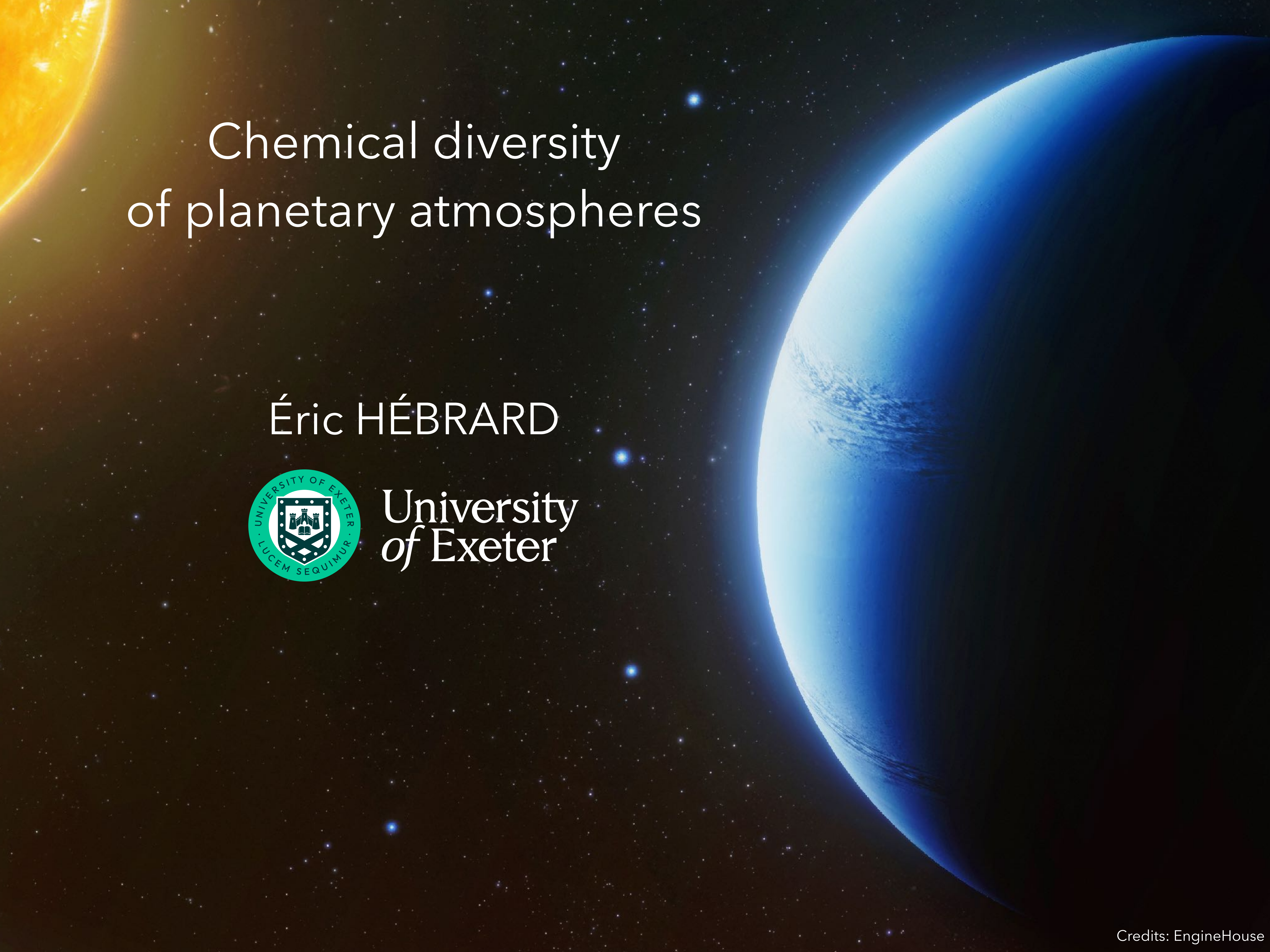
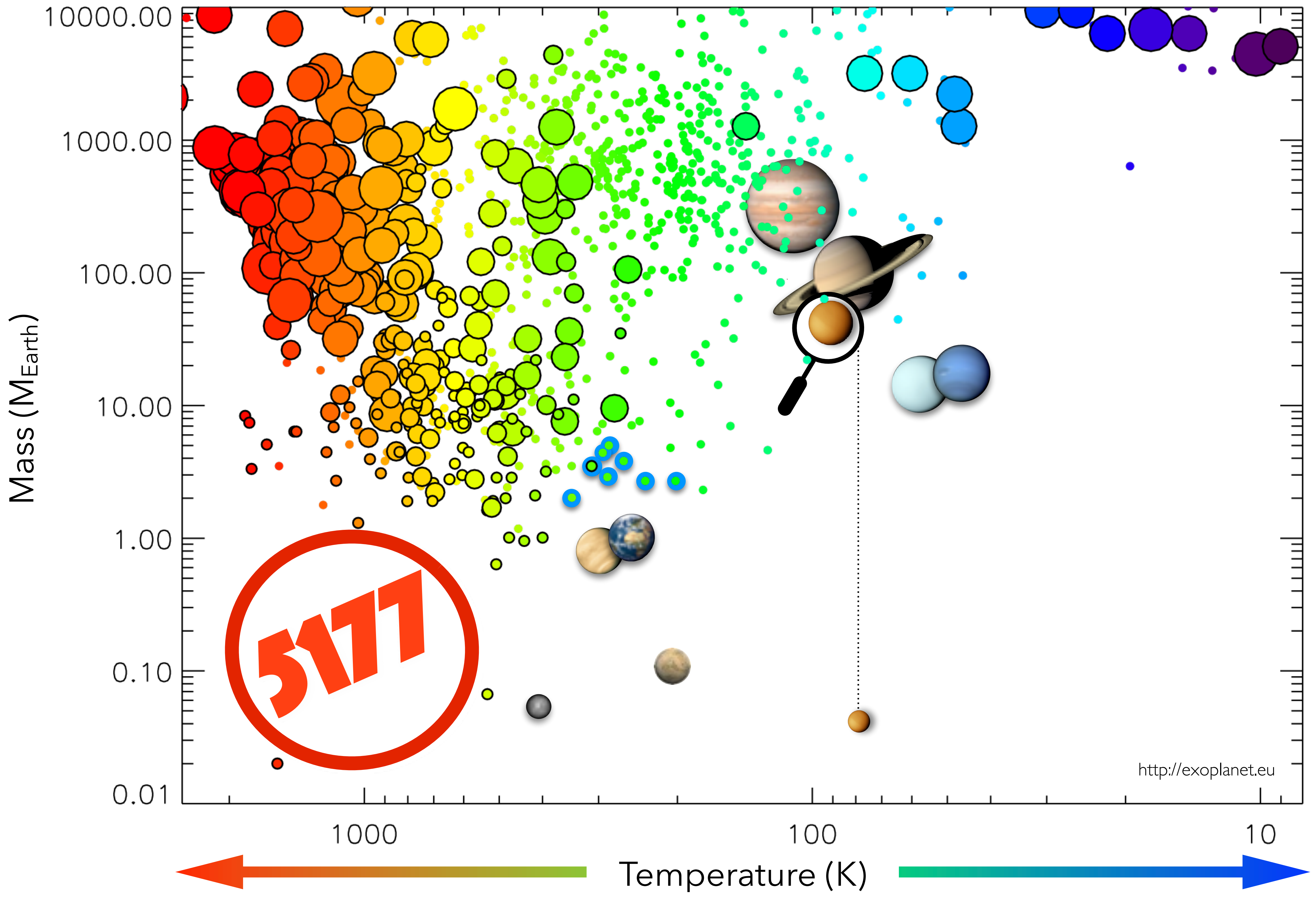


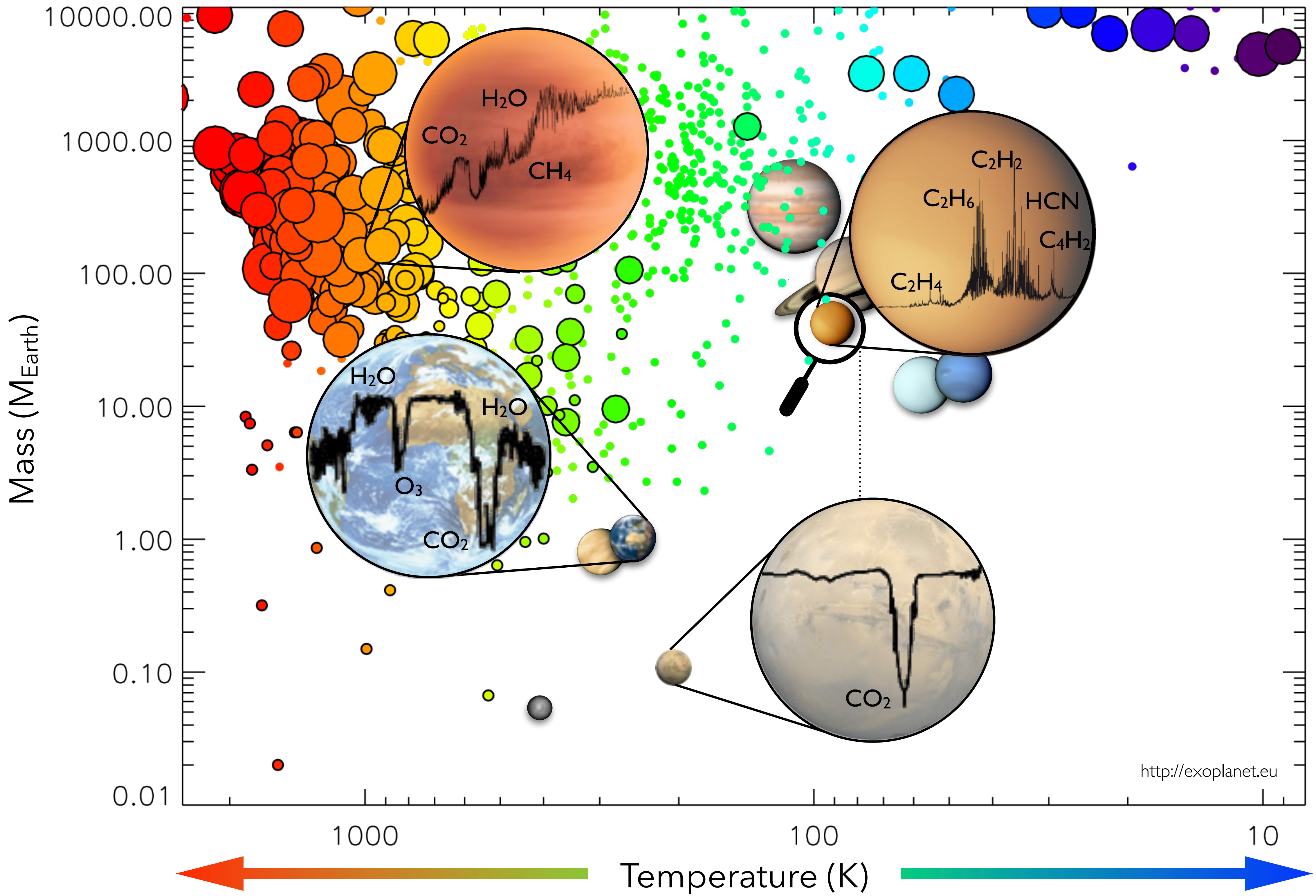
Chemical diversity of planetary atmospheres

Éric HÉBRARD

University of Exeter

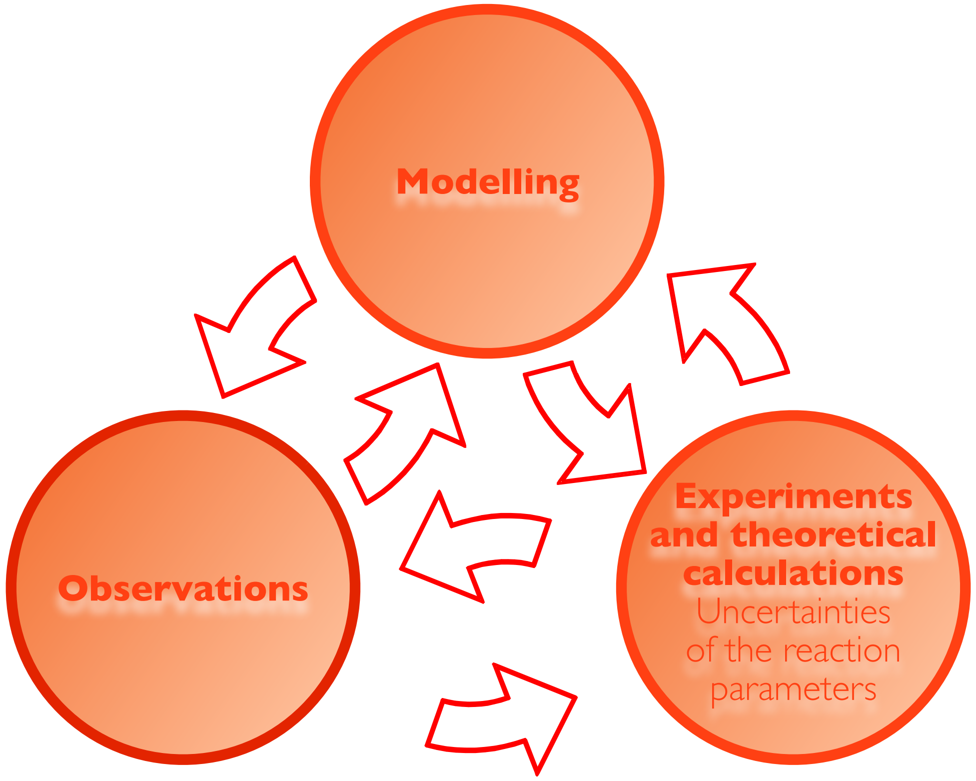
Credits: EngineHouse


Mass (M_{Earth})
10000.00
1000.00
100.00
10.00
1.00
0.10
0.01
1000
100
10
Temperature (K)
5177
http://exoplanet.eu


10000.00
1000.00
100.00
10.00
1.00
0.10
0.01
Mass (M_{Earth})
1000
100
10
Temperature (K)
H_2O
CO_2
CH_4
C_2H_2
C_2H_6
HCN
C_4H_2
C_2H_4
H_2O
H_2O
O_3
CO_2
CO_2
http://exoplanet.eu

Course overview

What - and how - do we know about
the **composition** of planetary atmospheres?



Modelling

Observations

Experiments and theoretical calculations
Uncertainties of the reaction parameters

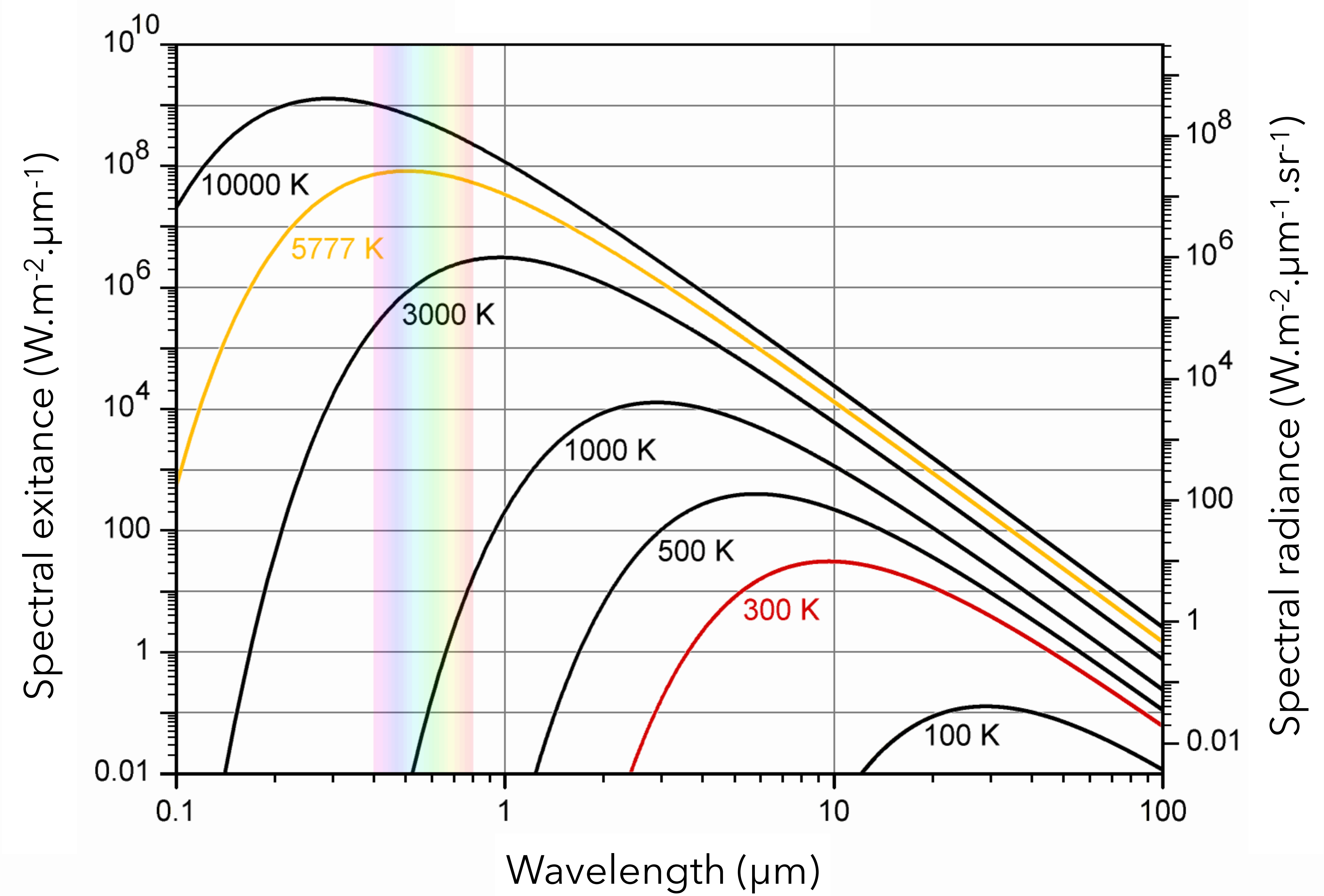
Course overview

What - and how - do we know about
the **composition** of planetary atmospheres?

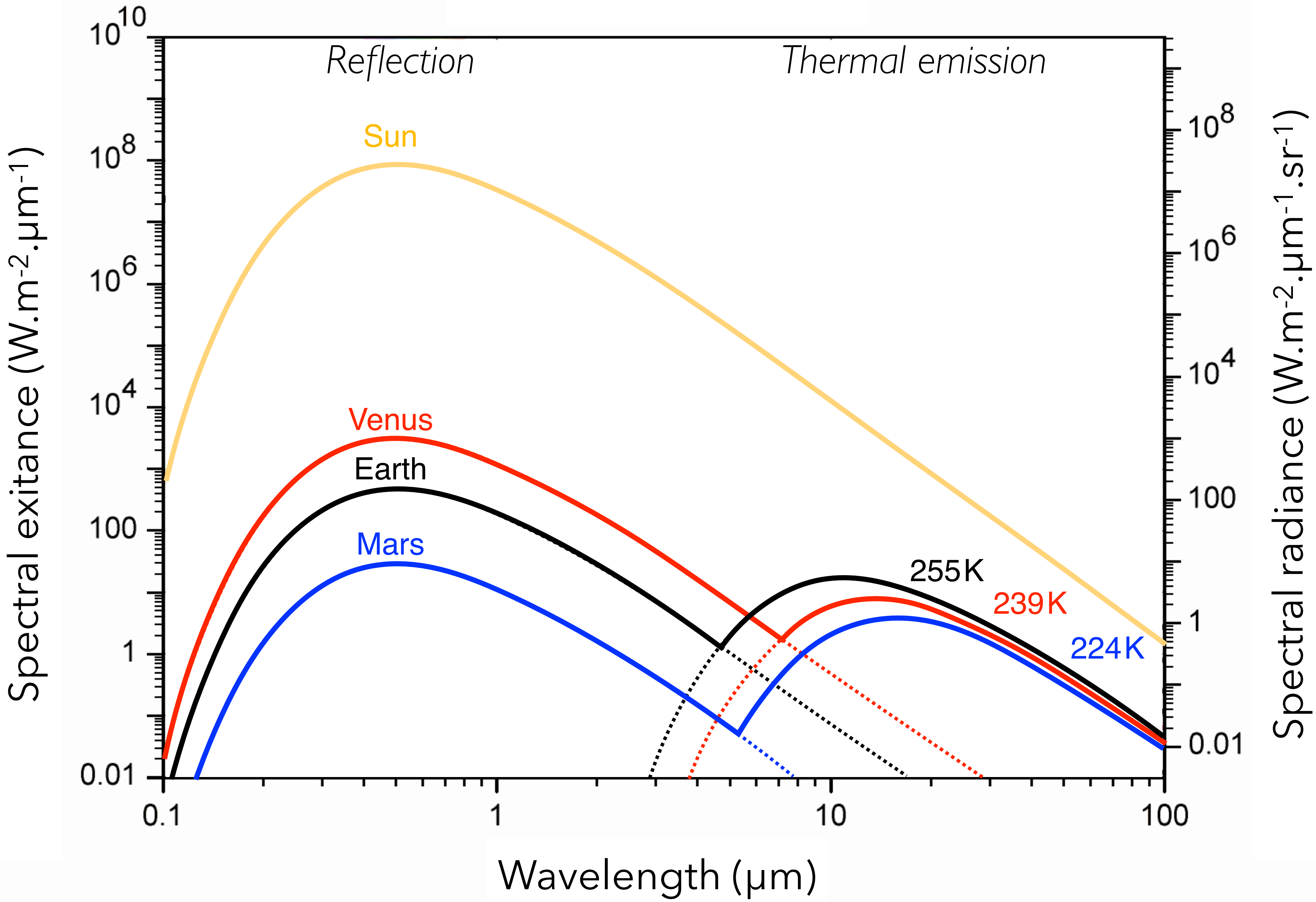
Case studies - examples for our own Solar System and beyond…

Planetary spectra

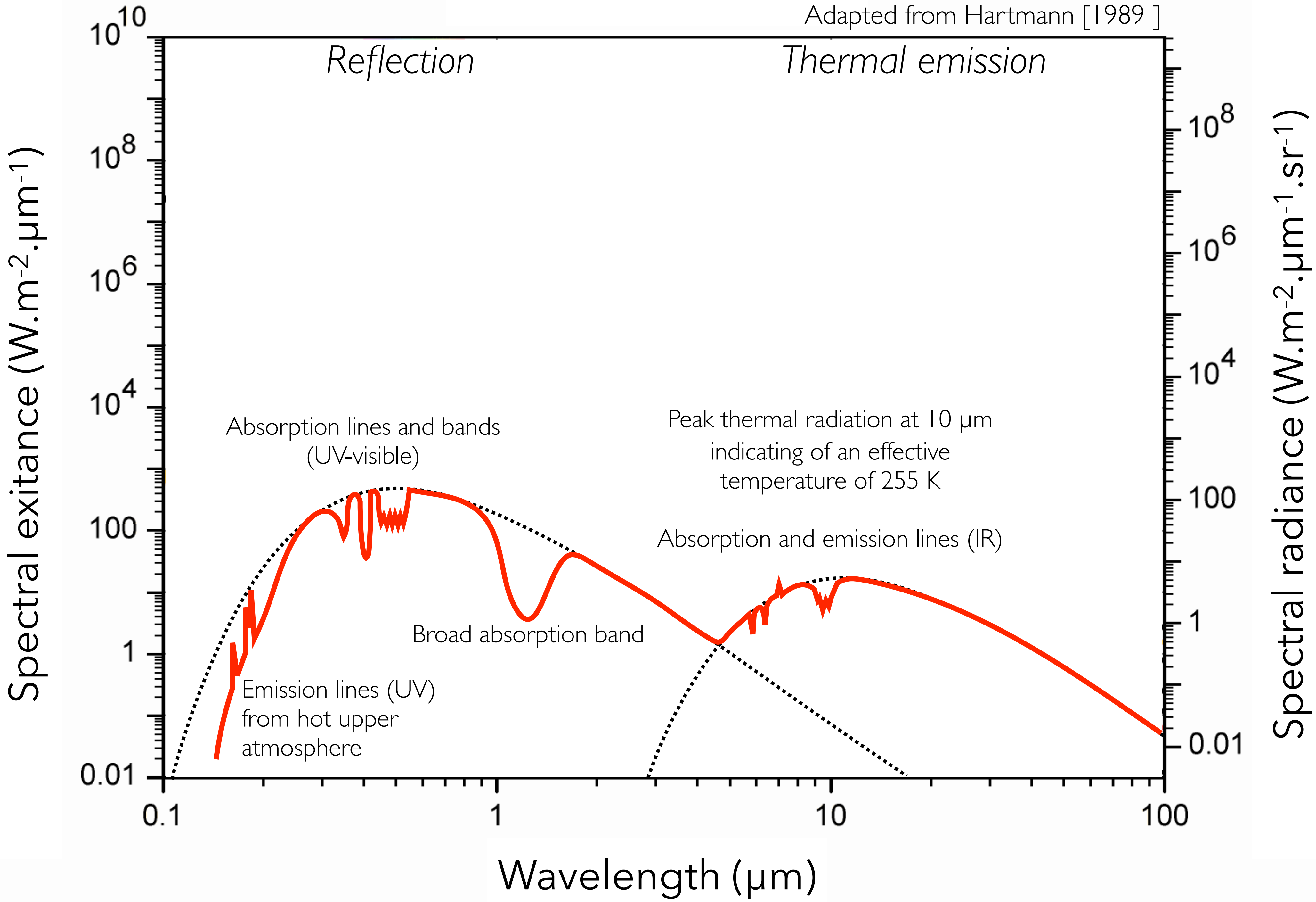
From blackbody radiation…



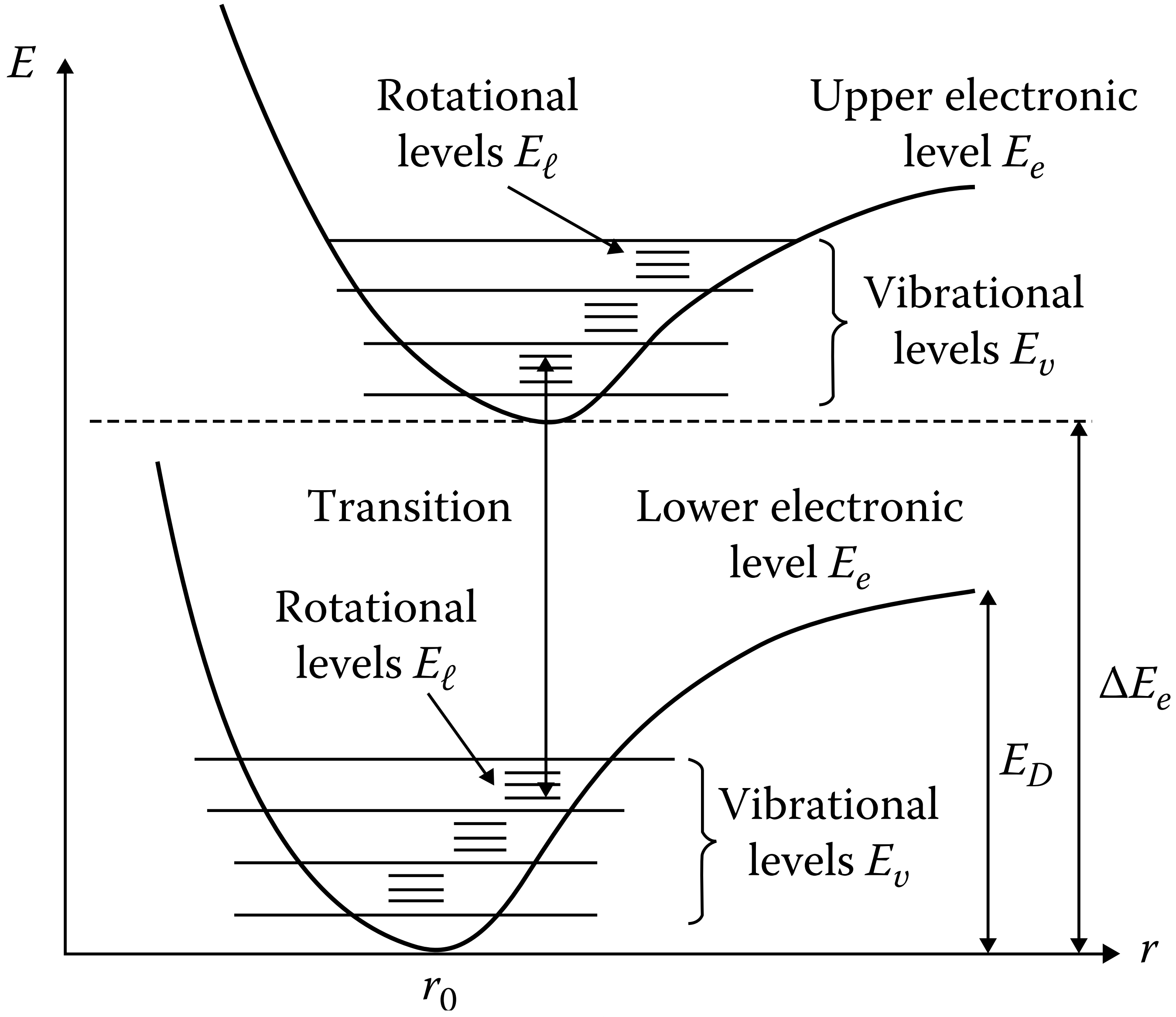
… to energy balance…

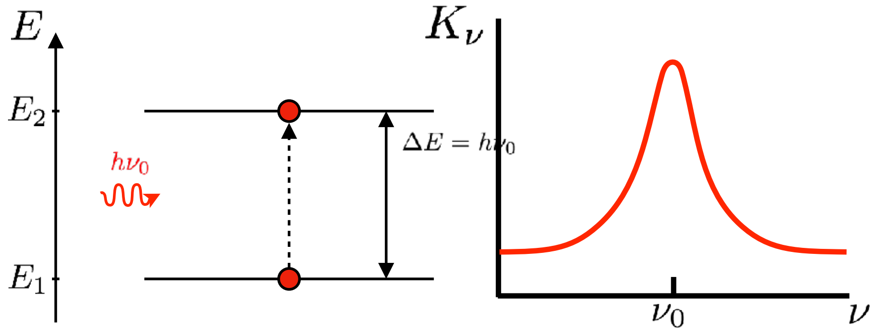


…to planetary spectrum



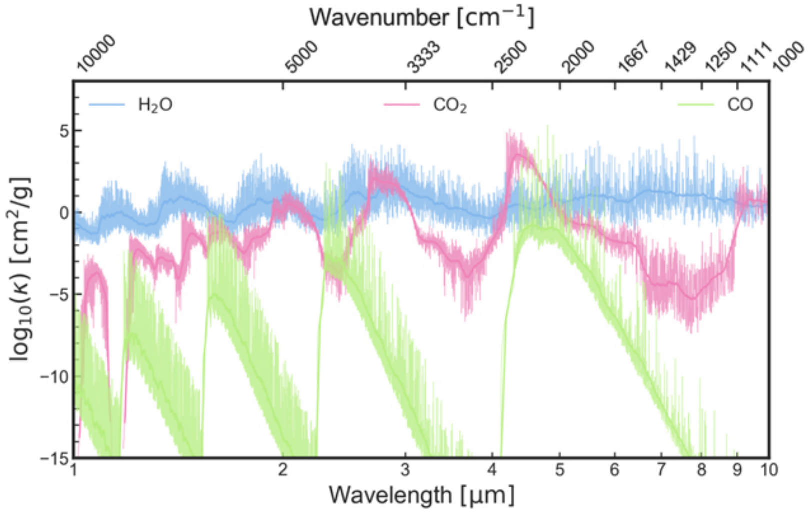
Opacities

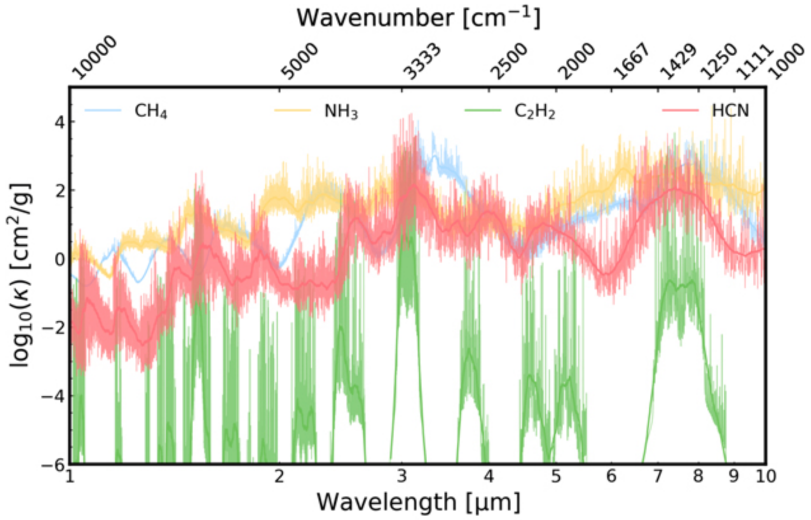

E
Rotational levels E_ℓ
Upper electronic level E_e
Vibrational levels E_v
Transition
Lower electronic level E_e
Rotational levels E_ℓ
Vibrational levels E_v
ΔE_e
E_D
r
r_0

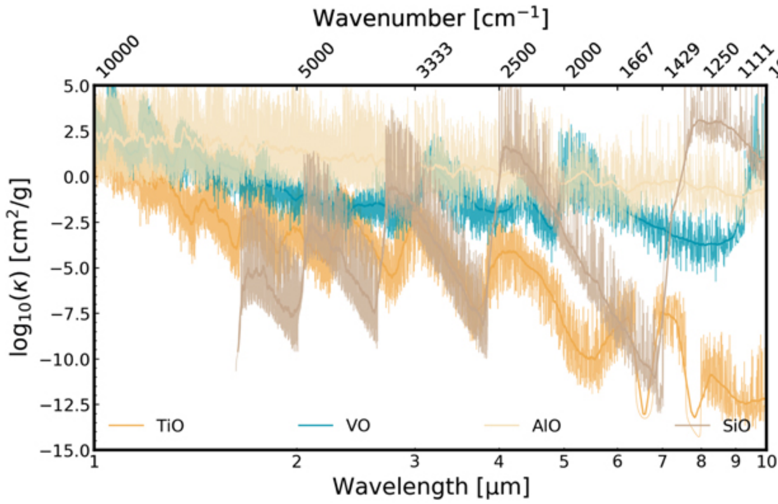

E
E_2
E_1
$h\nu_0$
$\Delta E = h\nu_0$
K_ν
ν_0
ν

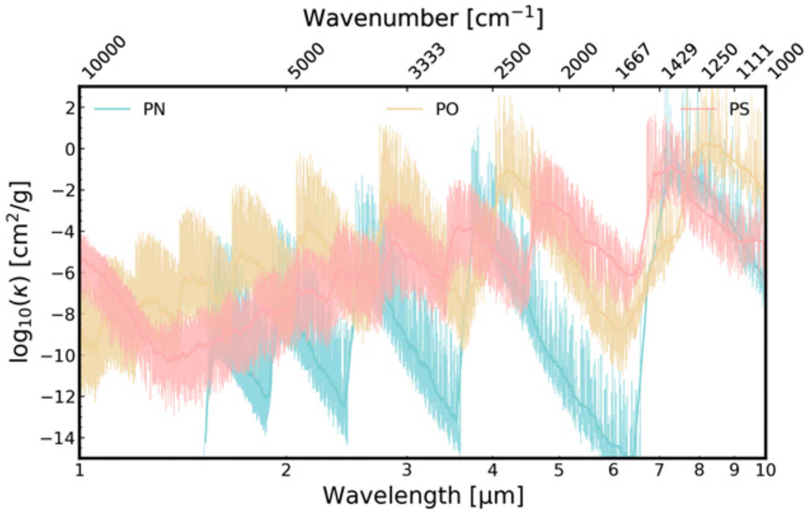
Opacities

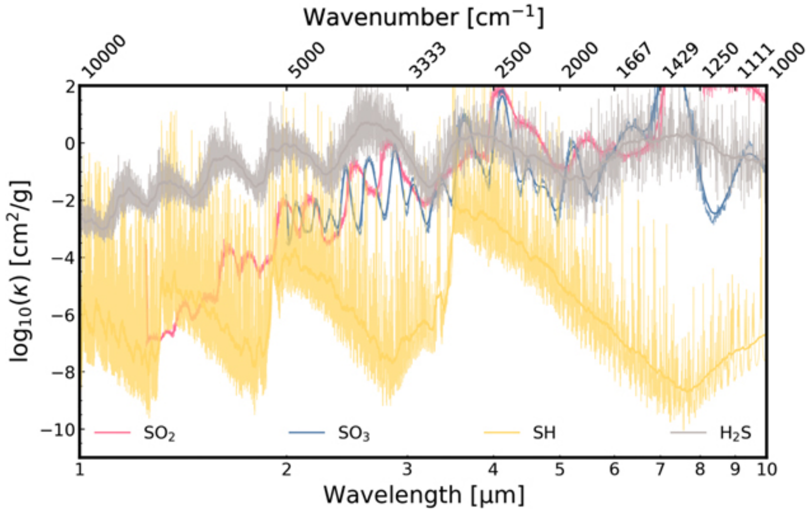
Grimm et al. [2021]

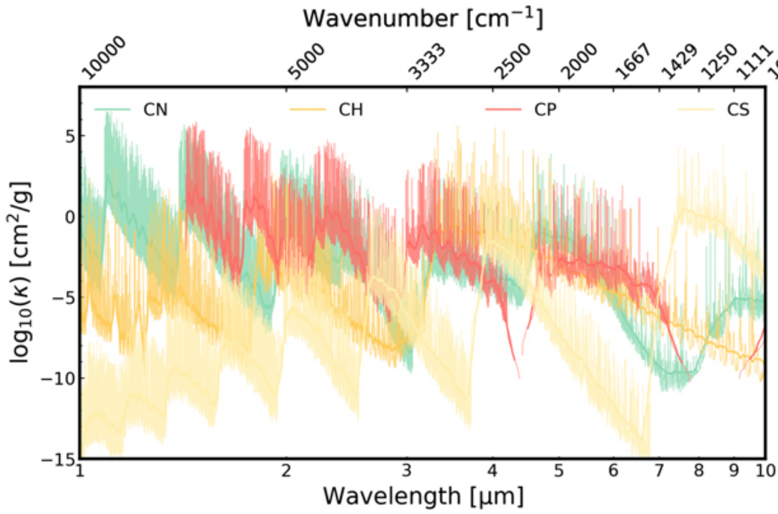


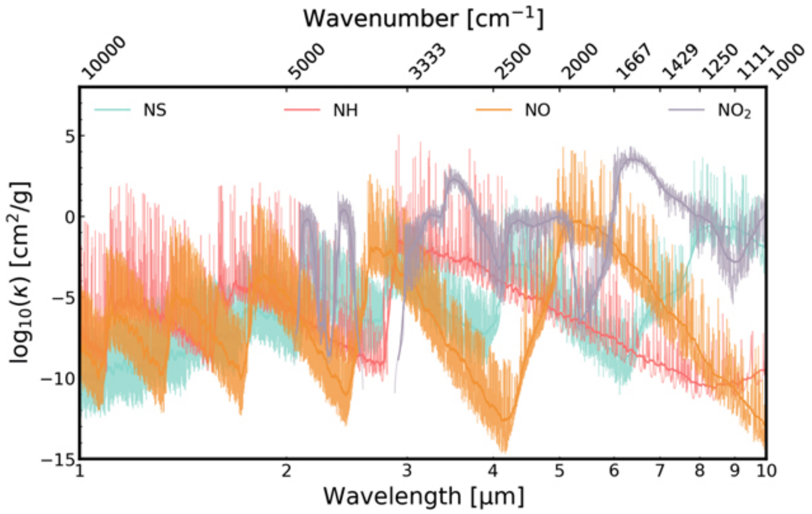


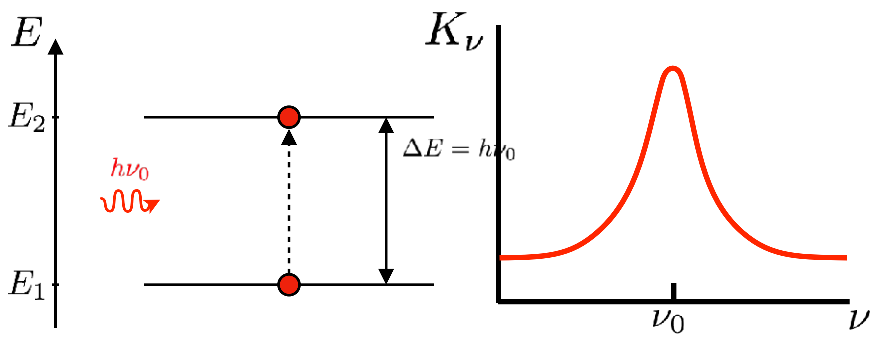


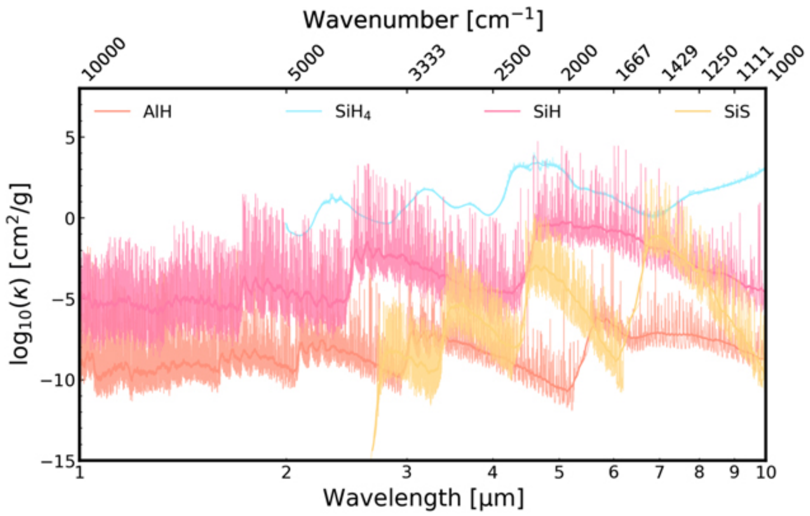




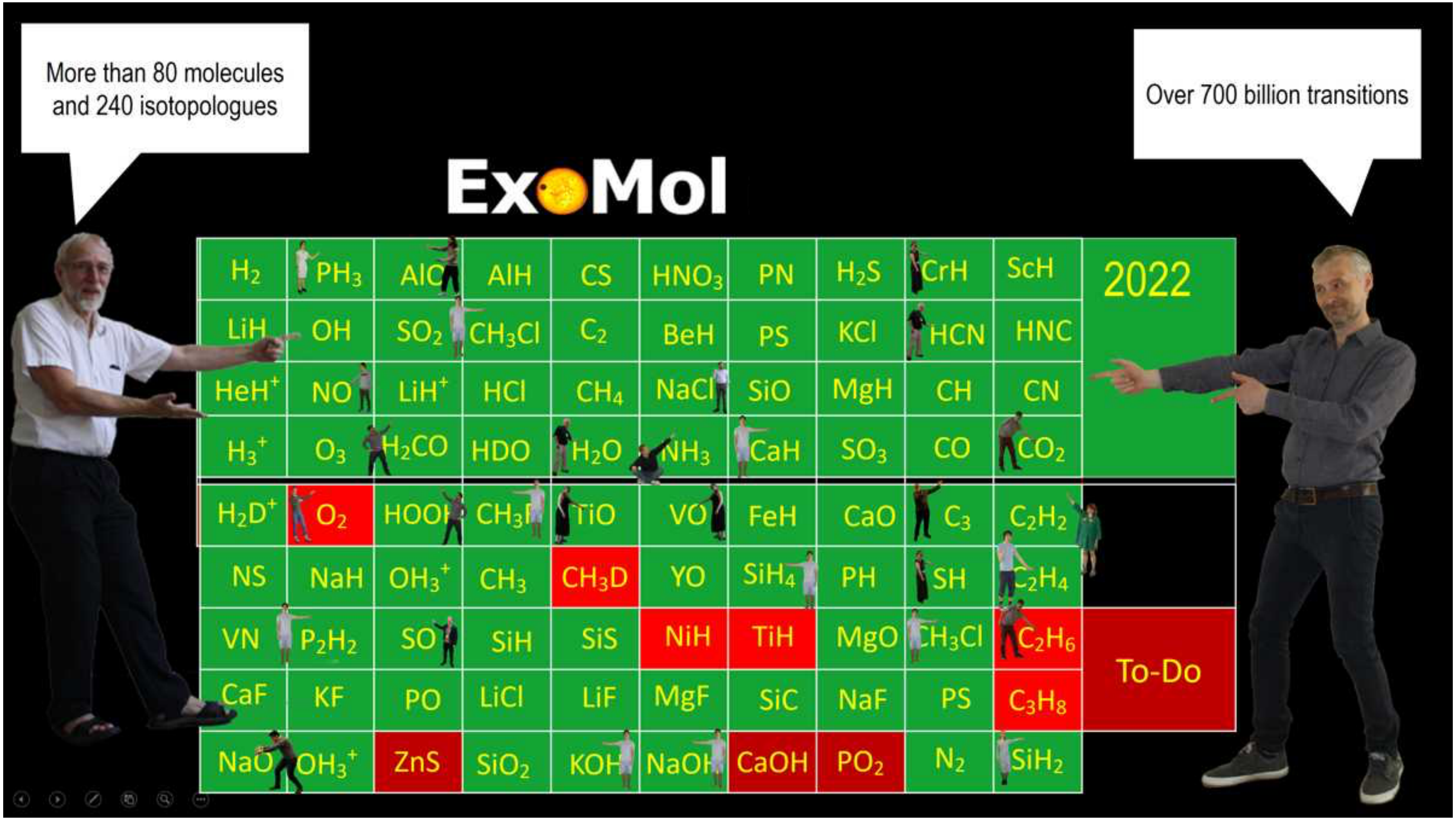








Opacities



More than 80 molecules and 240 isotopologues

Over 700 billion transitions

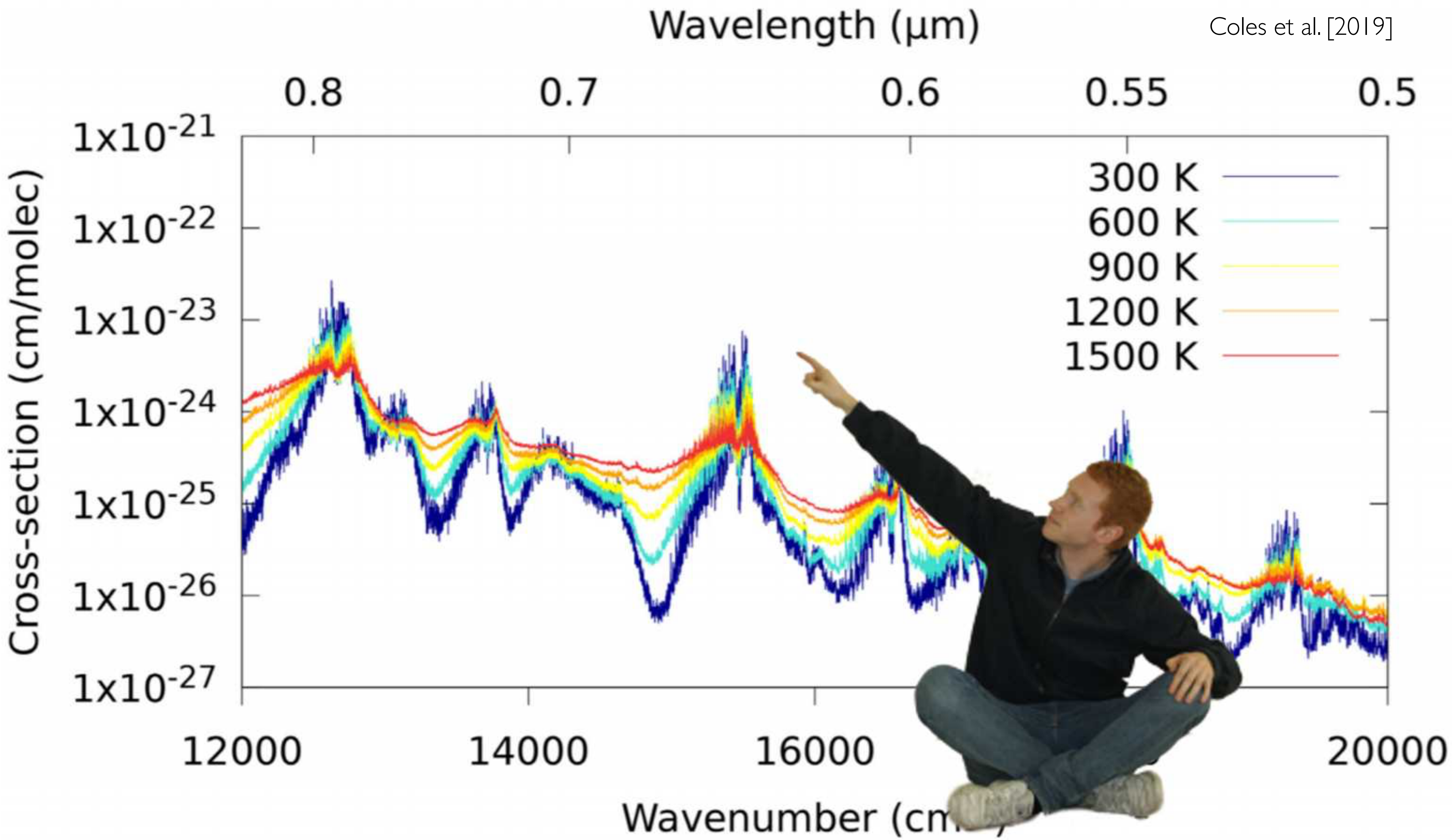
ExoMol

H_2	PH_3	AlO	AlH	CS	HNO_3	PN	H_2S	CrH	ScH
LiH	OH	SO_2	CH_3Cl	C_2	BeH	PS	KCl	HCN	HNC
HeH^+	NO	LiH^+	HCl	CH_4	NaCl	SiO	MgH	CH	CN
H_3^+	O_3	H_2CO	HDO	H_2O	NH_3	CaH	SO_3	CO	CO_2
H_2D^+	O_2	HOOH	CH_3F	TiO	VO	FeH	CaO	C_3	C_2H_2
NS	NaH	OH_3^+	CH_3	CH_3D	YO	SiH_4	PH	SH	C_2H_4
VN	P_2H_2	SO	SiH	SiS	NiH	TiH	MgO	CH_3Cl	C_2H_6
CaF	KF	PO	LiCl	LiF	MgF	SiC	NaF	PS	C_3H_8
NaO	OH_3^+	ZnS	SiO_2	KOH	NaOH	CaOH	PO_2	N_2	SiH_2

2022

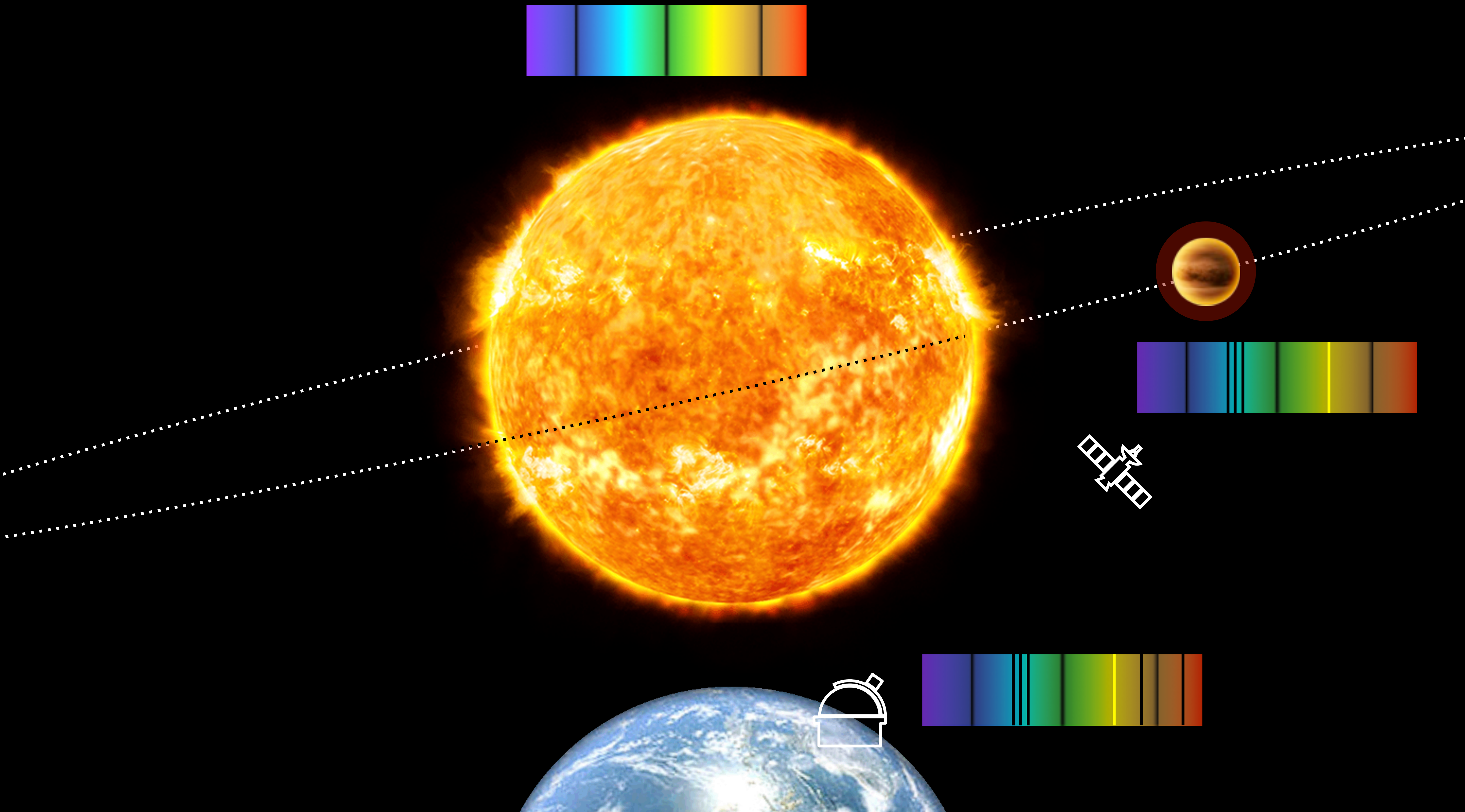
To-Do

Opacities

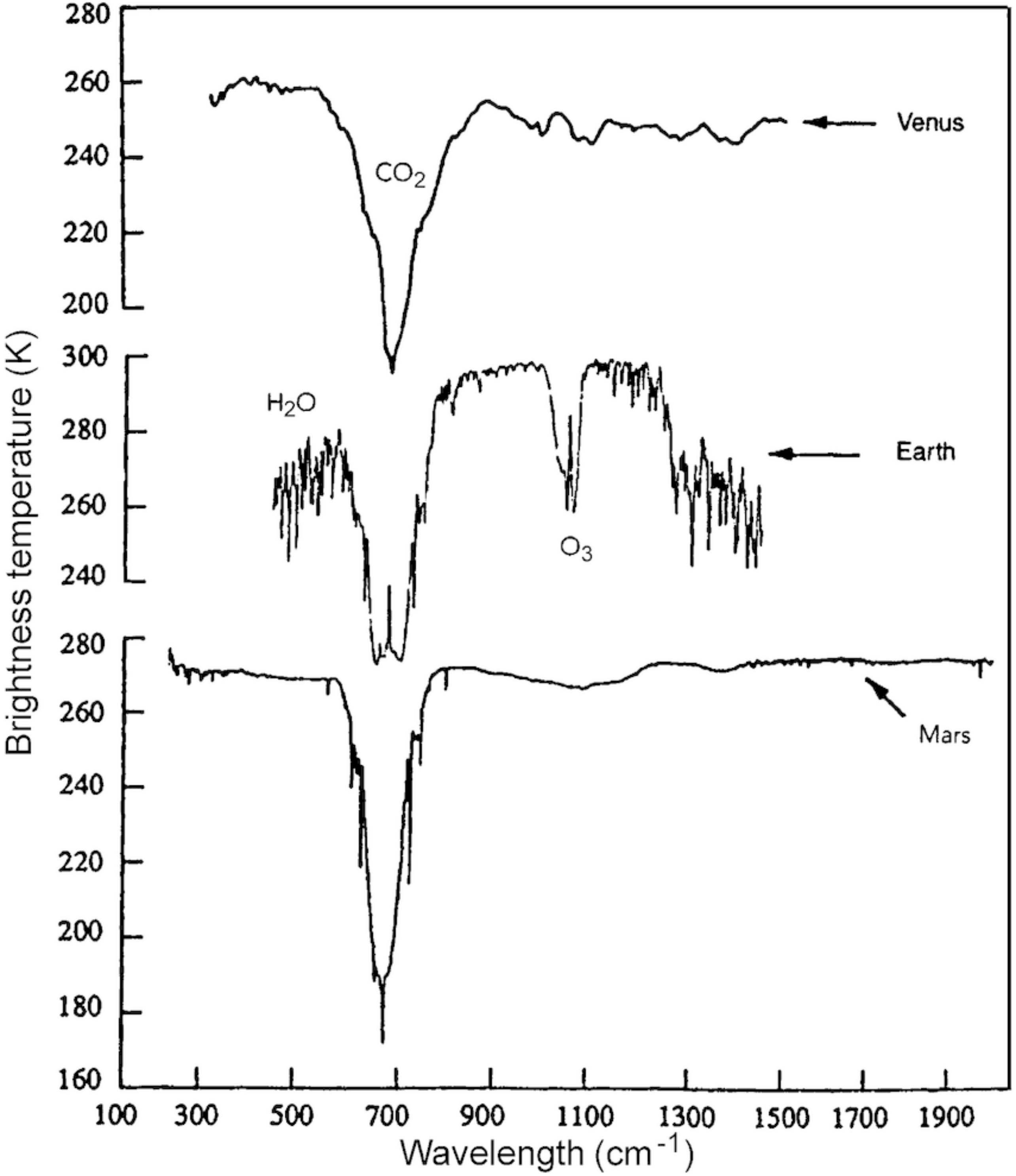


Coles et al. [2019]

Observations

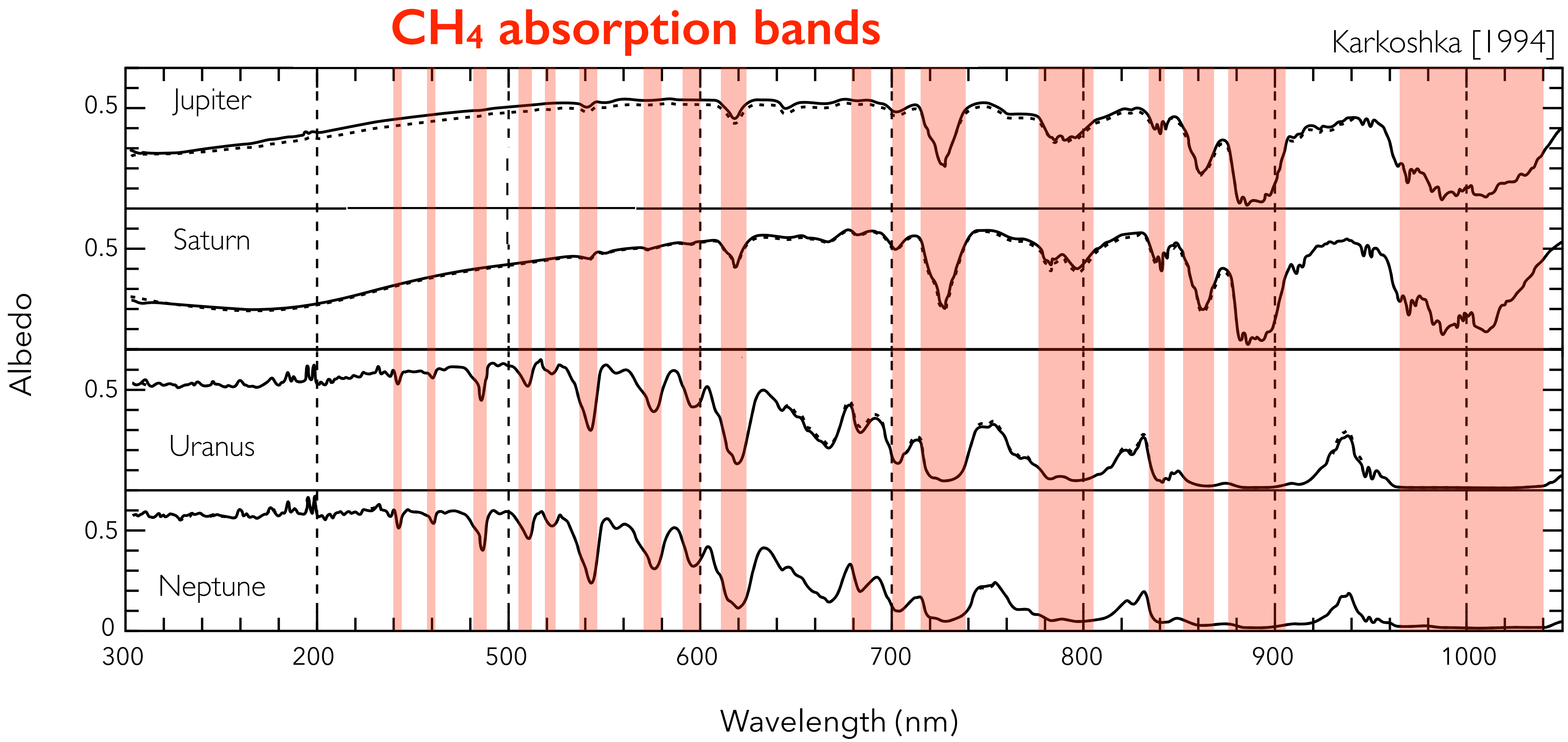


Terrestrial planets

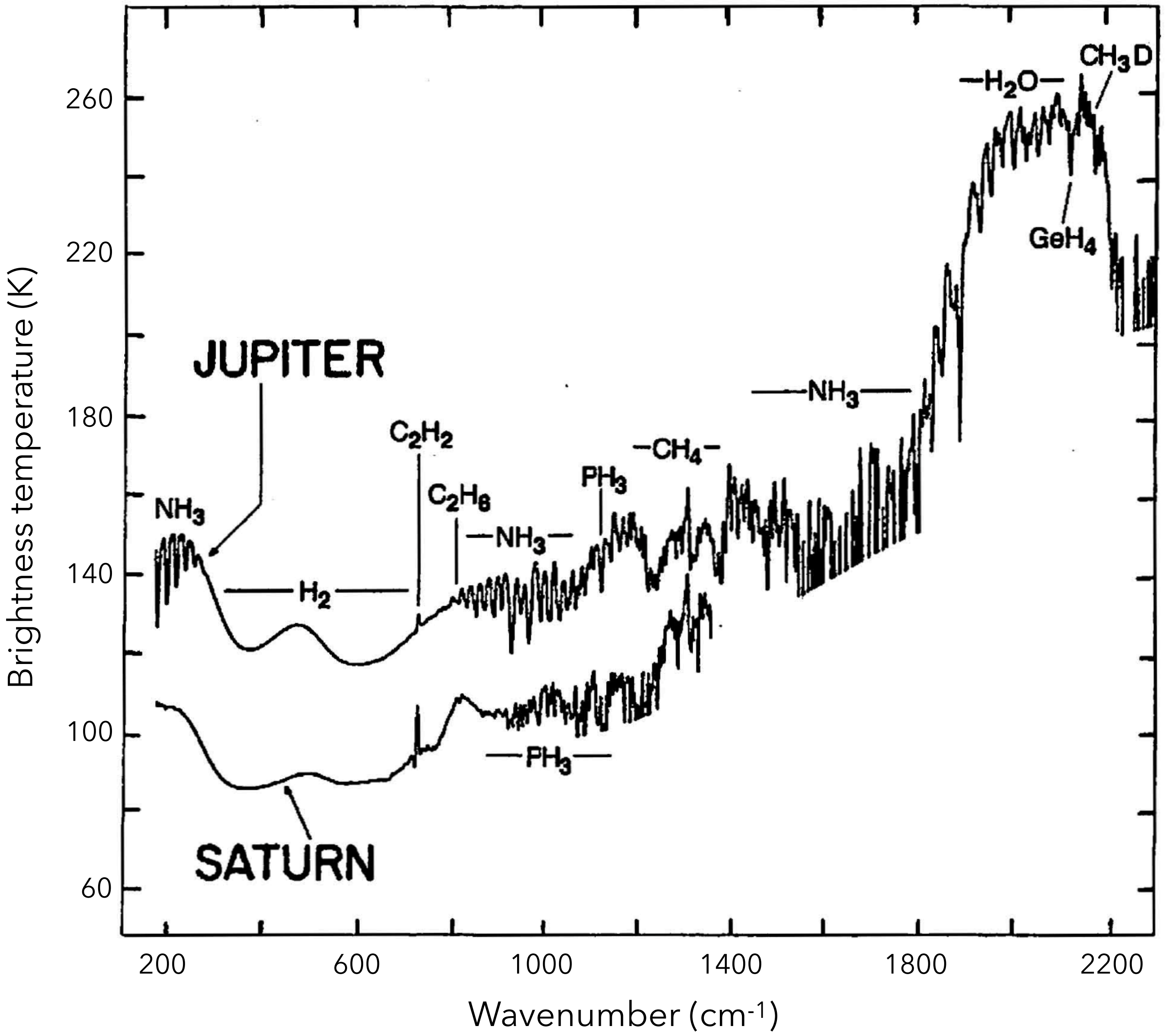


adapted from Hanel [1992]

Giant planets

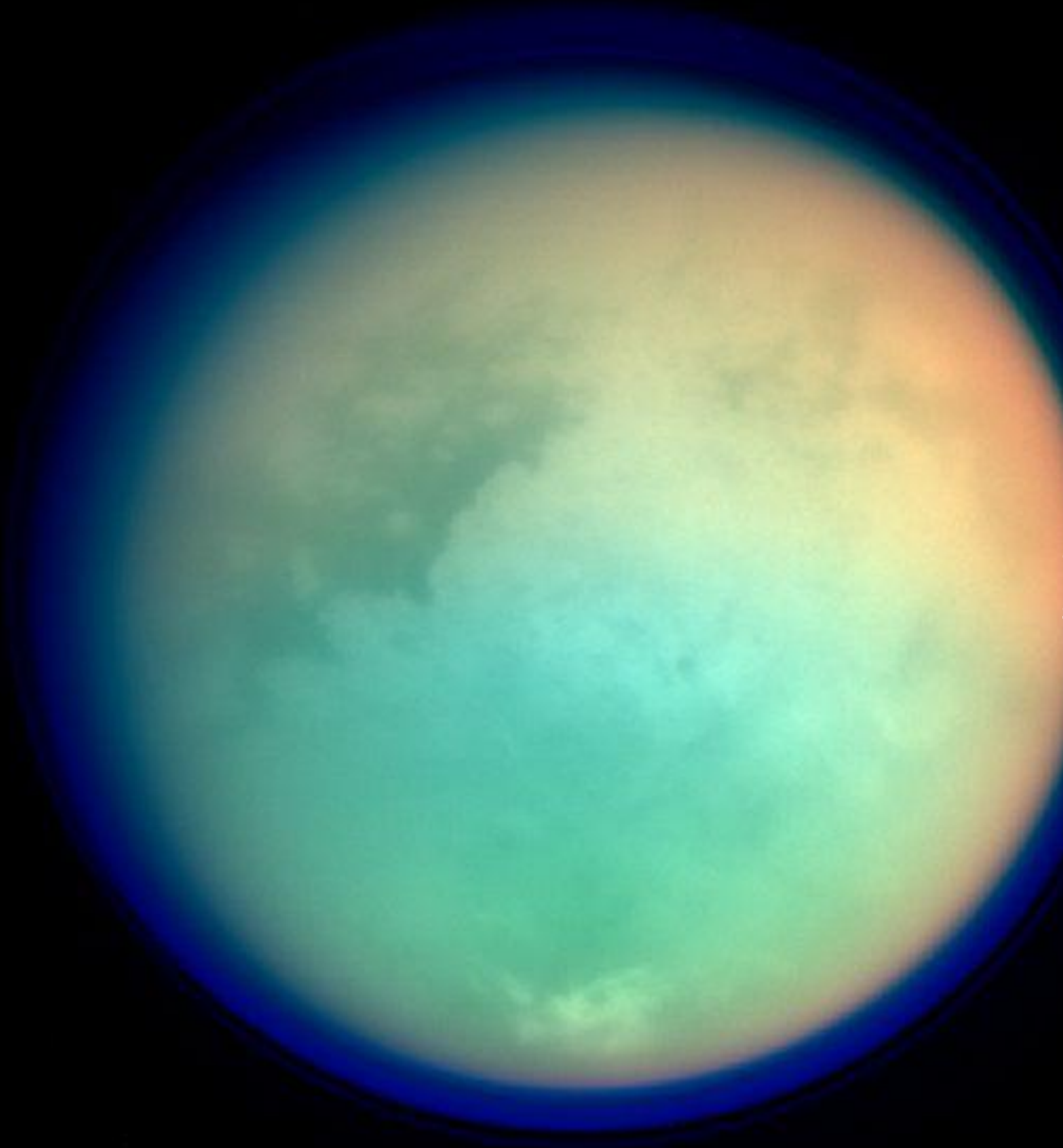


Jupiter and Saturn

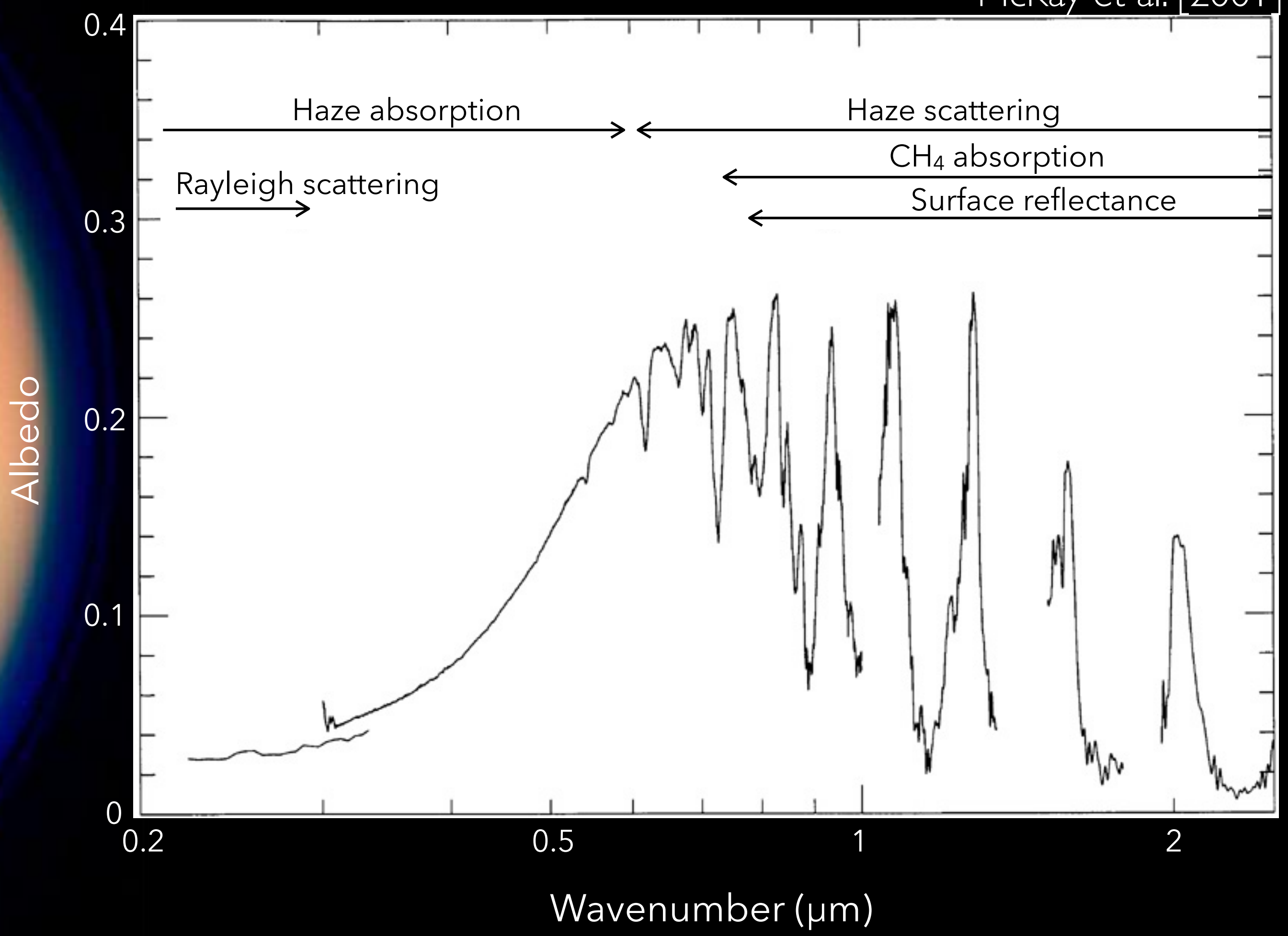


adapted from Hanel [1992]

Titan

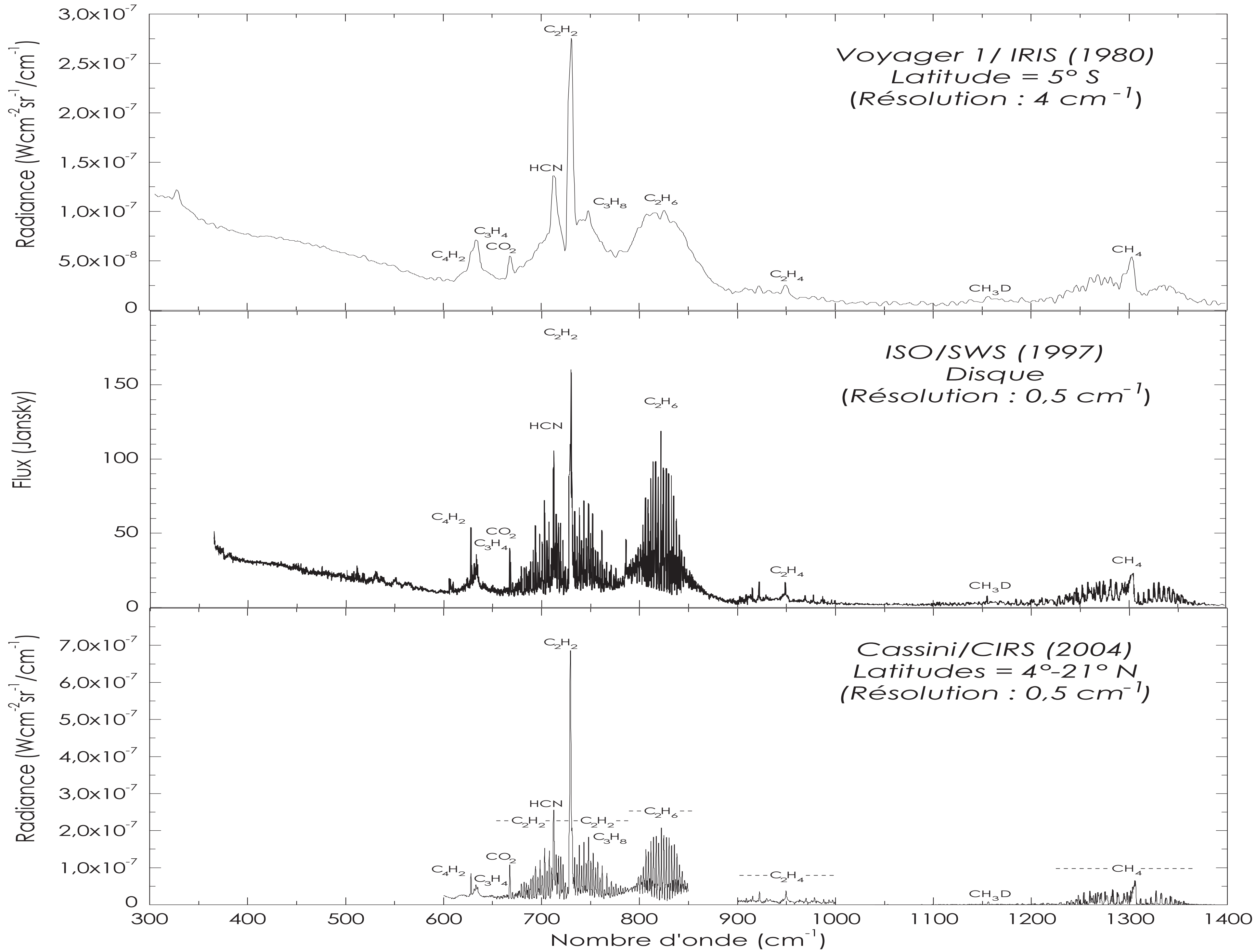


McKay et al. [2001]



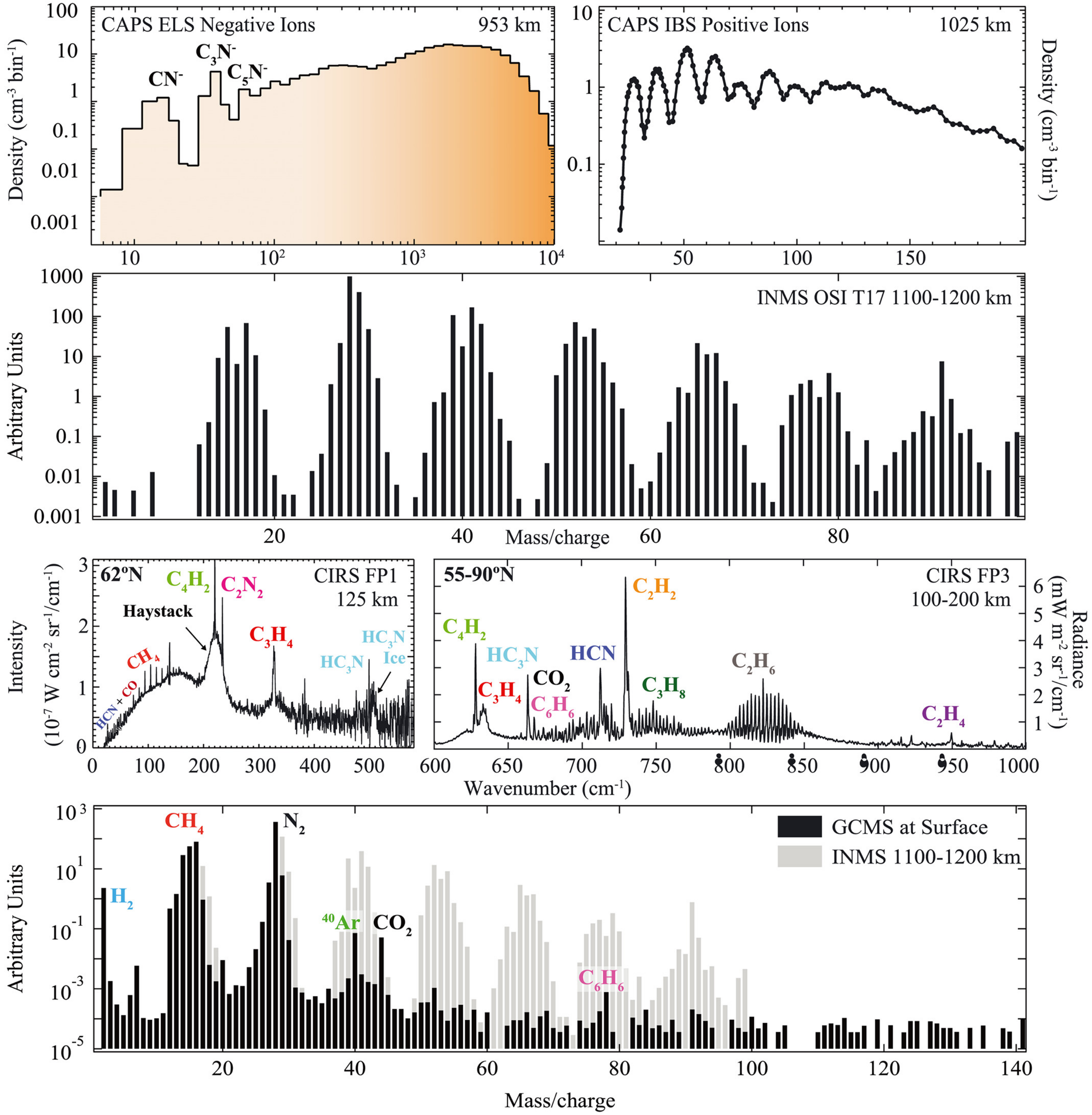
Credits : NASA, JPL, Space Science Institute

Titan

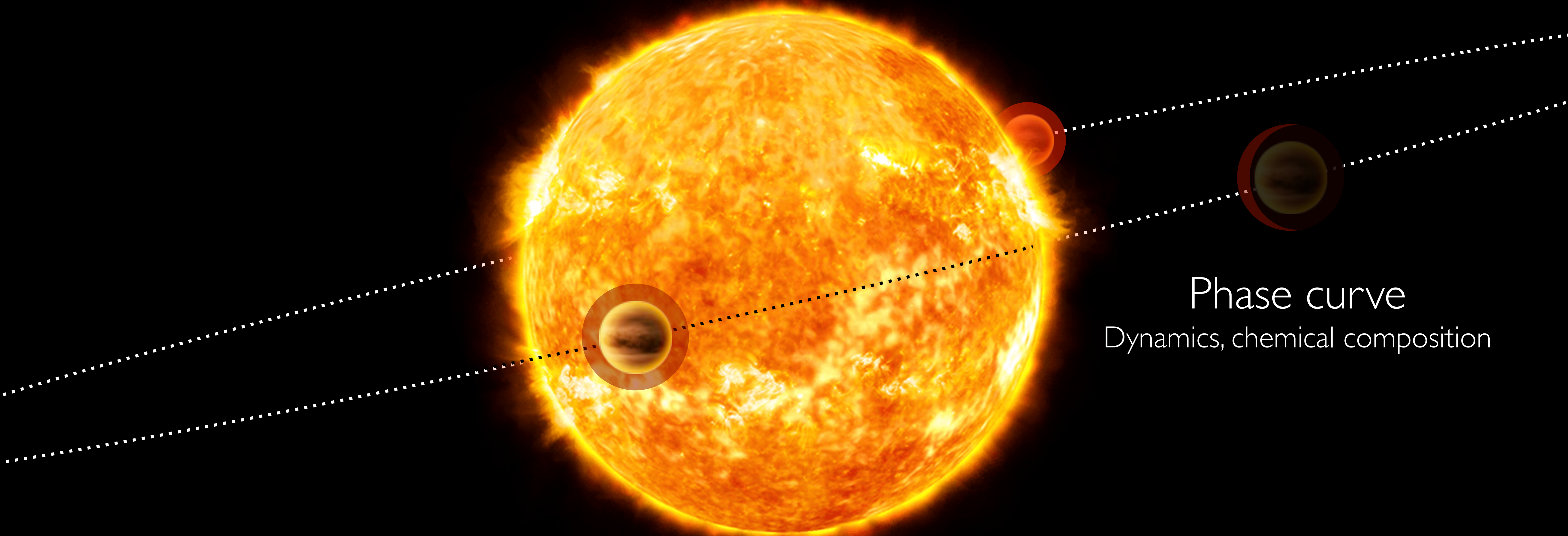

Voyager 1/ IRIS (1980)
Latitude = 5° S
(Résolution : 4 cm^{-1})
Radiance (Wcm^{-2}sr^{-1}/cm^{-1})
3,0x10^{-7}
2,5x10^{-7}
2,0x10^{-7}
1,5x10^{-7}
1,0x10^{-7}
5,0x10^{-8}
0
C_2H_2
HCN
C_3H_8
C_2H_6
C_3H_4
C_4H_2
CO_2
C_2H_4
CH_3D
CH_4
ISO/SWS (1997)
Disque
(Résolution : 0,5 cm^{-1})
Flux (Jansky)
150
100
50
0
Cassini/CIRS (2004)
Latitudes = 4°-21° N
(Résolution : 0,5 cm^{-1})
7,0x10^{-7}
6,0x10^{-7}
5,0x10^{-7}
4,0x10^{-7}
3,0x10^{-7}
2,0x10^{-7}
1,0x10^{-7}
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
Nombre d'onde (cm^{-1})

Titan

Hörst et al. [2017]



Exoplanets



Secondary eclipse/direct imaging

Temperature structure, chemical composition, wind speeds

Phase curve

Dynamics, chemical composition

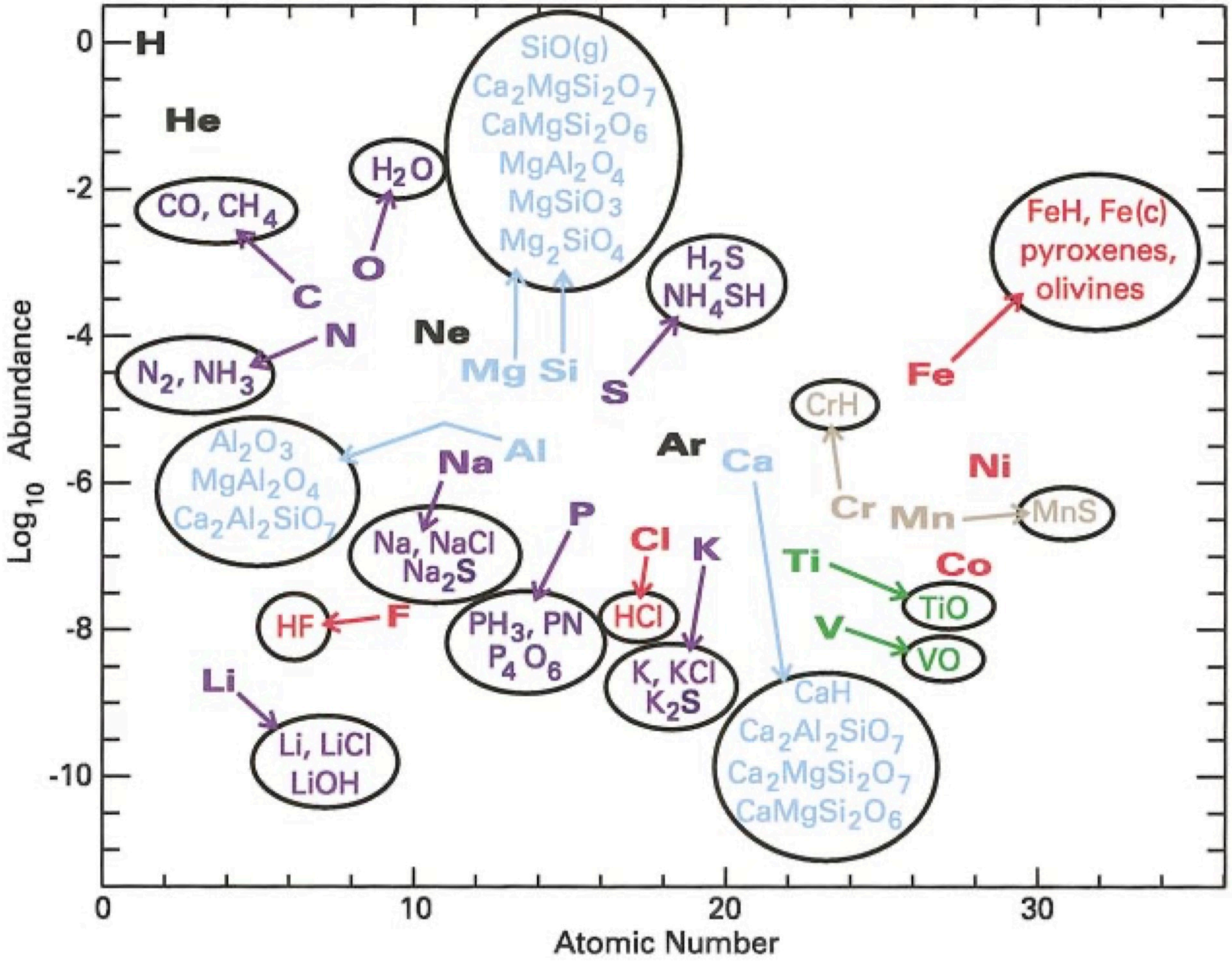
Primary eclipse

Chemical composition, haziness+cloudiness

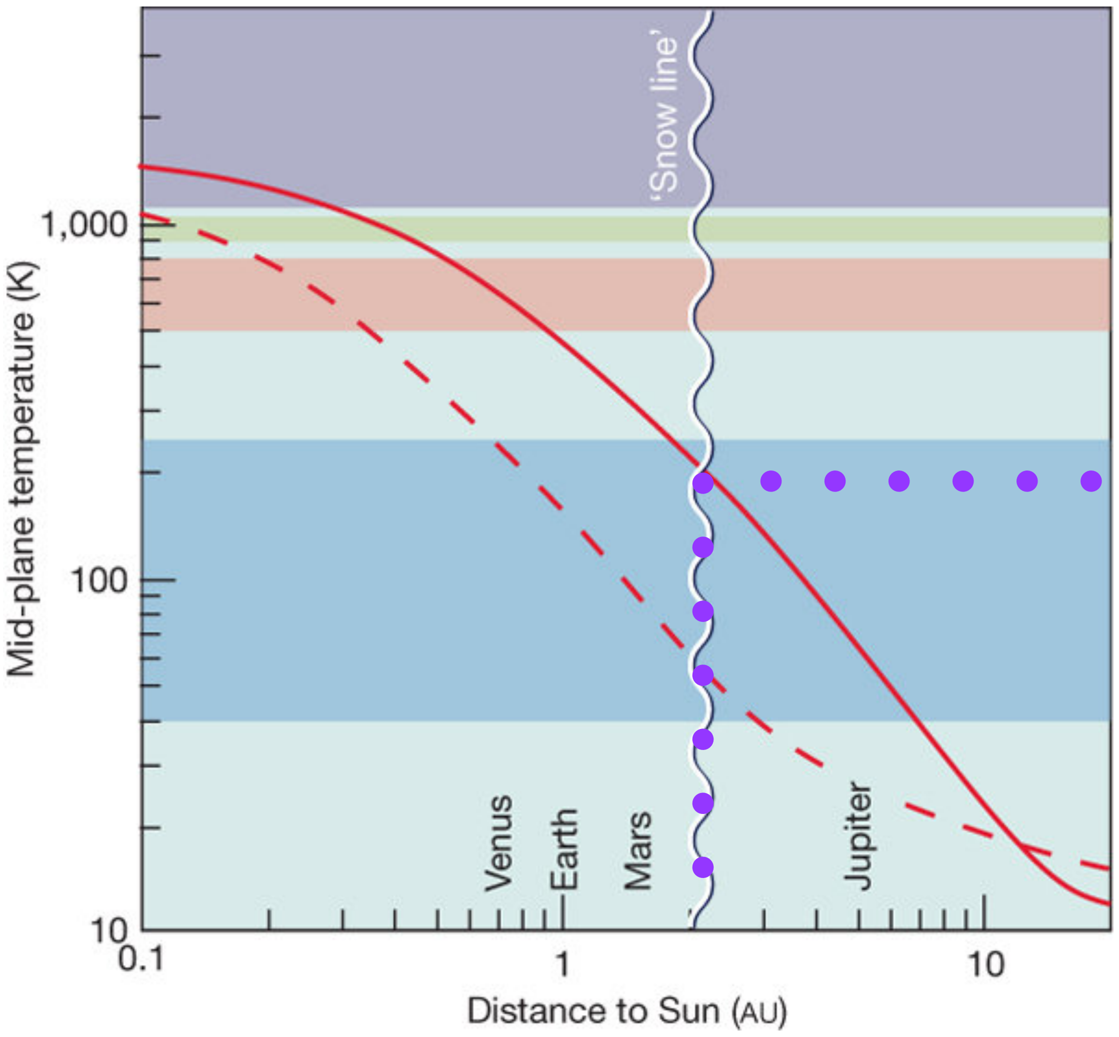
Origin of atmospheres
(in a nutshell)

Elemental abundances

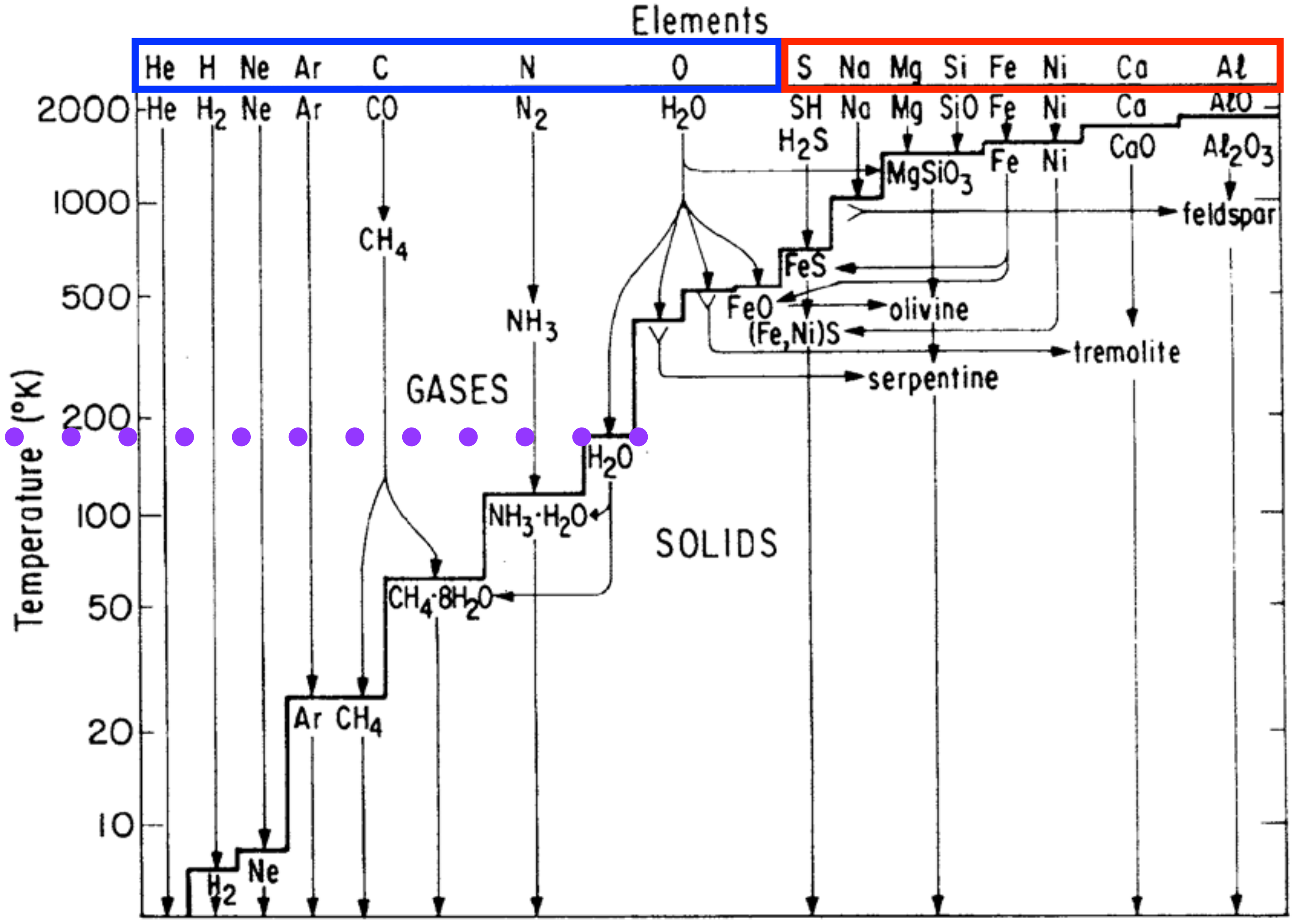
Burrows et al. [2001]



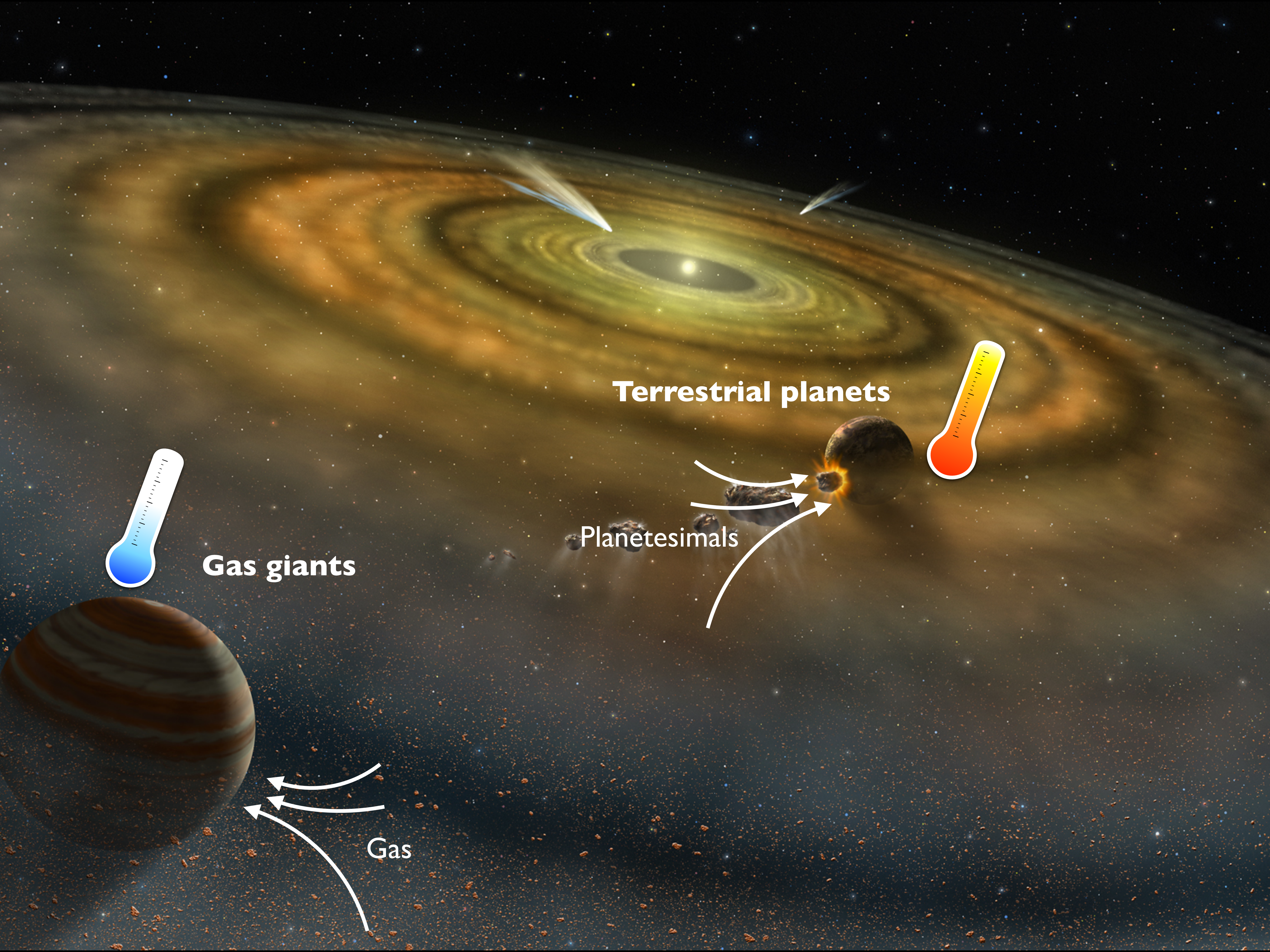
Temperature and condensation



Thermal structure
of the solar nebula.
(Albarède [2009])



Condensation sequence of most abundant elements
in the solar nebula.
(Barshay and Lewis [1976])



Terrestrial planets

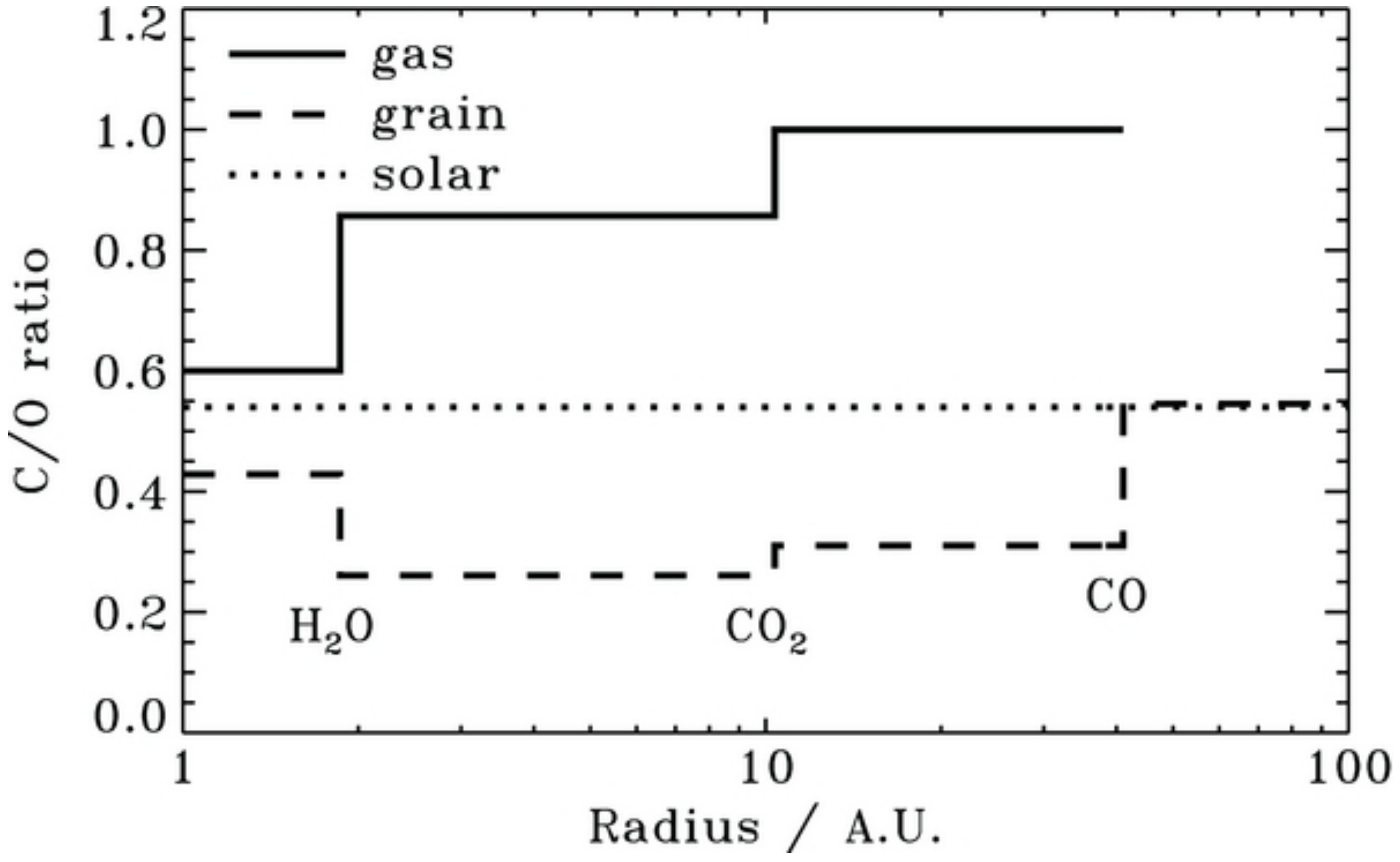
Planetesimals

Gas giants

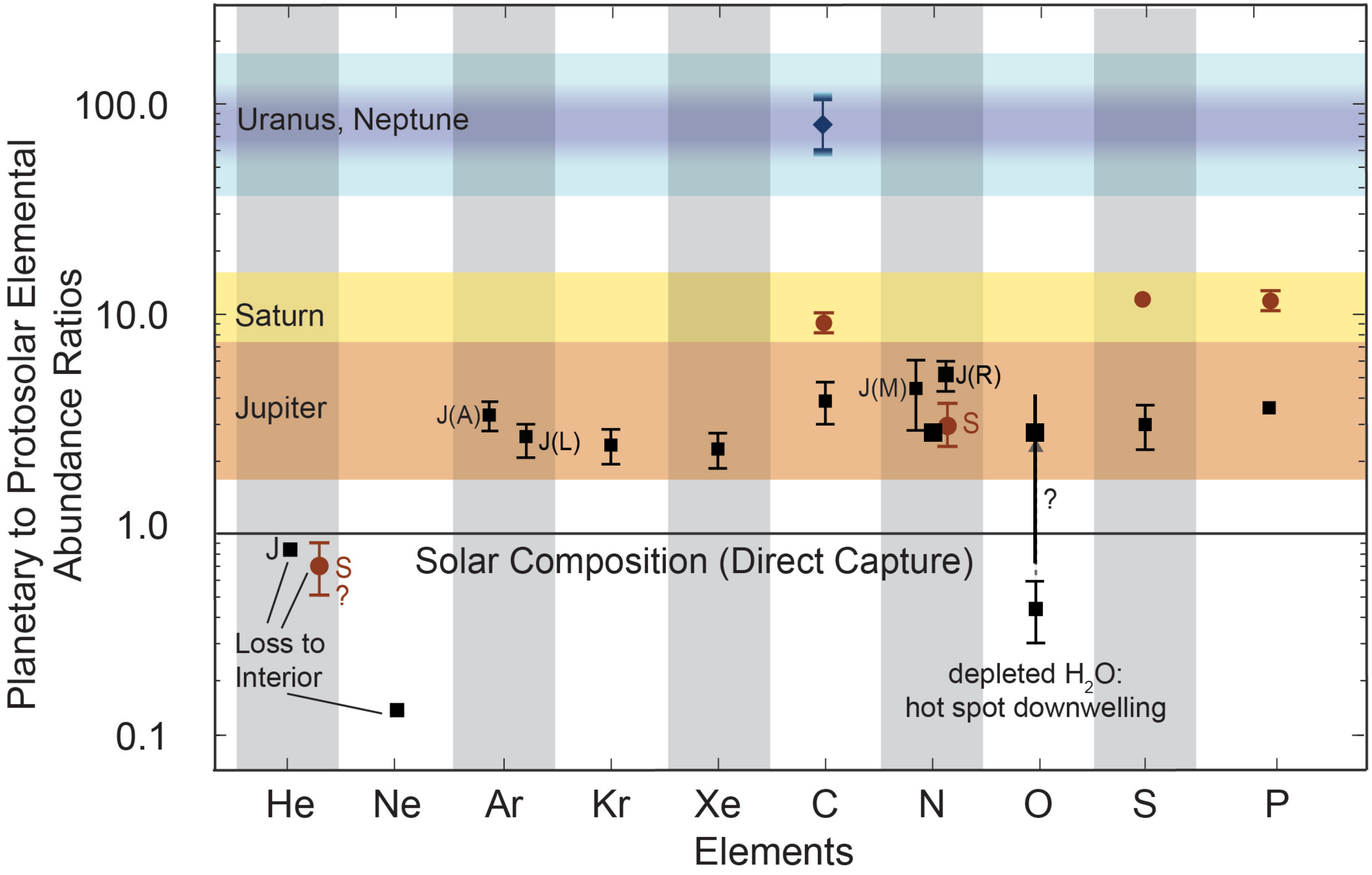
Gas

C/O ratio

Oberg et al. [2011]



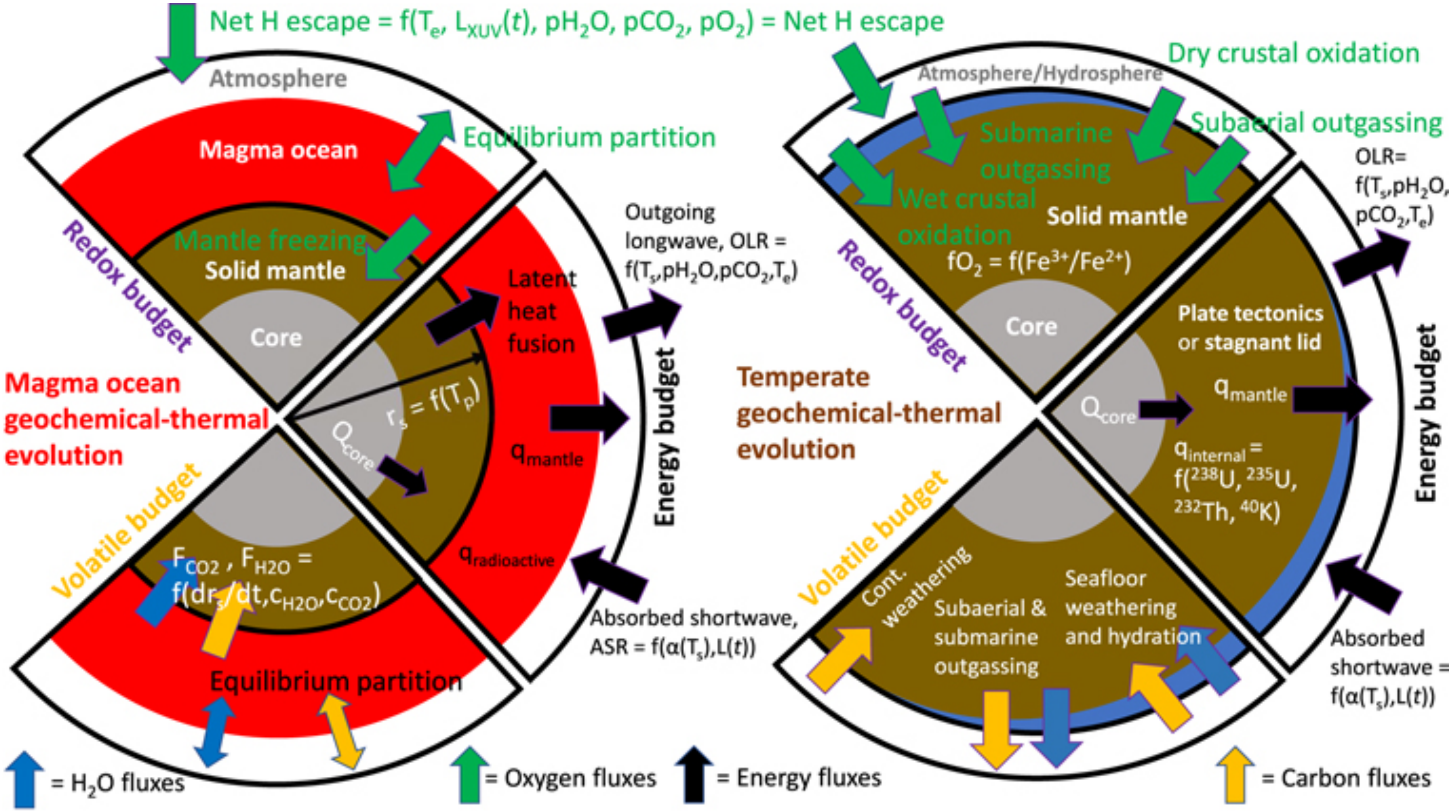
Atmospheres of giant planets



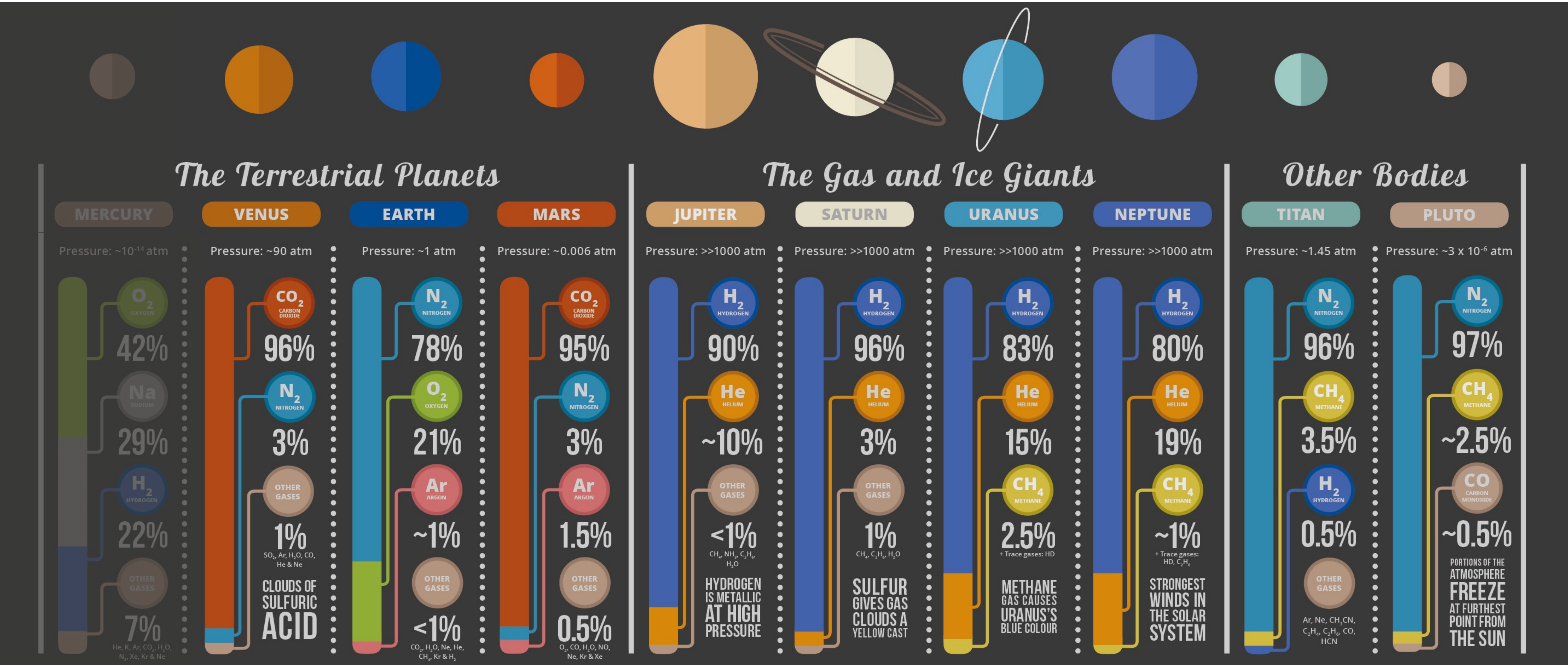
adapted from Atreya et al. [2016]

Atmospheres of terrestrial planets

Krissansen-Totton and Fortney [2022]

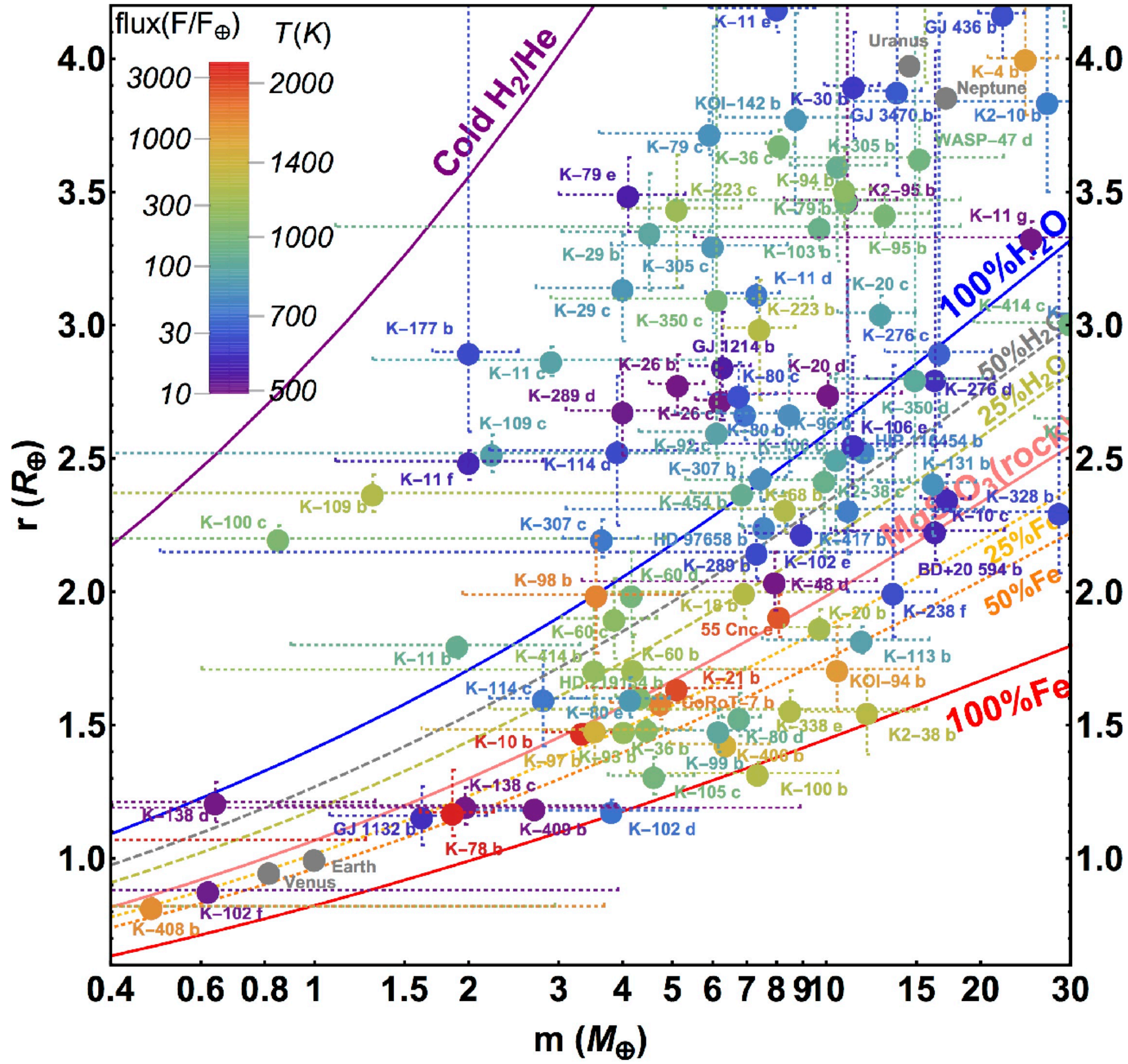


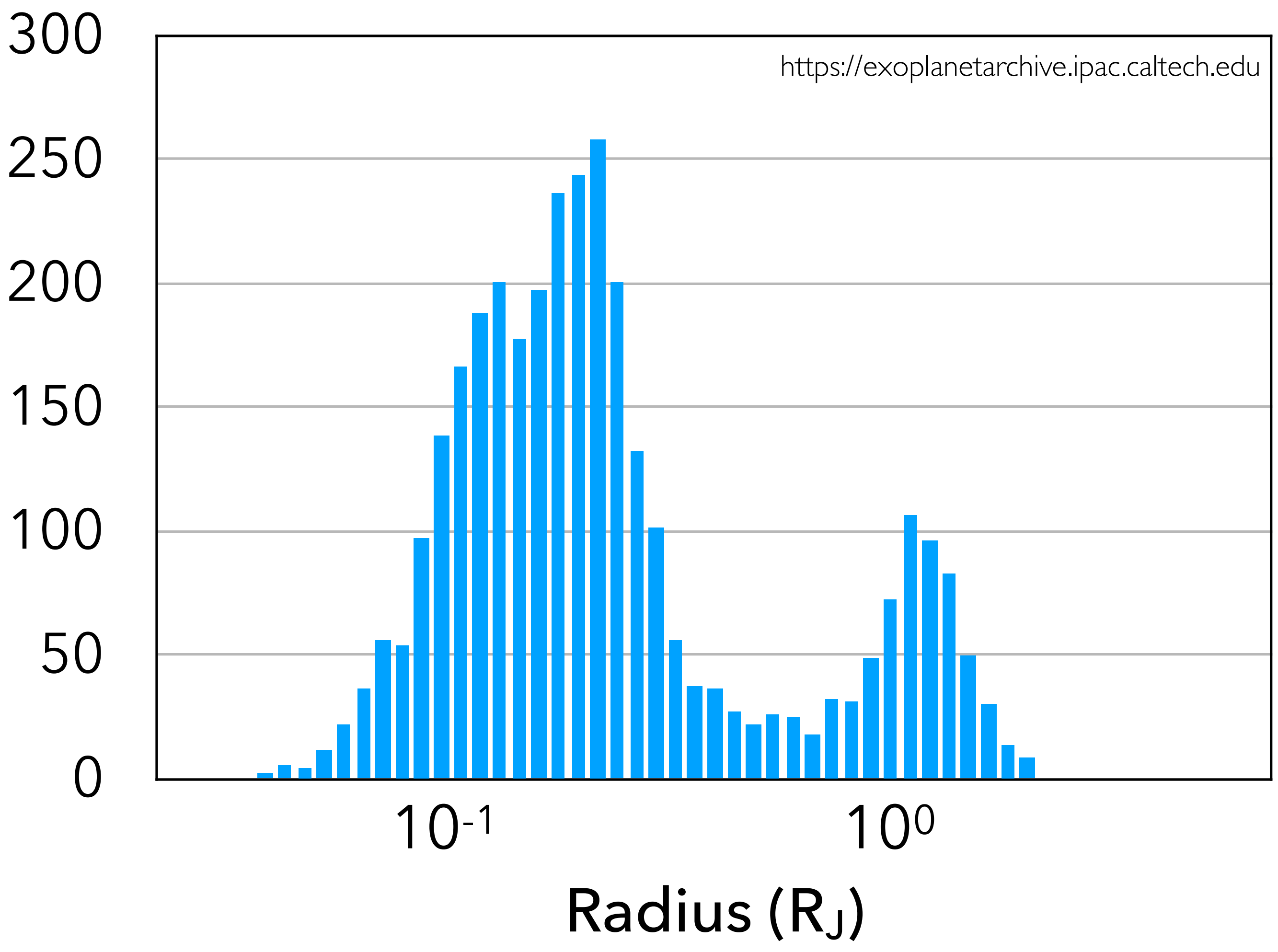
Atmospheres of the Solar System



Three planetary classes to rule them all ?

Exo-atmospheres

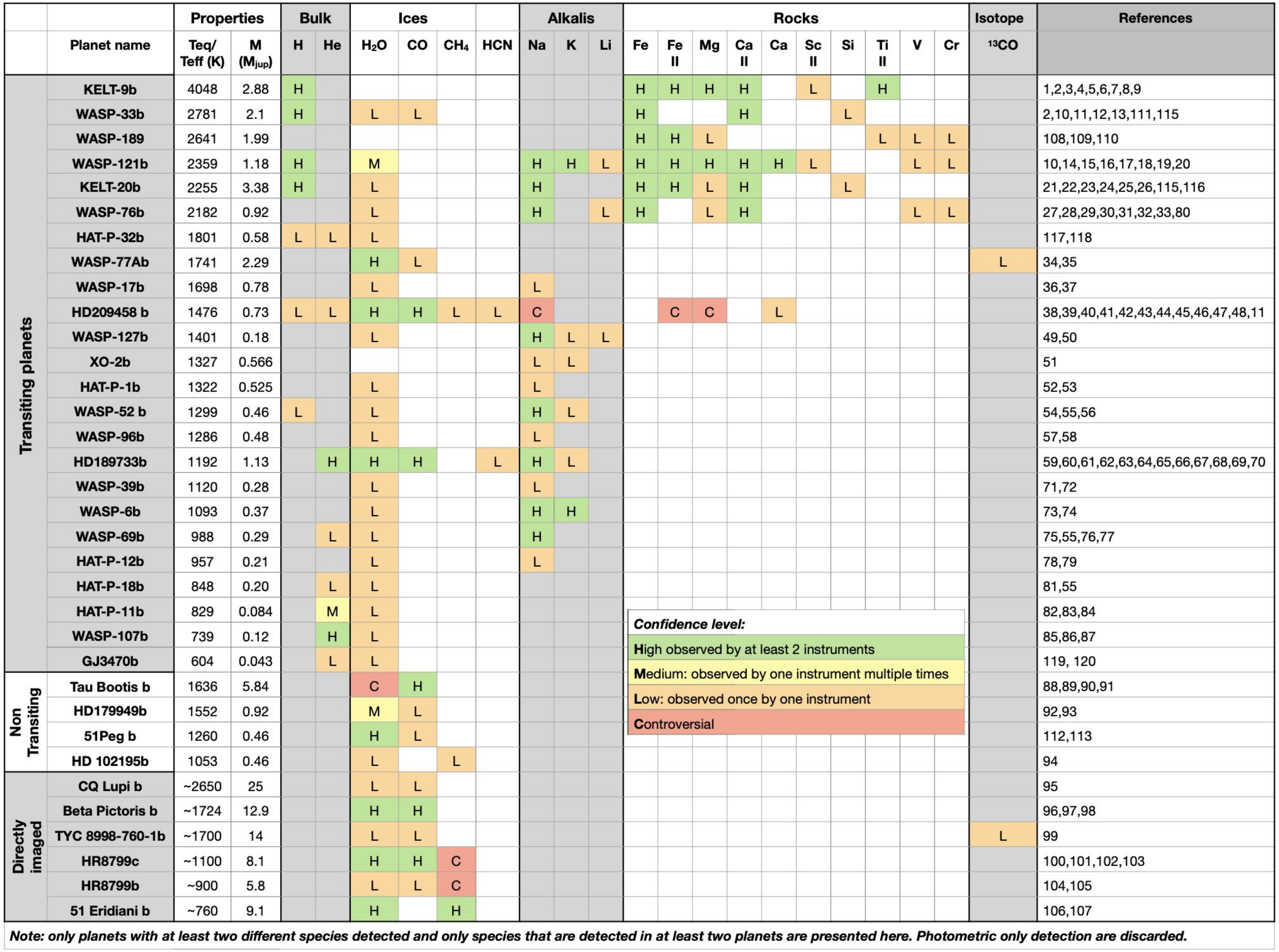




Other planetary systems contain planets
very different from ours (hot Jupiters, super-Earths, mini-Neptunes, iron planets. . .)

Exo-atmospheres

Credits: Vivien Parmentier, @V_Parmentier



		Properties		Bulk		Ices				Alkalis			Rocks										Isotope	References
	Planet name	Teq/ Teff (K)	M (M_{jup})	H	He	H_2O	CO	CH_4	HCN	Na	K	Li	Fe	Fe II	Mg	Ca II	Ca	Sc II	Si	Ti II	V	Cr	^{13}CO	
Transiting planets	KELT-9b	4048	2.88	H									H	H	H	H		L		H				1,2,3,4,5,6,7,8,9
	WASP-33b	2781	2.1	H		L	L						H			H			L					2,10,11,12,13,111,115
	WASP-189	2641	1.99										H	H	L					L	L	L		108,109,110
	WASP-121b	2359	1.18	H		M				H	H	L	H	H	H	H	H	L			L	L		10,14,15,16,17,18,19,20
	KELT-20b	2255	3.38	H		L				H			H	H	L	H			L					21,22,23,24,25,26,115,116
	WASP-76b	2182	0.92			L				H		L	H		L	H					L	L		27,28,29,30,31,32,33,80
	HAT-P-32b	1801	0.58	L	L	L																		117,118
	WASP-77Ab	1741	2.29			H	L																L	34,35
	WASP-17b	1698	0.78			L				L														36,37
	HD209458 b	1476	0.73	L	L	H	H	L	L	C				C	C		L							38,39,40,41,42,43,44,45,46,47,48,11
	WASP-127b	1401	0.18			L				H	L	L												49,50
	XO-2b	1327	0.566							L	L													51
	HAT-P-1b	1322	0.525			L				L														52,53
	WASP-52 b	1299	0.46	L		L				H	L													54,55,56
	WASP-96b	1286	0.48			L				L														57,58
	HD189733b	1192	1.13		H	H	H		L	H	L													59,60,61,62,63,64,65,66,67,68,69,70
	WASP-39b	1120	0.28			L				L														71,72
	WASP-6b	1093	0.37			L				H	H													73,74
	WASP-69b	988	0.29		L	L				H														75,55,76,77
	HAT-P-12b	957	0.21			L				L														78,79
	HAT-P-18b	848	0.20		L	L																		81,55
	HAT-P-11b	829	0.084		M	L																		82,83,84
	WASP-107b	739	0.12		H	L																		85,86,87
	GJ3470b	604	0.043		L	L																		119, 120
Non Transiting	Tau Bootis b	1636	5.84			C	H																	88,89,90,91
	HD179949b	1552	0.92			M	L																	92,93
	51Peg b	1260	0.46			H	L																	112,113
	HD 102195b	1053	0.46			L		L																94
Directly imaged	CQ Lupi b	~2650	25			L	L																	95
	Beta Pictoris b	~1724	12.9			H	H																	96,97,98
	TYC 8998-760-1b	~1700	14			L	L																L	99
	HR8799c	~1100	8.1			H	H	C																100,101,102,103
	HR8799b	~900	5.8			L	L	C																104,105
	51 Eridiani b	~760	9.1			H		H																106,107

Confidence level:

- 🟩 **H**igh observed by at least 2 instruments
- 🟨 **M**edium: observed by one instrument multiple times
- 🟧 **L**ow: observed once by one instrument
- 🟥 **C**ontroversial

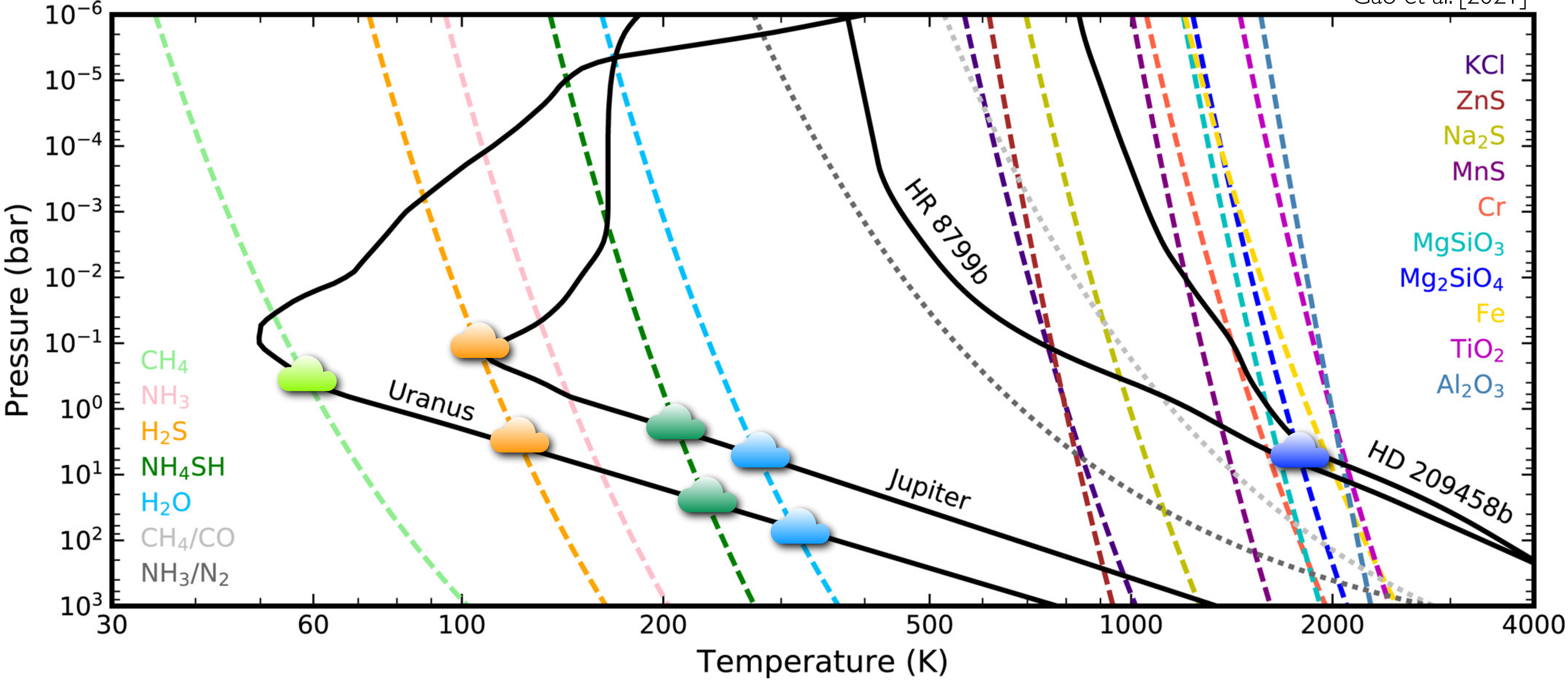
Note: only planets with at least two different species detected and only species that are detected in at least two planets are presented here. Photometric only detection are discarded.

Exo-atmospheres

$H_2O_{(g)} \longrightarrow H_2O_{(s,l)}$

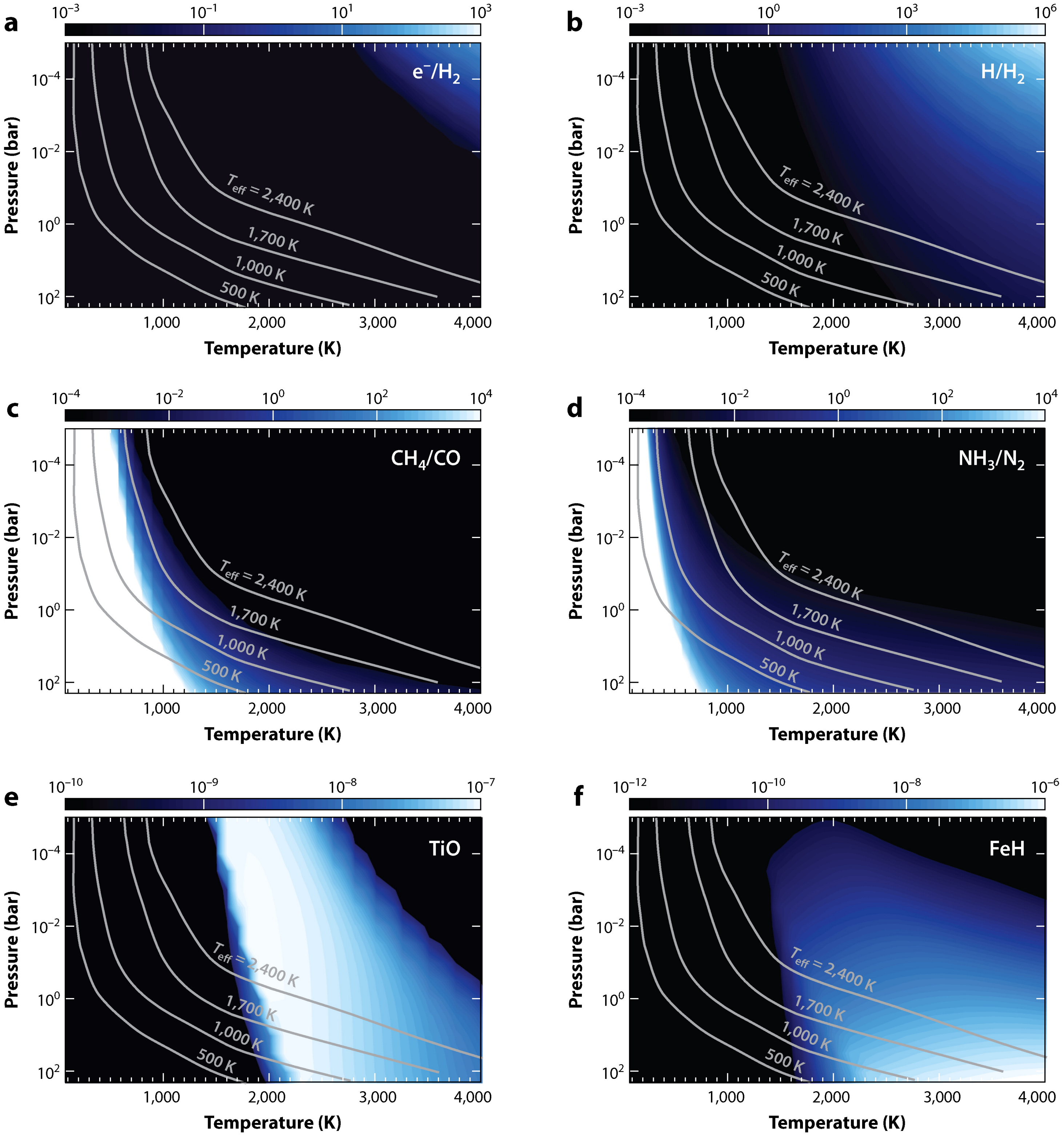
$2Mg_{(g)} + 3H_2O_{(g)} + SiO_{(g)} \longrightarrow Mg_2SiO_{4(s,l)} + 3H_{2(g)}$

Gao et al. [2021]



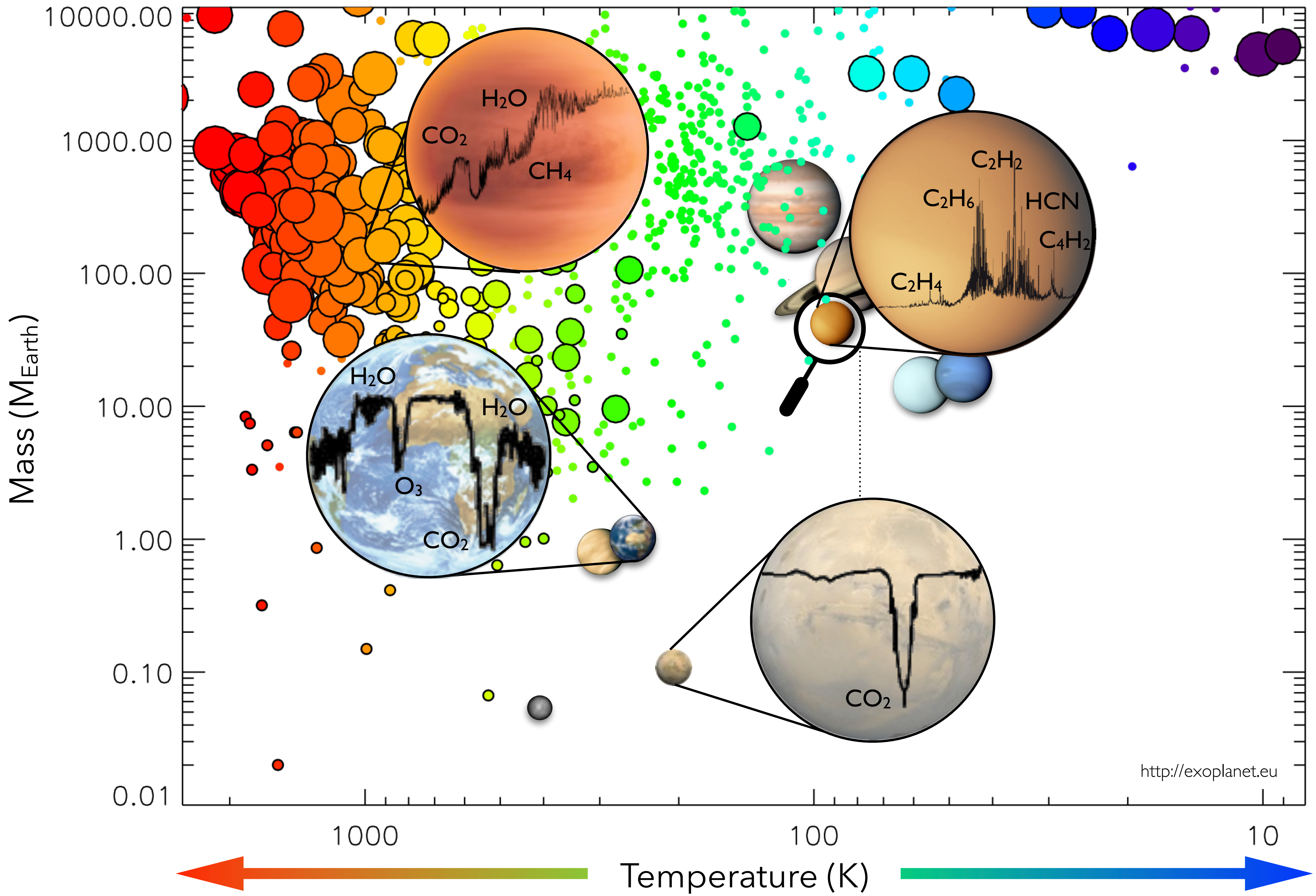
Exo-atmospheres

Marley and Robinson [2015]



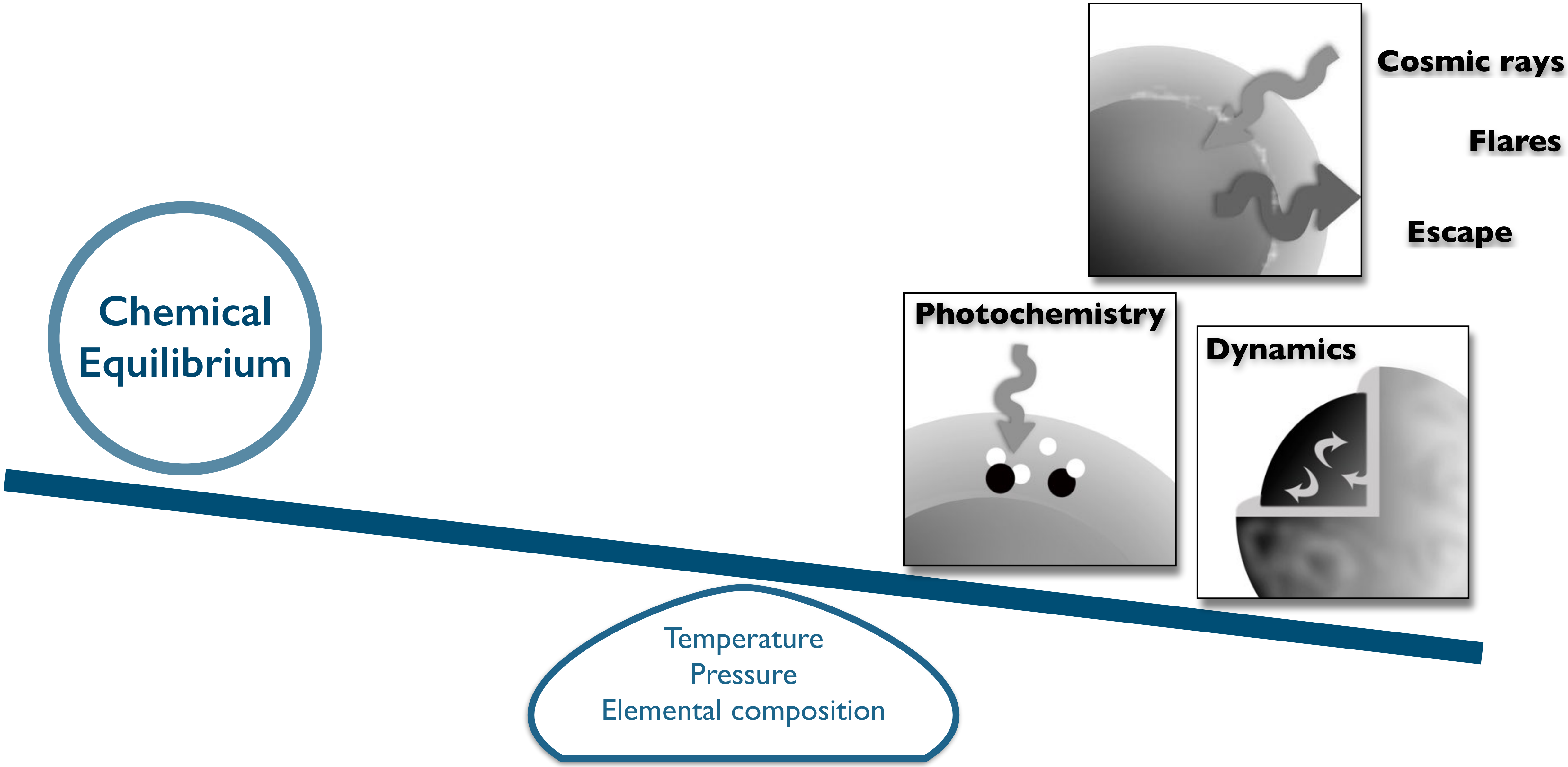
Chemical diversity of planetary atmospheres

Eric Hébrard



Chemical disequilibrium

How to explain the deviations from chemical composition observed in planetary atmospheres?



Cosmic rays

Flares

Escape

Photochemistry

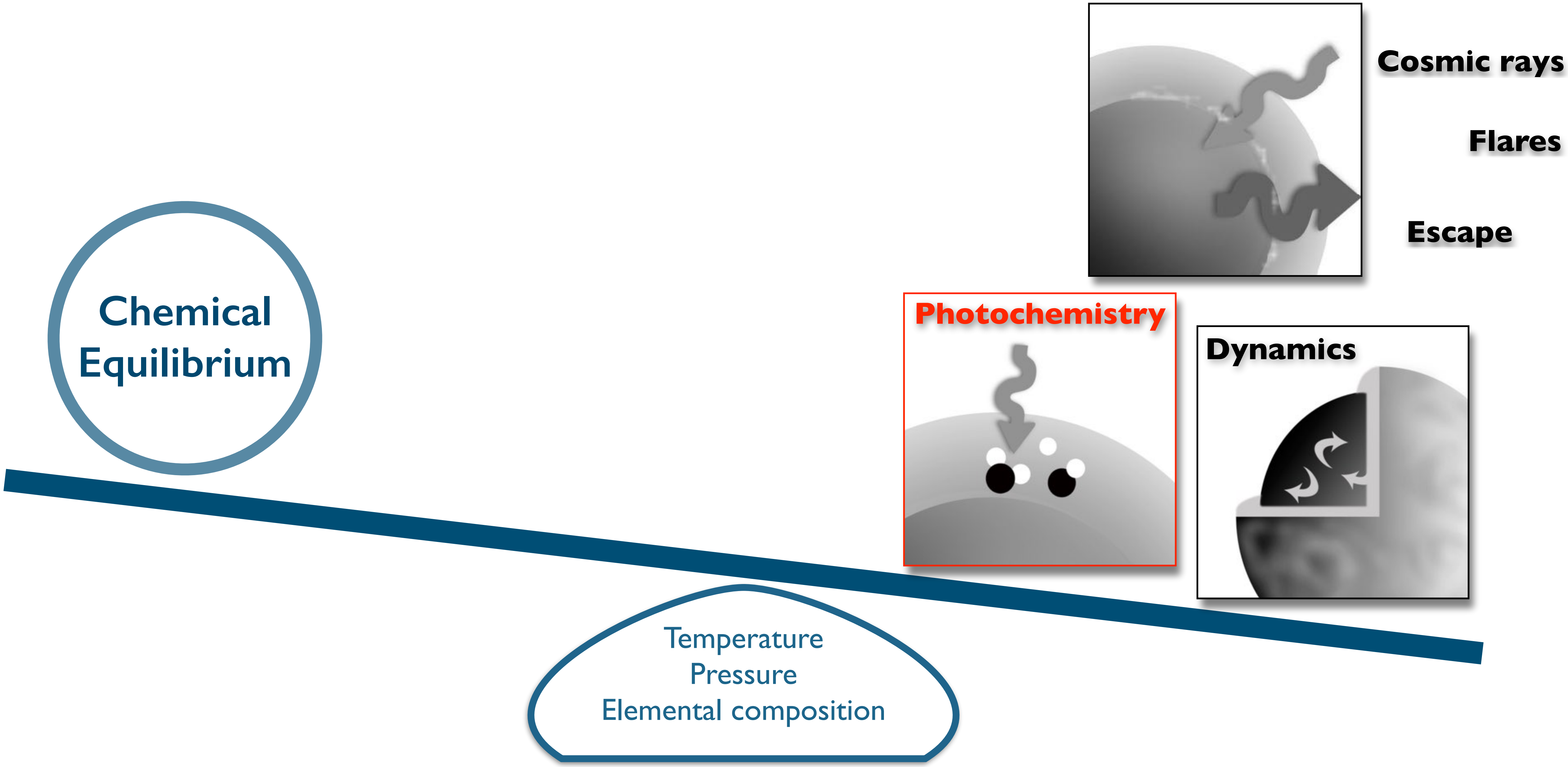
Dynamics

Chemical Equilibrium

Temperature
Pressure
Elemental composition

Chemical disequilibrium

How to explain the deviations from chemical composition observed in planetary atmospheres?



Cosmic rays

Flares

Escape

Chemical Equilibrium

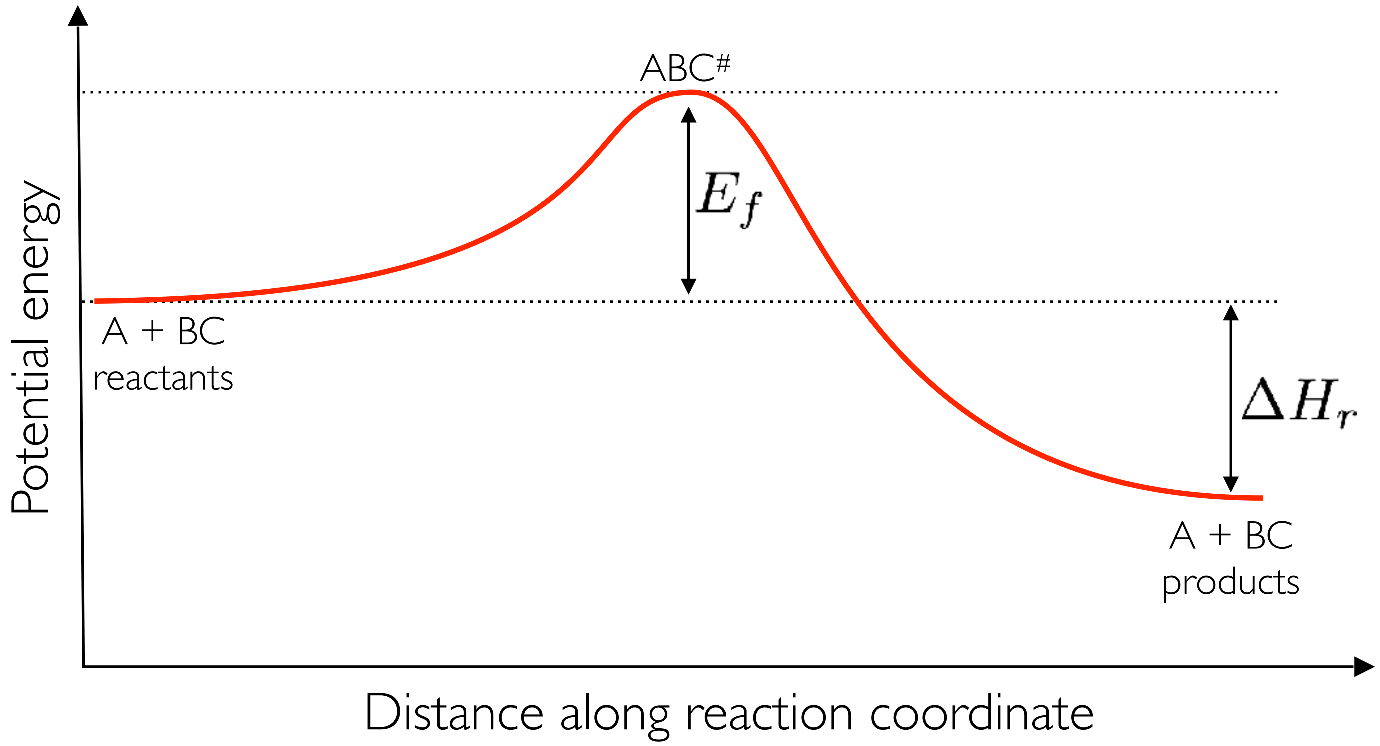
Photochemistry

Dynamics

Temperature
Pressure
Elemental composition

Thermodynamics

Can a reaction occur ?



$\Delta H_r > 0$ Endothermic reaction

$\Delta H_r < 0$ Exothermic reaction

$\Delta G_r = \Delta H_r - T\Delta S_r < 0$ for spontaneous reaction

Thermodynamics

How fast does a reaction occur ?

General form : aA + bB → cC + dD

Rate : $-\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[D]}{\mathrm{d}t}$ (molecule cm^{-3} s^{-1})

Elementary reactions

Unimolecular : 1 molecule falls apart

A → products

Rate : $-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]$

Rate constant unit : s^{-1}

Bimolecular : 2 molecules collide and react

A + B → C + D

Rate : $-\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{\mathrm{d}[D]}{\mathrm{d}t} = k[A][B]$

Rate constant unit : cm^3 $\mathrm{molecule}^{-1}$ s^{-1}

Termolecular : 3 molecules collide "simultaneously" and react

A + B + M → AB + M

Rate : $-\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{\mathrm{d}[AB]}{\mathrm{d}t} = k[A][B][M]$

Rate constant unit : cm^6 $\mathrm{molecule}^{-2}$ s^{-1}

Half-lives and lifetimes

Half-life = ***$t_{1/2}$*** = time for concentration of species to fall to 1/2 present value

Natural lifetime = "lifetime" = ***τ*** = time for concentration of species to fall to 1/e of present value

Note that lifetime of species does not depend on its own concentration

Unimolecular : 1 molecule falls apart

A → products

$$t^A_{1/2} = \frac{-\ln(1/2)}{k} \qquad \tau^A = \frac{1}{k}$$

Bimolecular : 2 molecules collide and react

A + B → C + D

$$t^A_{1/2} = \frac{-\ln(1/2)}{k[B]} \qquad \tau^A = \frac{1}{k[B]}$$

Termolecular : 3 molecules collide "simultaneously" and react

A + B + M → AB + M

$$t^A_{1/2} = \frac{-\ln(1/2)}{k[B][M]} \qquad \tau^A = \frac{1}{k[B][M]}$$

Half-lives and lifetimes

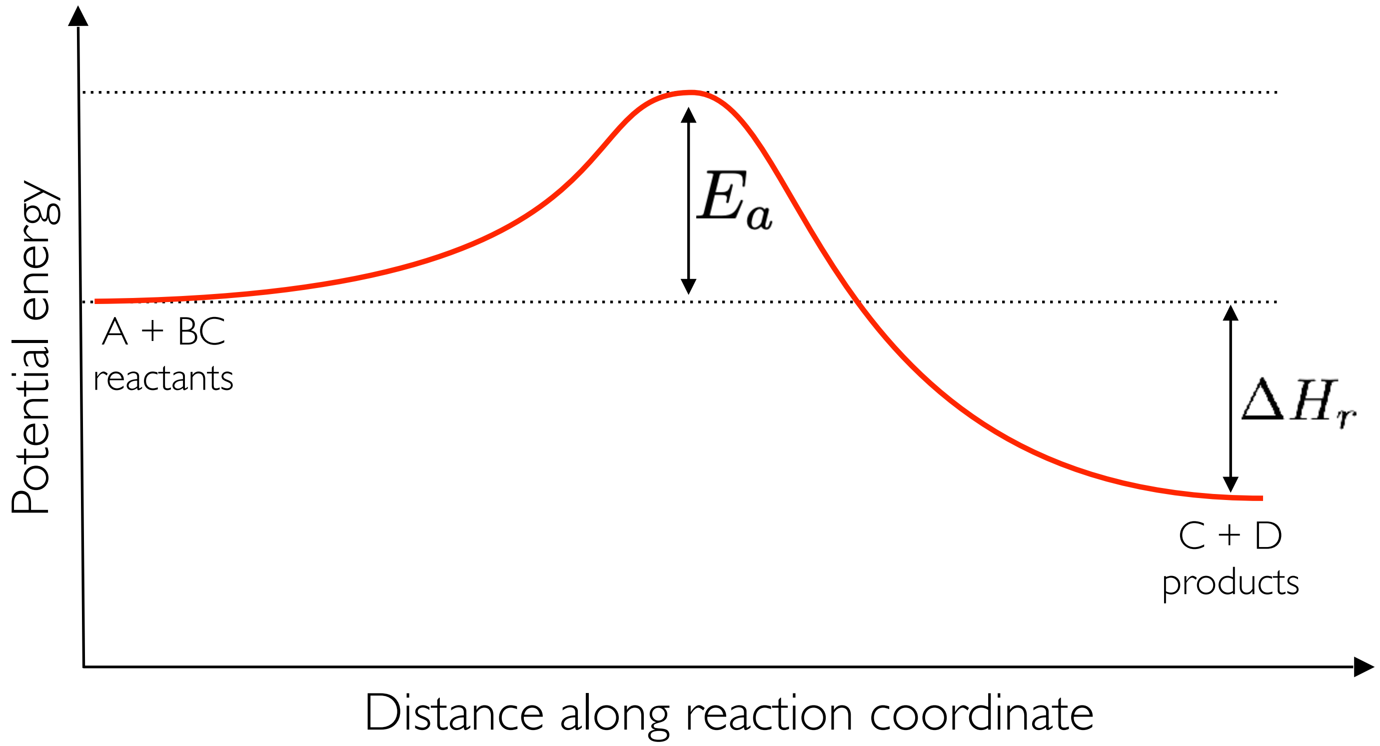
Old CFC = CFC-11 = $CFCl_3$
New(ish) HCFC = HCFC-21 = $CHFCl_2$

Assumptions:
(1) Lifetimes determined by reaction with hydroxyl radical (OH)
(2) Typical concentration of OH in troposphere : $[OH] \sim 1 \times 10^{6}$ molecule cm^{-3}
(3) Rate coefficients at room temperature :
$k_{CFC\text{-}11} < 5.0 \times 10^{-18}$ cm^{3} molecule^{-1} s^{-1} and $k_{HCFC\text{-}21} = 2.5 \times 10^{-14}$ cm^{3} molecule^{-1} s^{-1}

Lifetimes :
$\tau_{CFC\text{-}11} = 1 / k[OH] = 1 / (5.0\times10^{-18} \times 10^{6}) = 2\times10^{11}$ s = 6340 years
$\tau_{HCFC\text{-}21} = 1 / k[OH] = 1 / (2.5\times10^{-14} \times 10^{6}) = 4\times10^{7}$ s = 1.2 years

Collision theory

$$A + B \underset{k_r}{\overset{kf}{\rightleftarrows}} C + D$$



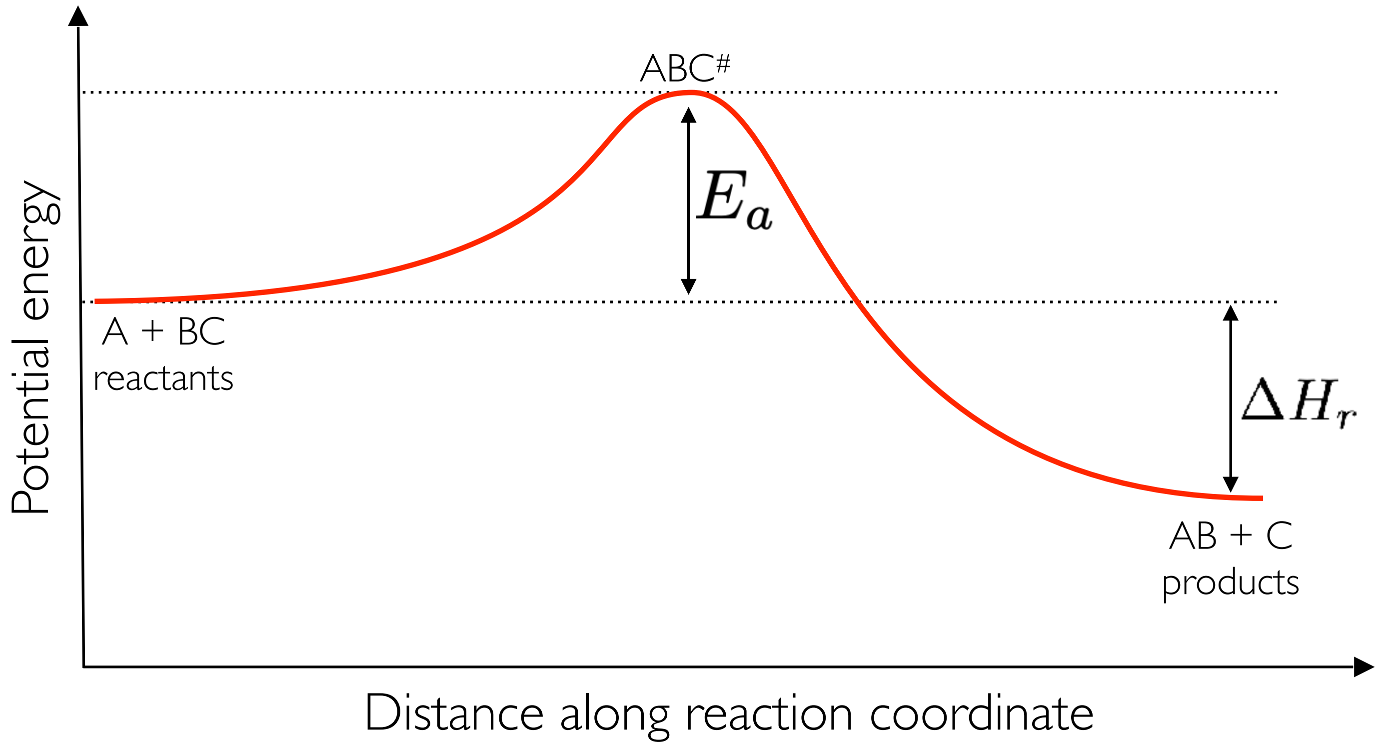
$$Z = \rho_{N_\mathrm{A}} \rho_{N_\mathrm{B}} \sigma_\mathrm{col} \sqrt{\frac{8 k_\mathrm{B} T}{\pi \mu_\mathrm{AB}}}$$

$$\sigma_\mathrm{col} = \pi \left(r_\mathrm{A} + r_\mathrm{B} \right)^2$$

$$k = Z \exp\left(-\frac{E_\mathrm{a}}{RT} \right)$$

Transition State Theory

$$A + BC \underset{k_r}{\overset{kf}{\rightleftarrows}} ABC^{\#} \xrightarrow{k_p} AB + C$$

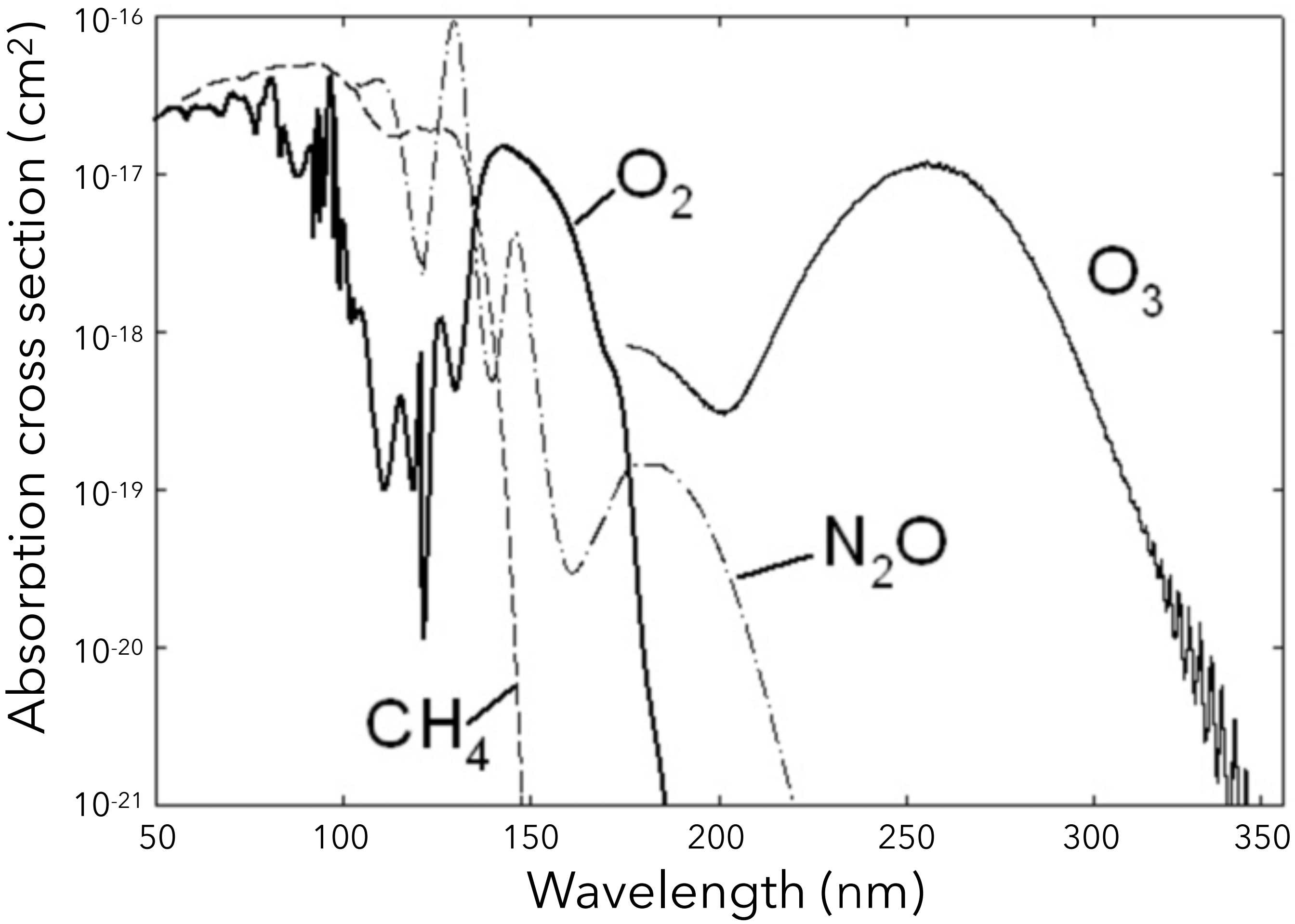


$$K_{eq} = \frac{k_f}{k_r} = \frac{[ABC^{\#}]}{[A][BC]} \qquad K_{eq} = \mathrm{e}^{-\frac{\Delta G^{\#}}{RT}} = \mathrm{e}^{\frac{\Delta S^{\#}}{R}} \mathrm{e}^{-\frac{\Delta H^{\#}}{RT}}$$

$$k = \frac{k_B T}{h} K_{eq} = \frac{k_B T}{h} \mathrm{e}^{-\frac{\Delta G^{\#}}{RT}} = \frac{k_B T}{h} \mathrm{e}^{\frac{\Delta S^{\#}}{R}} \mathrm{e}^{-\frac{\Delta H^{\#}}{RT}}$$

Photoabsorption cross sections

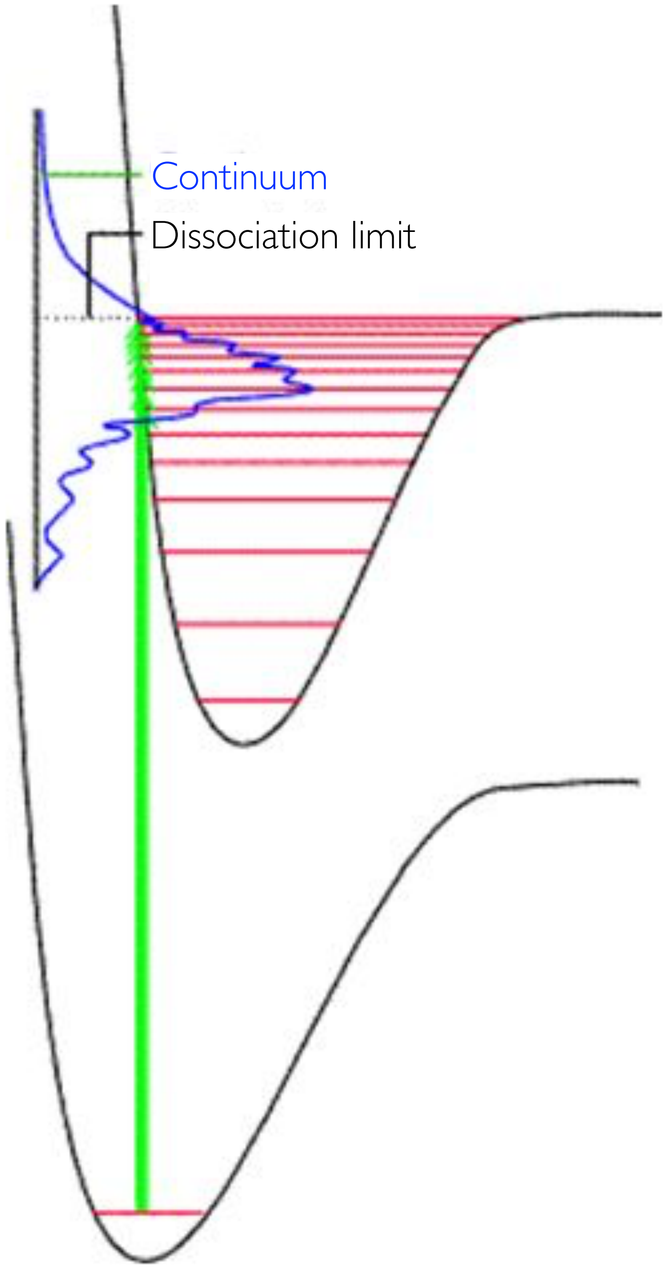
Effective area of the molecule that a photon needs to traverse in order to be absorbed.
The larger the absorption cross section, the easier it is to photoexcite the molecule.



$$d\tau_\nu = \sigma_\nu \rho_N dz$$

Absorption cross section [L^2]

Photodissociation



Species	Dissociation energy threshold (eV)	Dissociation wavelength threshold (nm)
CO	11.11	111.6
N_2	9.76	127.0
CO_2	5.46	227.0
O_2	5.12	242.1
H_2O	5.12	242.1
H_2	4.48	276.7
CH_4	4.45	278.5
NH_3	3.9	317.8

Photodissociation rates

A + hν → B + C

Rate : $-\frac{\mathrm{d}[A]}{\mathrm{d}t} = \frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{\mathrm{d}[C]}{\mathrm{d}t} = J_A[A]$ (molecule cm^{-3} s^{-1})

$$J_A = \int_\lambda \sigma_A(\lambda)\phi_A(\lambda)F(\lambda)d\lambda$$ Photolysis rate (s^{-1})

$\sigma_A(\lambda)$ – wavelength-dependent cross section of A (cm^2 molecule^{-1})

$\Phi_A(\lambda)$ – wavelength-dependent quantum yield for photolysis

$F(\lambda)$ – spectral actinic flux density (photons cm^{-2} s^{-1})

$$t^A_{1/2} = \frac{-\ln(1/2)}{J_A} \qquad \tau^A = \frac{1}{J_A}$$

Photodissociation rates

$$A + h\nu \rightarrow B + C$$

$$\text{Rate}: -\frac{\mathrm{d}[A]}{\mathrm{d}t} = \frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{\mathrm{d}[C]}{\mathrm{d}t} = J_A[A] \;\; (\text{molecule cm}^{-3}\ \text{s}^{-1})$$

$$J_A = \int_\lambda \sigma_A(\lambda)\phi_A(\lambda)F(\lambda)d\lambda \qquad \text{Photolysis rate } (\text{s}^{-1})$$

$\sigma_A(\lambda)$ – wavelength-dependent cross section of A ($\text{cm}^2\ \text{molecule}^{-1}$)

$$\Phi_A(\lambda) - \frac{\text{Number of excited molecules proceeding by pathway } i}{\text{Total number of photons absorbed}}$$

E.g. :

$$\overset{h\nu}{NO_3} \rightarrow NO_3^* \rightarrow NO_2 + O$$
$$\rightarrow NO + O_2$$
$$\rightarrow NO_3 \ h\nu$$

$$\sum_i \Phi_{A_i}(\lambda) = 1$$

Important chemical cycles (for terrestrial planets)

Ozone cycle

Photodissociation :	$\overset{h\nu}{O_2} \rightarrow O + O$ ($\lambda < 240$ nm)	J_1
Recombination :	$O + O_2 + M \rightarrow O_3 + M$	k_1
Photodissociation :	$\overset{h\nu}{O_3} \rightarrow O_2 + O$ ($\lambda < 1100$ nm)	J_2
Recombination :	$O + O_3 \rightarrow O_2 + O_2$	k_2

$$\frac{\mathrm{d[O]}}{\mathrm{d}t} = 2J_1(z)[\mathrm{O_2}] + J_2(z)[\mathrm{O_3}] - k_1[\mathrm{O}][\mathrm{O_2}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}]$$

$$\frac{\mathrm{d[O_3]}}{\mathrm{d}t} = k_1[\mathrm{O}][\mathrm{O_2}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}] - J_2(z)[\mathrm{O_3}]$$

$$[\mathrm{O}] = \frac{2J_1(z)\,[\mathrm{O_2}] + J_2(z)\,[\mathrm{O_3}]}{k_2\,[\mathrm{O_3}]} \qquad [\mathrm{O_3}] = \frac{k_1[\mathrm{O}]\,[\mathrm{O_2}]\,[\mathrm{M}]}{k_2[\mathrm{O}] + J_2(z)}$$

- Ozone (O_3) formation usually mediated by aerosols (Mars)
- Spatial distribution of ozone on Earth due to dynamics.

CO cycle

Photodissociation :

$\overset{h\nu}{CO_2} \rightarrow CO + O$ ($\lambda < 169$ nm)

Recombination :

$\cancel{CO + O + M \rightarrow CO_2 + M}$ (spin-forbidden)

$O + O + M \rightarrow O_2 + M$

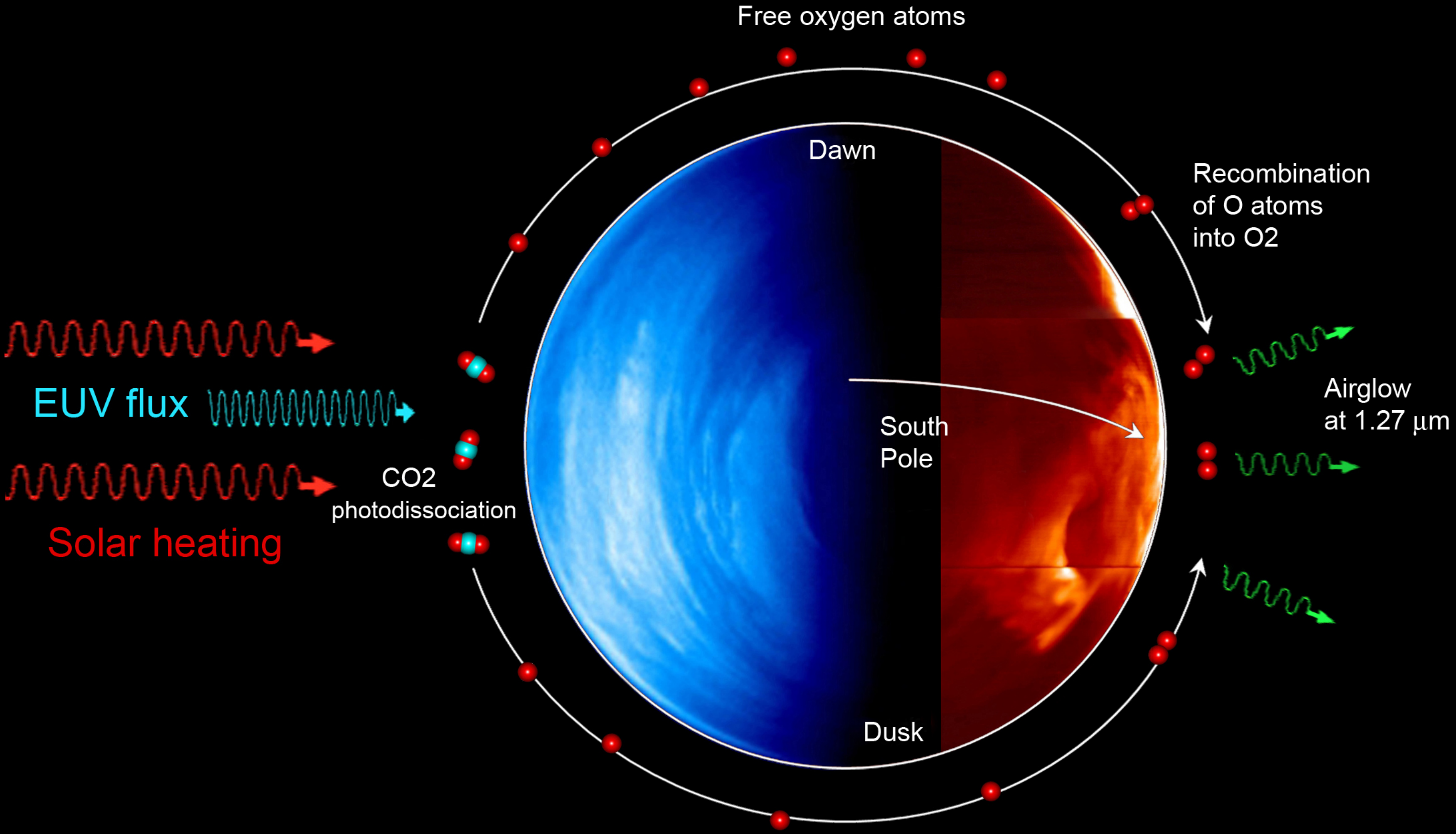
$2CO_2 \rightarrow 2CO + O_2$

Disagreement with the observed
low abundances of CO and O_2

\+

CO$_2$ stability problem

Venus



Free oxygen atoms

Dawn

Recombination
of O atoms
into O2

EUV flux

Solar heating

CO2
photodissociation

South
Pole

Airglow
at 1.27 µm

Dusk

Credits : ESA/VIRTIS/INAF-IASF/Obs. de Paris-LESIA/Universidad del País Vasco

CO cycle

$h\nu$

Photodissociation : $CO_2 \rightarrow CO + O$ ($\lambda < 169$ nm)

Recombination : ~~$CO + O + M \rightarrow CO_2 + M$~~ (spin-forbidden)

$O + O + M \rightarrow O_2 + M$

$h\nu$

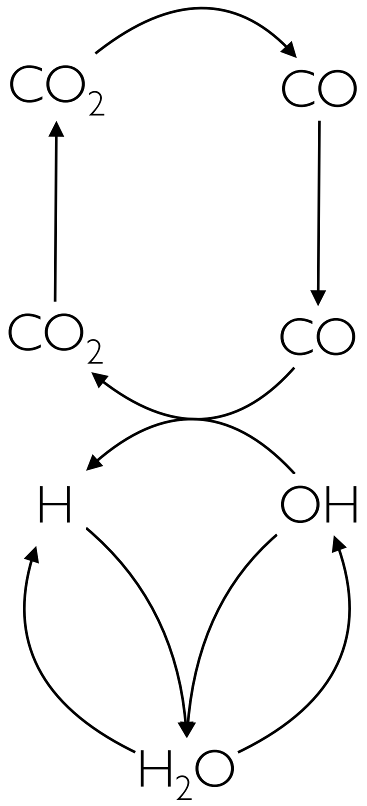
Photodissociation : $O_2 \rightarrow O + O$ ($\lambda < 240$ nm)

$h\nu$

$H_2O \rightarrow OH + H$ ($\lambda < 210$ nm)

Recombination : $OH + H + M \rightarrow H_2O + M$

Oxidation : $CO + OH \rightarrow CO_2 + H$



Fundamental role of H_2O, even at low abundances

- If H_2O is present, this limits the amount of CO (almost non-existent on Earth)
- Mars and Venus have a lot less H_2O than Earth, and a lot more CO (though still small compared to CO_2)
- Spatial distribution of CO gives info on dynamics.

CO cycle on Mars

$h\nu$

Photodissociation : $CO_2 \rightarrow CO + O$ ($\lambda < 169$ nm)

Recombination : ~~$CO + O + M \rightarrow CO_2 + M$~~ (spin-forbidden)

$O + O + M \rightarrow O_2 + M$

$h\nu$

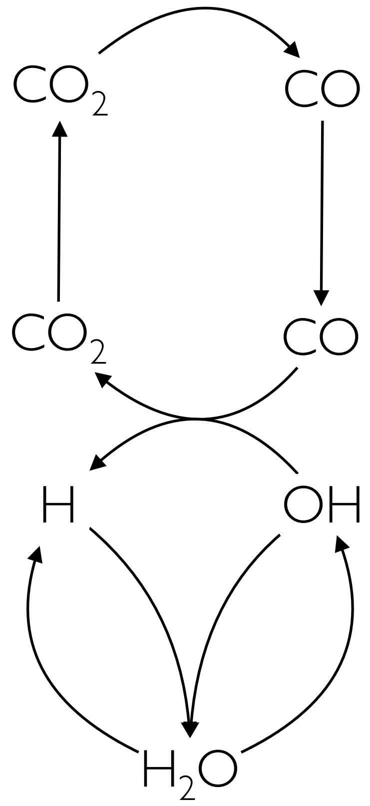
Photodissociation : $O_2 \rightarrow O + O$ ($\lambda < 240$ nm)

$h\nu$

$H_2O \rightarrow OH + H$ ($\lambda < 210$ nm)

Recombination : $OH + H + M \rightarrow H_2O + M$

Oxidation : $CO + OH \rightarrow CO_2 + H$



$$\begin{array}{l} O + O_2 + M \rightarrow O_3 + M \\ H + O_3 \rightarrow OH + O_2 \\ CO + OH \rightarrow CO_2 + H \\ \hline CO + O \rightarrow CO_2 \end{array}$$

$$\begin{array}{l} H + O_2 + M \rightarrow HO_2 + M \\ O + HO_2 \rightarrow OH + O_2 \\ CO + OH \rightarrow CO_2 + H \\ \hline CO + O \rightarrow CO_2 \end{array}$$

$$\begin{array}{l} 2 \times (H + O_2 + M \rightarrow HO_2 + M) \\ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \\ H_2O_2 + h\nu \rightarrow OH + OH \\ 2 \times (CO + OH \rightarrow CO_2 + H) \\ \hline 2CO + O_2 \rightarrow 2CO_2 \end{array}$$

HO_x radicals used as catalysts in the recombination of CO and O

CO cycle on Venus

$h\nu$

Photodissociation : $CO_2 \rightarrow CO + O$ $(\lambda < 169\ \text{nm})$

Recombination : ~~$CO + O + M \rightarrow CO_2 + M$~~ (spin-forbidden)

$O + O + M \rightarrow O_2 + M$

$h\nu$

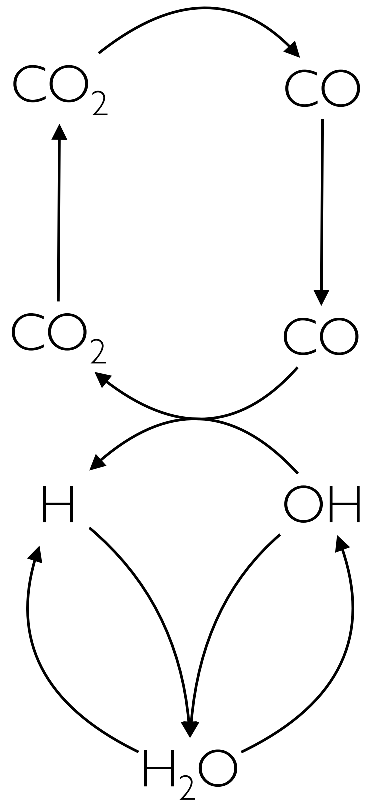
Photodissociation : $O_2 \rightarrow O + O$ $(\lambda < 240\ \text{nm})$

$h\nu$

$H_2O \rightarrow OH + H$ $(\lambda < 210\ \text{nm})$

Recombination : $OH + H + M \rightarrow H_2O + M$

Oxidation : $CO + OH \rightarrow CO_2 + H$



$CO + O + \text{aerosol} \rightarrow CO_2 + \text{aerosol}$

Aerosols used as heterogeneous catalysts

$Cl + CO + M \rightarrow ClCO + M$ (chloroformyl radical)

$ClCO + O_2 + M \rightarrow ClC(O)O_2 + M$ (peroxycholorformyl radical)

$ClC(O)O_2 + O \rightarrow CO_2 + O_2 + Cl$

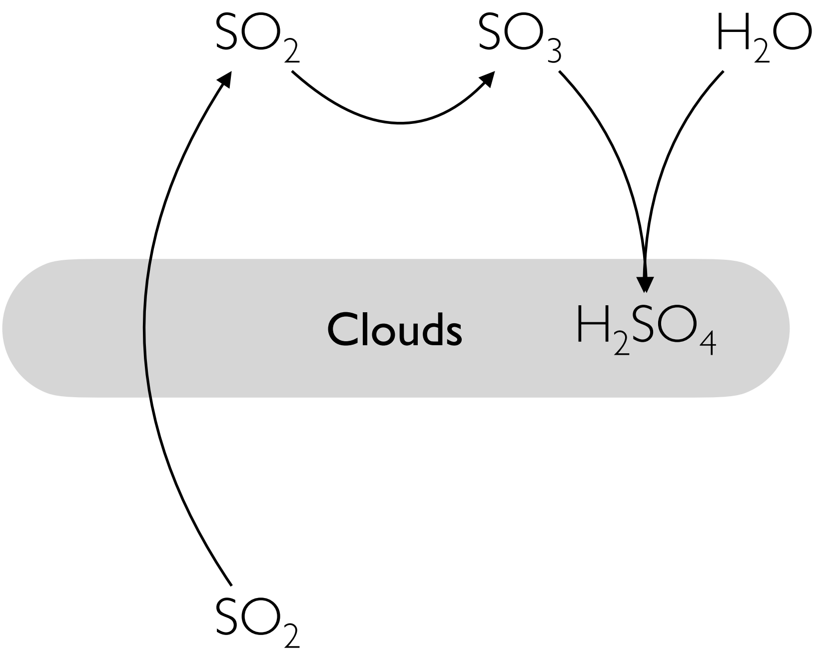
$CO + O \rightarrow CO_2$

Cl radicals used as catalysts in the recombination of CO and O

Sulfur cycle

Oxydation : $SO_2 + O + M \rightarrow SO_3 + M$

Condensation : $SO_3 + H_2O \rightarrow H_2SO_4$ (aerosols)



- Major source of SO_2 is volcanic outgassing
- SO_2 is an important greenhouse gas
- H_2SO_4 aerosols have an anti-greenhouse effect
- Applications : Earth, Venus, early Mars(?)

Sulfur cycle on Venus

$h\nu$

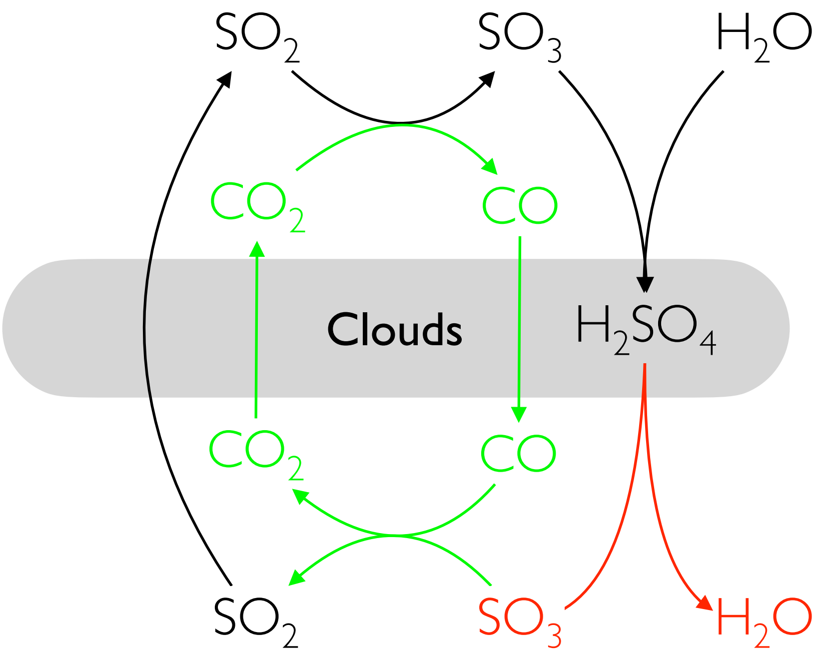
Photodissociation : $CO_2 \rightarrow CO + O$ ($\lambda < 169$ nm)

Oxydation : $SO_2 + O + M \rightarrow SO_3 + M$

Condensation : $SO_3 + H_2O \rightarrow H_2SO_4$ (aerosols)

Recycling : $H_2SO_4 \rightarrow SO_3 + H_2O$

$SO_3 + CO \rightarrow SO_2 + CO_2$



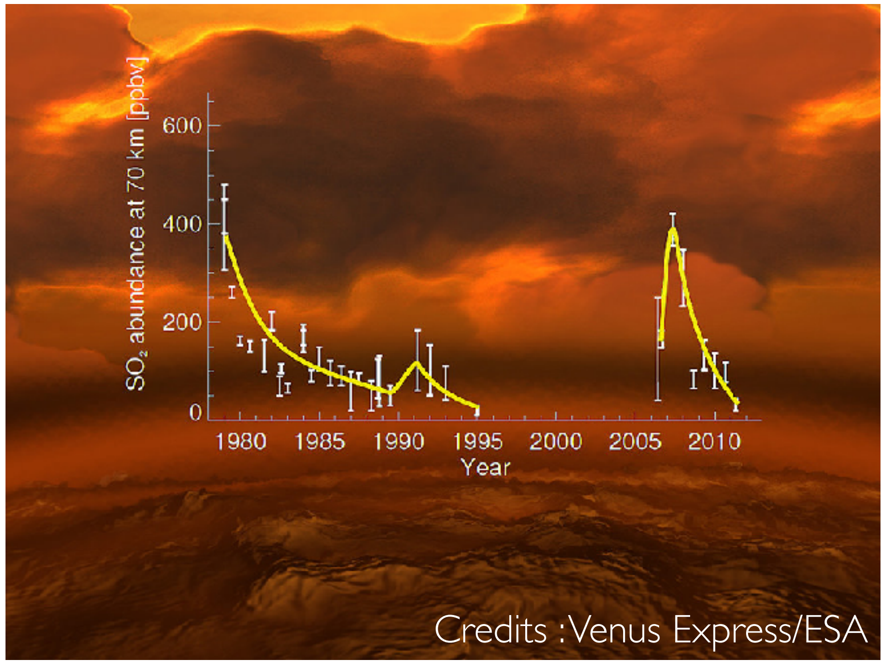
SO_2 SO_3 H_2O

CO_2 CO

Clouds H_2SO_4

CO_2 CO

SO_2 SO_3 H_2O



Credits : Venus Express/ESA