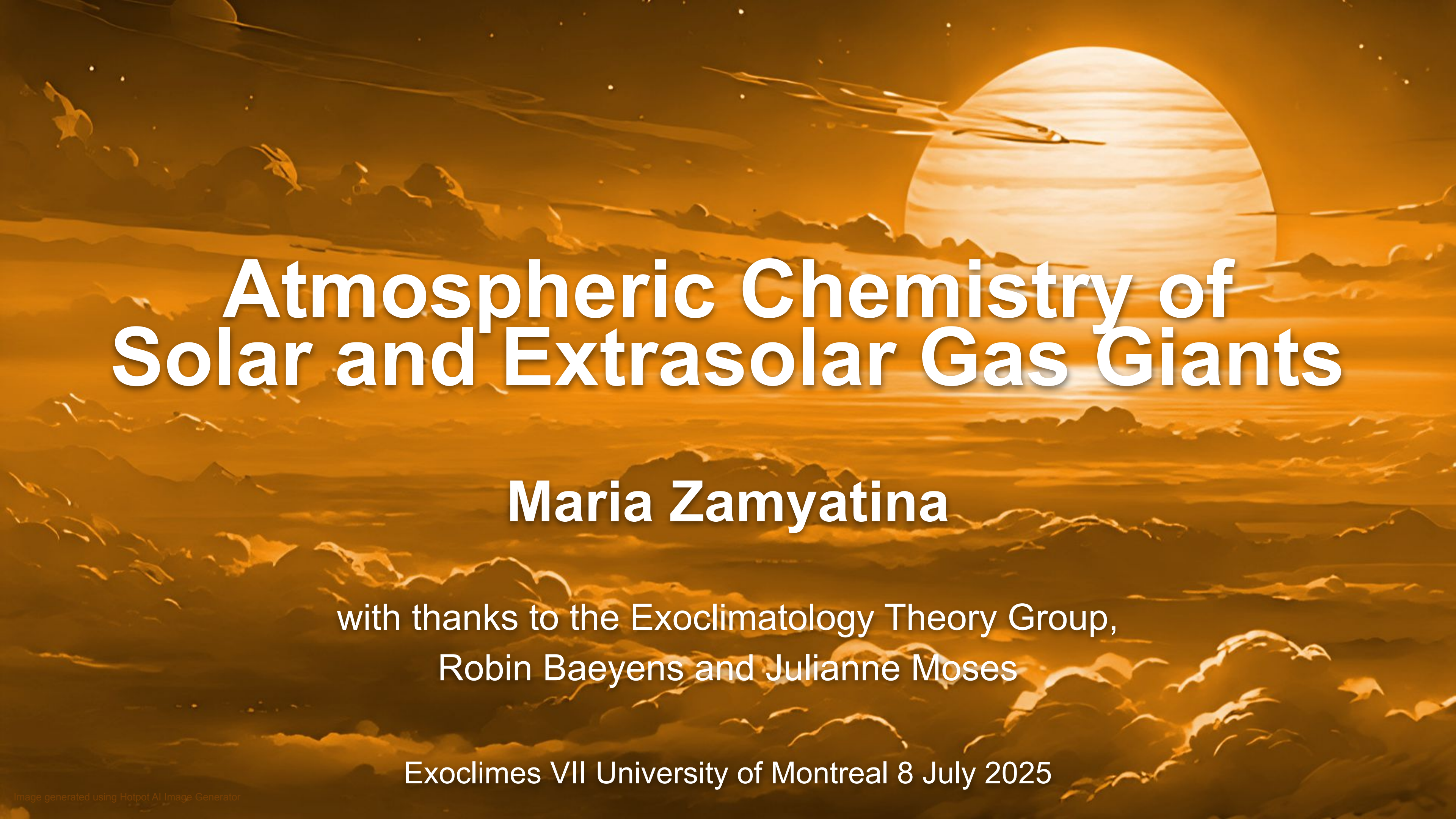


Atmospheric Chemistry of Solar and Extrasolar Gas Giants

Maria Zamyatina

with thanks to the Exoclimatology Theory Group,
Robin Baeyens and Julianne Moses

Exoclimes VII University of Montreal 8 July 2025

Outline

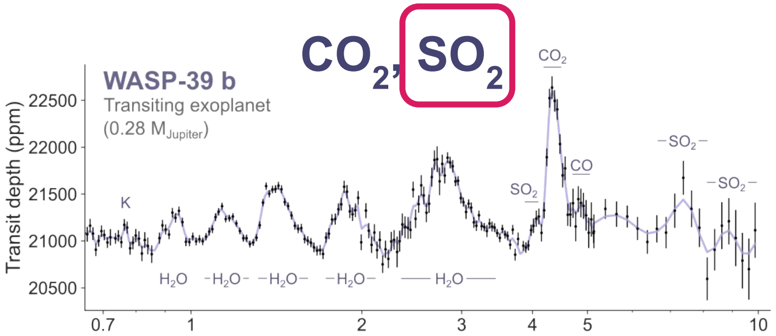
- Big questions
- Some chemical detection firsts with JWST
- Sulphur dioxide (SO_2)
  - What we can learn from SO_2
- Methane (CH_4)
  - The “missing methane” problem
- Chemical networks
- Lessons from the Solar System

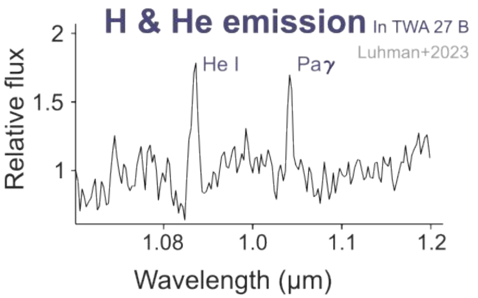
Big questions

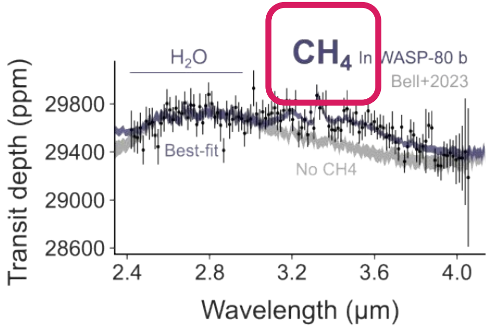
- How do planets form?
- How do planets get their atmospheres?
- How chemically diverse are planetary atmospheres?
- What processes affect atmospheric composition?

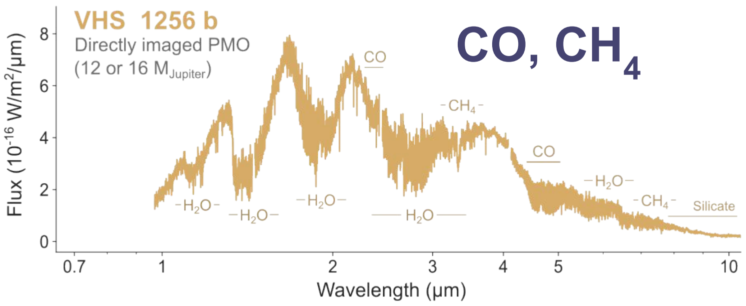
What can the observed atmospheric composition tell us about the past and the present of a planet?

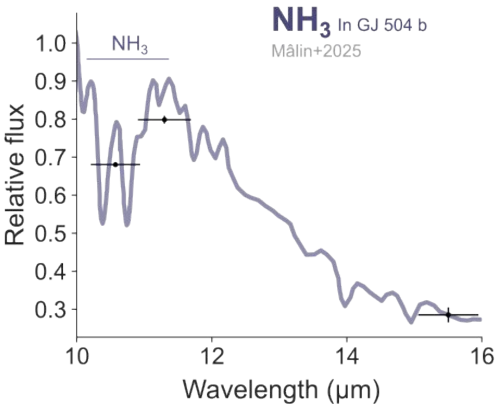
JWST extrasolar-gas-giant firsts

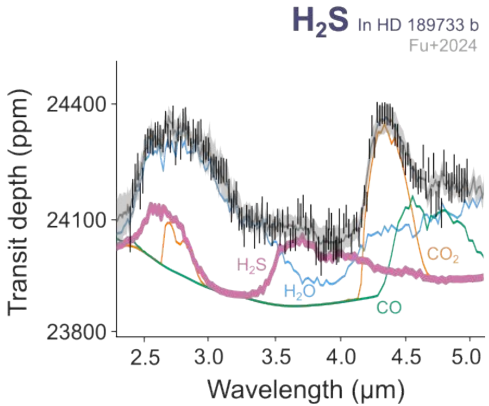












Espinoza,Perrin2025

Why do we care about **sulphur**?

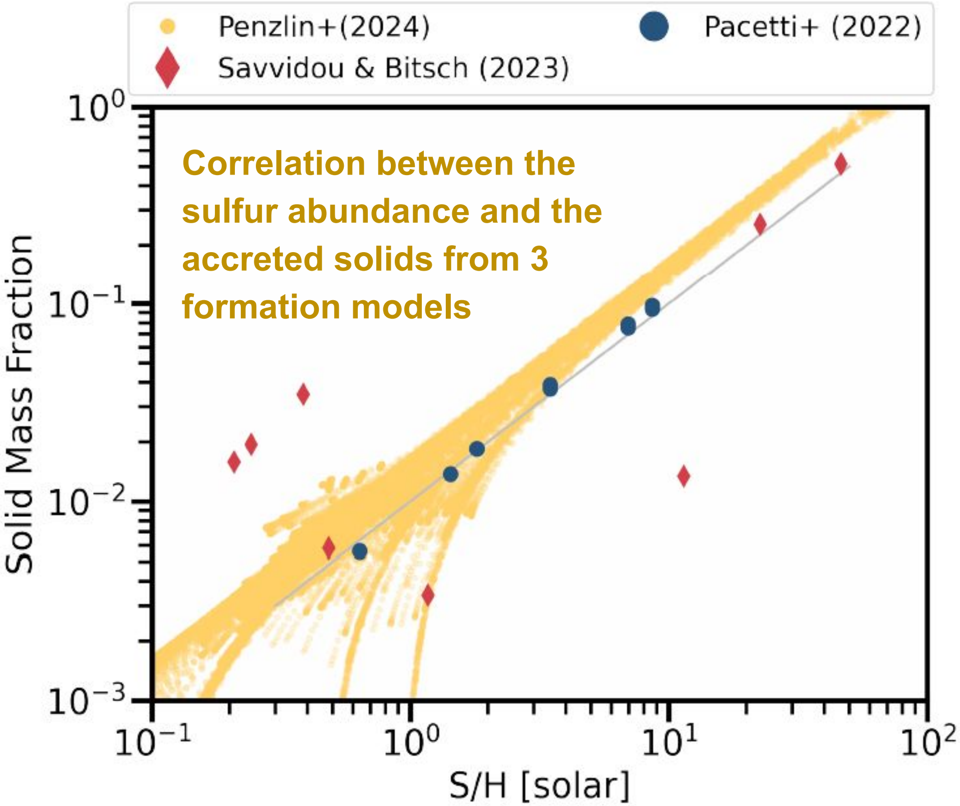
<u>**S** is abundant and of intermediate volatility</u>

- tracer for the **amount of solid material accreted by planets** during their formation
- helps **distinguish between competing models of planet formation**, complementing C, O, Si, Na, Fe

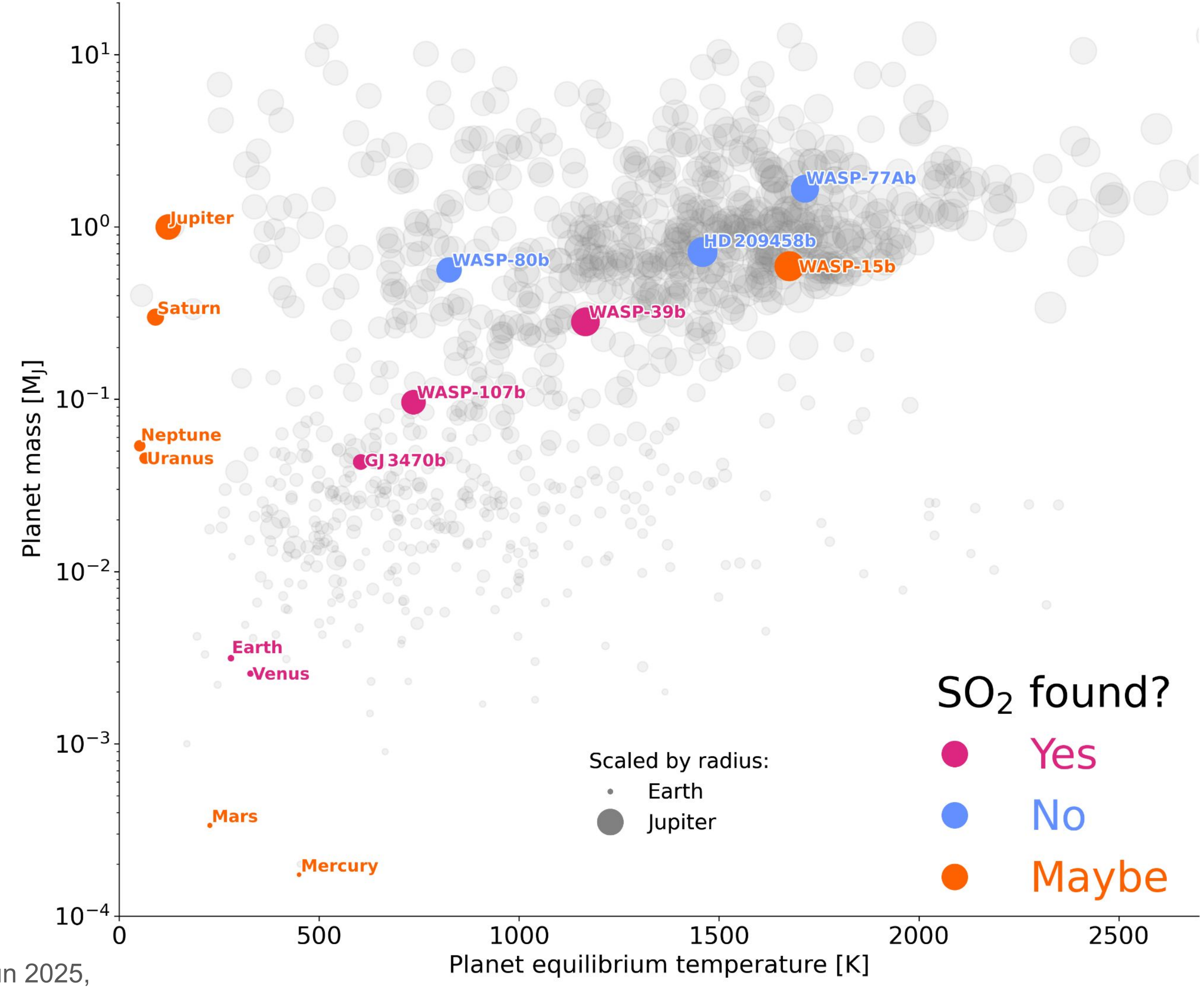
<u>Planet formation problem</u>: **S can sublimate into H_2S** at lower temperatures and may **modify planet's S/O**

<u>**S** chemistry</u> in H_2-rich atmospheres is **poorly known**

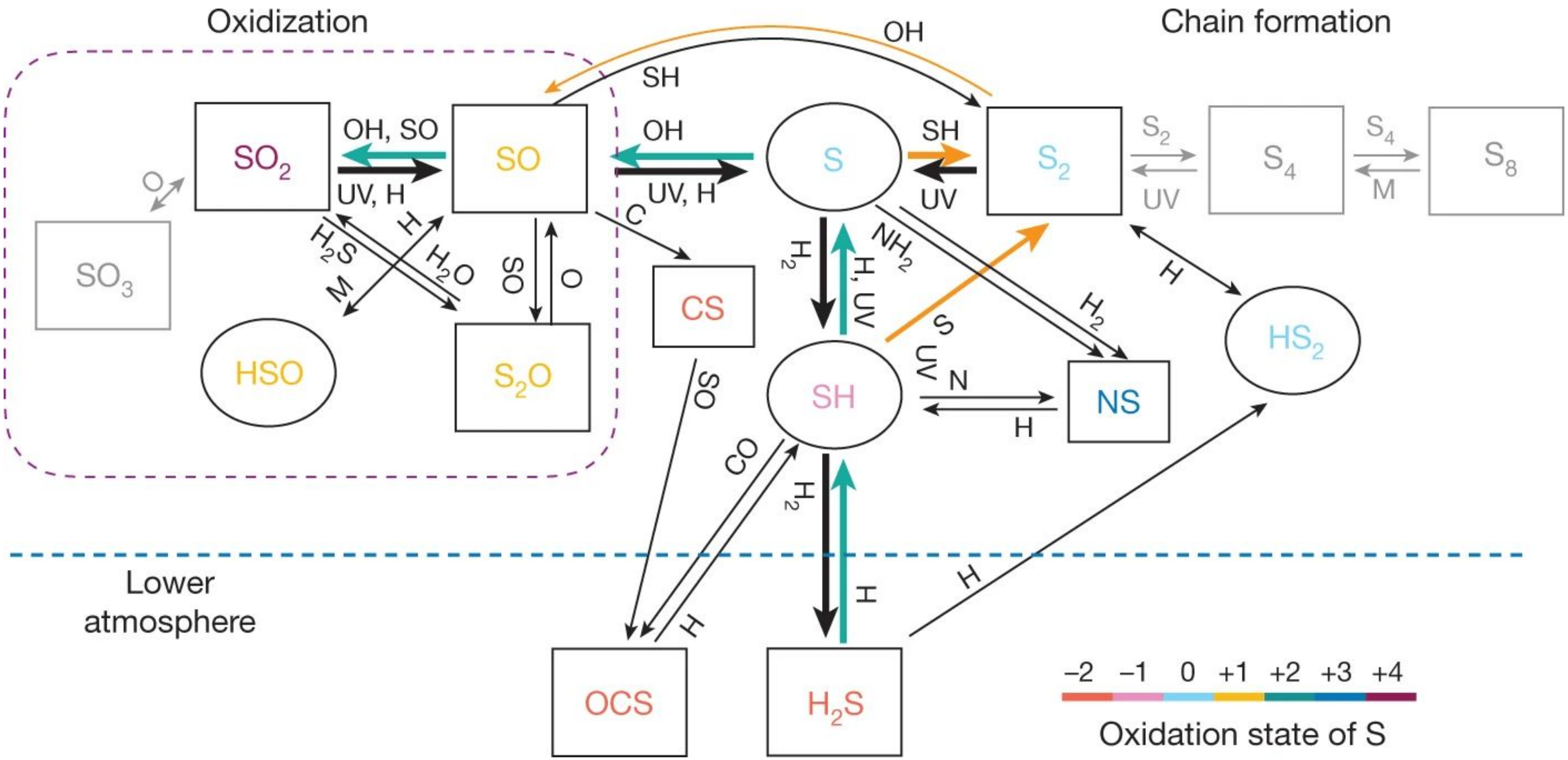
- **SO_2** is a **thermodynamically unstable** form of sulfur, because it is highly oxidised
- **SO_2** detection means that H_2S, a thermodynamically stable form of sulfur, is oxidised to SO_2
- **SO_2**: **tracer for atmospheric dynamics and metallicity** of giant planets



Feinstein,Booth,Bergner+2025

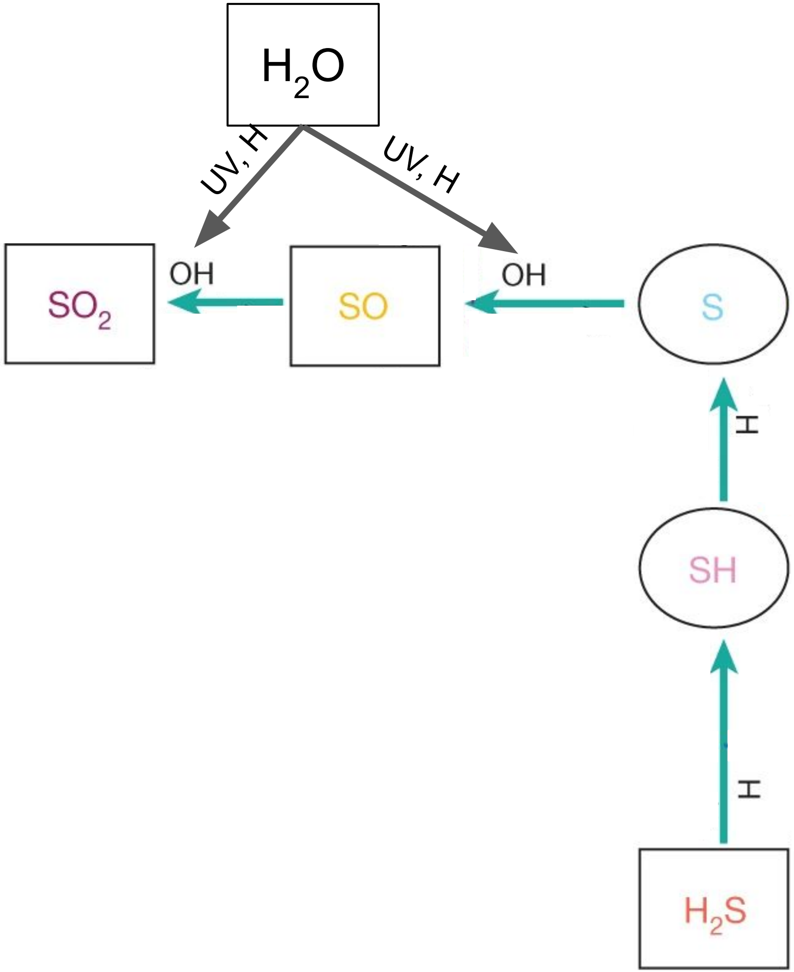


Southworth2011 TEPCat Jun 2025,
ExoAtmospheres Database

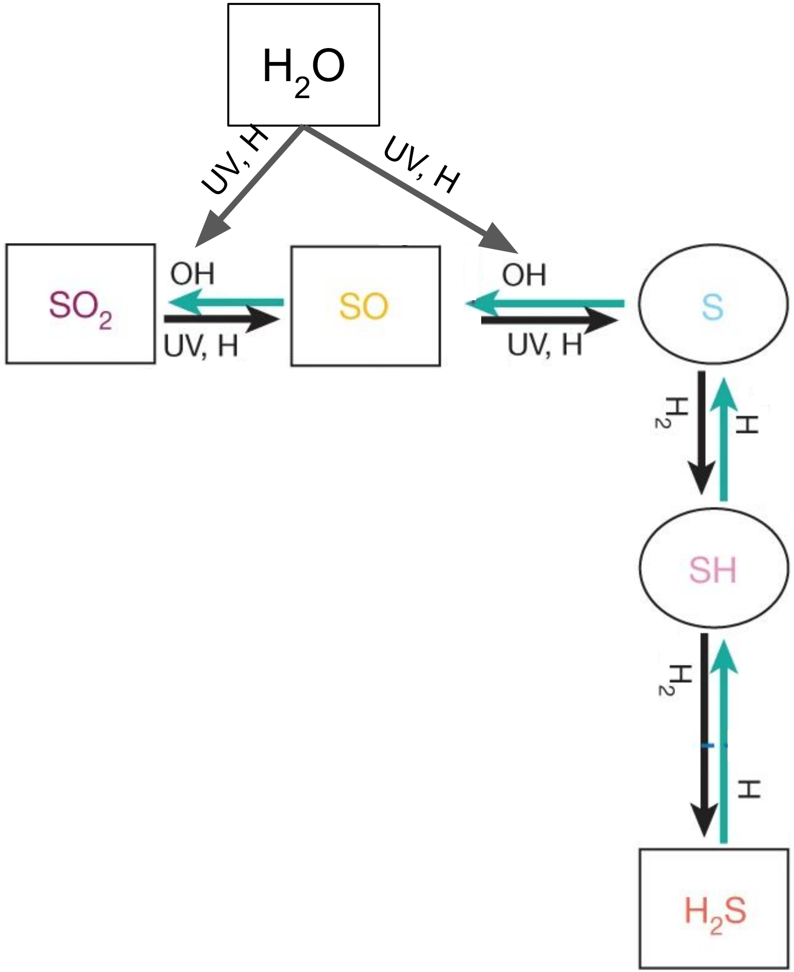


Oxidization
Chain formation
Lower atmosphere
SO2
SO3
SO
HSO
S2O
CS
S
SH
S2
S4
S8
HS2
NS
OCS
H2S
OH, SO
UV, H
OH
SH
UV
OH
SH
−2 −1 0 +1 +2 +3 +4
Oxidation state of S

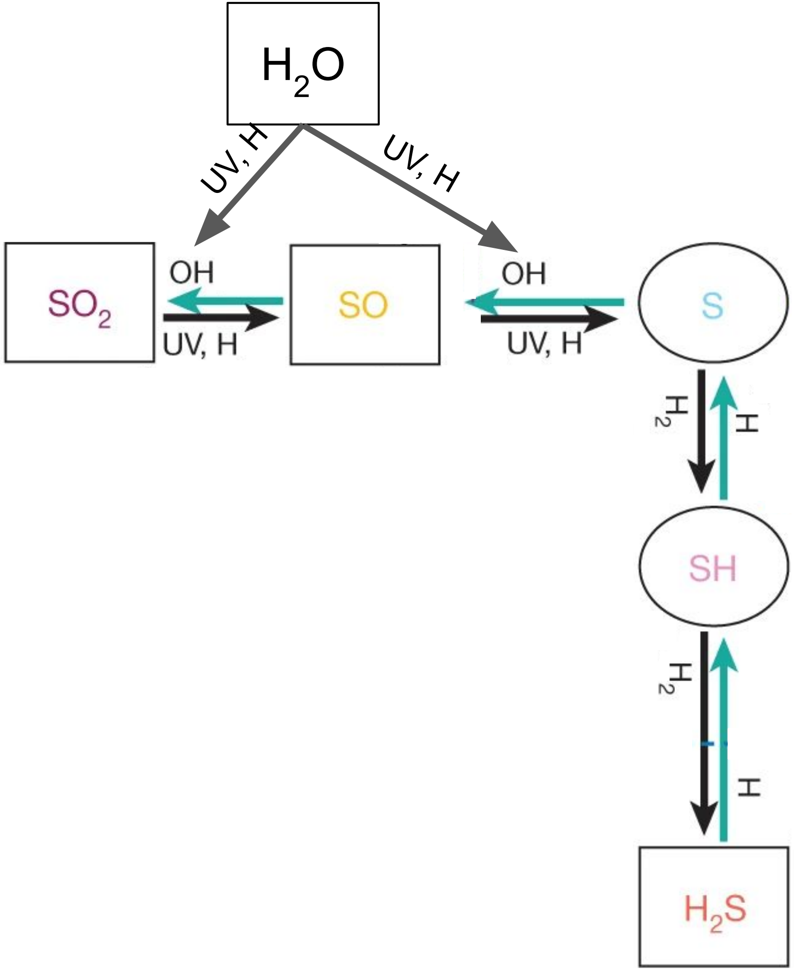
Tsai+2023a

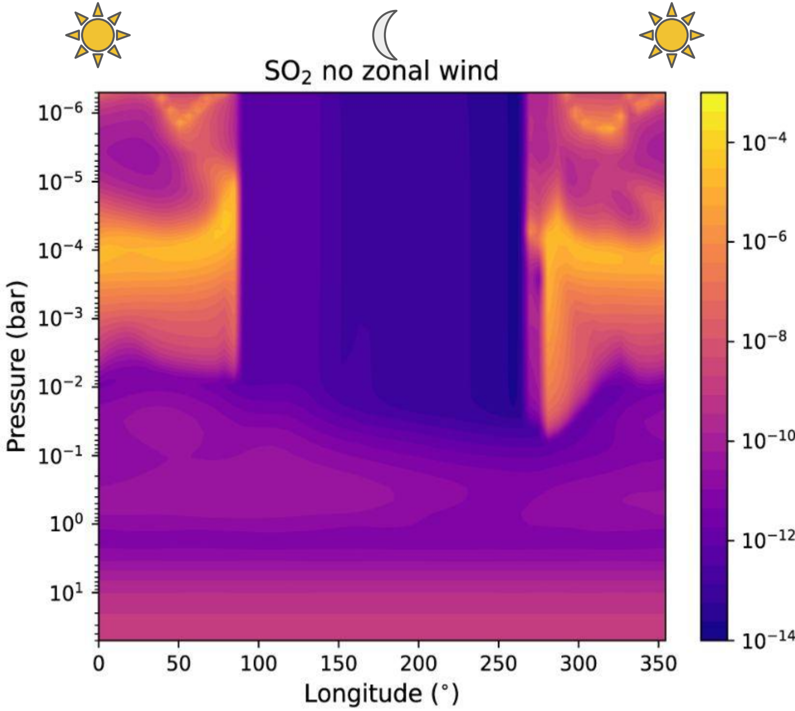


Tsai+2023a



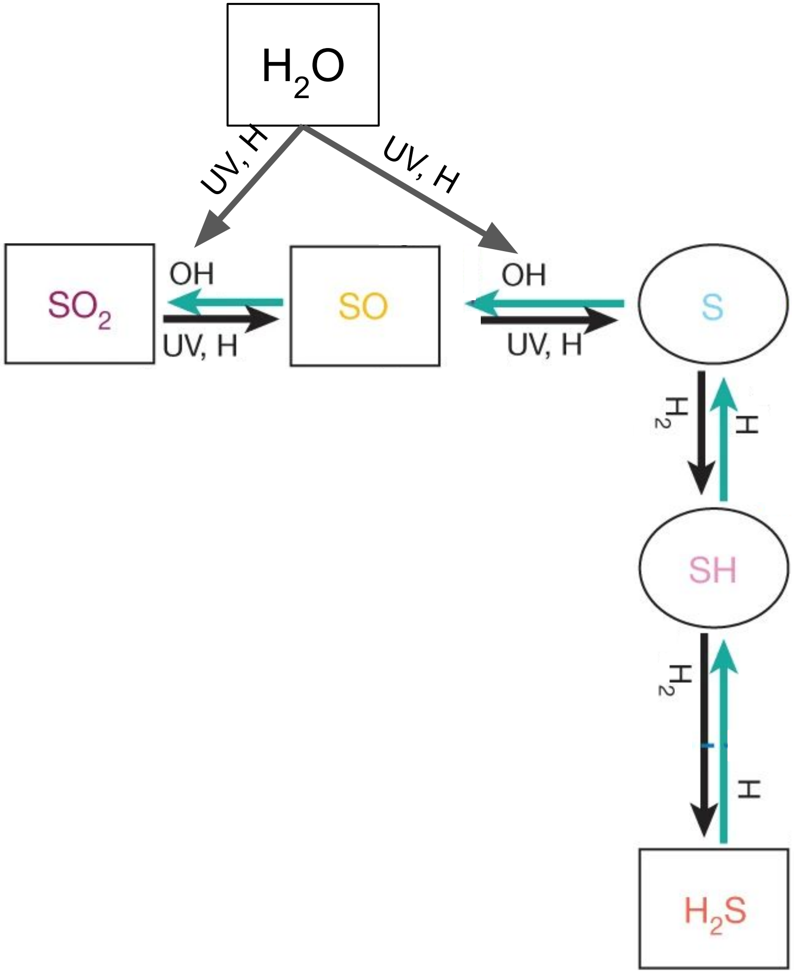
Tsai+2023a

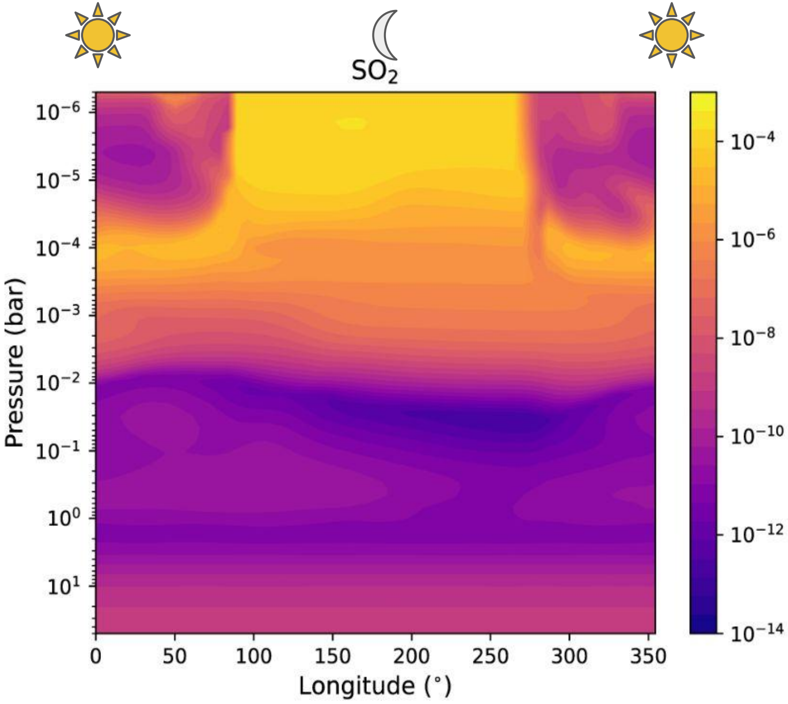




No horizontal transport

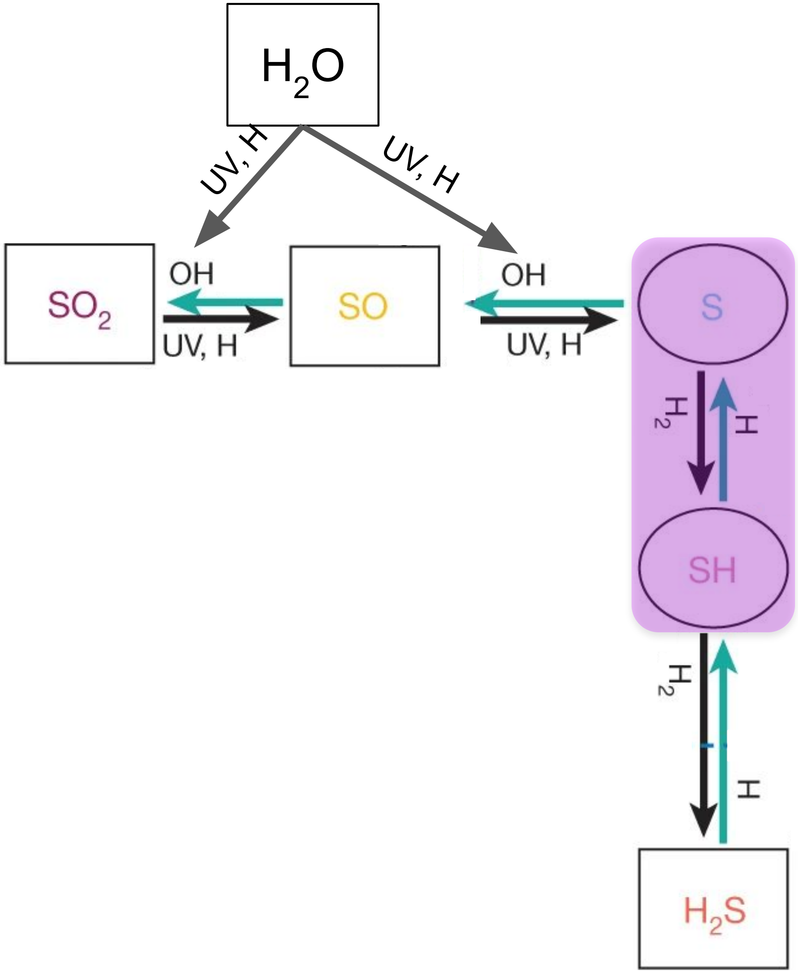
Tsai+2023a,b

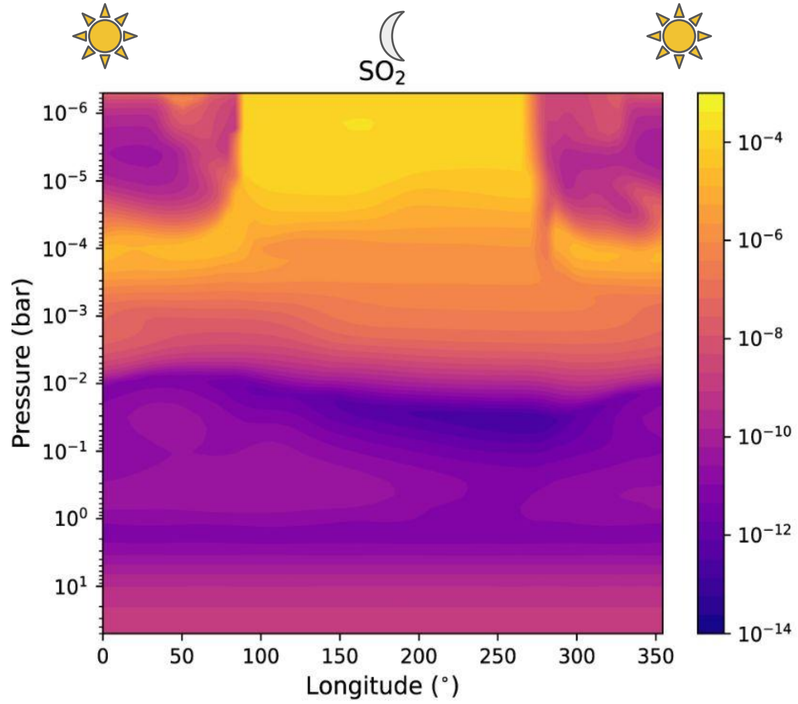




With horizontal transport

Tsai+2023a,b


H_2O
UV, H
UV, H
SO_2
OH
UV, H
SO
OH
UV, H
S
H_2
H
SH
H_2
H
H_2S


SO_2
Pressure (bar)
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
0
50
100
150
200
250
300
350
Longitude (°)
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}

Tsai+2023a,b

Need lab data!

Table 4. Sulfur Reaction Rate Coefficient Data Needed for Exoplanet Studies

Reaction[a]			Notes[b]
$S + S_3$	$\longrightarrow$	$S_2 + S_2$	Need data
$S + S_4$	$\longrightarrow$	$S_2 + S_3$	Need data
$S + SH$	$\longrightarrow$	$S_2 + H$	Some data exist; need accurate values and T dependence
$S + HS_2$	$\longrightarrow$	$S_2 + SH$	Sendt et al. (2002); need extension to lower & higher T
$S + CO + M$	$\longrightarrow$	$OCS + M$	† Need low and high pressure limits and their T dependence
$S + CS + M$	$\longrightarrow$	$CS_2 + M$	† Need low and high pressure limits and their T dependence
$S + HCS$	$\longrightarrow$	$CS_2 + H$	† Alzueta et al. (2019) estimate; need confirmation
$S_2 + H + M$	$\longrightarrow$	$HS_2 + M$	Sendt et al. (2002); need confirmation and extension to lower T
$S_2 + S_2 + M$	$\longrightarrow$	$S_4 + M$	† Some data exist; need accurate values and T dependence
$S_4 + S_4 + M$	$\longrightarrow$	$S_8 + M$	† Need low and high pressure limits and their T dependence
$SH + H$	$\longrightarrow$	$H_2 + S$	Some data exist; need accurate values and T dependence
$SH + H + M$	$\longrightarrow$	$H_2S + M$	Need low and high pressure limits and T dependence
$SH + S_3$	$\longrightarrow$	$HS_2 + S_2$	Need data
$SH + S_4$	$\longrightarrow$	$HS_2 + S_3$	Need data
$SH + SH$	$\longrightarrow$	$H_2S + S$	† Some data exist; need accurate values and T dependence
$SH + HS_2$	$\longrightarrow$	$H_2S + S_2$	† Sendt et al. (2002); need extension to lower T
$SH + H_2S_2$	$\longrightarrow$	$H_2S + HS_2$	Sendt et al. (2002); need extension to lower T
$SH + CS$	$\longrightarrow$	$CS_2 + H$	† Alzueta et al. (2019); need confirmation and T dependence
$SH + HCS$	$\longrightarrow$	$H_2S + CS$	Need data
$SH + OCS$	$\longrightarrow$	$CO + HS_2$	† Need data and T dependence
$HS_2 + H$	$\longrightarrow$	$SH + SH$	Sendt et al. (2002); need confirmation
$HS_2 + H$	$\longrightarrow$	$H_2 + S_2$	Sendt et al. (2002); need extension to lower T
$HS_2 + H$	$\longrightarrow$	$H_2S + S$	Sendt et al. (2002); need extension to lower T
$HS_2 + HS_2$	$\longrightarrow$	$H_2S_2 + S_2$	Sendt et al. (2002); need extension to lower T
$HS_2 + CS$	$\longrightarrow$	$CS_2 + SH$	Need data and T dependence
$CS + SO$	$\longrightarrow$	$CO + S_2$	Need data and T dependence
$CS + SO$	$\longrightarrow$	$OCS + S$	Need data and T dependence
$HOSO + H$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + O$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + OH$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + S$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + SH$	$\longrightarrow$	products	Need data and product branching ratios
$S_2O + H$	$\longrightarrow$	$SO + OH$	Need data

[a] M represents any third body such as the dominant background gas.
[b] † represents particularly pressing need.

Credit: Julianne Moses
Baeyens+ RASTI (in prep.)

Many reactions involving C-S bond

Table 4. Sulfur Reaction Rate Coefficient Data Needed for Exoplanet Studies

Reaction[a]			Notes[b]
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$S_4 + S_4 + M$	$\longrightarrow$	$S_8 + M$	† Need low and high pressure limits and their T dependence
$SH + H$	$\longrightarrow$	$H_2 + S$	Some data exist; need accurate values and T dependence
$SH + H + M$	$\longrightarrow$	$H_2S + M$	Need low and high pressure limits and T dependence
$SH + S_3$	$\longrightarrow$	$HS_2 + S_2$	Need data
$SH + S_4$	$\longrightarrow$	$HS_2 + S_3$	Need data
$SH + SH$	$\longrightarrow$	$H_2S + S$	† Some data exist; need accurate values and T dependence
$SH + HS_2$	$\longrightarrow$	$H_2S + S_2$	† Sendt et al. (2002); need extension to lower T
$SH + H_2S_2$	$\longrightarrow$	$H_2S + HS_2$	Sendt et al. (2002); need extension to lower T
$SH + CS$	$\longrightarrow$	$CS_2 + H$	† Alzueta et al. (2019); need confirmation and T dependence
$SH + HCS$	$\longrightarrow$	$H_2S + CS$	Need data
$SH + OCS$	$\longrightarrow$	$CO + HS_2$	† Need data and T dependence
$HS_2 + H$	$\longrightarrow$	$SH + SH$	Sendt et al. (2002); need confirmation
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$HOSO + H$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + O$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + OH$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + S$	$\longrightarrow$	products	Need data and product branching ratios
$HOSO + SH$	$\longrightarrow$	products	Need data and product branching ratios
$S_2O + H$	$\longrightarrow$	$SO + OH$	Need data

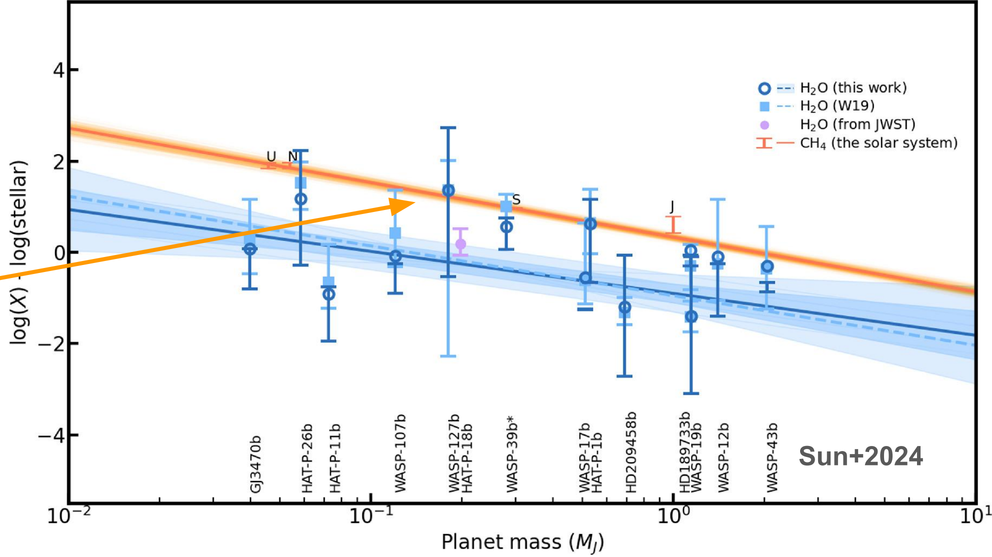
[a] M represents any third body such as the dominant background gas.
[b] † represents particularly pressing need.

Credit: Julianne Moses
Baeyens+ RASTI (in prep.)

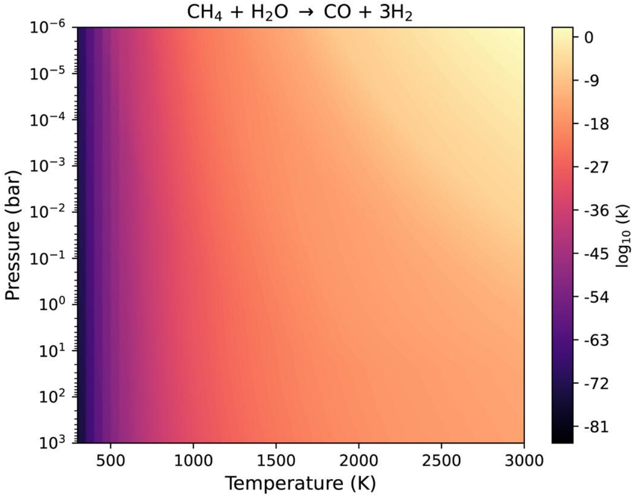
S chemistry is affected by C chemistry, and one of the key C species in giant planet atmospheres is CH_4

Why care about CH_4?

- CH_4 is a **proxy for metallicity** for the solar system giants
- CH_4 is a **haze** precursor
- CH_4 depletion as a **proxy for the deep atmosphere** temperature

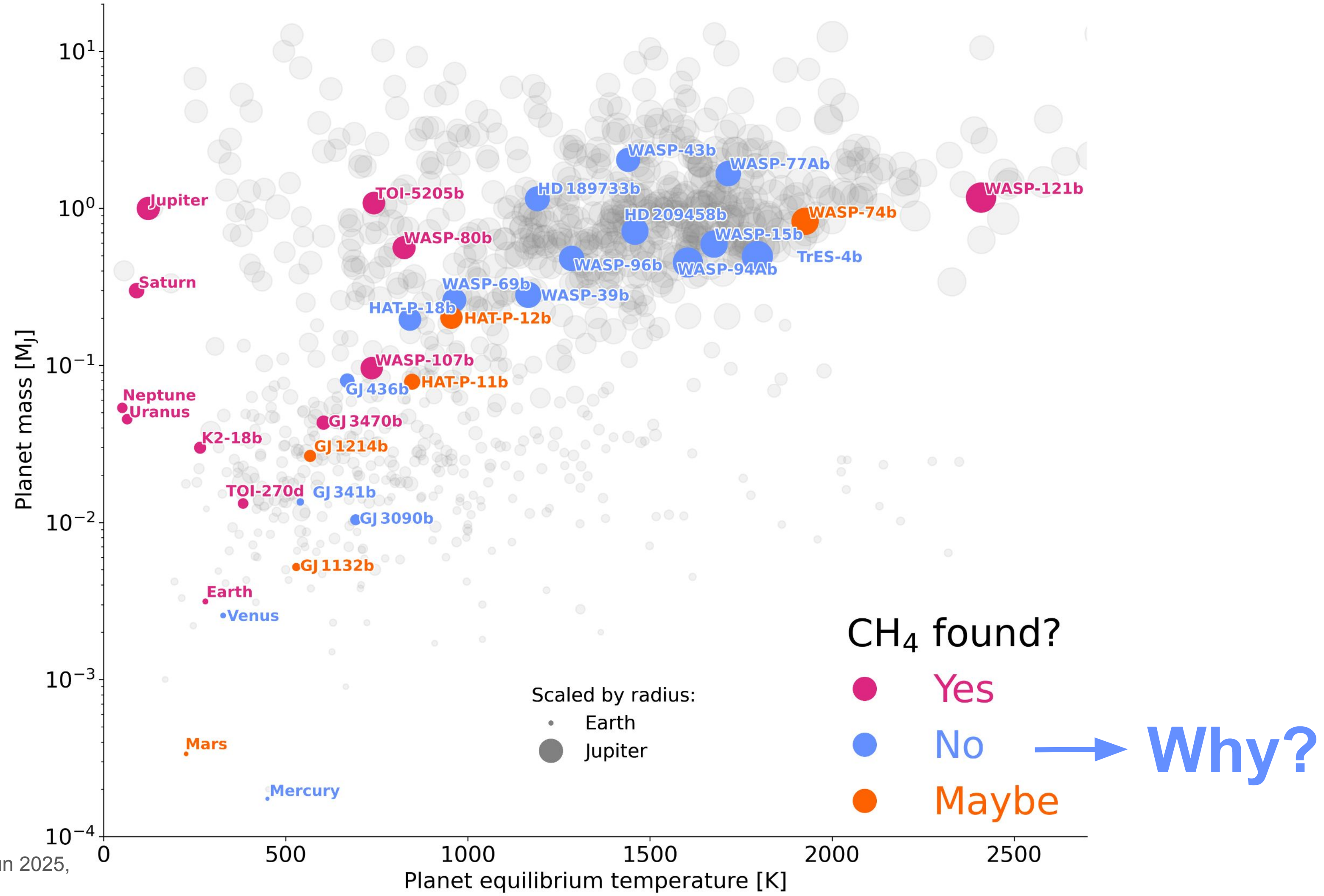


- CH_4 holds **most carbon at low temperatures**, while CO dominates at high temperatures
- But: CH_4-CO transition is smooth

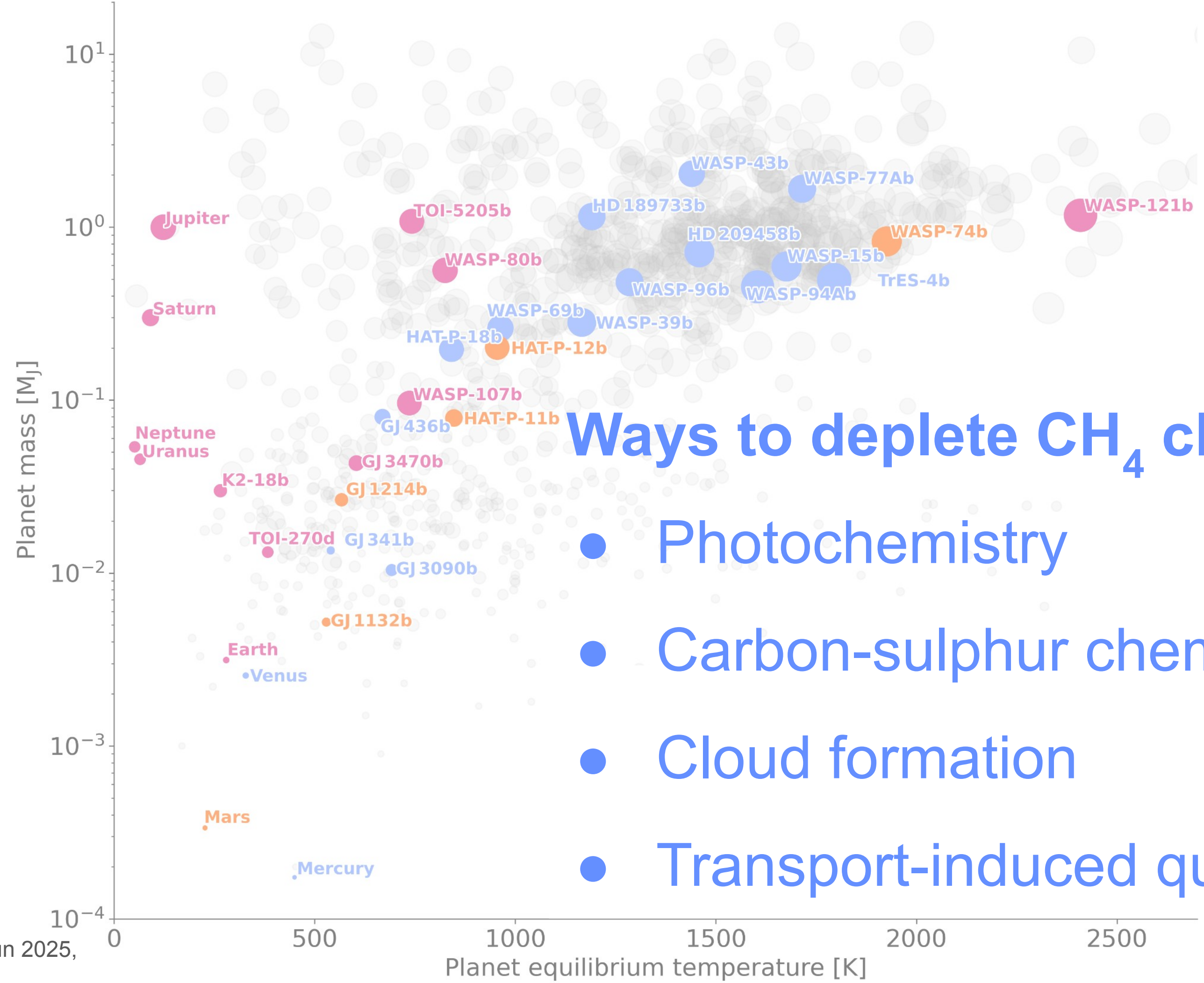


Tsai+2022

Atreya+18, Welbanks+2019, Sing+2024, JWST GO-3557



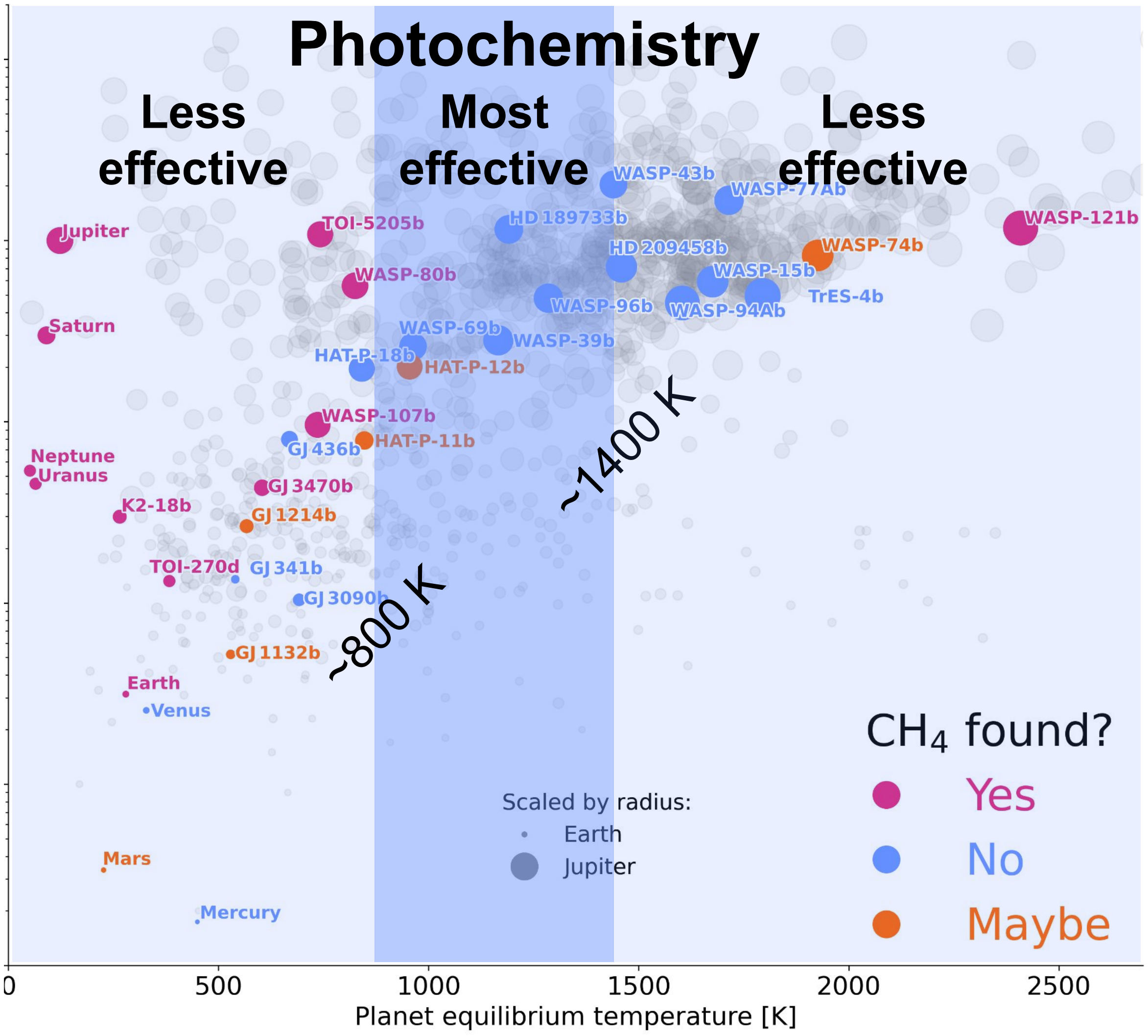
Southworth2011 TEPCat Jun 2025, ExoAtmospheres Database



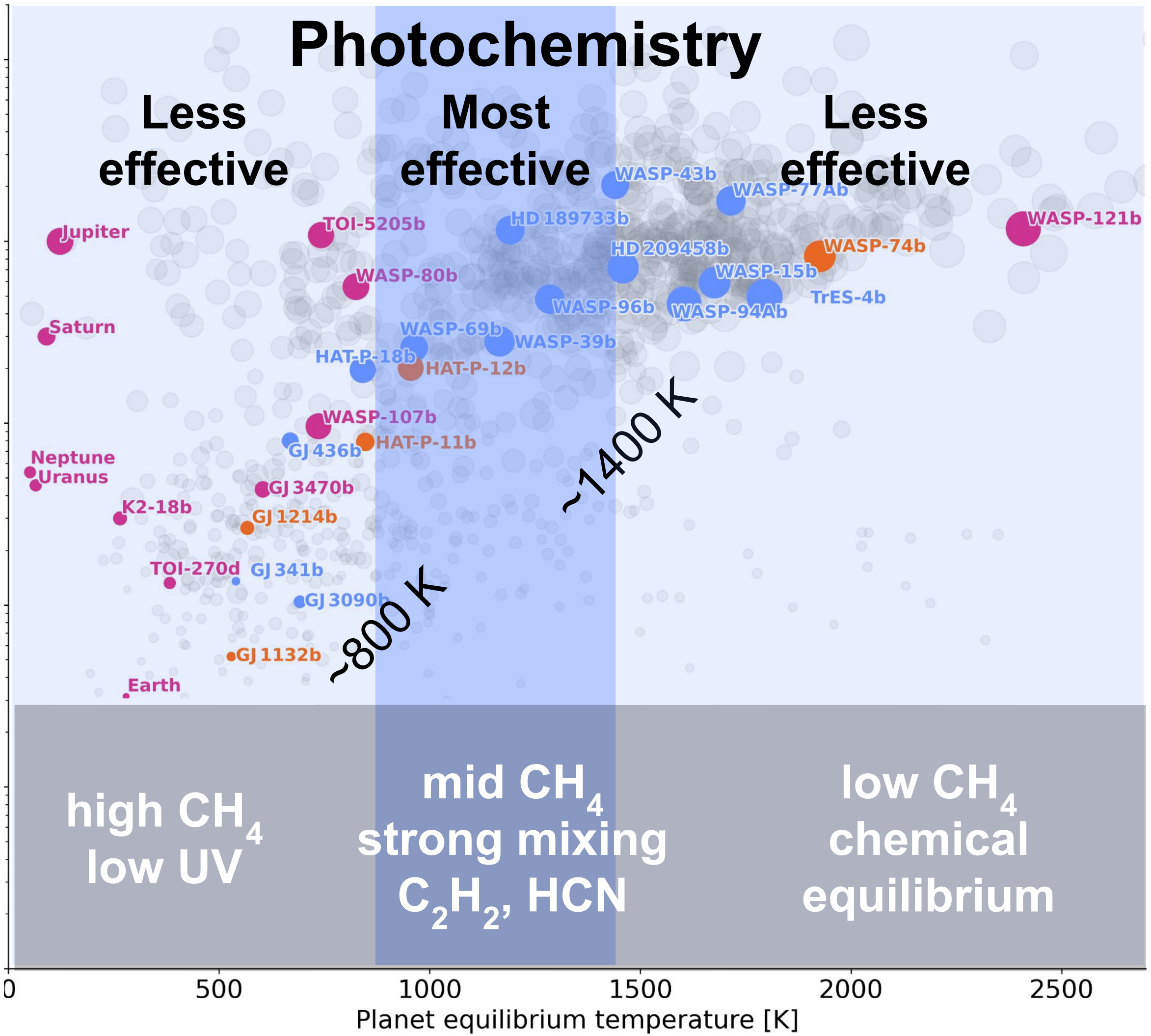
Ways to deplete CH_4 chemically:

- Photochemistry
- Carbon-sulphur chemistry
- Cloud formation
- Transport-induced quenching

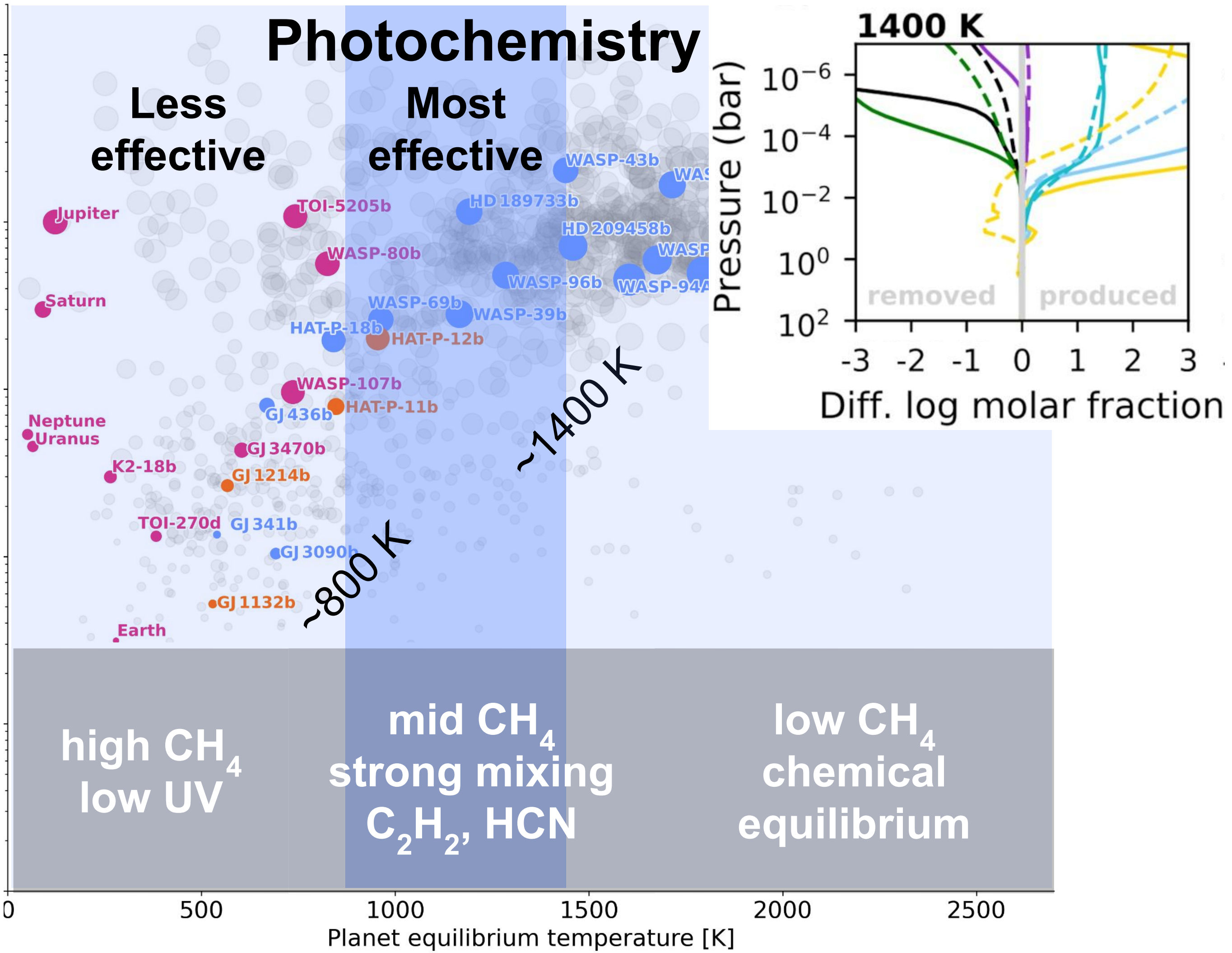
Southworth2011 TEPCat Jun 2025,
ExoAtmospheres Database



Baeyens+2022

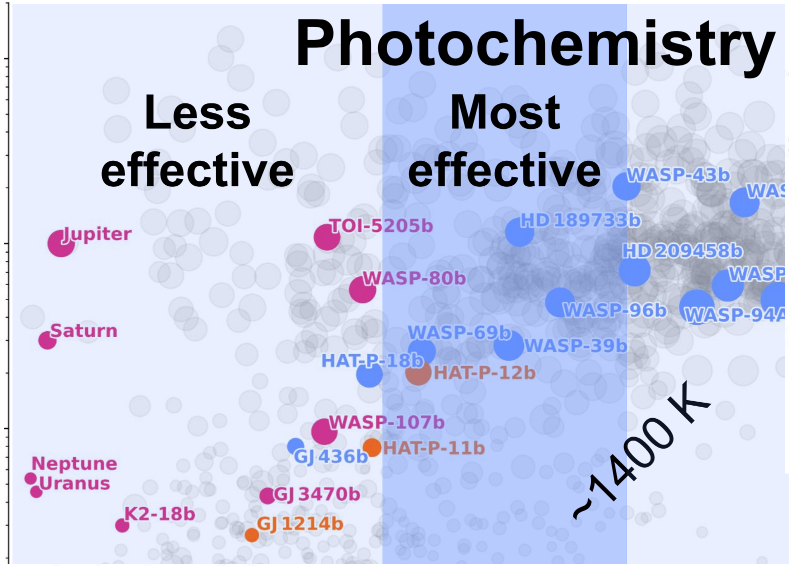


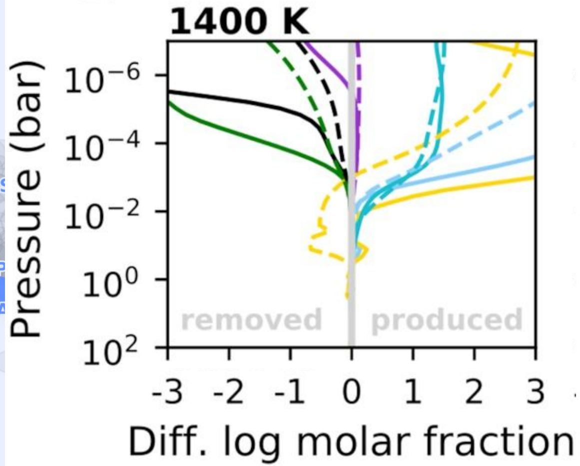
Baeyens+2022



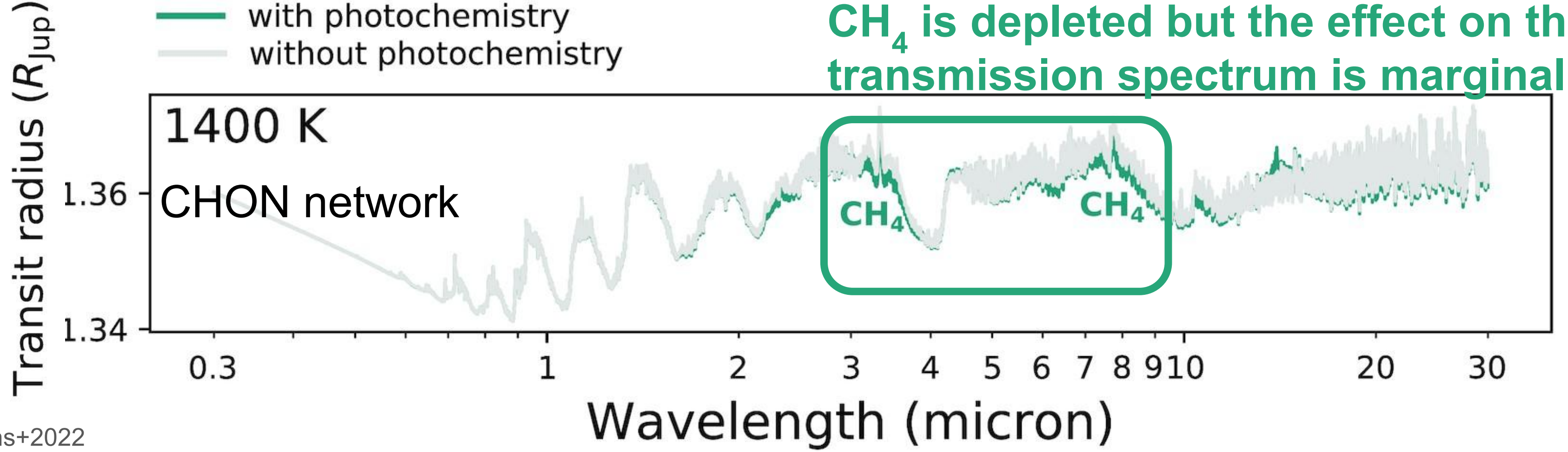
Baeyens+2022

Photochemistry





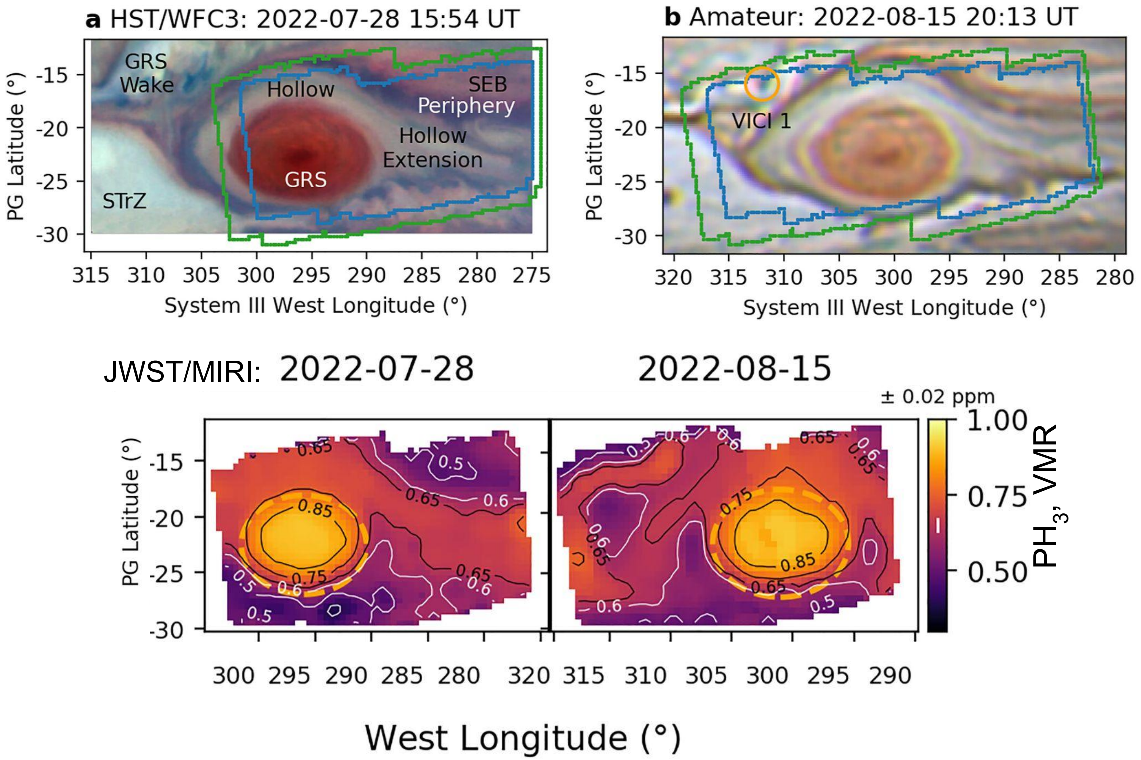
CH$_4$ is depleted but the effect on the transmission spectrum is marginal



Baeyens+2022

Lessons from the solar system:
Phosphine in Jupiter's Great Red Spot

- Excess in PH_3 and aerosols coincides with still unidentified red chromophore
- **Aerosols shield PH_3 from UV** in this long-lived anticyclone



Harkett+2024

CH_4 depletion due to: **Carbon-sulphur chemistry**

Carbon-sulphur chemistry depletes CH_4 & does it **differently in different chemical networks**. E.g.:

$CH_4 + H \rightarrow \mathbf{CH_3} + H_2$

Key difference

Veillet+2025 CHONS

$\mathbf{CH_3} + S \rightarrow CH_2S + H$

$\mathbf{CH_2S} + H \rightarrow CHS + HS_2$

$CHS + S_2 \rightarrow \mathbf{CS} + HS_2$

Tsai+2023a CHONS

$\mathbf{CH_3} + H \rightarrow {}^1CH_2 + H_2$

${}^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2$

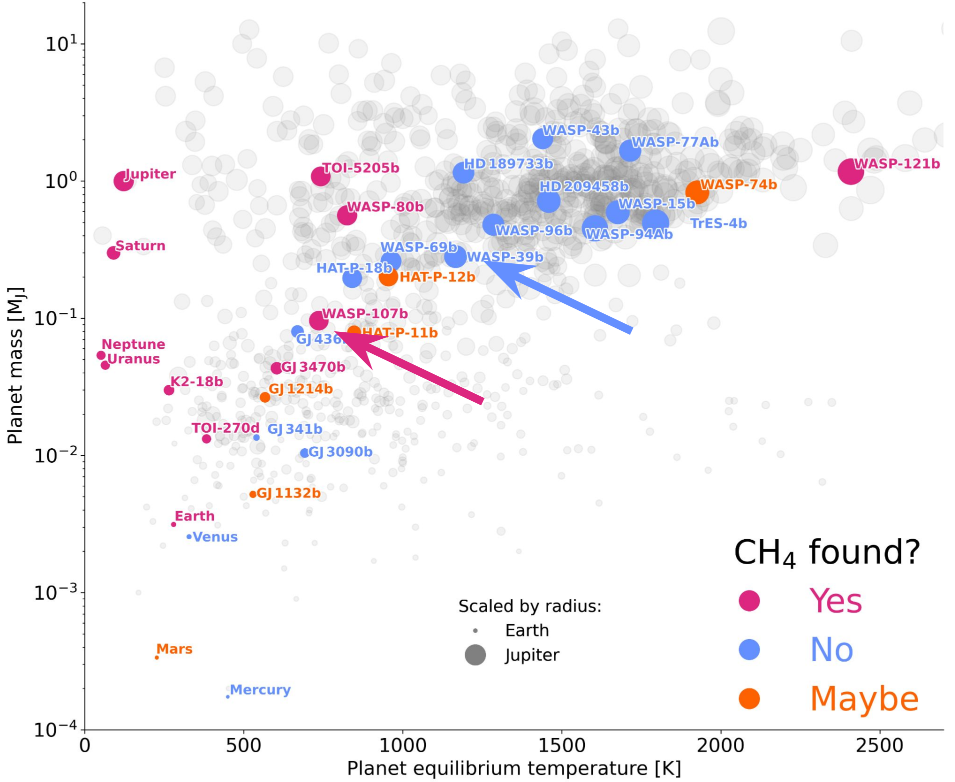
${}^3CH_2 + S \rightarrow CHS + H$

$CHS + H \rightarrow \mathbf{CS} + H_2$

$\mathbf{CS} + SO \rightarrow OCS + S$

$OCS + H \rightarrow CO + SH$

$CO + OH \rightarrow CO_2 + H$



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Carbon-sulphur chemistry depletes CH_4 & does it **differently in different chemical networks**. E.g.:

$CH_4 + H \rightarrow$ **CH_3** $+ H_2$

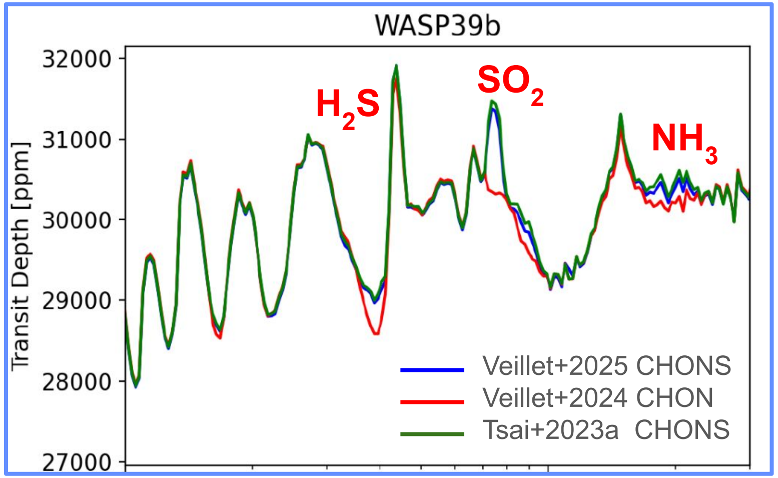
Key difference

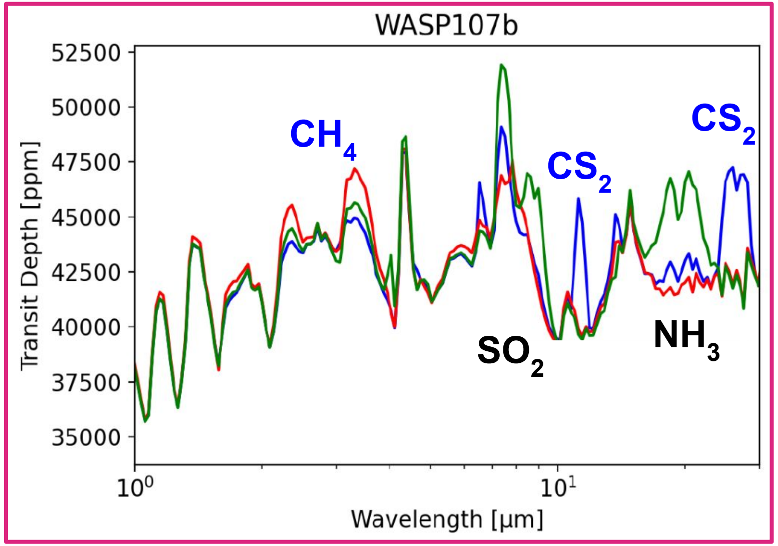
Veillet+2025 CHONS	Tsai+2023a CHONS
CH_3 $+ S \rightarrow CH_2S + H$	**CH_3** $+ H \rightarrow {}^1CH_2 + H_2$
CH_2S $+ H \rightarrow CHS + HS_2$	${}^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2$
$CHS + S_2 \rightarrow$ **CS** $+ HS_2$	${}^3CH_2 + S \rightarrow CHS + H$
	$CHS + H \rightarrow$ **CS** $+ H_2$

CS $+ SO \rightarrow OCS + S$

$OCS + H \rightarrow CO + SH$

$CO + OH \rightarrow CO_2 + H$





Veillet+2025

Aside:
Families of chemical networks for giant planets

Last updated	C	H	O	N	S	P	Cl	Model	Species	Notes
Moses+2013	✅	✅	✅	✅	❌	❌	❌	KINETICS	92	originally developed for solar system
Hu+2015	✅	✅	✅	✅	✅	❌	❌	MEAC	111	originally developed for rocky exoplanets
Gao+2016, Johnson+2022	✅	✅	✅	✅	✅	❌	❌	EPACRIS	varies	computer-aided chemical reaction network generator
Hobbs2021	✅	✅	✅	✅	✅	❌	❌	LEVI	a lot	STAND
Tsai+2021	✅	✅	✅	✅	✅	❌	❌	VULCAN	96	open source, widely used
Tsai+2022	✅	✅	✅	✅	❌	❌	❌	Exo-FMS	12	MINI-CHEM
Lee+2024	❌	✅	✅	❌	❌	✅	❌	VULCAN	32	phosphorus
Wogan+2024	✅	✅	✅	✅	✅	❌	✅	Photochem	111	Zahnle, chlorine
Veillet+2025	✅	✅	✅	✅	✅	❌	❌	FRECKLL	226	verified against combustion experiments

Sorry if I missed your “family”! Please let me know.

New laboratory & ab initio data are needed!

CH_4 depletion due to: **Cloud formation**

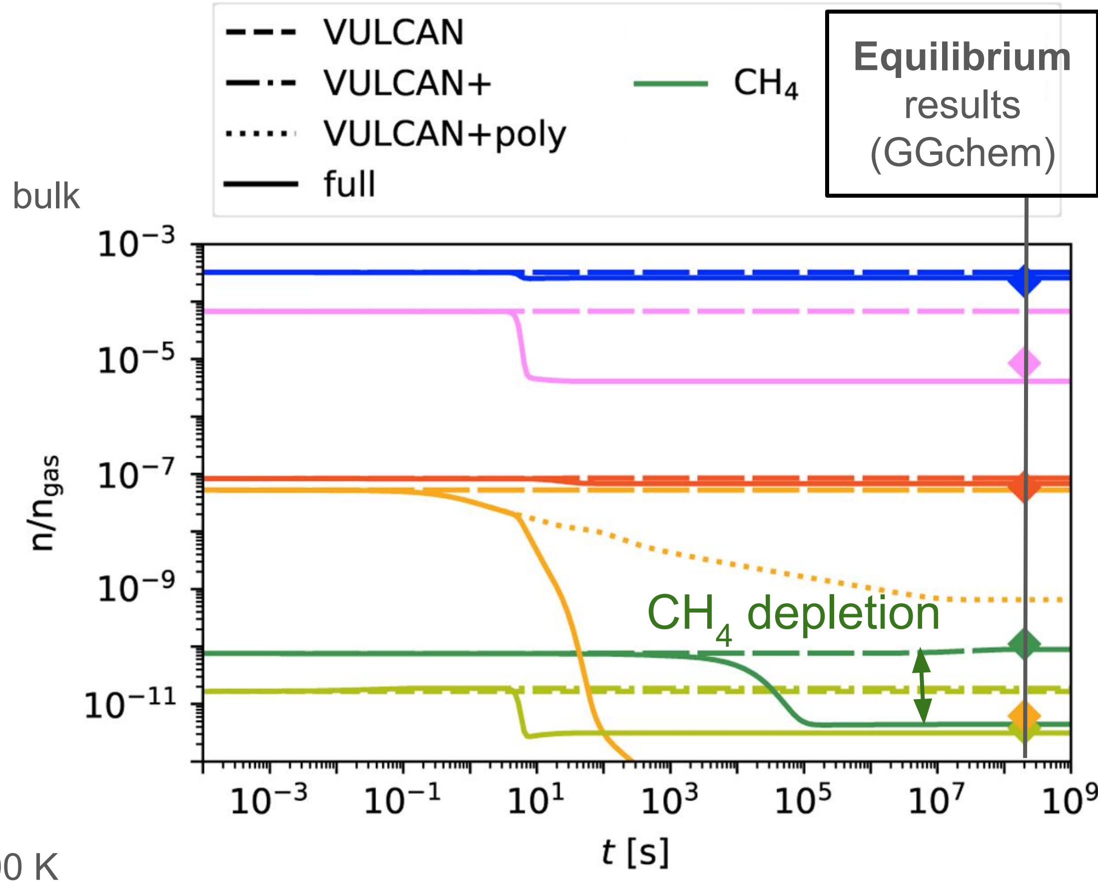
- Kinetic cloud formation model
- Cycling between surface reactions of cloud bulk growth:

$$2\,SiO \rightarrow 2\,SiO[s]$$
$$2\,SiO[s] + 3\,H_2 \rightarrow 2\,SiH + 2\,H_2O$$
$$2\,SiH + 4\,H_2O \rightarrow 2\,SiO_2[s] + 4\,H_2 + 2H$$
$$2\,SiO_2[s] + 2\,H_2 \rightarrow 2\,SiO + 2\,H_2O$$
net: $\mathbf{H_2 \rightarrow 2\,H}$

- Depletion via:

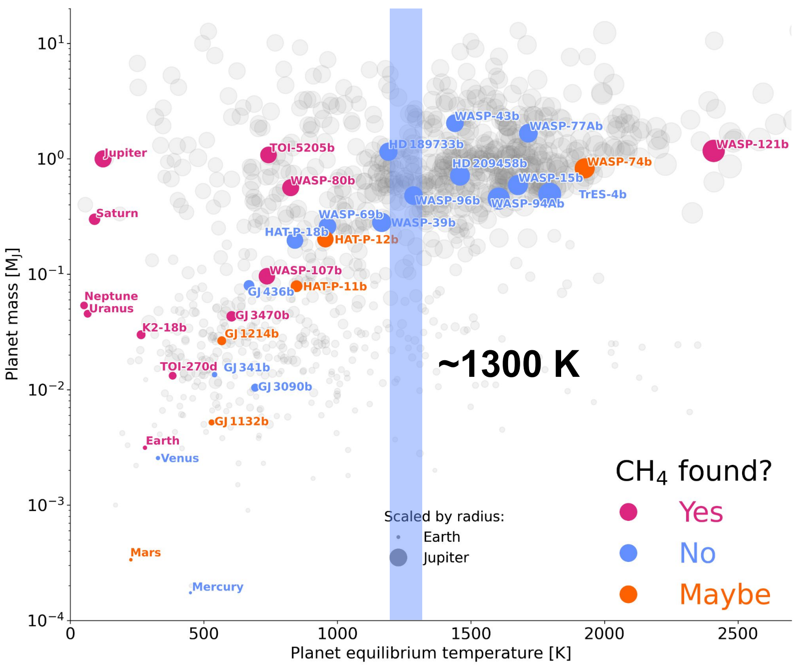
$$CH_4 + \mathbf{H} \rightarrow CH_3 + H_2$$
$$CH_3 + \mathbf{H} \rightarrow CH_2 + H_2$$
$$CH_2 + \mathbf{H} \rightarrow CH + H_2$$
$$CH + H_2O \rightarrow H_2CO + H$$

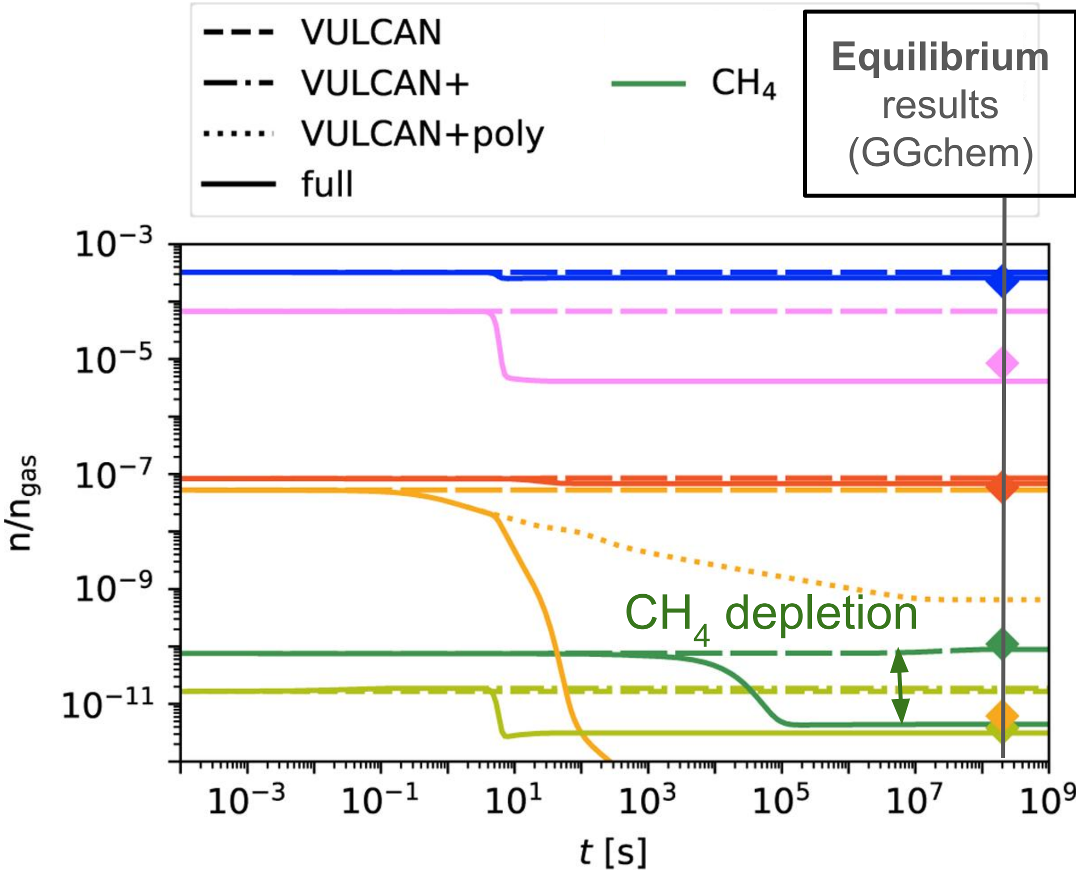
- CH_4 changes largest at $<10^{-3}$ bar and ~1300 K



Kiefer+2024

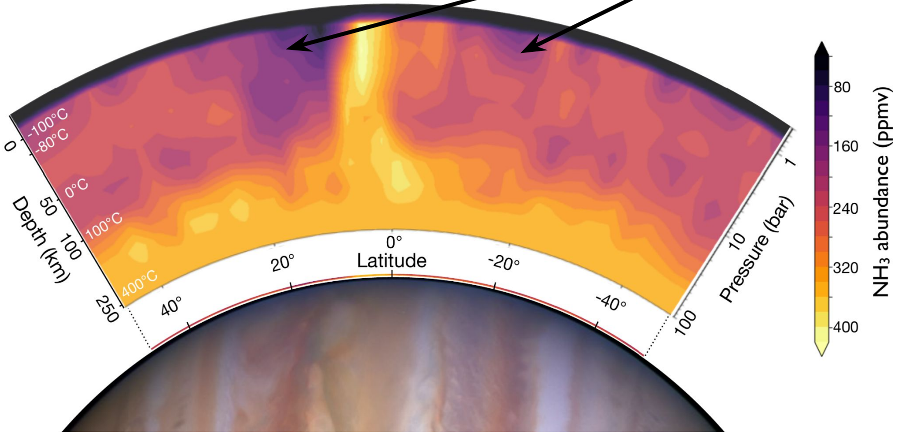
CH_4 depletion due to: **Cloud formation**





Kiefer+2024

Lessons from the solar system:
Storm-driven NH_3 depletion on Jupiter



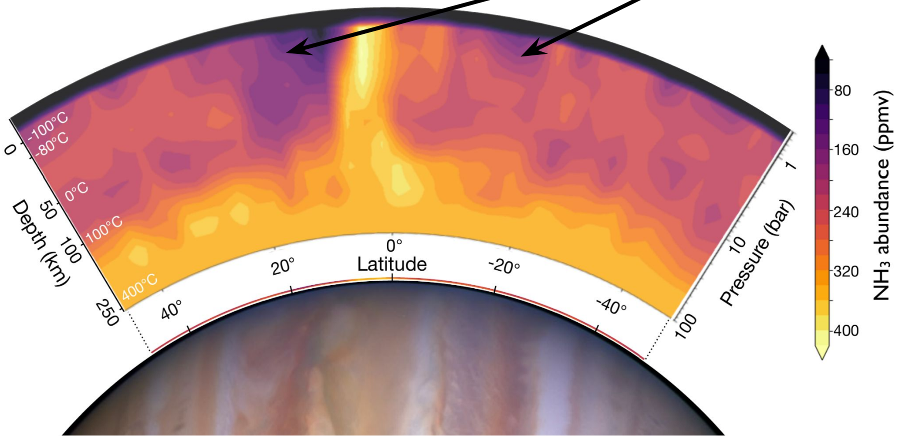
From a press release:

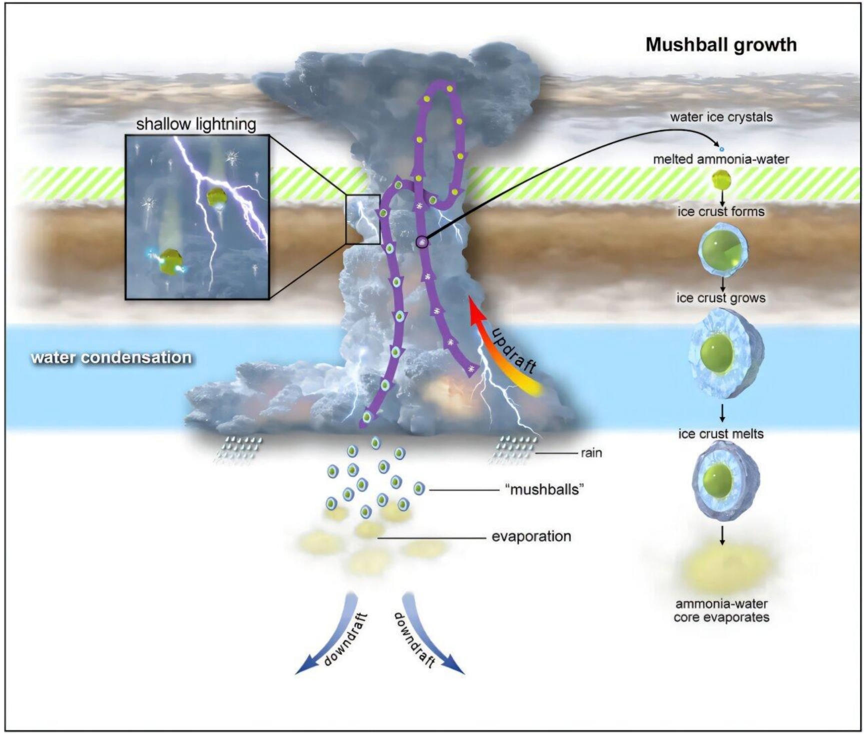
"Imke and I both were like, '**There's no way in the world this is true**,'" said Moeckel, … "**So many things have to come together to actually explain this, it seems so exotic. I basically spent three years trying to prove this wrong. And I couldn't prove it wrong.**"

- Observation: NH_3 depletion correlates with enhanced lightning activity

Li+2017, Guillot+2023, Moeckel+2025

Lessons from the solar system:
Storm-driven NH_3 depletion on Jupiter



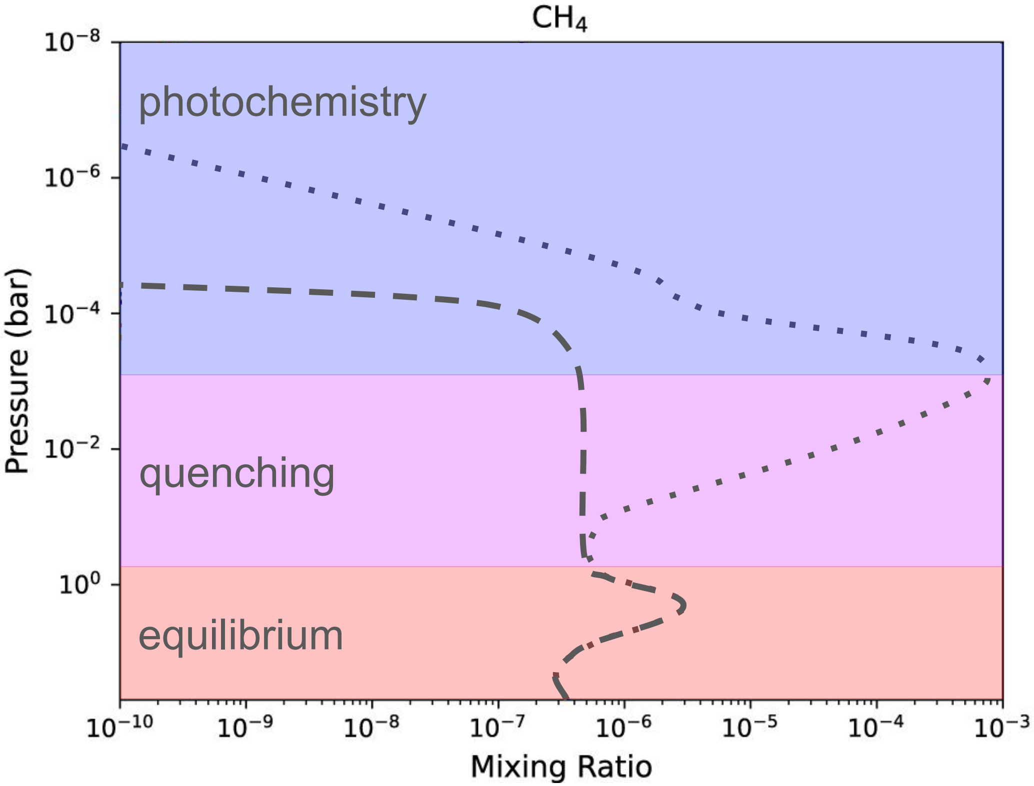


- Observation: NH_3 depletion correlates with enhanced lightning activity
- Theory: NH_3 vapour helps melt H_2O ice crystals at low temperatures (-85C), forming H_2O-NH_3 mushballs
    - net effect: downward transport of NH_3

Li+2017, Guillot+2023, Moeckel+2025

Likely happens on all solar and colder extrasolar giants!

CH_4 depletion due to:
Transport-induced quenching



equilibrium

kinetics + vertical diffusion

$\tau_{chem} > \tau_{adv}$

$\tau_{chem} = \tau_{adv}$

$\tau_{chem} < \tau_{adv}$

homogenisation by wind

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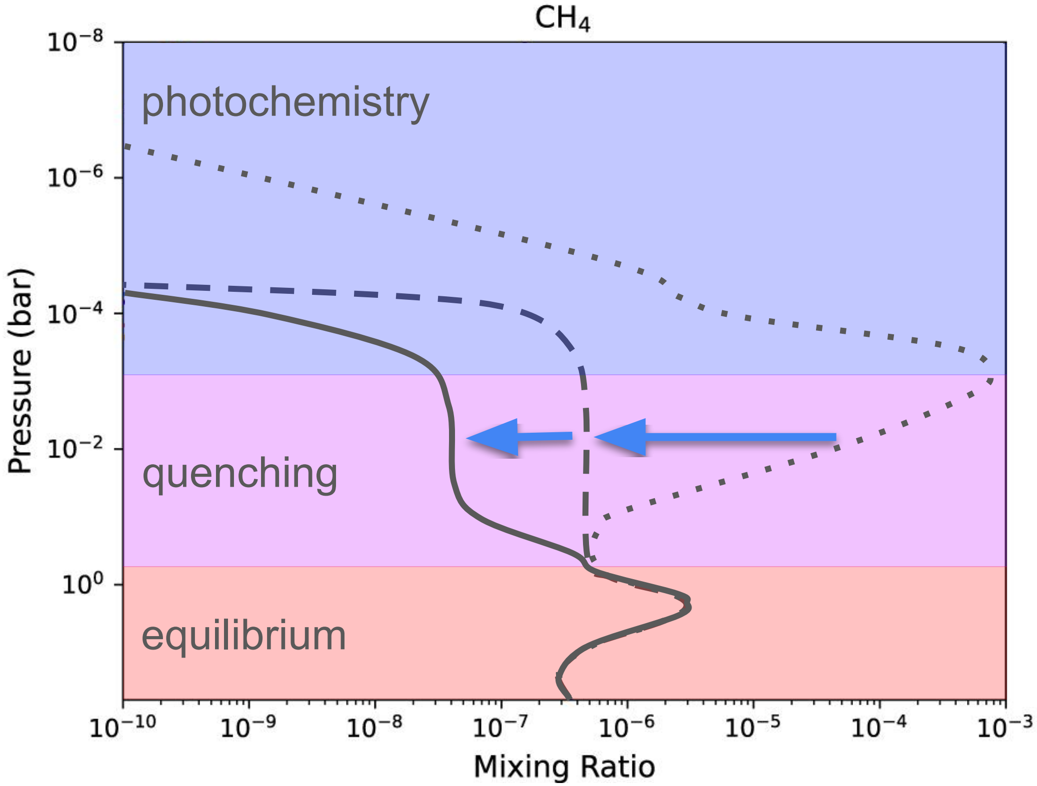

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kinetics + vertical and horizontal diffusion

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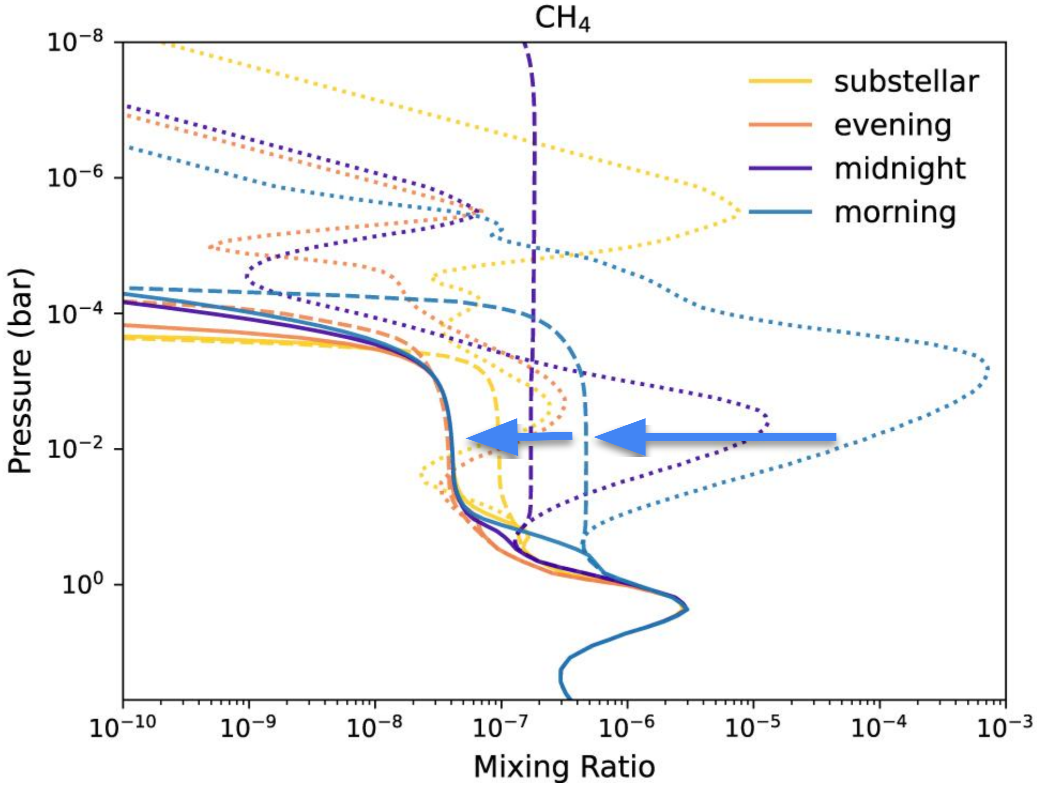


equilibrium

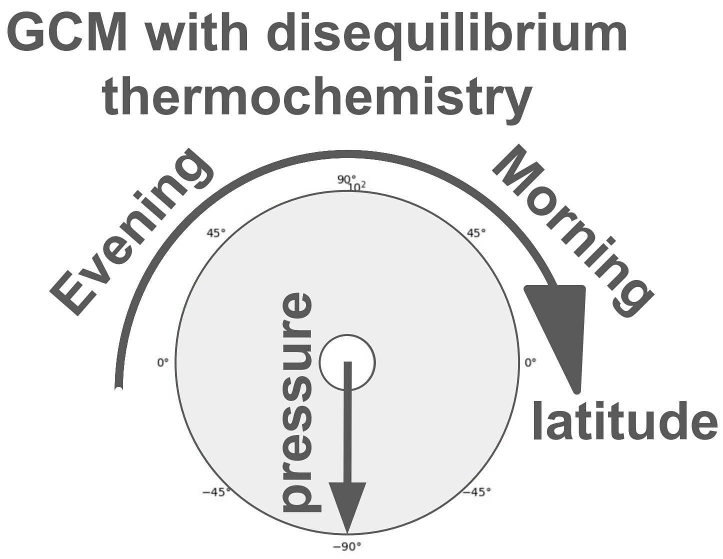
kinetics + vertical diffusion

kinetics + vertical and horizontal diffusion

Depletion by up to 3-4 orders of magnitude!

Tsai+2023

CH$_4$ depletion due to:
Transport-induced quenching



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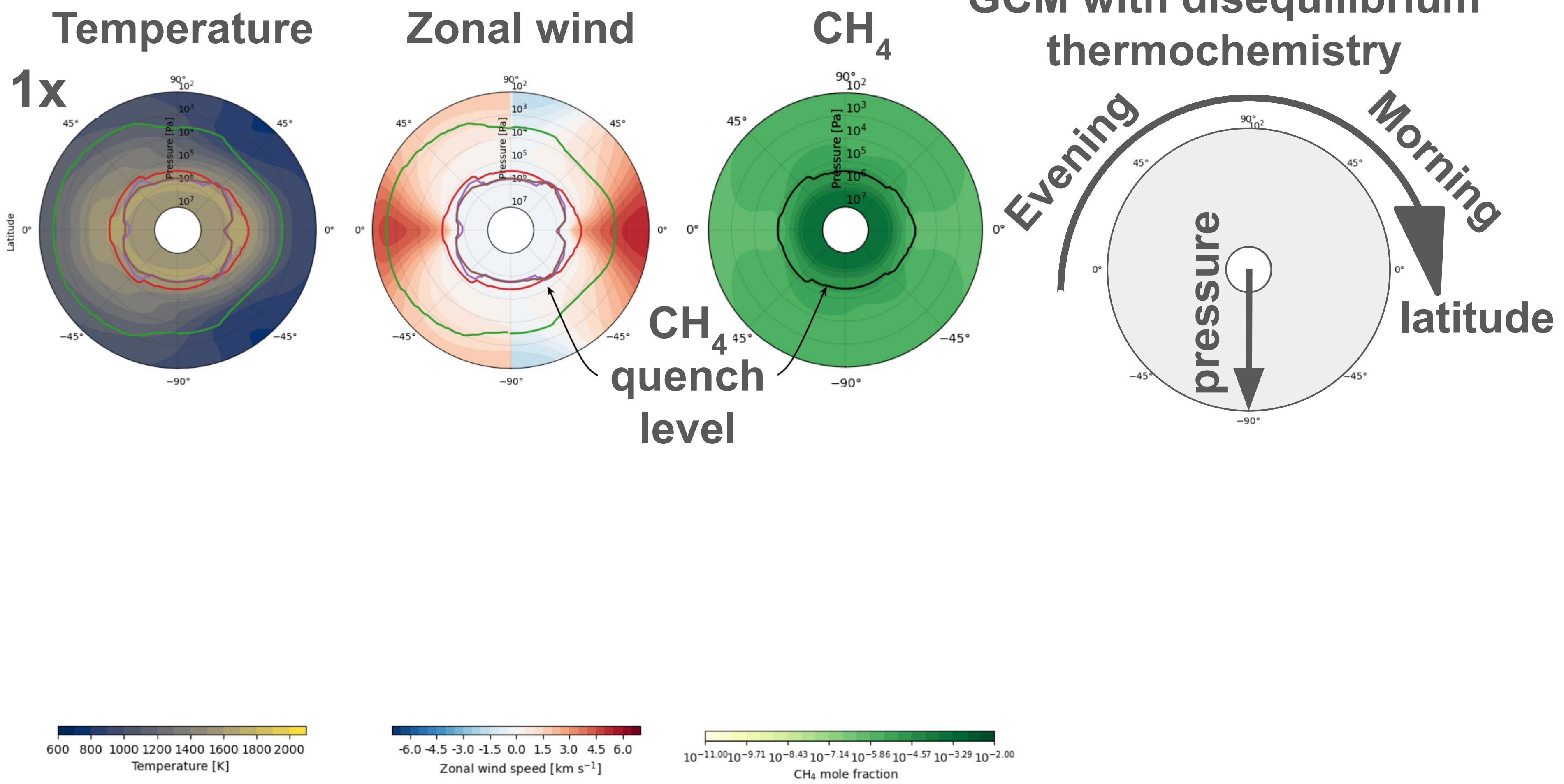
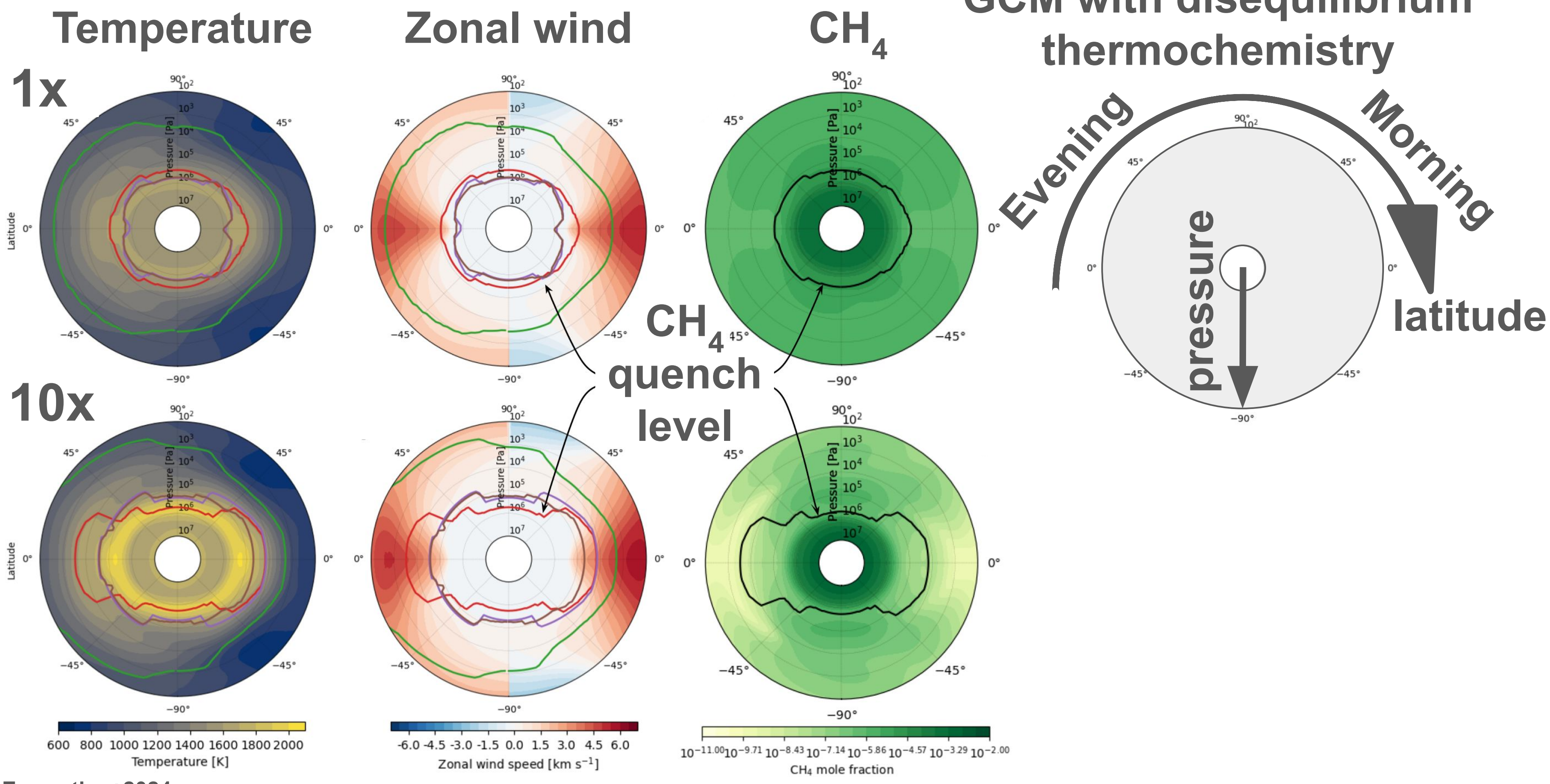


Zamyatina+2024

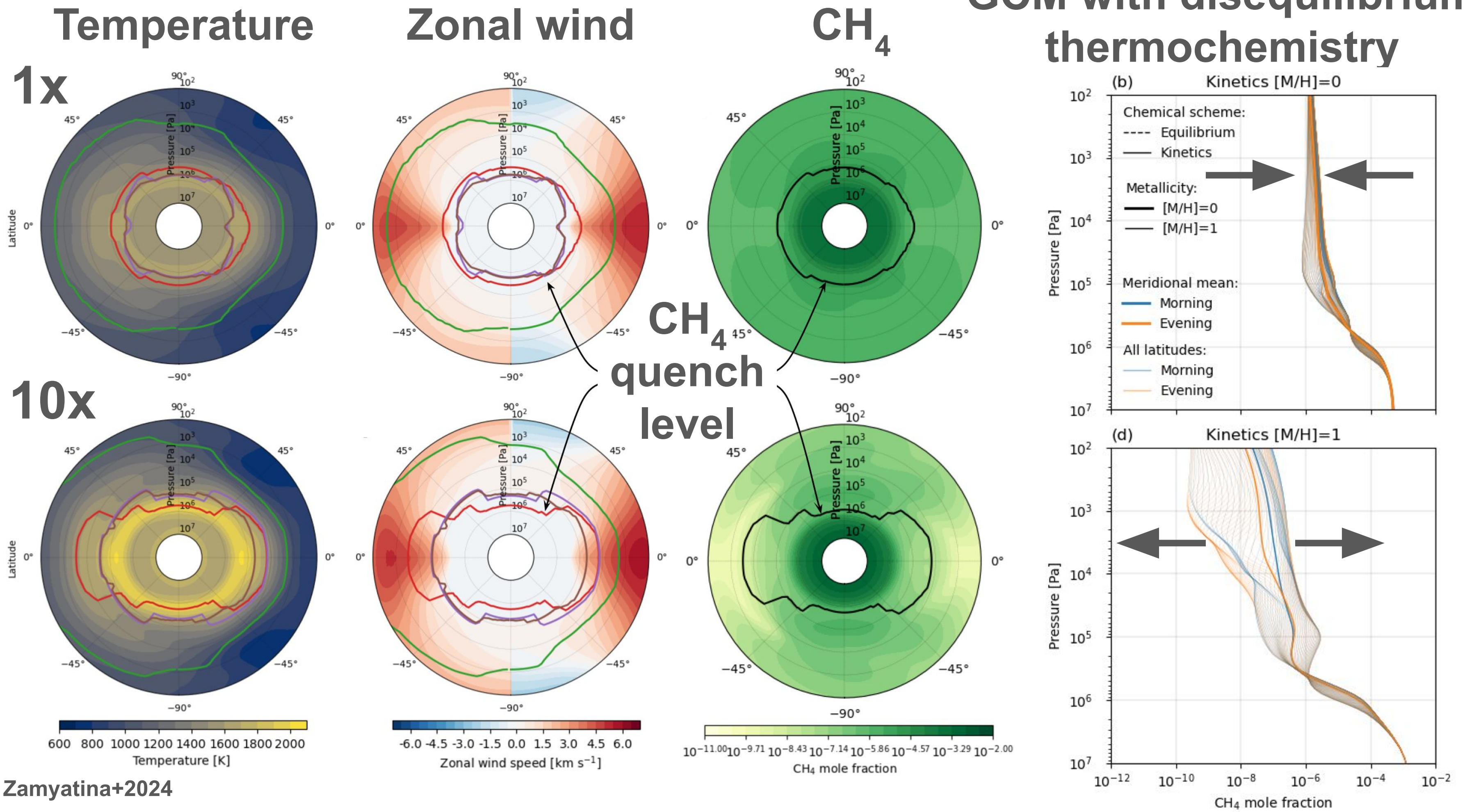
CH$_4$ depletion due to: **Transport-induced quenching**



Zamyatina+2024

CH_4 depletion due to: **Transport-induced quenching**

GCM with disequilibrium thermochemistry



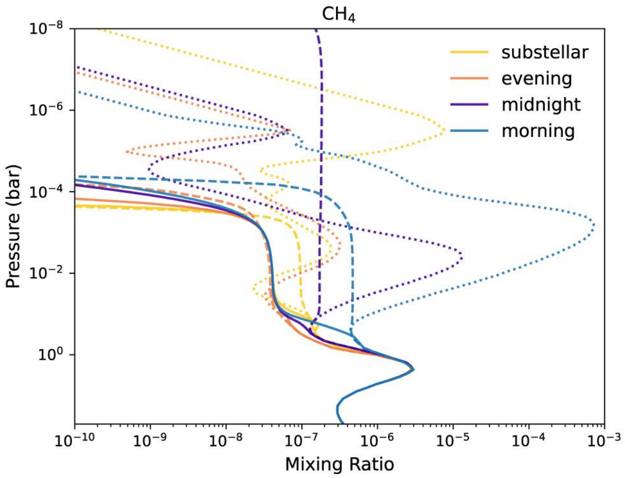
Zamyatina+2024

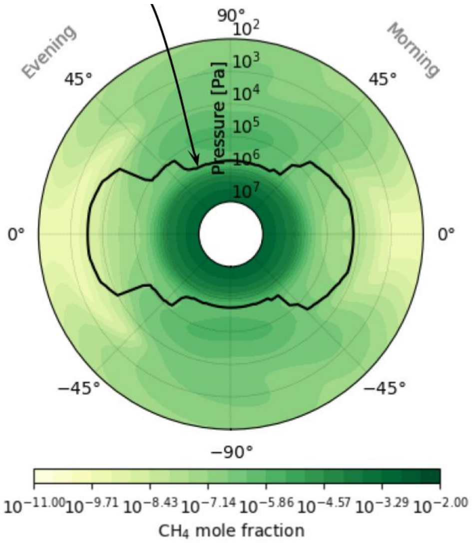
Summary of:
Transport-induced quenching

- Quenching - homogenisation of gas-phase composition by wind
- CH_4 is readily homogenised
- CH_4 is enhanced or depleted depending on where it quenches
  - CH_4 could be more depleted if it quenches inside the region of fast equatorial winds

Implication:

- **Be careful when using CH_4 depletion as a deep atmosphere thermometer**





Tsai+2023, **Zamyatina+2024**

Summary

- Ever increasing wealth of chemical species detections allows for a detailed study of atmospheric processes
  - **Keep moving from "just detections" to processes**
- **Keep increasing the complexity of disequilibrium chemistry models**
  - "Atmospheres are not simple, one-dimensional constructs", they are a highly coupled but beautiful mess
- Sulphur story is unraveling and there is more to come
- **Keep reporting non-detections**
  - CH_4 non-detections could be caused by photochemistry, C-S coupling, cloud formation, transport-induced quenching - **likely all together and more**
- Keep looking at the Solar System when interpreting extrasolar observations
- Need more chemical kinetics data