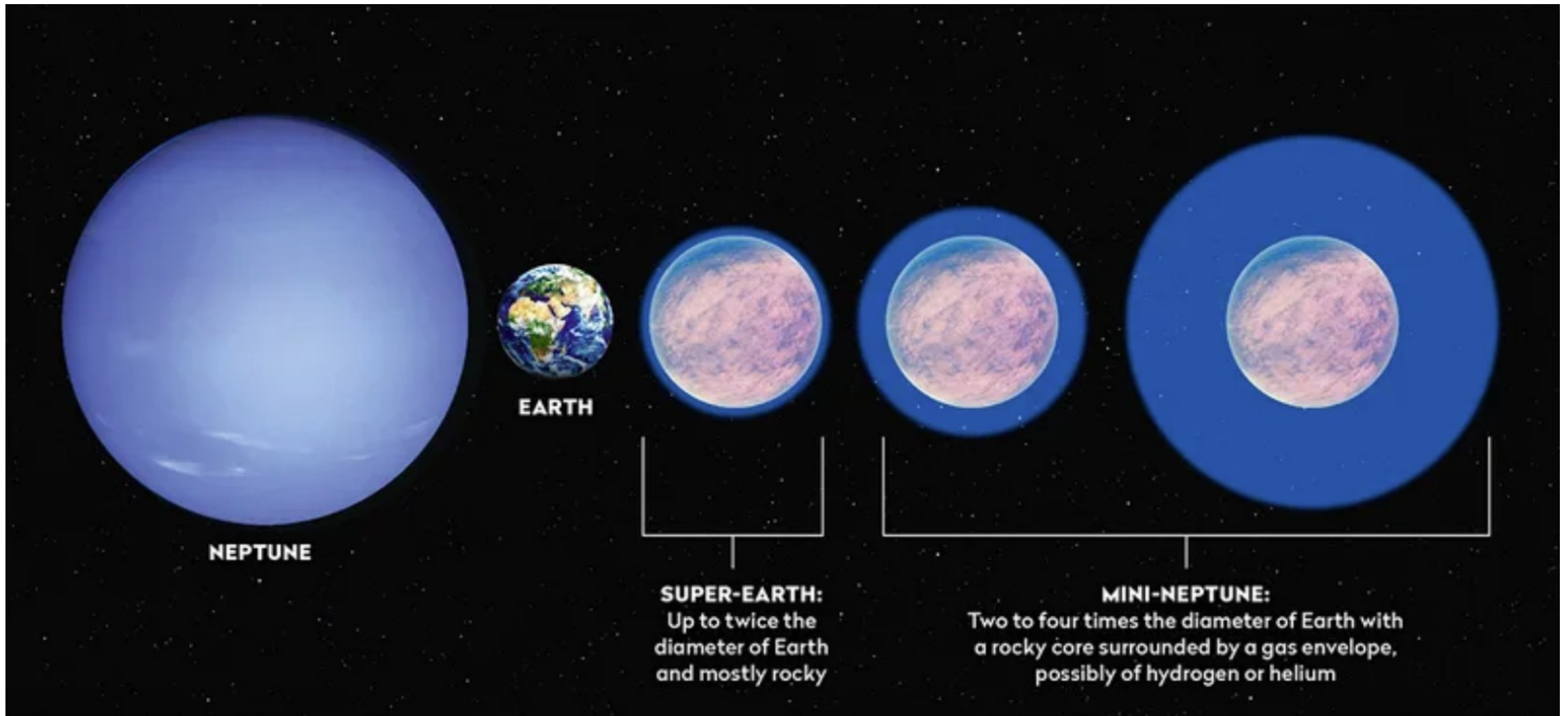


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Solutions remain degenerate!

Conclusions

- To explain their bulk densities, sub-Neptunes have low mean molecular weight envelopes (< 5 kg/mol) between $\sim 0.5 - 3\%$ the total planet mass
- This generates pressures up to ~ 10 GPa and temperatures up to ~ 4000 K
- At these conditions, silicate components evaporate, forming SiH_4 , and behaviour is strongly non-ideal
- If metallicity is sufficiently high CH_4 also forms, and is observed in the photosphere of temperate sub-Neptunes, unlike SiH_4 which condenses
- Hotter sub-Neptunes, in particular, are O-rich and contain H_2O in their atmospheres, potentially reflecting miscibility in their interiors



Atmospheric diversity on abiotic rocky worlds - atmodeller



OPEN ACCESS

An Oxidation Gradient Straddling the Small Planet Radius Valley

Collin Cherubim, Robin Wordsworth, Dan J. Bower, Paolo A. Sossi, Danica Adams, and Renyu Hu
Published 2025 April 10 • © 2025. The Author(s). Published by the American Astronomical Society.

[The Astrophysical Journal](#), Volume 983, Number 2

Citation Collin Cherubim et al 2025 *ApJ* 983 97


DOI 10.3847/1538-4357/adbca9

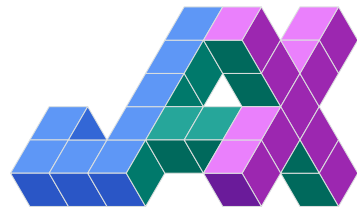
JOURNAL ARTICLE

Silane–methane competition in sub-Neptune atmospheres as a diagnostic of metallicity and magma oceans

Kaustubh Hakim , Dan J Bower, Fabian L Seidler, Paolo A Sossi

Monthly Notices of the Royal Astronomical Society, Volume 546, Issue 2, February 2026, stag133, <https://doi.org/10.1093/mnras/stag133>

Published: 20 January 2026 **Article history** 



OPEN ACCESS

Diversity of Low-mass Planet Atmospheres in the C–H–O–N–S–Cl System with Interior Dissolution, Nonideality, and Condensation: Application to TRAPPIST-1e and Sub-Neptunes

Dan J. Bower, Maggie A. Thompson, Kaustubh Hakim, Meng Tian, and Paolo A. Sossi

Published 2025 December 4 • © 2025. The Author(s). Published by the American Astronomical Society.

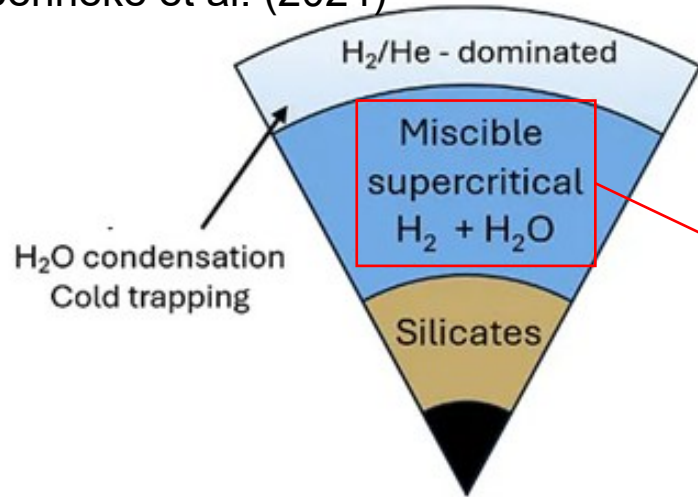
[The Astrophysical Journal](#), Volume 995, Number 1

Citation Dan J. Bower et al 2025 *ApJ* 995 59

DOI 10.3847/1538-4357/ae1479

Mixing in atmospheres of other worlds

Benneke et al. (2024)



Stratified Mini-Neptune
(cool)

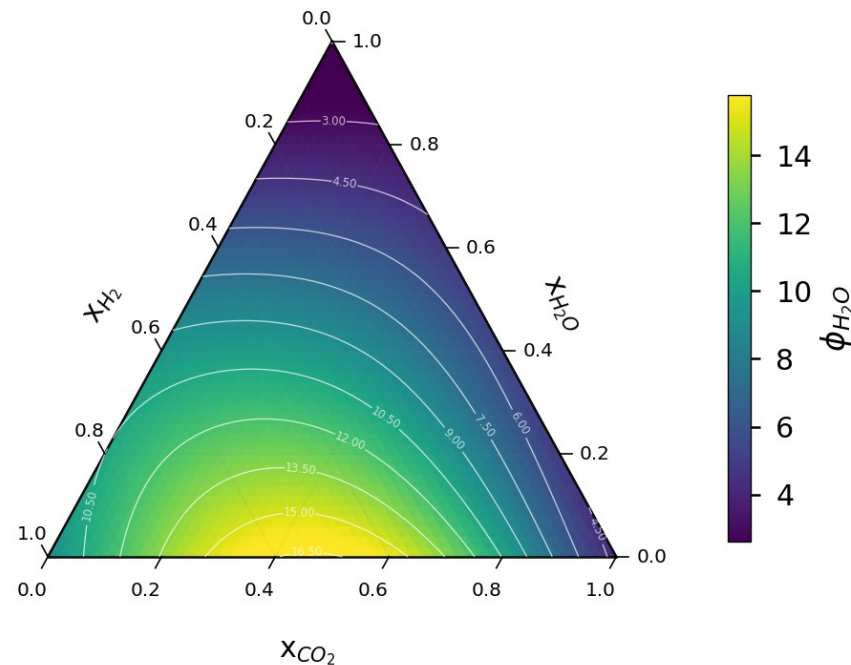
Yuna Yu



MSc.(Geneva/ETH)
Sept. 2024 – Jul 2025
w/ P.Sossi, D. Bower, C. Lovis

- Structures of sub-Neptunes depend on properties of supercritical fluids
- Pressures > 1 GPa and Temperatures > 1000 K in deep envelope

Aim: Determine volumes of mixed fluids in C-O-H system



- Deviation from ideal gas given by fugacity coefficient:
- $\phi = \text{fugacity}/\text{pressure}$
- H₂O strongly non-ideal in H₂-rich fluids

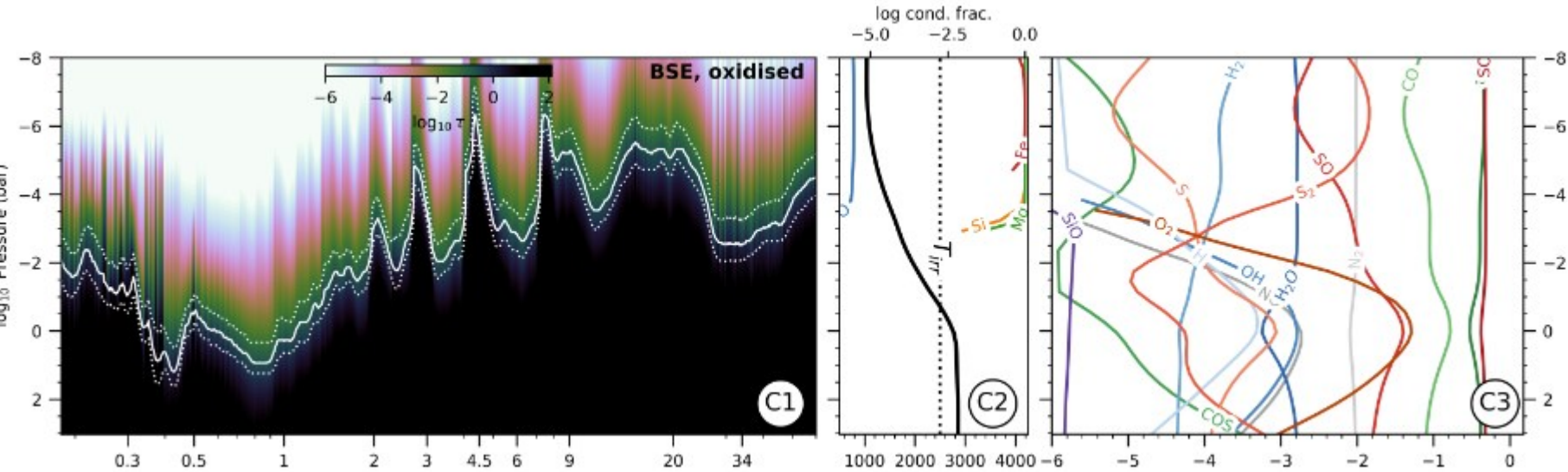
Favours phase separation in sub-Neptunes

Volatile-bearing mineral atmospheres of hot rocky exoplanets as probes of interior state and composition

Fabian L. Seidler¹, Paolo A. Sossi¹, Dan J. Bower¹, and Brice-Olivier Demory^{2,3}



- Mineral + CHONS atmospheres
- Spectra of Earth-like and Sun-like atmospheres
- Application to 55-Cnc-e



55-Cnc-e likely has a reducing atmosphere (no SO₂)