

# Clouds and haze on exoplanets and brown dwarfs



© Manchu & Fossé

Benjamin Charnay

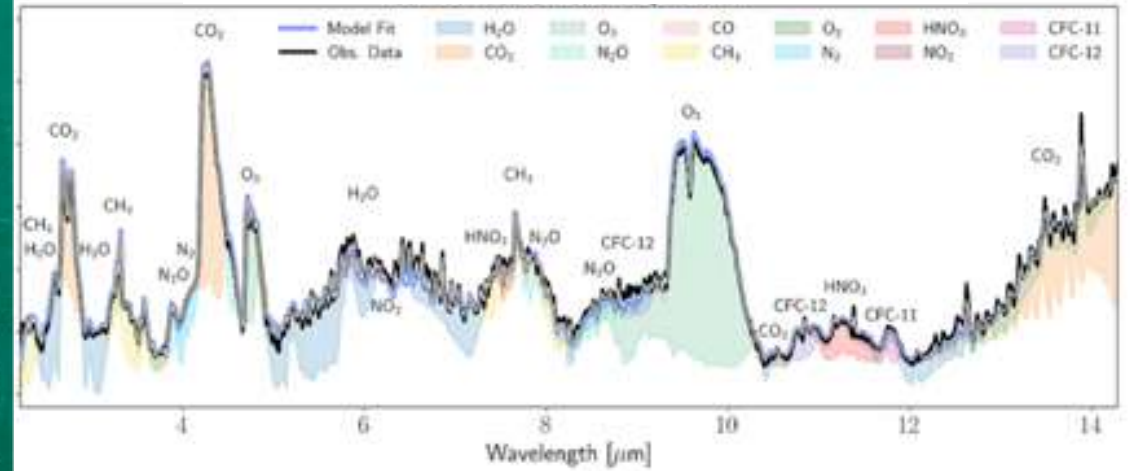
Ariel School, 2023, Biarritz

# Cycle 3 proposal deadline: October 25, 2023

I have a great idea for a JWST proposal: detecting  $\text{N}_2\text{O}$  and DMS as hints for life on Trappist-1 e !!!



Trappist-1 e transmission spectrum



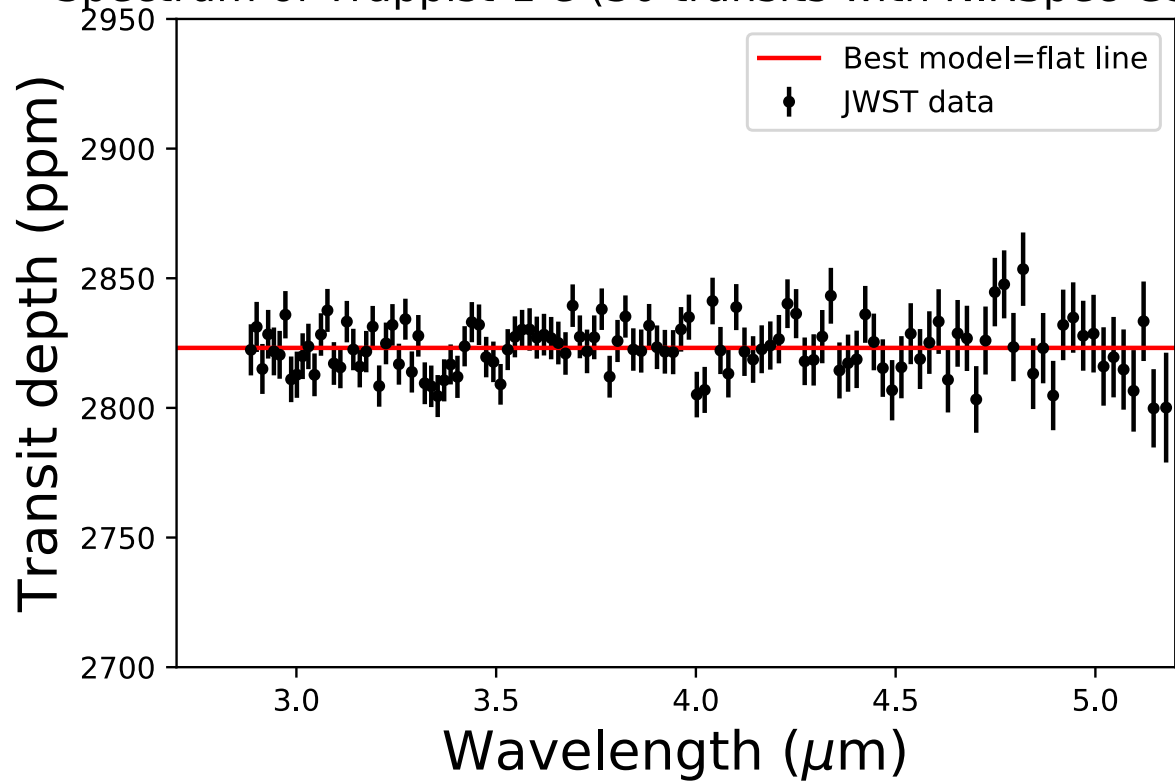
My JWST  
proposal is accepted !!!



I received the JWST data  
!!!



Spectrum of Trappist-1 e (30 transits with NIRSpec-G395M)



**Lesson from observations: most of exoplanets are cloudy or hazy**



# Clouds/haze impact on exoplanetary atmospheres

- Atmospheric composition/chemistry
- Radiative transfert (scattering & absorption)
- Atmospheric dynamics
- Temperature and climate

➔ **Atmospheric retrieval**



**Clouds seen by astronomers**



**Clouds seen by atmospheric scientists**

# Aerosols in exoplanetary atmospheres: clouds or haze

## Condensate clouds

(thermodynamic phase change)



## Haze

(non-equilibrium chemistry)





Clouds/haze are everywhere












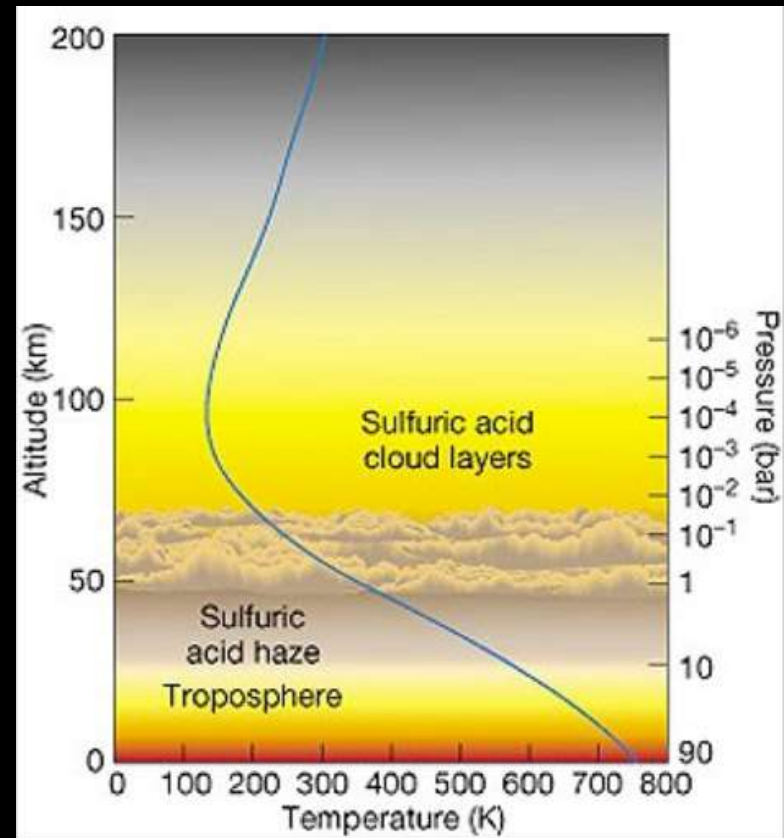
	 <b>Clouds</b>	 <b>Haze</b>
 <b>Venus</b>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub> and other heavier photochemical products like S <sub>8</sub> (?)
 <b>Earth</b>	H <sub>2</sub> O	Smog
 <b>Mars</b>	H <sub>2</sub> O, CO <sub>2</sub>	No haze (but lots of dust)
 <b>Jupiter</b>  <b>Saturn</b>	H <sub>2</sub> O, NH <sub>3</sub> , NH <sub>4</sub> SH	Forms from NH <sub>3</sub> , CH <sub>4</sub> , H <sub>2</sub> S, etc. photochemistry
 <b>Titan</b>	CH <sub>4</sub> , HCN, C <sub>4</sub> N <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , other organics	Forms from CH <sub>4</sub> , N <sub>2</sub> , CO, etc. photochemistry
 <b>Uranus</b>  <b>Neptune</b>	H <sub>2</sub> O, NH <sub>3</sub> , NH <sub>4</sub> SH CH <sub>4</sub> , H <sub>2</sub> S	Forms from NH <sub>3</sub> , CH <sub>4</sub> , H <sub>2</sub> S, etc. photochemistry
 <b>Triton</b>	N <sub>2</sub>	Forms from CH <sub>4</sub> , N <sub>2</sub> , CO, etc. photochemistry
 <b>Pluto</b>	N <sub>2</sub>	Forms from CH <sub>4</sub> , N <sub>2</sub> , CO, etc. photochemistry
 <b>Exoplanets</b>	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O alkali metals, iron, silicates, other, etc.	Yes. All the possible kinds.

Figure from Sarah Hörst

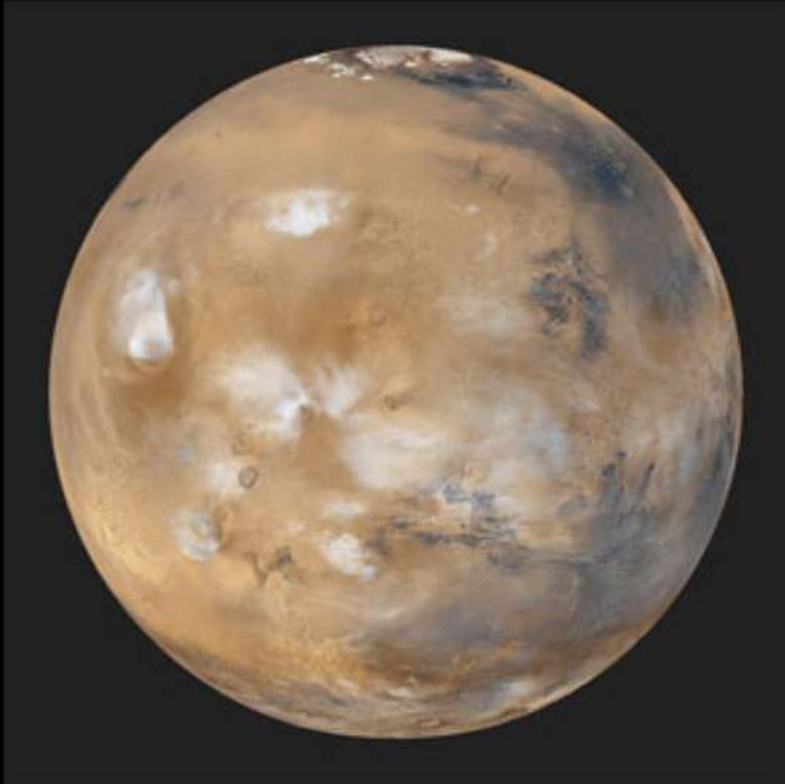
# Venus ( $\text{H}_2\text{SO}_4$ )



[Pioneer Venus, 1979]

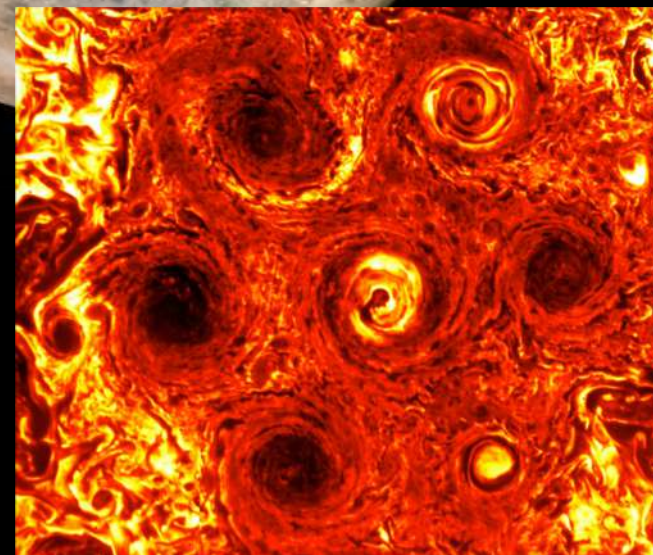
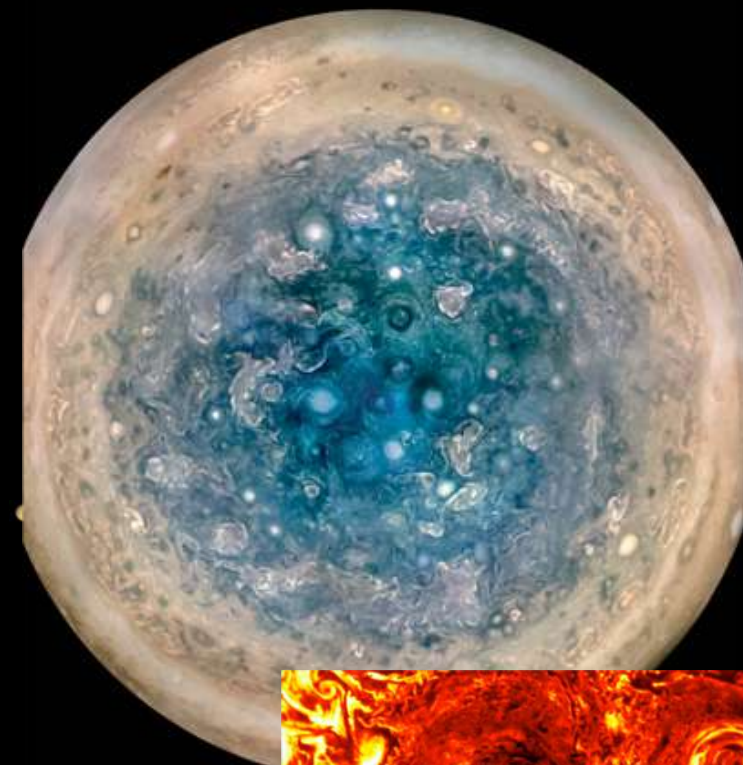


# Mars (H<sub>2</sub>O and CO<sub>2</sub>)



CO<sub>2</sub> clouds from Curiosity

# Jupiter (NH<sub>3</sub>, NH<sub>4</sub>SH, H<sub>2</sub>O, Photochemical haze)



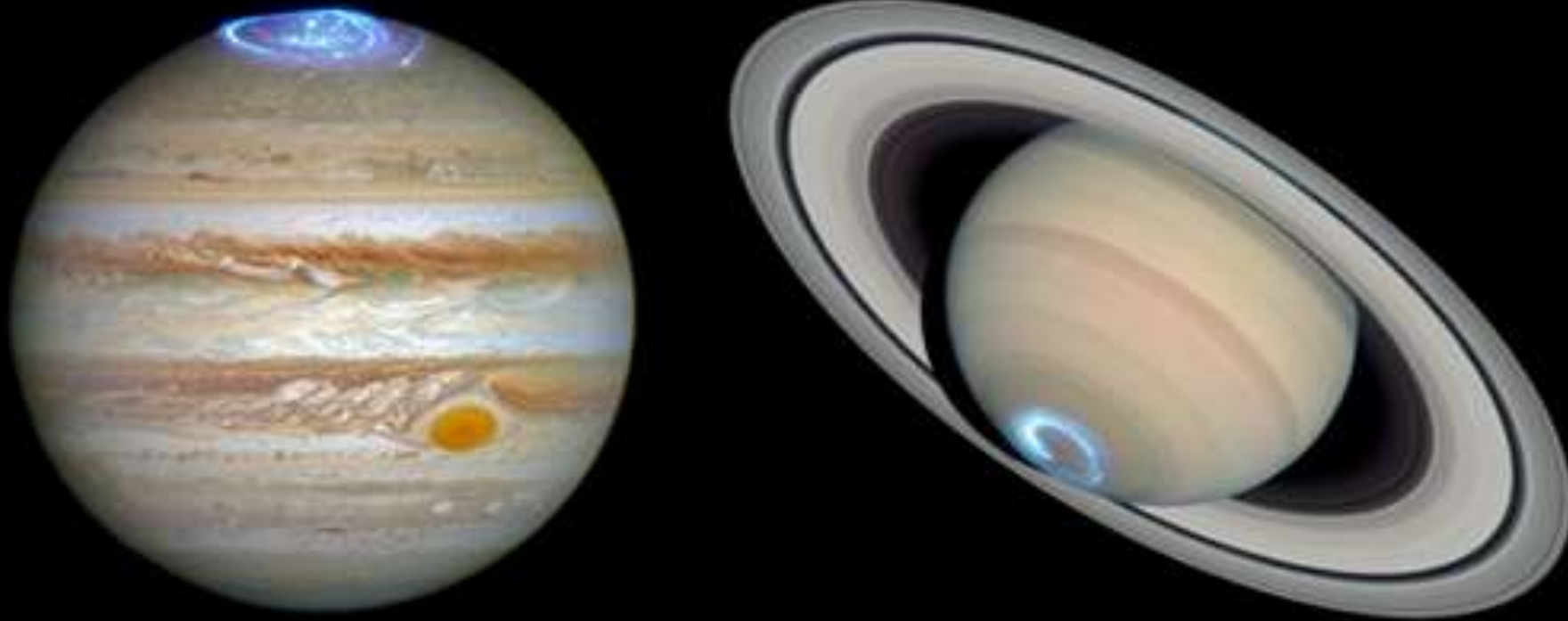
[Adriani et al. Nature 2018]

Saturn ( $\text{NH}_3$ ,  $\text{NH}_4\text{SH}$ ,  $\text{H}_2\text{O}$ , Photochemical haze)



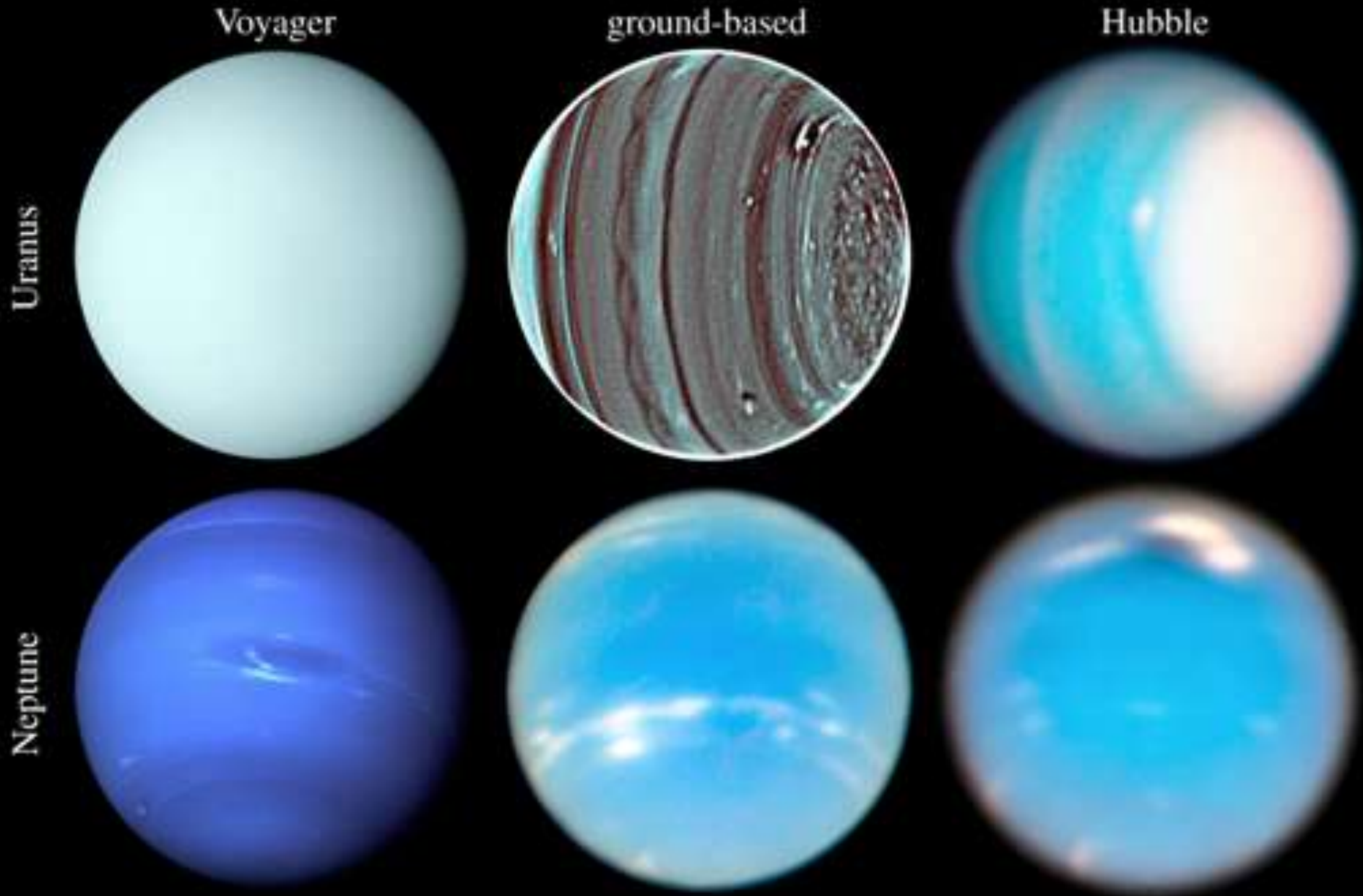
[Image Cassini-Huygens PIA14905]

# Aurorae on Jupiter & Saturn



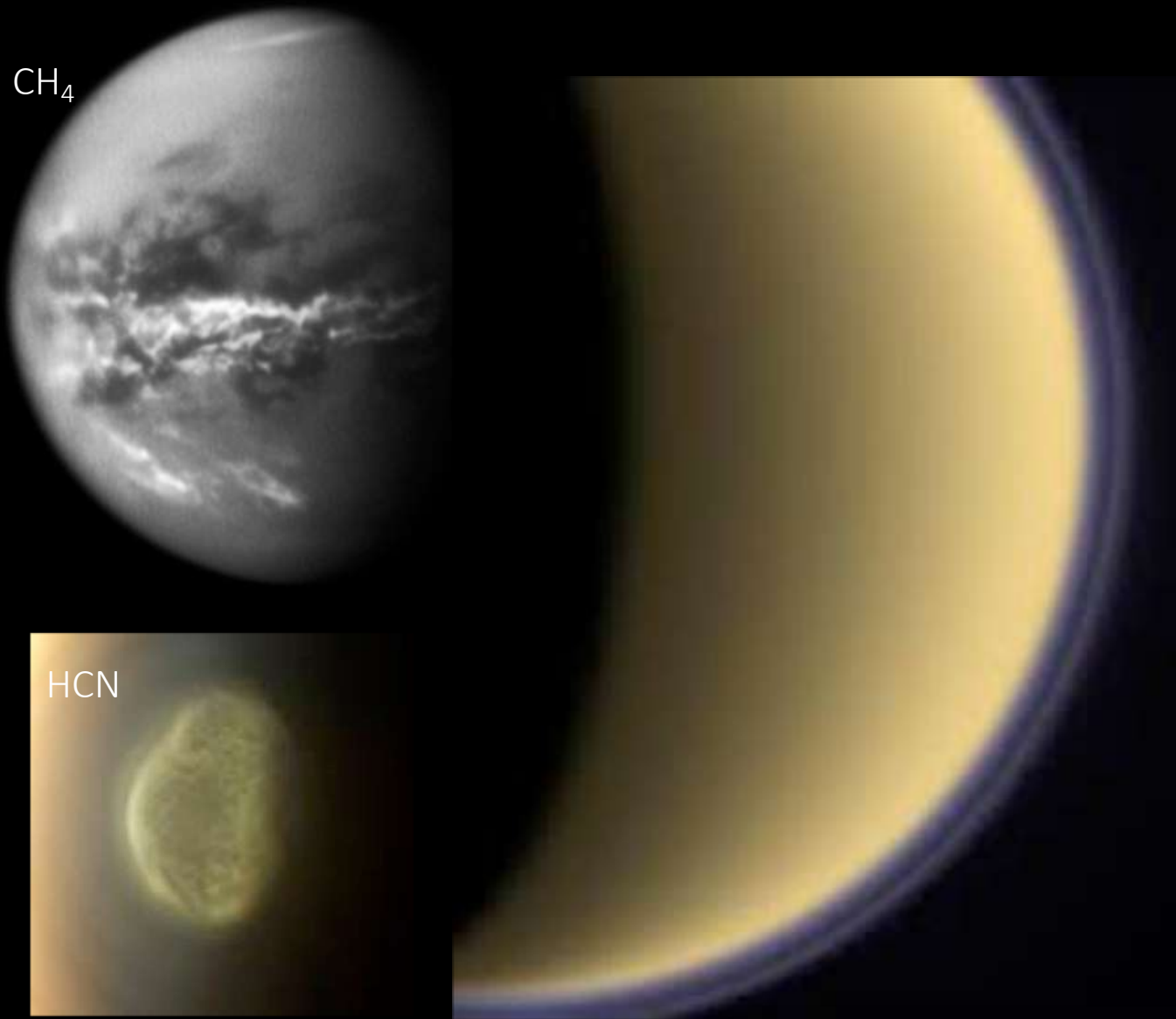
Auroral chemistry and hazes on Jupiter and Saturn

Ice giants: Uranus & Neptune ( $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{NH}_4\text{S}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ )

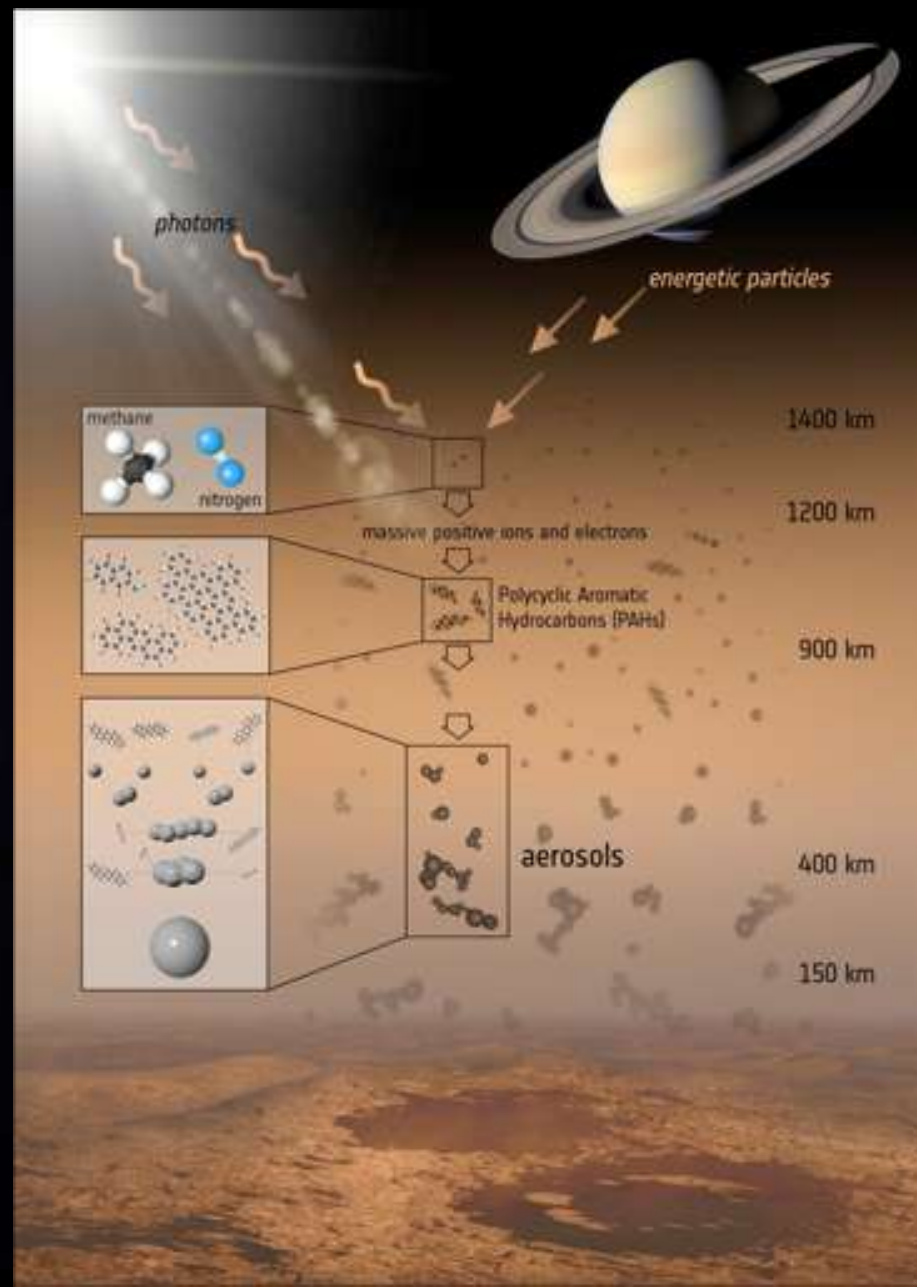


# Titan ( $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , HCN, photochemical haze)

$\text{CH}_4$

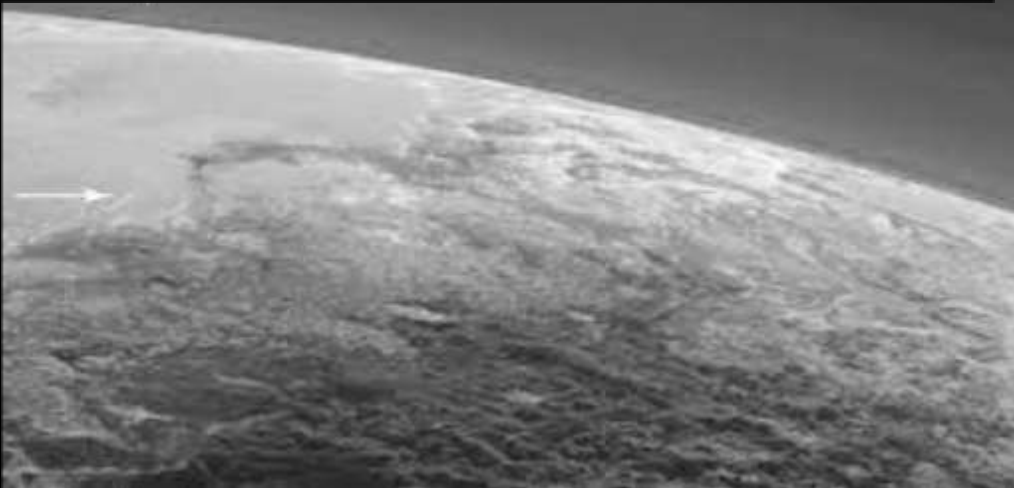


HCN



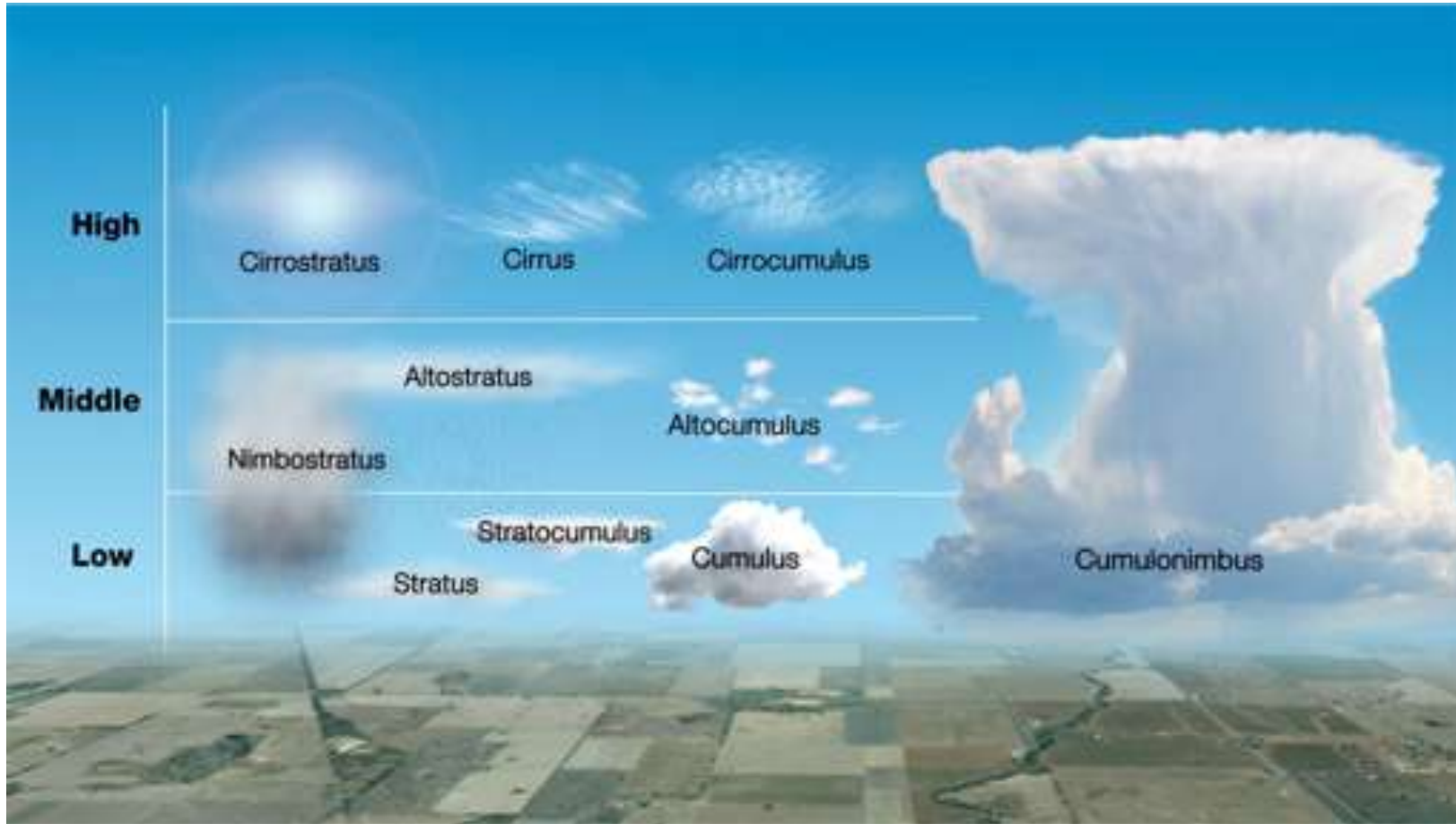


# Pluto (N<sub>2</sub>, photochemical haze)





# International Cloud Atlas



Luke Howard (1772-1864)

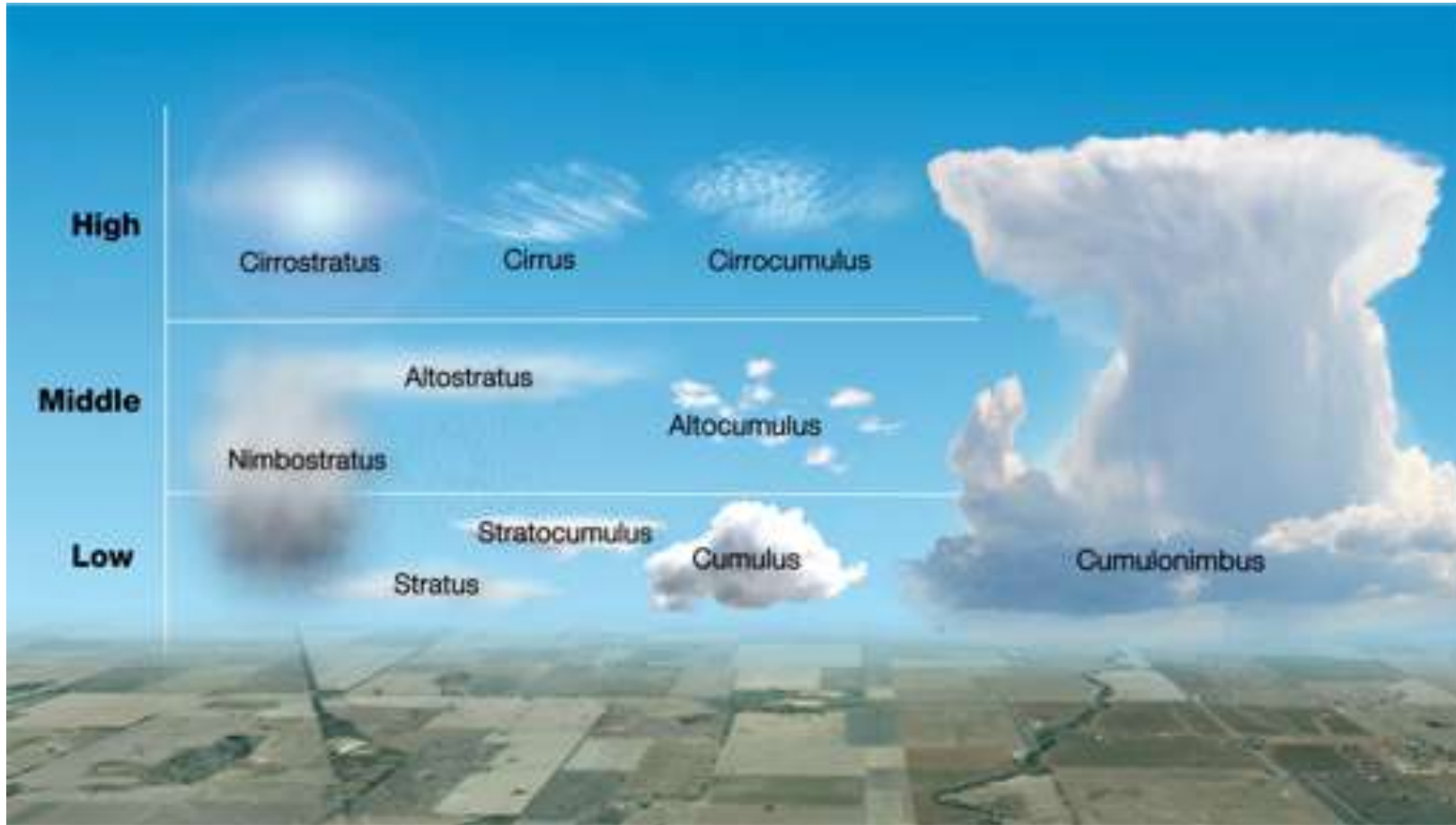
*Essay on the Modification of Clouds*



Main clouds are a combination of the following prefixes and suffixes:

- **Stratus/strato**: flat/layered and smooth
- **Cumulus/cumulo**: heaped up/puffy, like cauliflower
- **Cirrus/cirro**: high up/wispy
- **Alto**: medium level
- **Nimbus/Nimbo**: rain-bearing cloud

# International Cloud Atlas



« To be on cloud nine »



Main clouds are a combination of the following prefixes and suffixes:

- **Stratus/strato**: flat/layered and smooth
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- **Alto**: medium level
- **Nimbus/Nimbo**: rain-bearing cloud

# Cloud identification



*Cirrus*

# Cloud identification



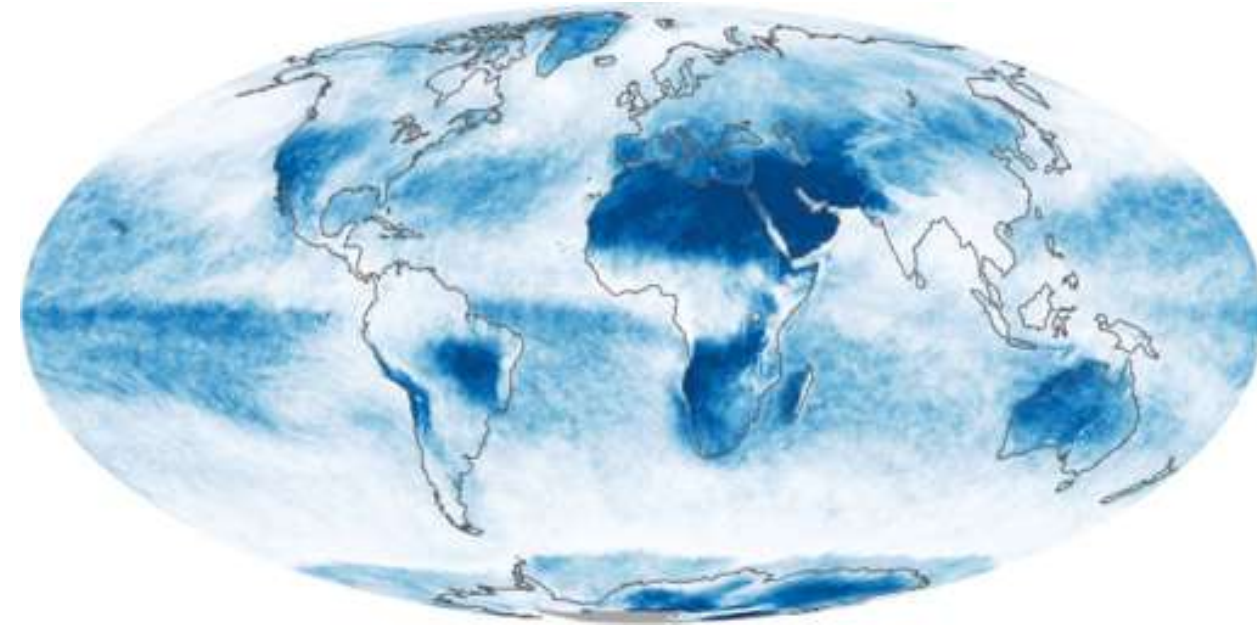
*Cirrocumulus*

# Cloud identification

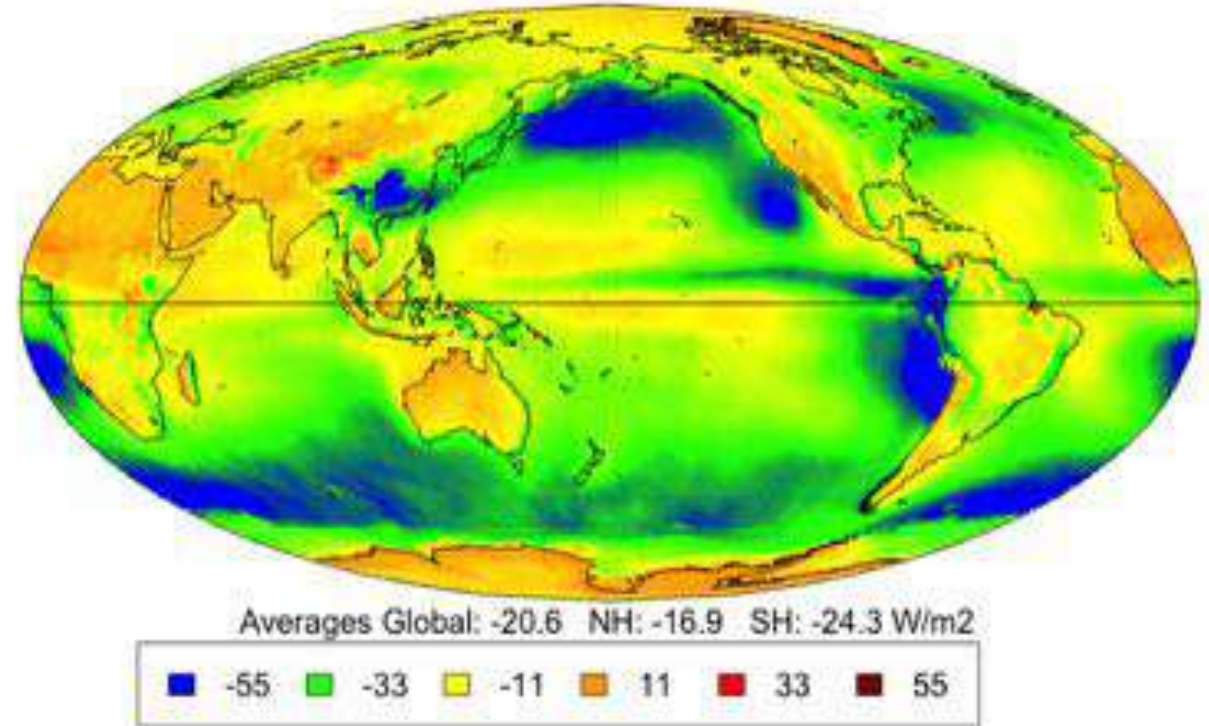


*Nimbostratus*

Map of cloud fraction



Net Cloud Radiative Effect (W/m<sup>2</sup>), CERES dataset



1) Scattering of stellar radiation

→ surface cooling by albedo effect

- Stronger effect for lower clouds (e.g. stratus)

2) Absorption/emission of thermal radiation

→ surface warming by greenhouse effect

- Stronger effect for upper clouds (e.g. cirrus)

Net cloud radiative forcing:

$$CRF = R_{\text{cloudy}} - R_{\text{clear}}$$

$$CRF = (ASR_{\text{cloudy}} - OLR_{\text{cloudy}}) - (ASR_{\text{clear}} - OLR_{\text{clear}})$$

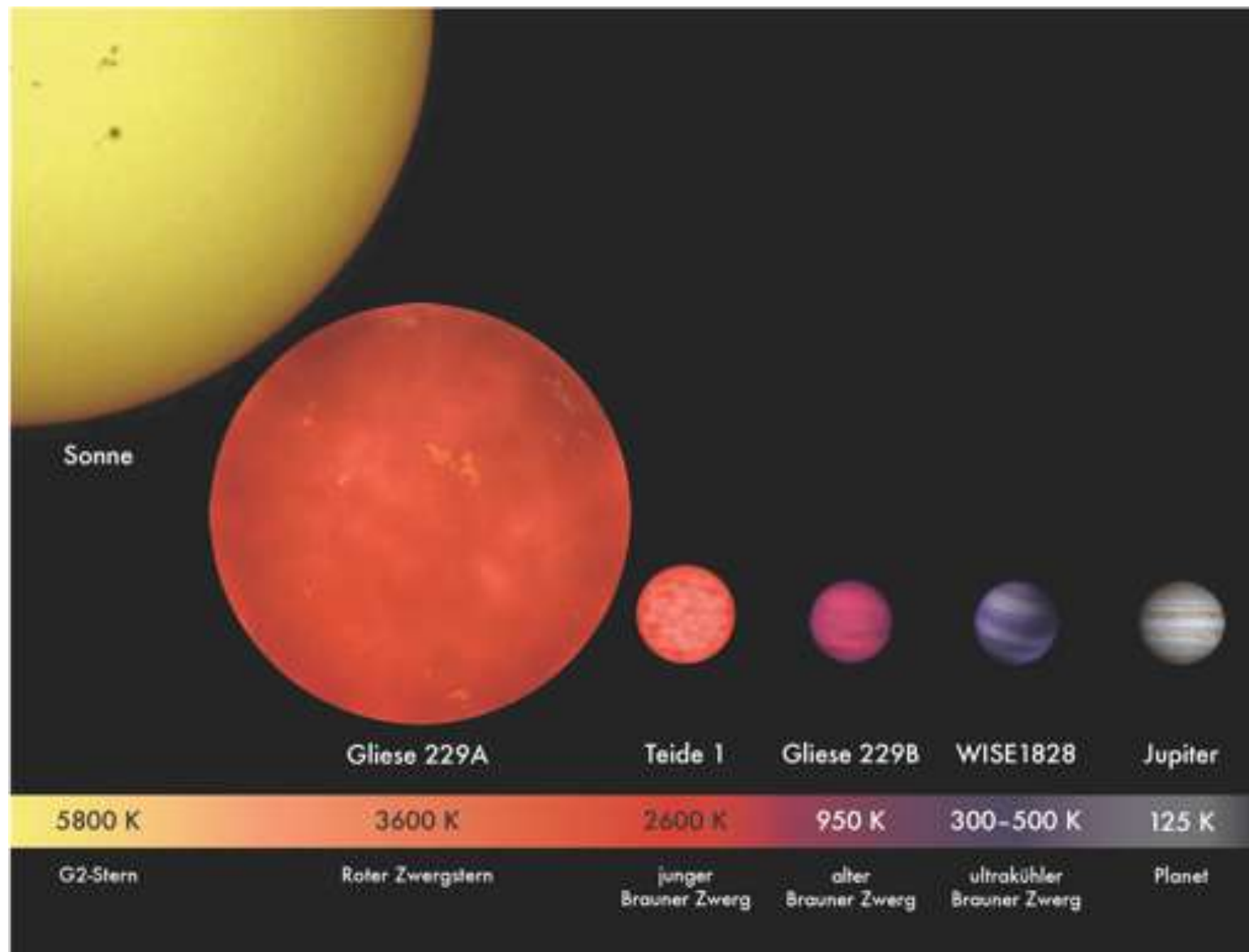
$$CRF = (ASR_{\text{cloudy}} - ASR_{\text{clear}}) + (OLR_{\text{clear}} - OLR_{\text{cloudy}})$$

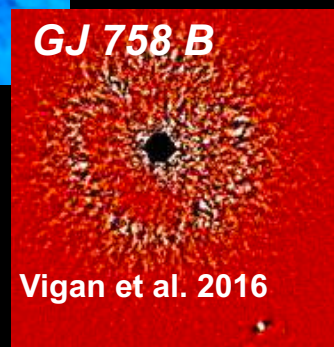
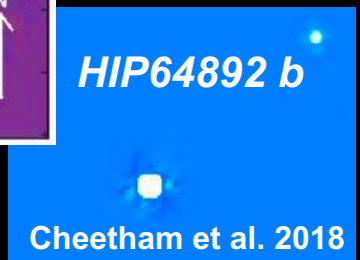
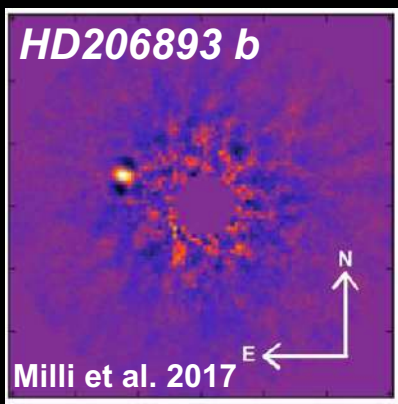
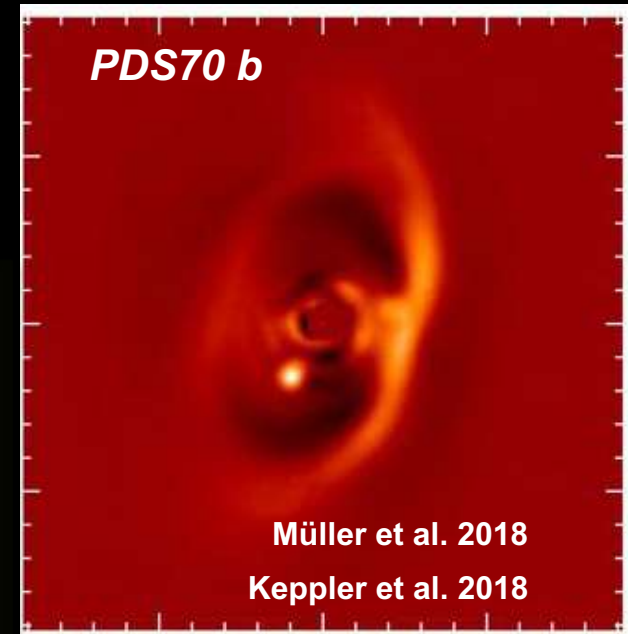
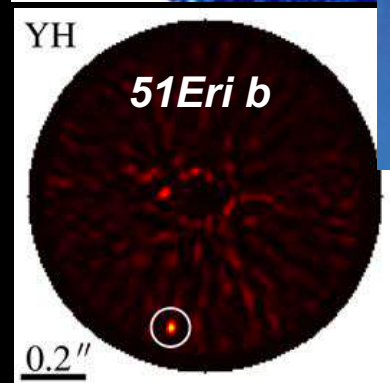
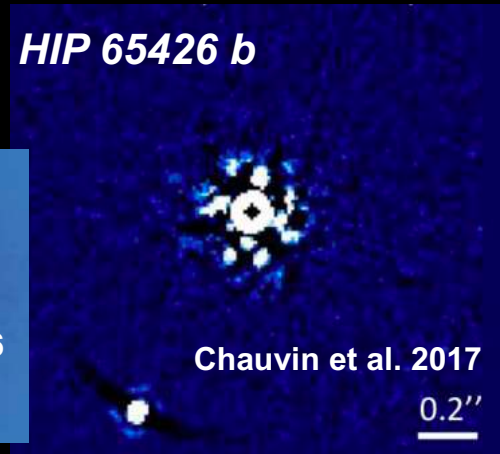
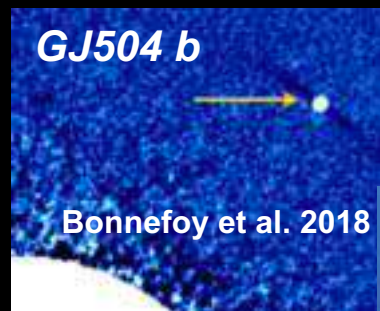
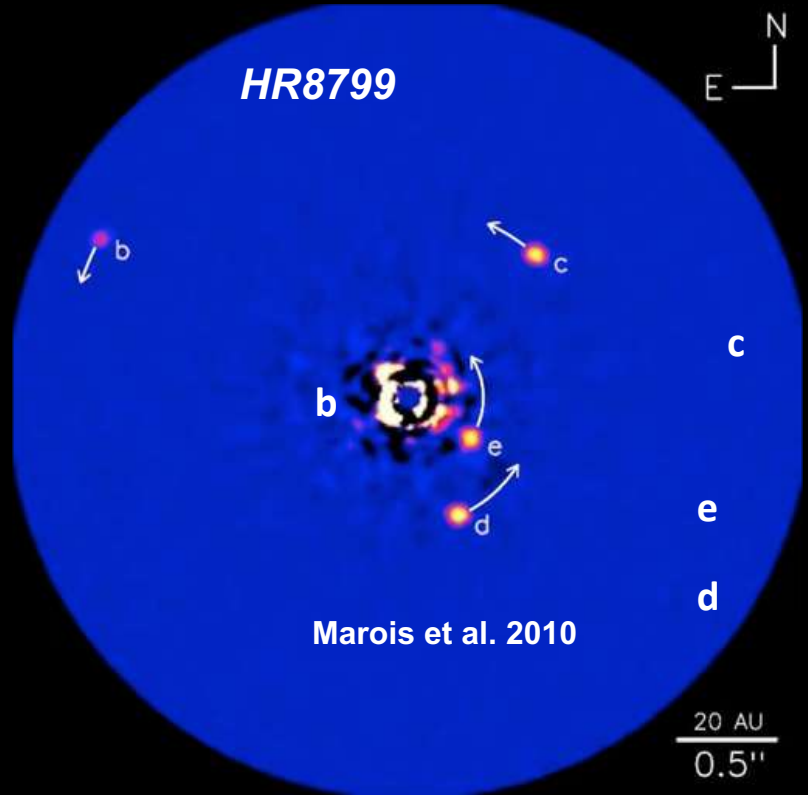
$$CRF = -20.6 \text{ W/m}^2$$



# Observations of clouds in brown dwarfs and young giant exoplanets

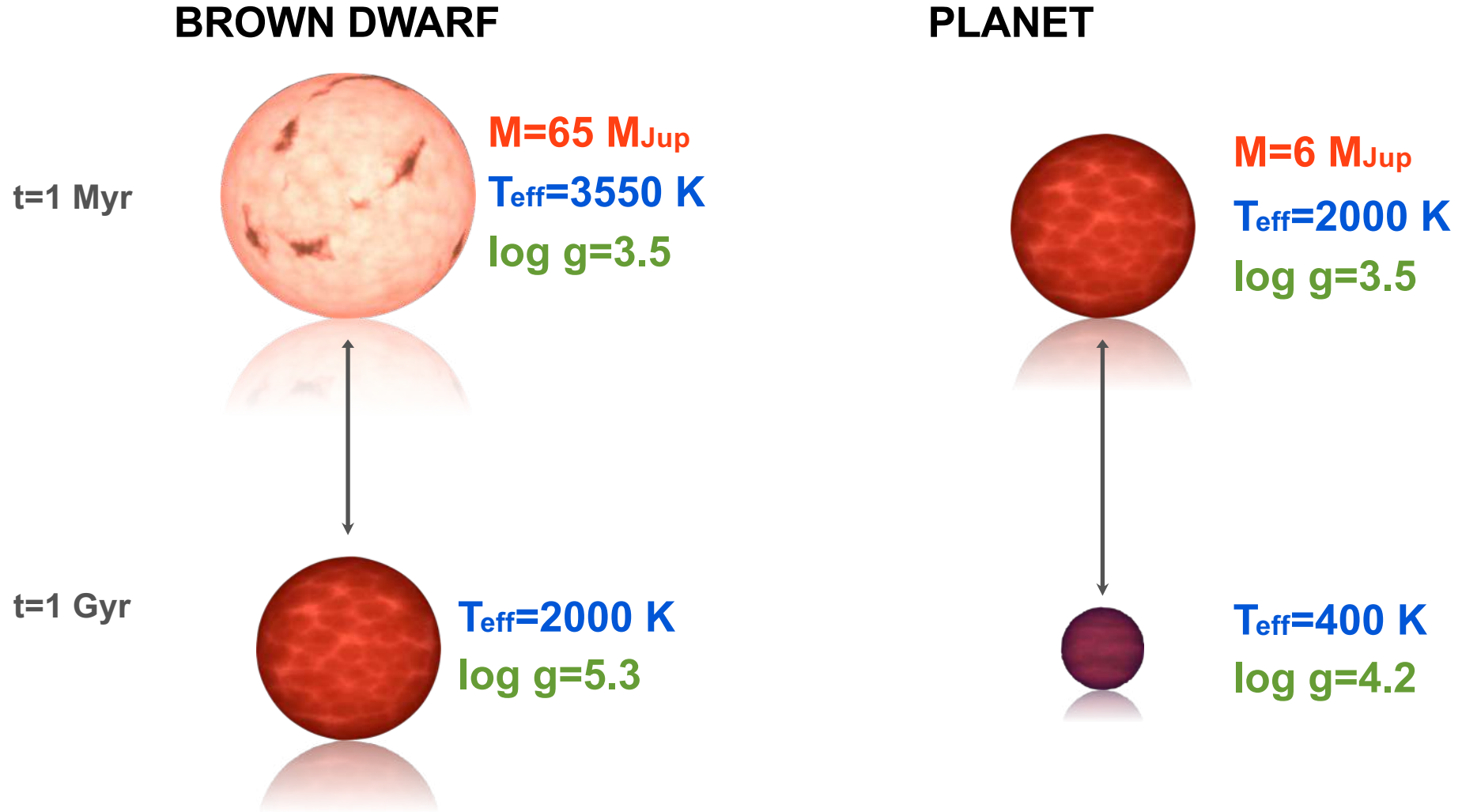
## Transitions in brown dwarfs





# Comparison brown dwarfs vs imaged giant planets

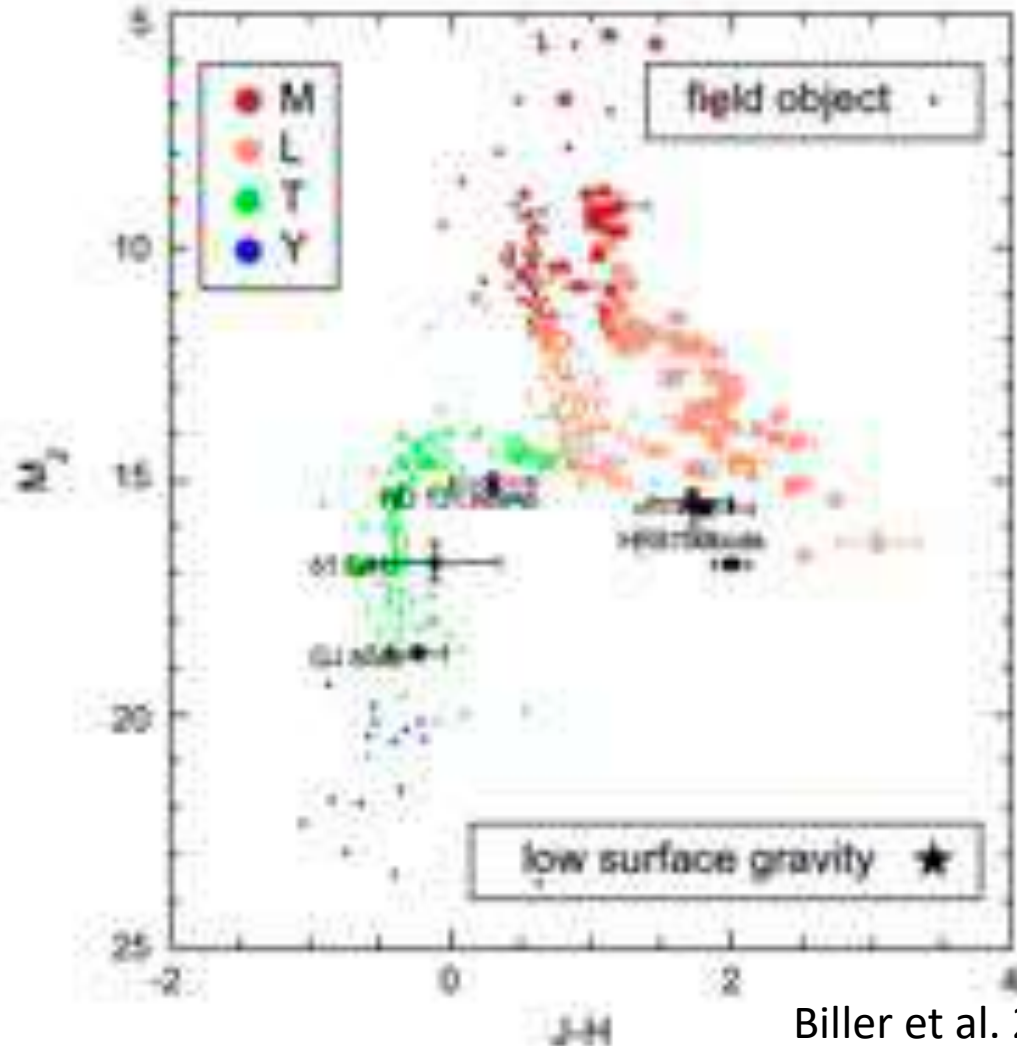
Imaged planets are young  $\Rightarrow$  low surface gravity



# Observations of clouds in brown dwarfs and young giant exoplanets

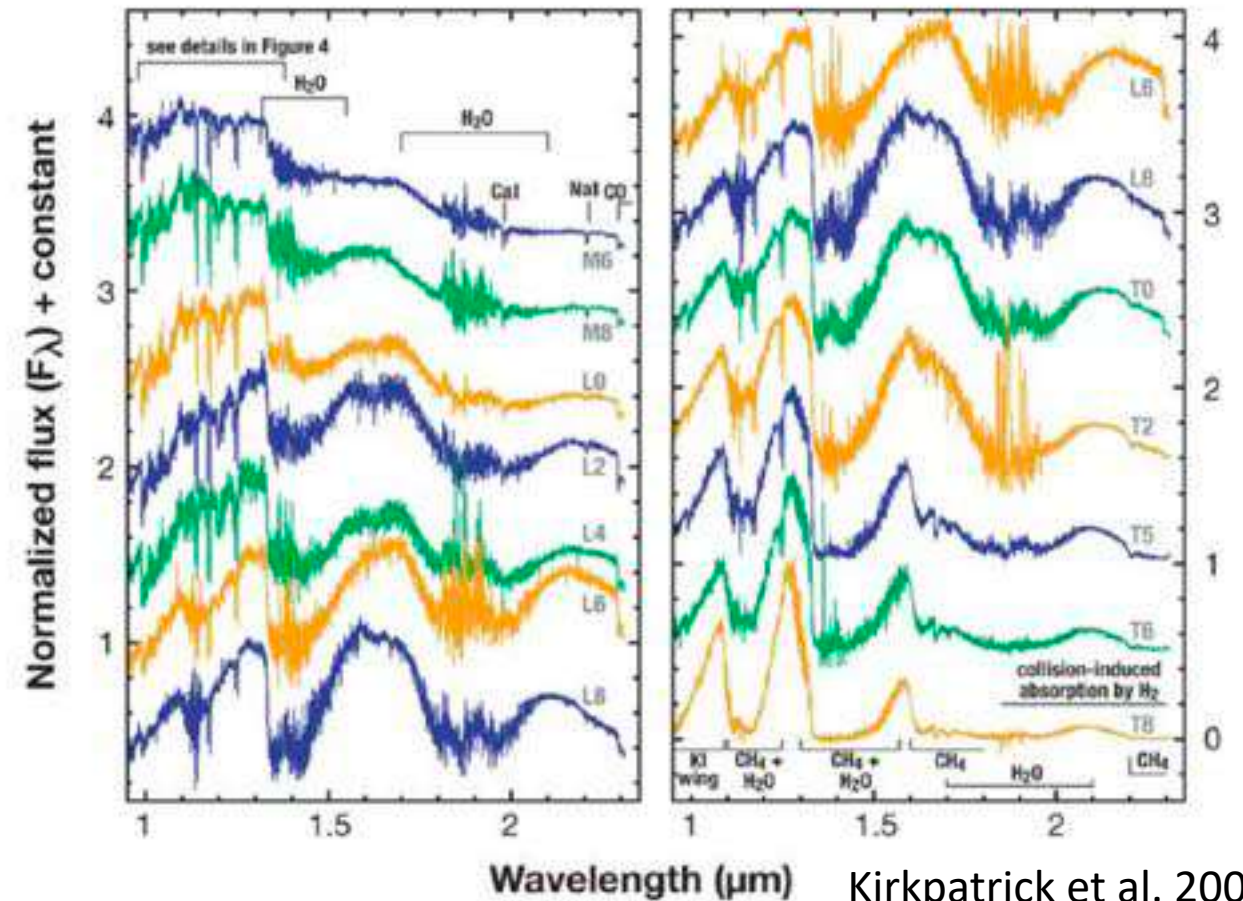
## Transitions in brown dwarfs

Photometric sequence



Biller et al. 2017

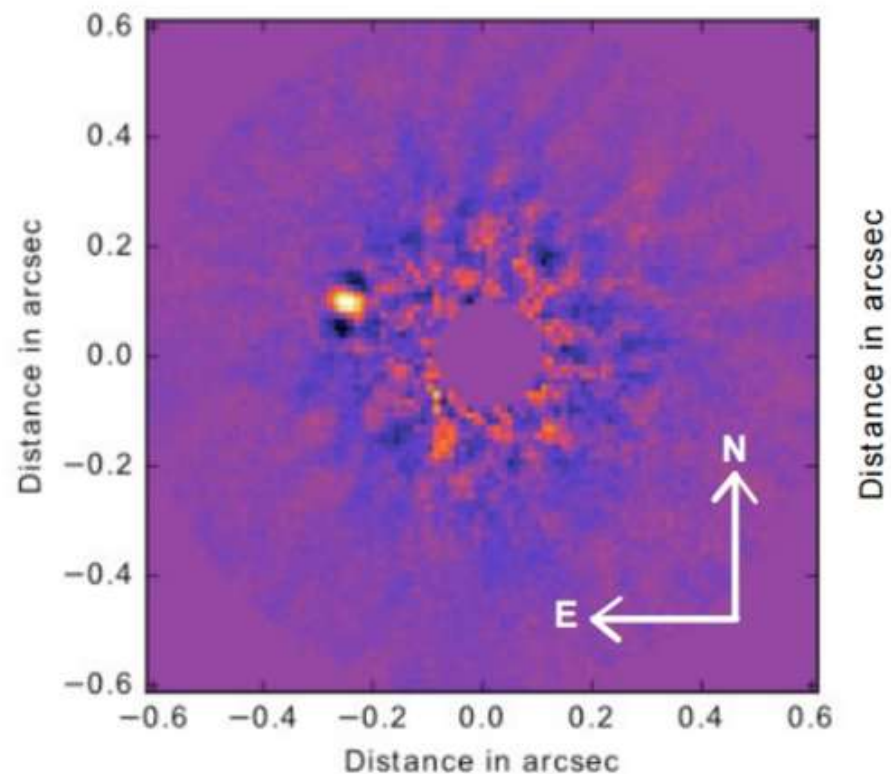
Spectroscopic sequence



Kirkpatrick et al. 2005

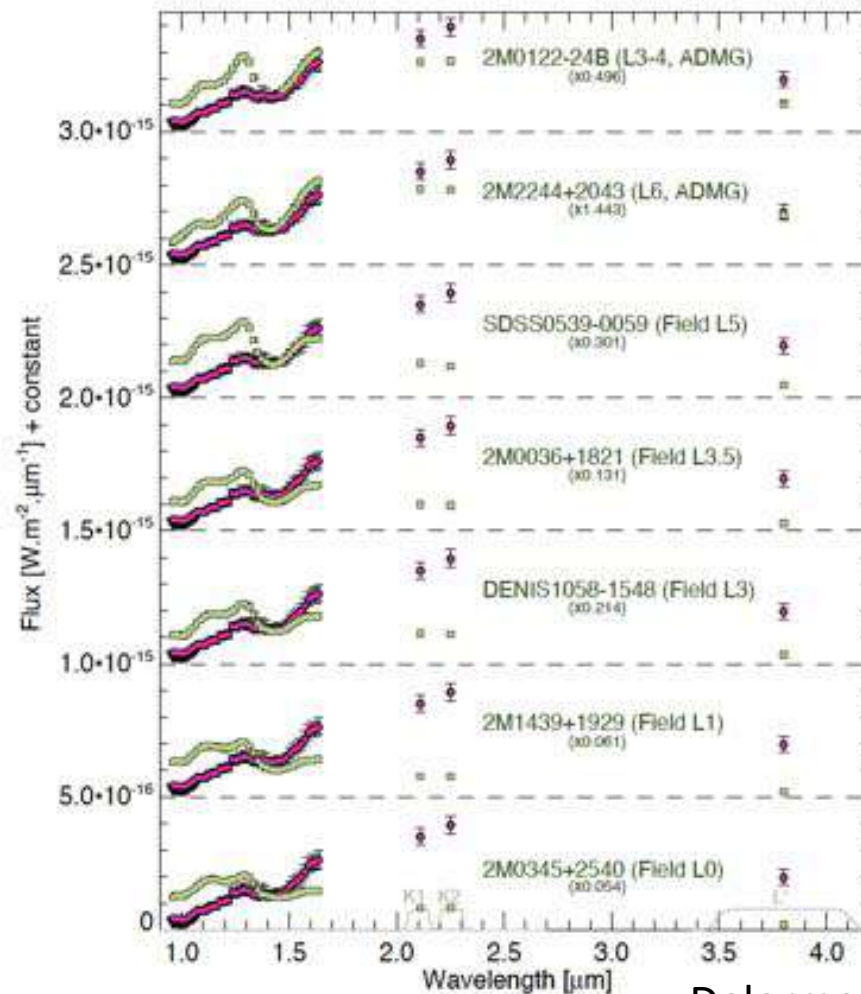
# Observations of clouds in brown dwarfs and young giant exoplanets

The red colors and featureless spectra of young giant exoplanets



Milli et al. 2017

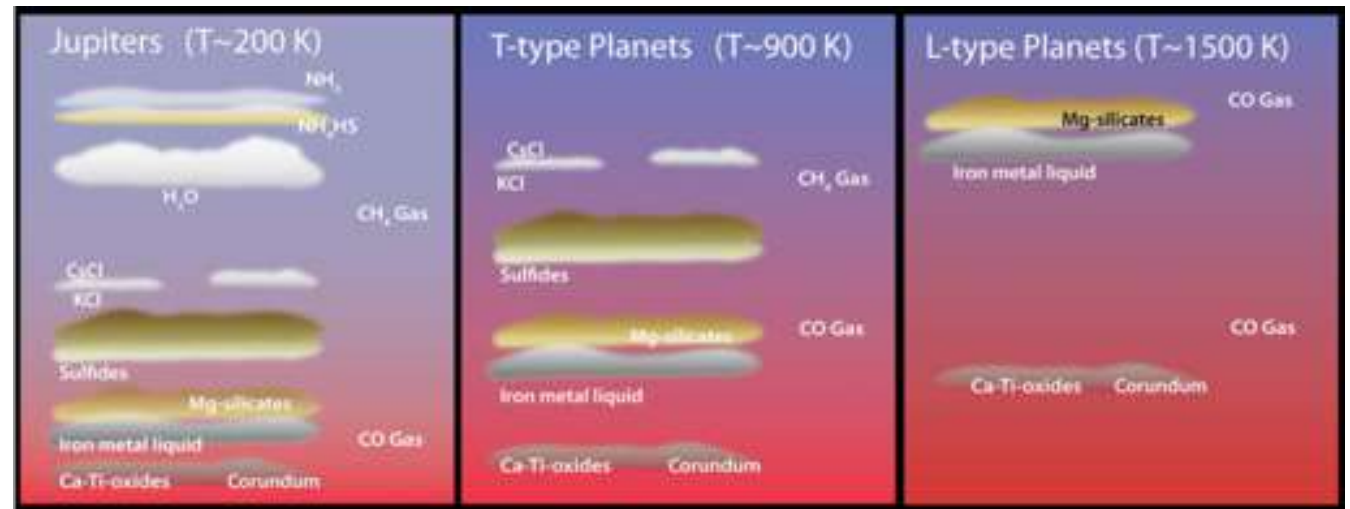
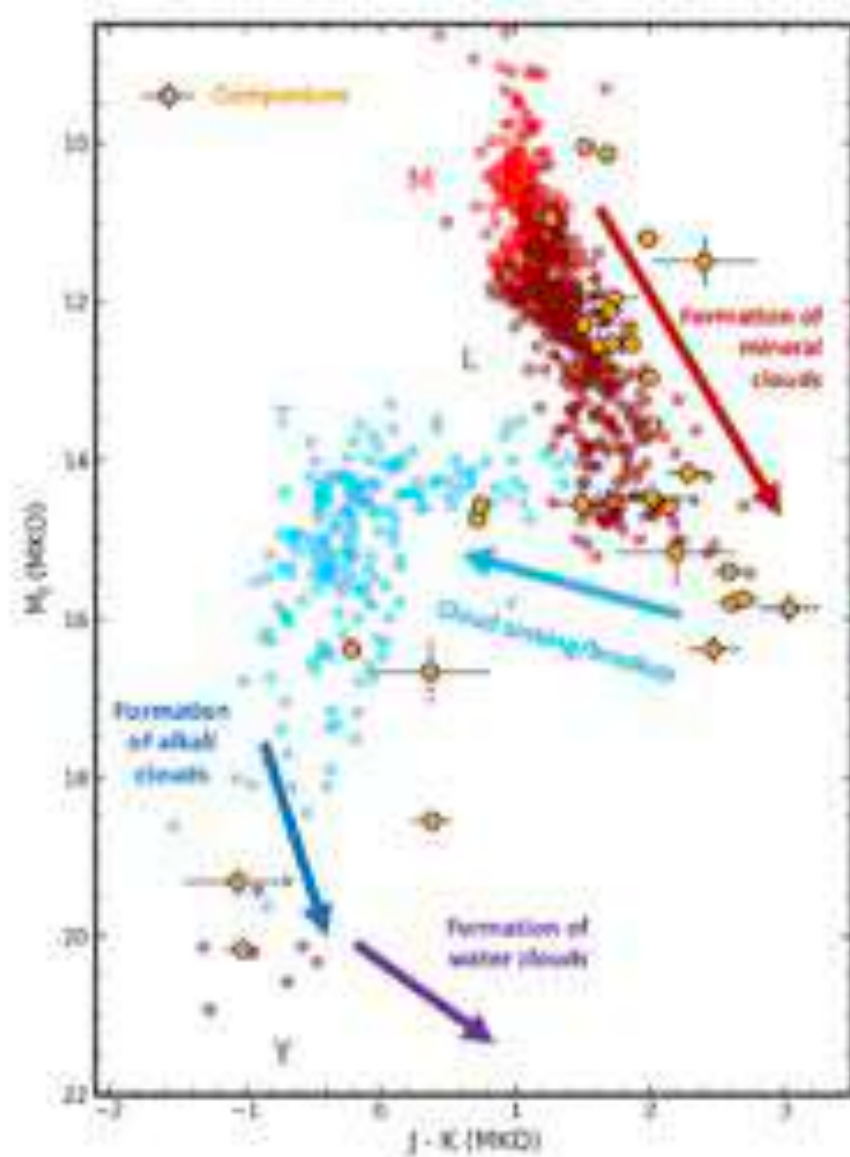
HD206893 b's spectrum = almost a black body



Delorme et al. 2017

# Observations of clouds in brown dwarfs and young giant exoplanets

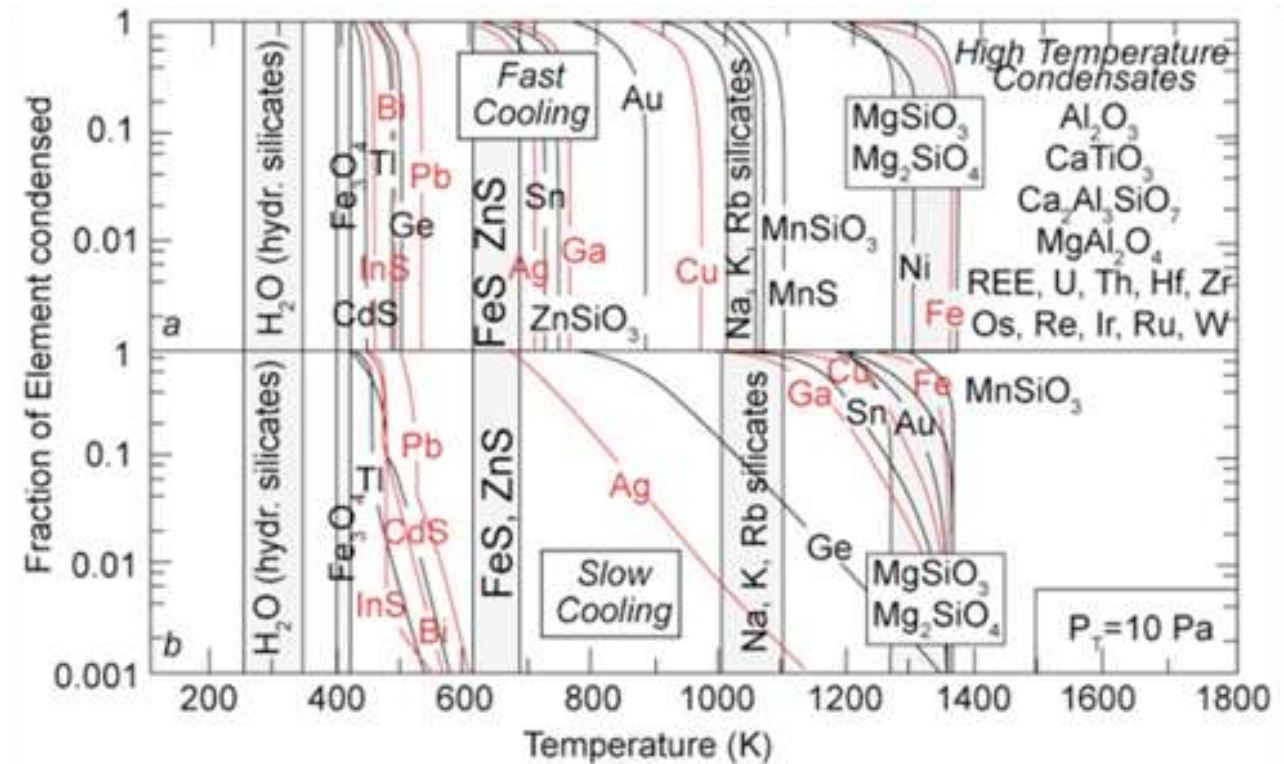
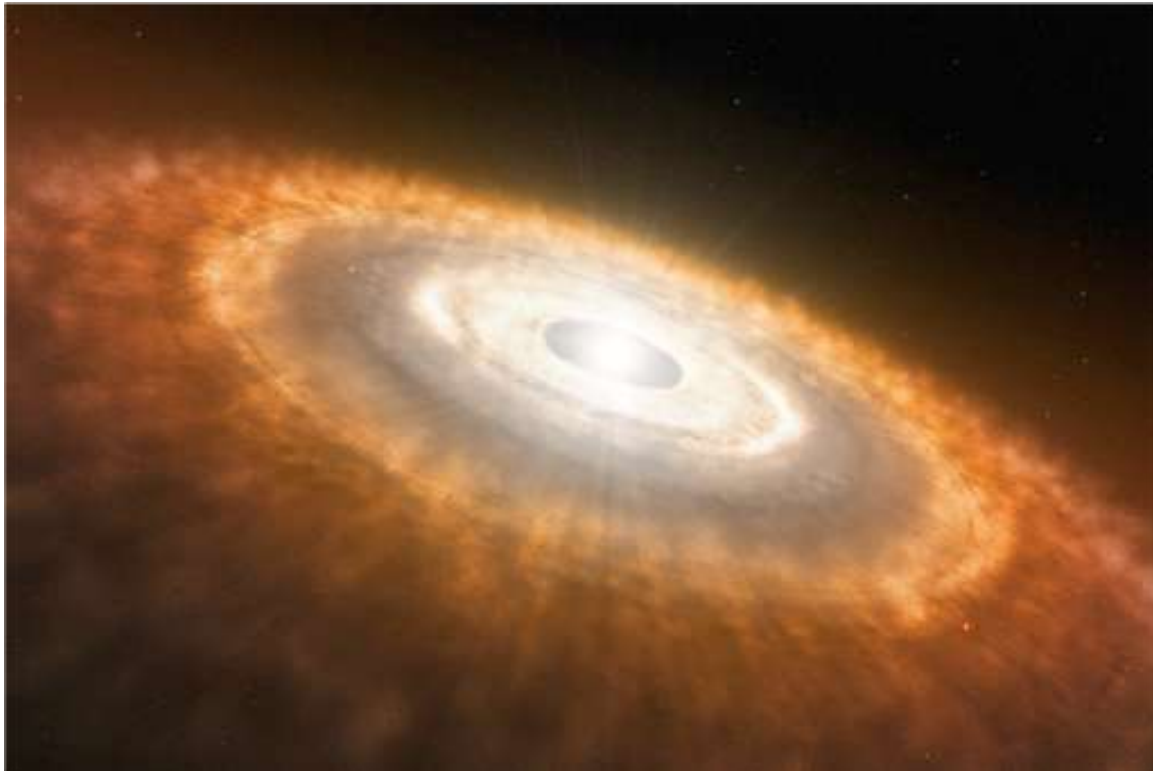
## Clouds as the driver of the LT-transition



Gao et al. 2020

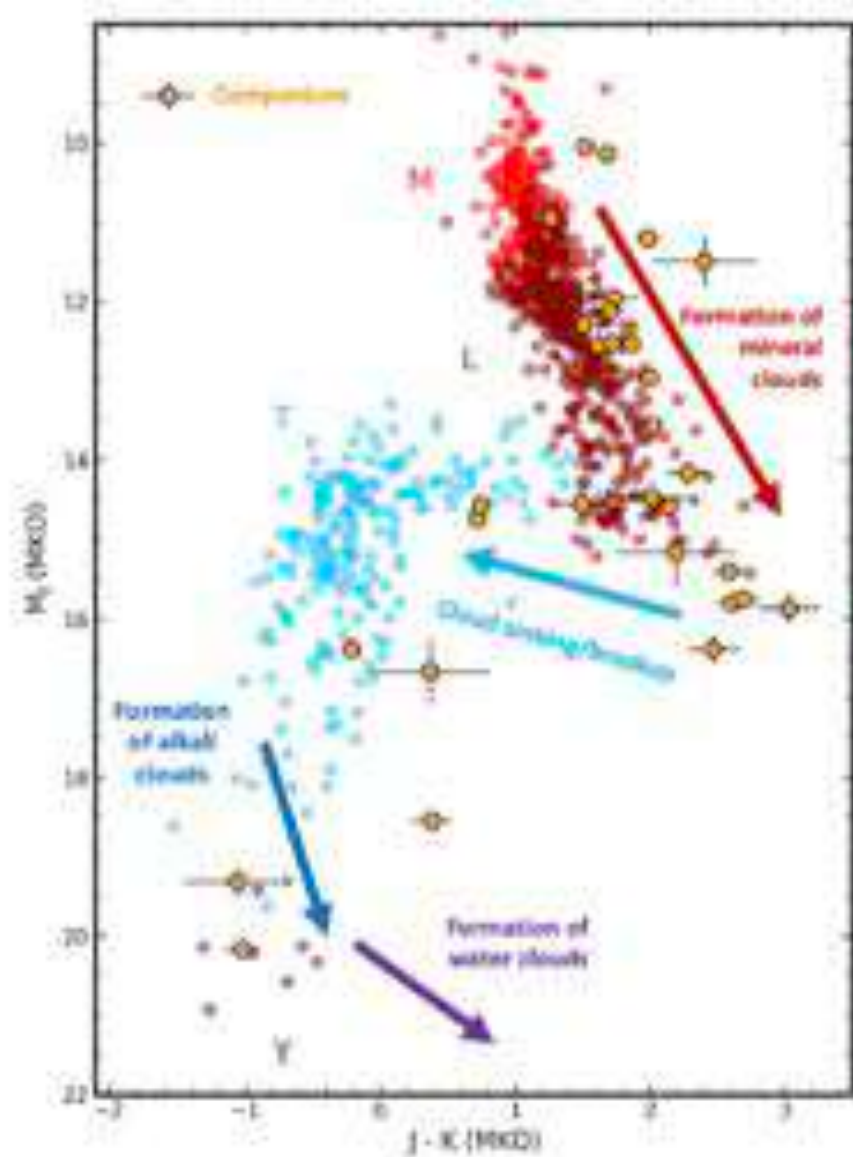
# Observations of clouds in brown dwarfs and young giant exoplanets

Analogy between cloud formation and the condensation sequence in protoplanetary disks

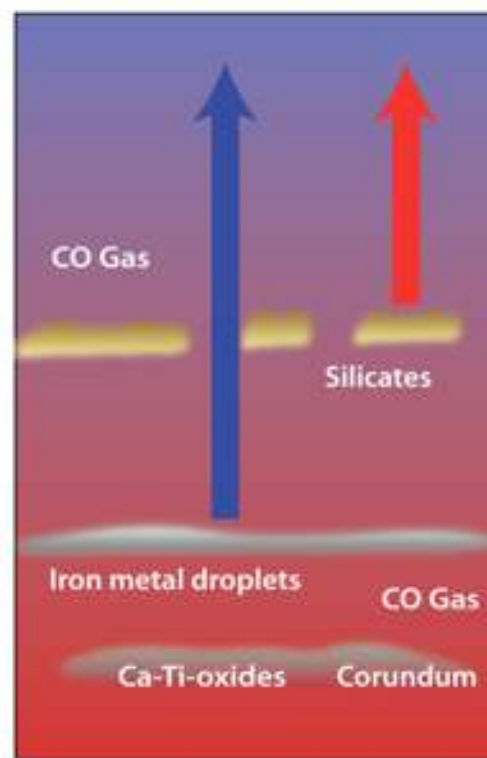


# Observations of clouds in brown dwarfs and young giant exoplanets

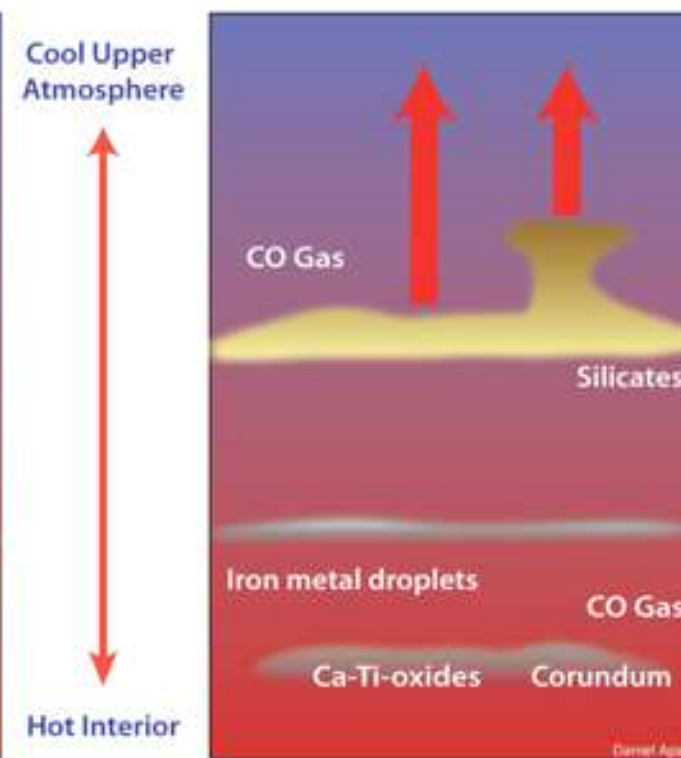
## Cloud inhomogeneities at the LT-transition



Cloud Holes : Large Color Variations



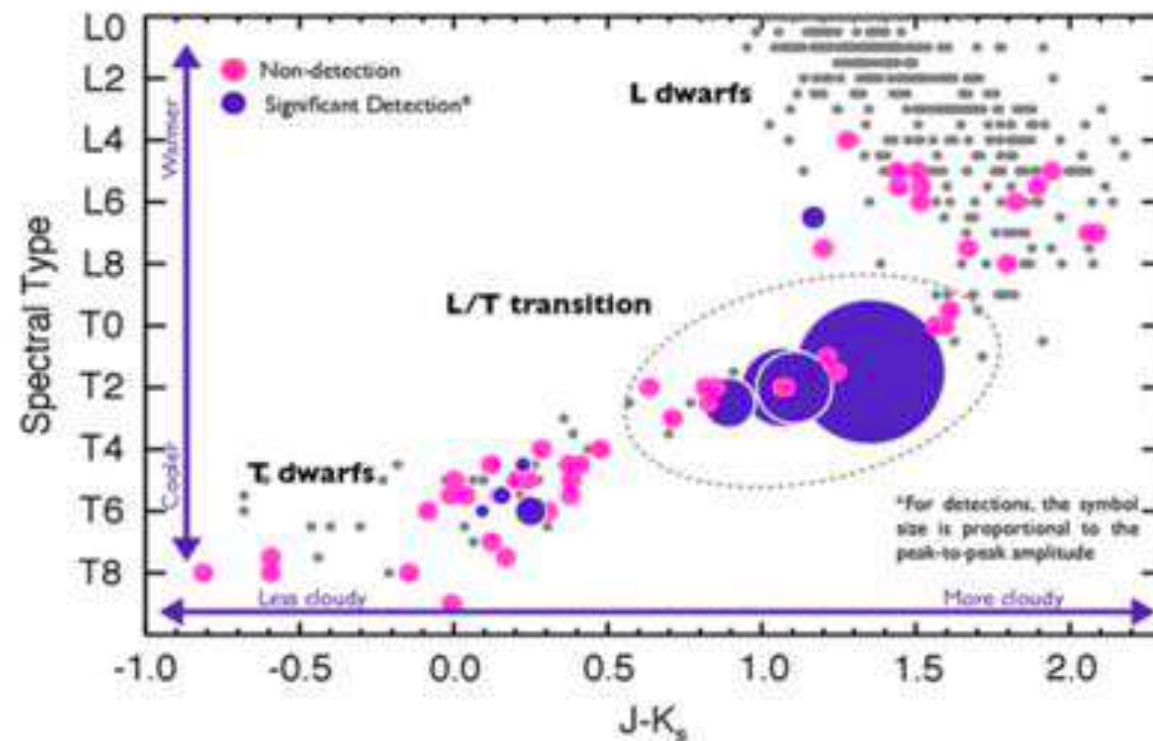
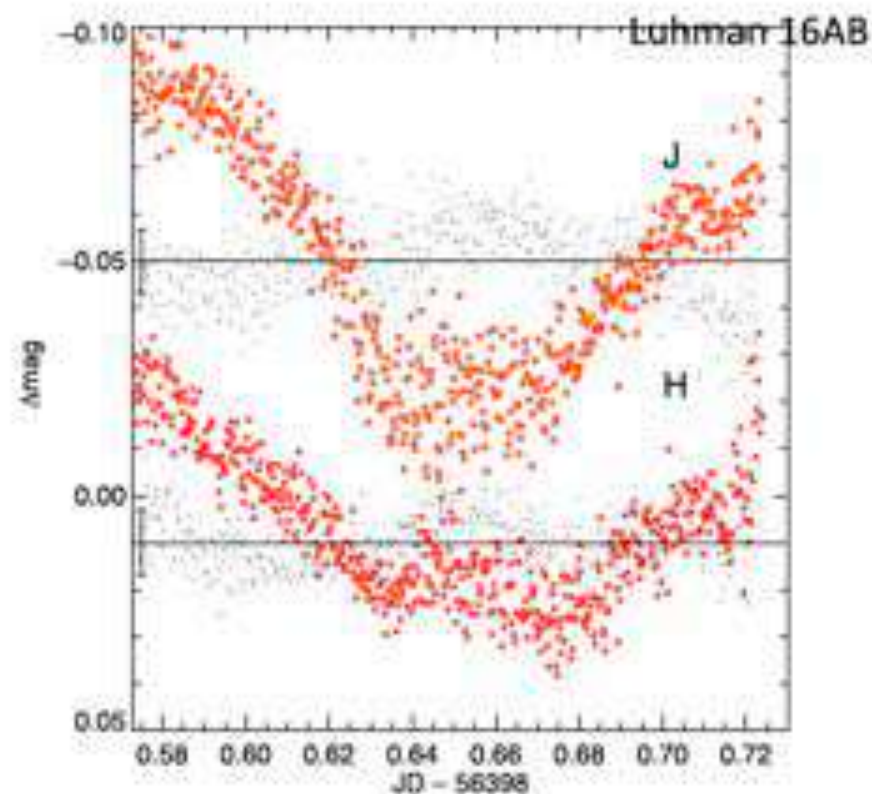
Cloud Thickness: Small Color Variations





# Observations of clouds in brown dwarfs and young giant exoplanets

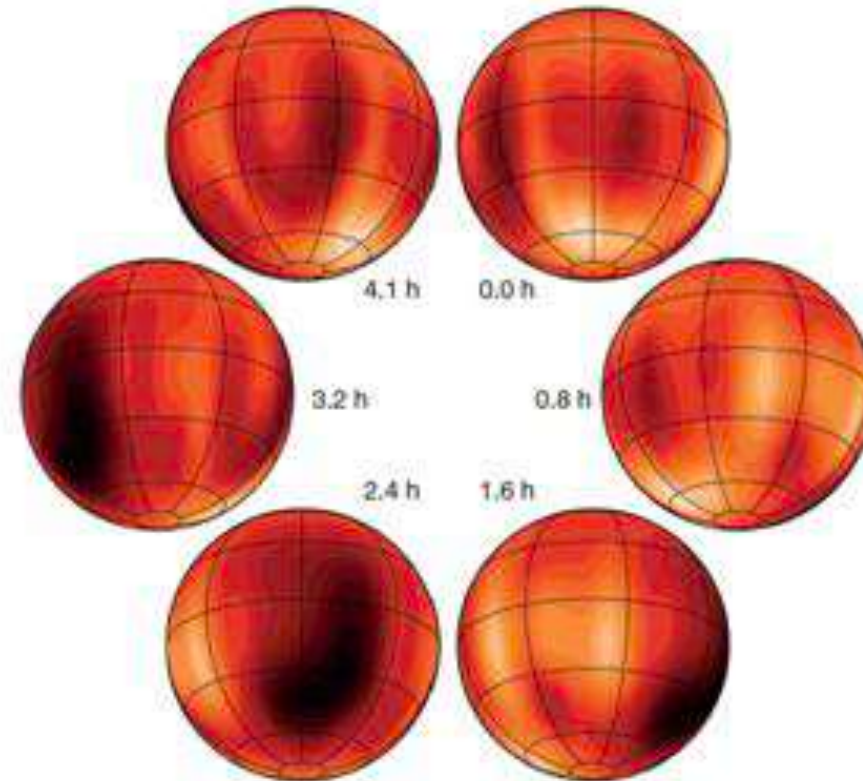
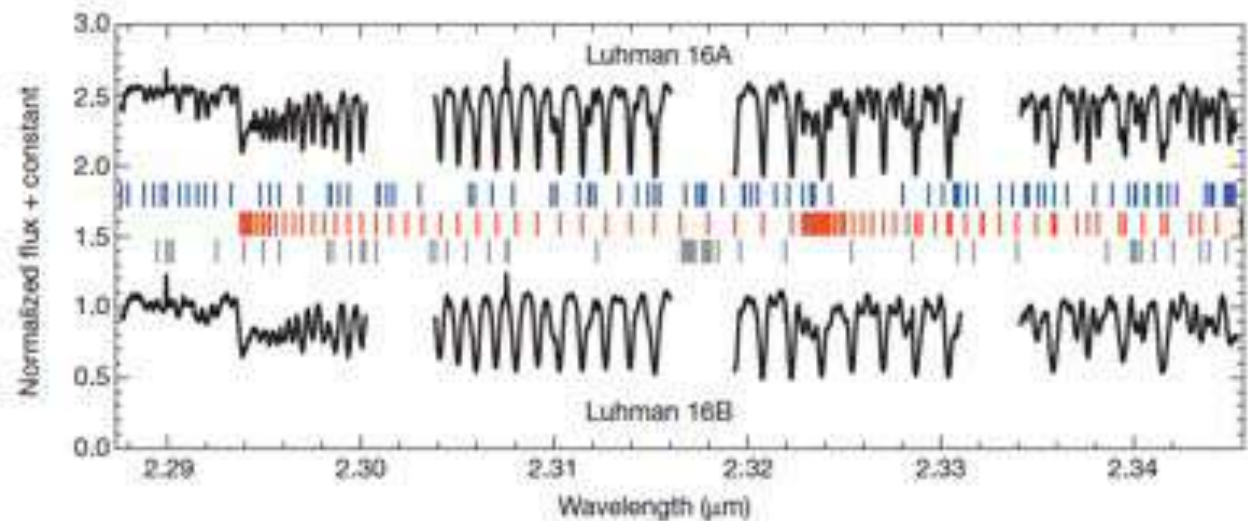
## Variability of brown dwarfs at the L-T transition



Biller et al. 2017

# Observations of clouds in brown dwarfs and young giant exoplanets

## Mapping of brown dwarfs at the LT-transition

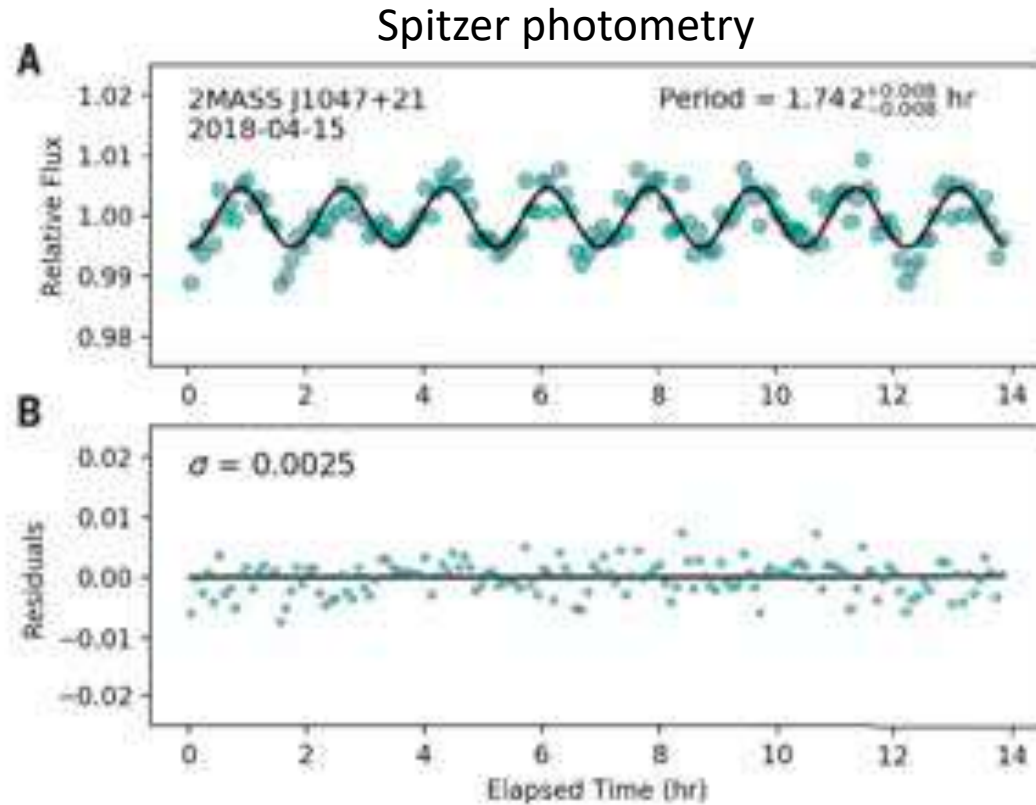


Crossfield et al. 2014

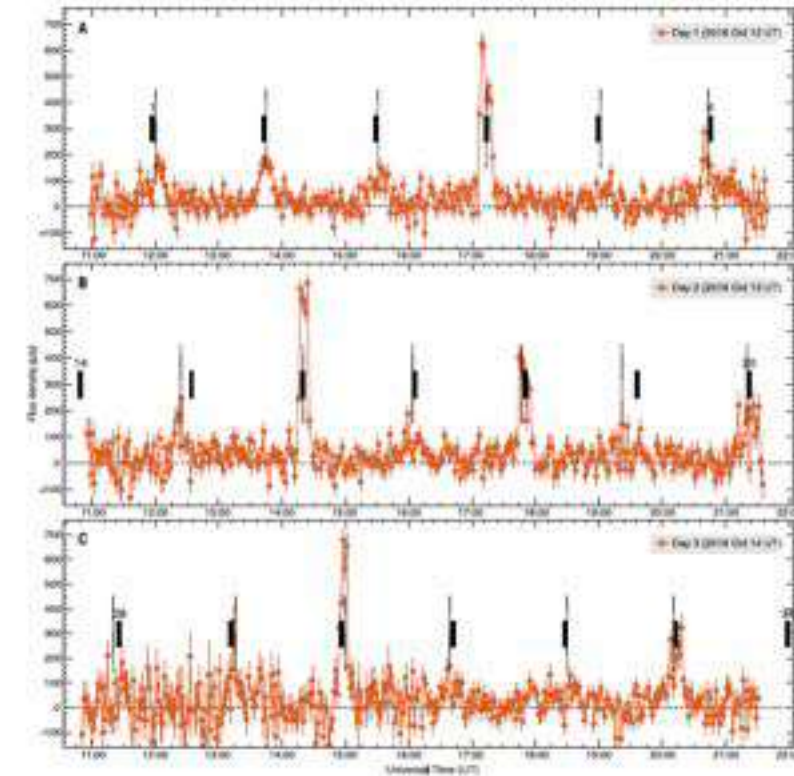
**Inhomogeneity in the cloud cover**

# Observations of clouds in brown dwarfs and young giant exoplanets

## Measurement of wind speed



## Radio light curve



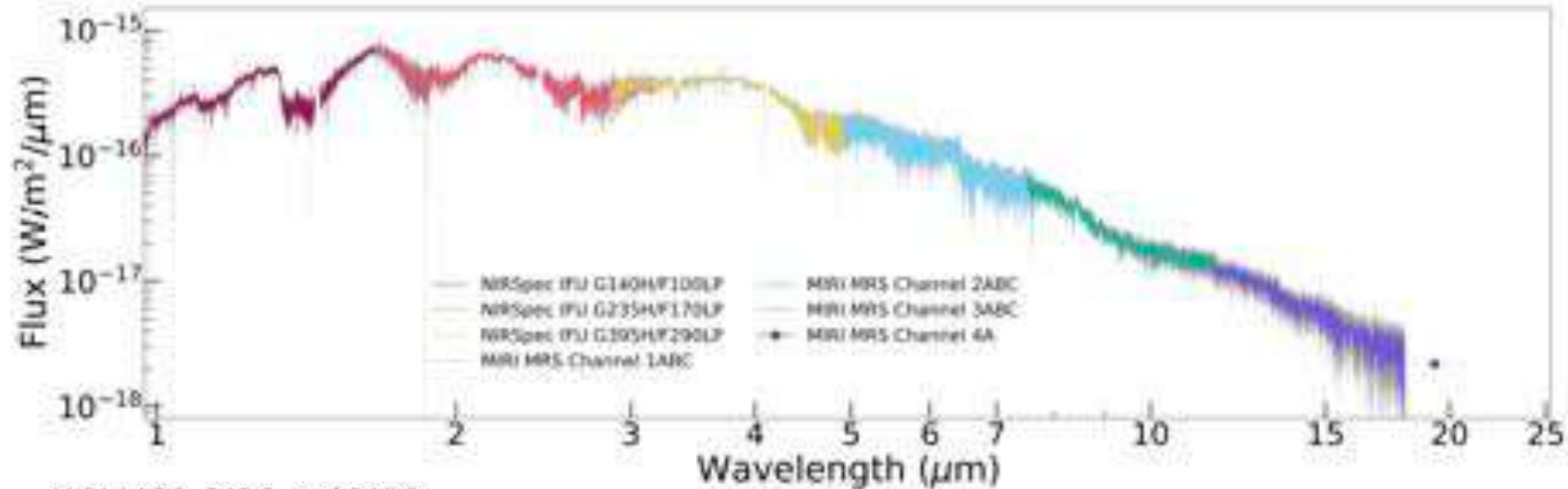
Allers et al. 2020

Difference between measured period from photometry (1.741h; clouds) and from radio emission ( $\sim 1.762$ h; interior)  
 $\Rightarrow$  Eastward jet with wind speed of  $650 \pm 310$  m/s

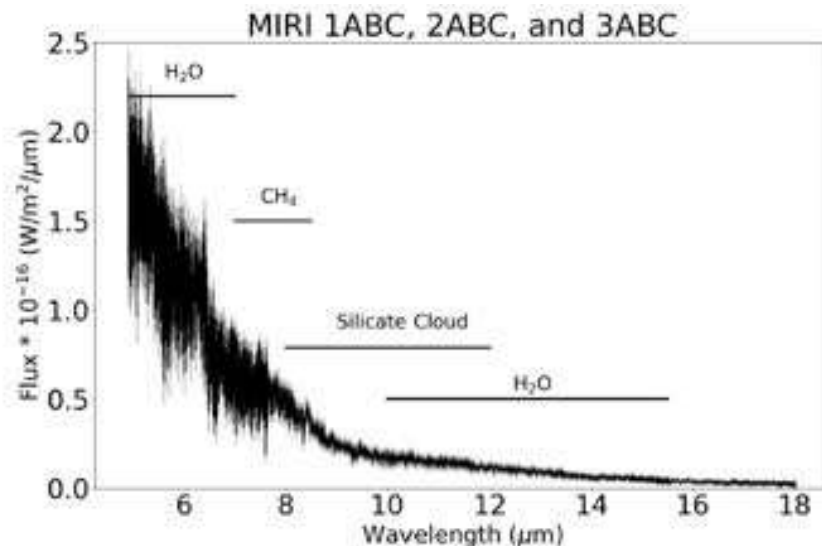
# Observations of clouds in brown dwarfs and young giant exoplanets

## Silicate feature

NIRSpec+MIRI spectrum of VHS 1256 b (ERS program)

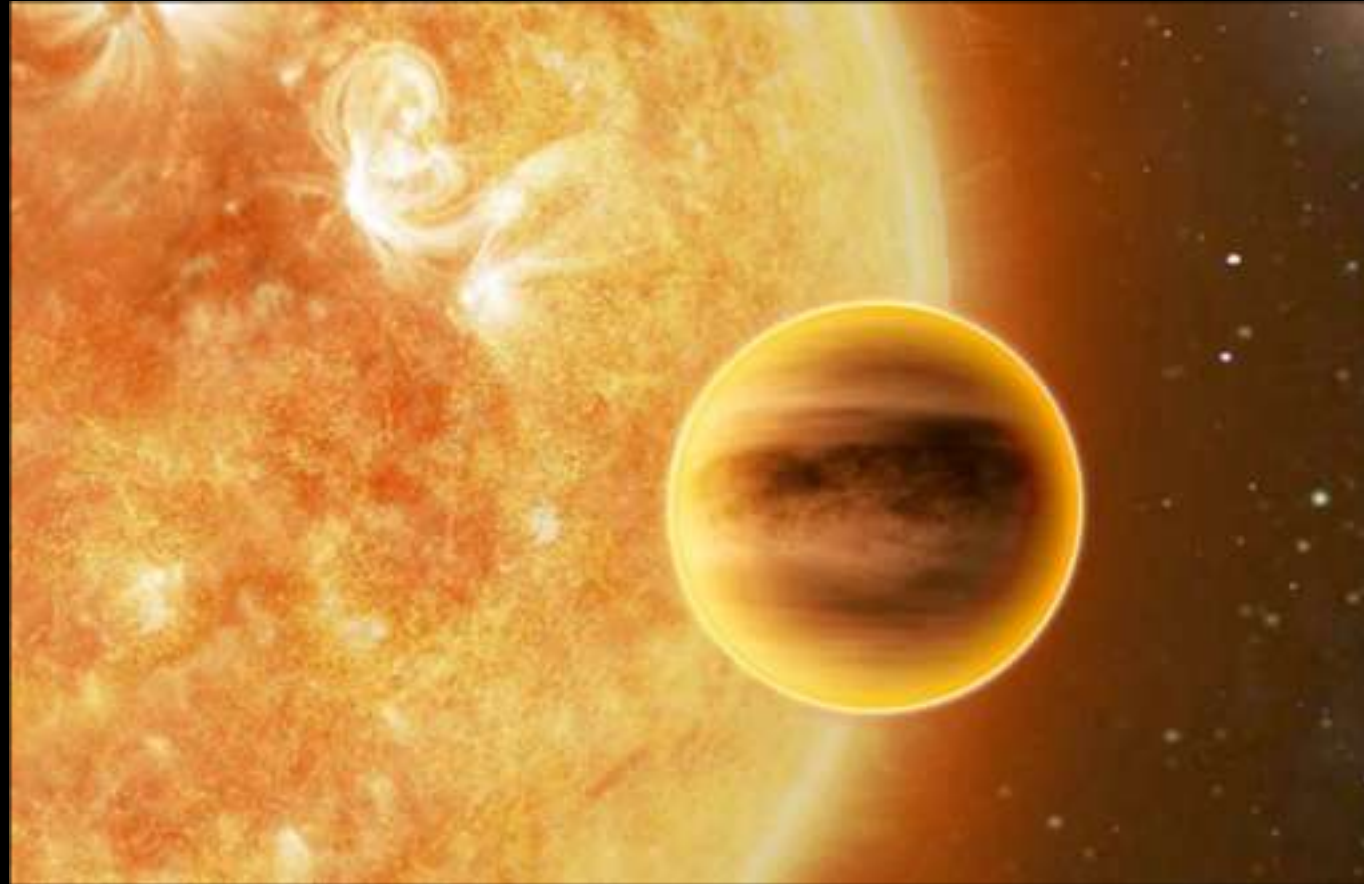


Miles et al. 2022



**Silicate absorbing band at 10  $\mu\text{m}$  !**

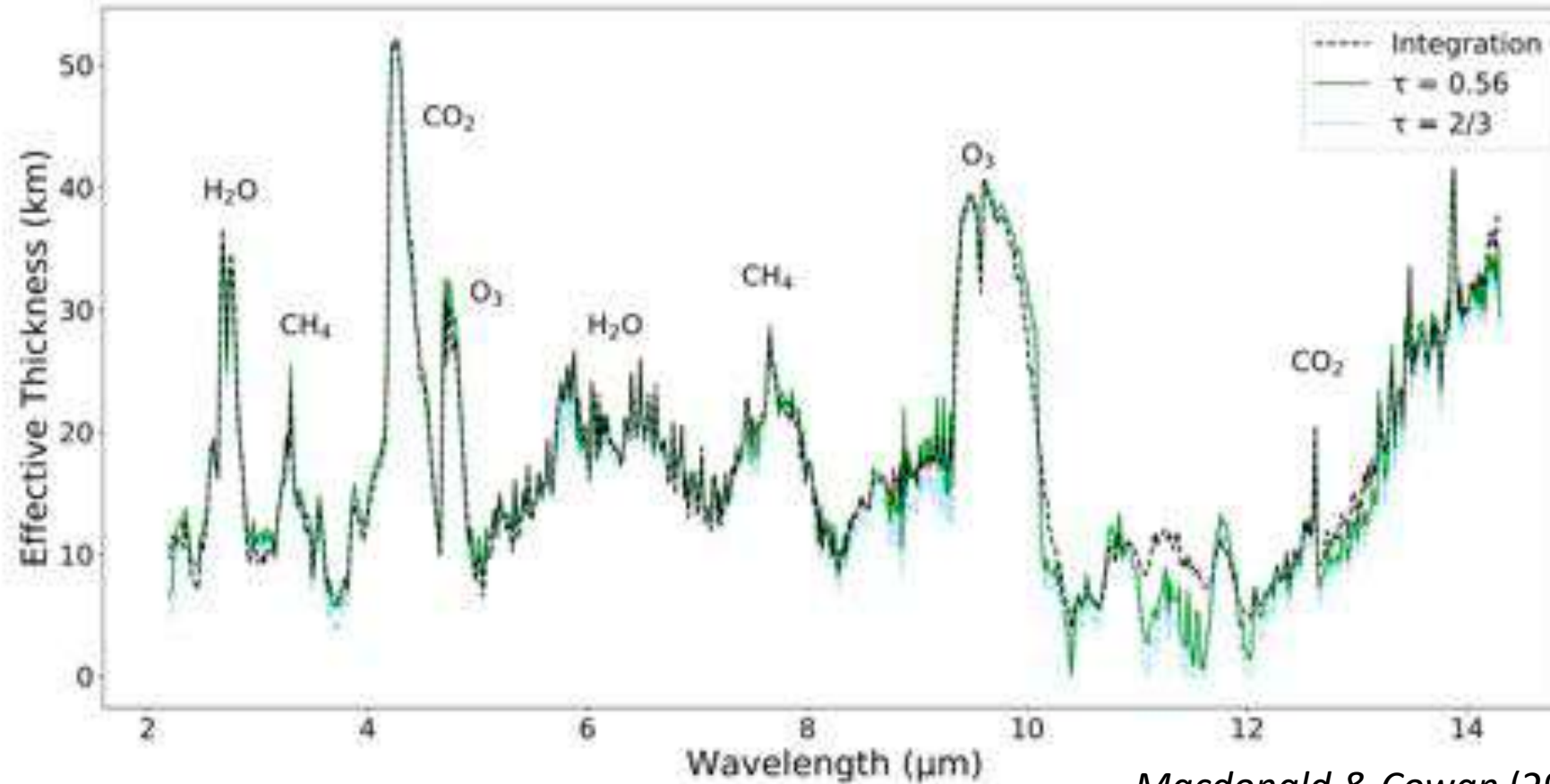
# Observation of clouds/haze for transiting exoplanets



# Observations of clouds & haze in exoplanets

## Transit spectroscopy

Synthetic Earth's transit spectrum



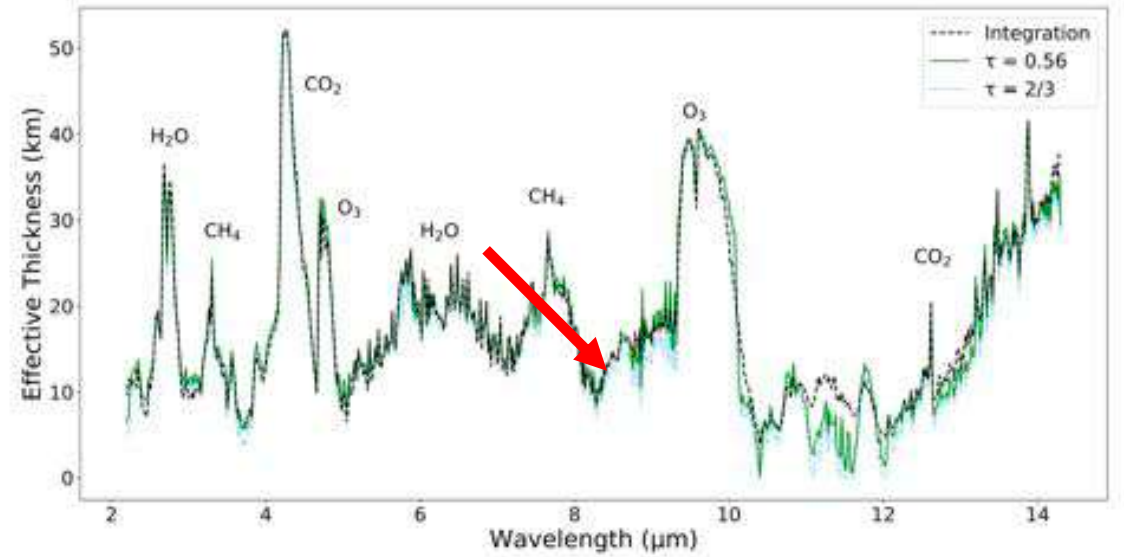
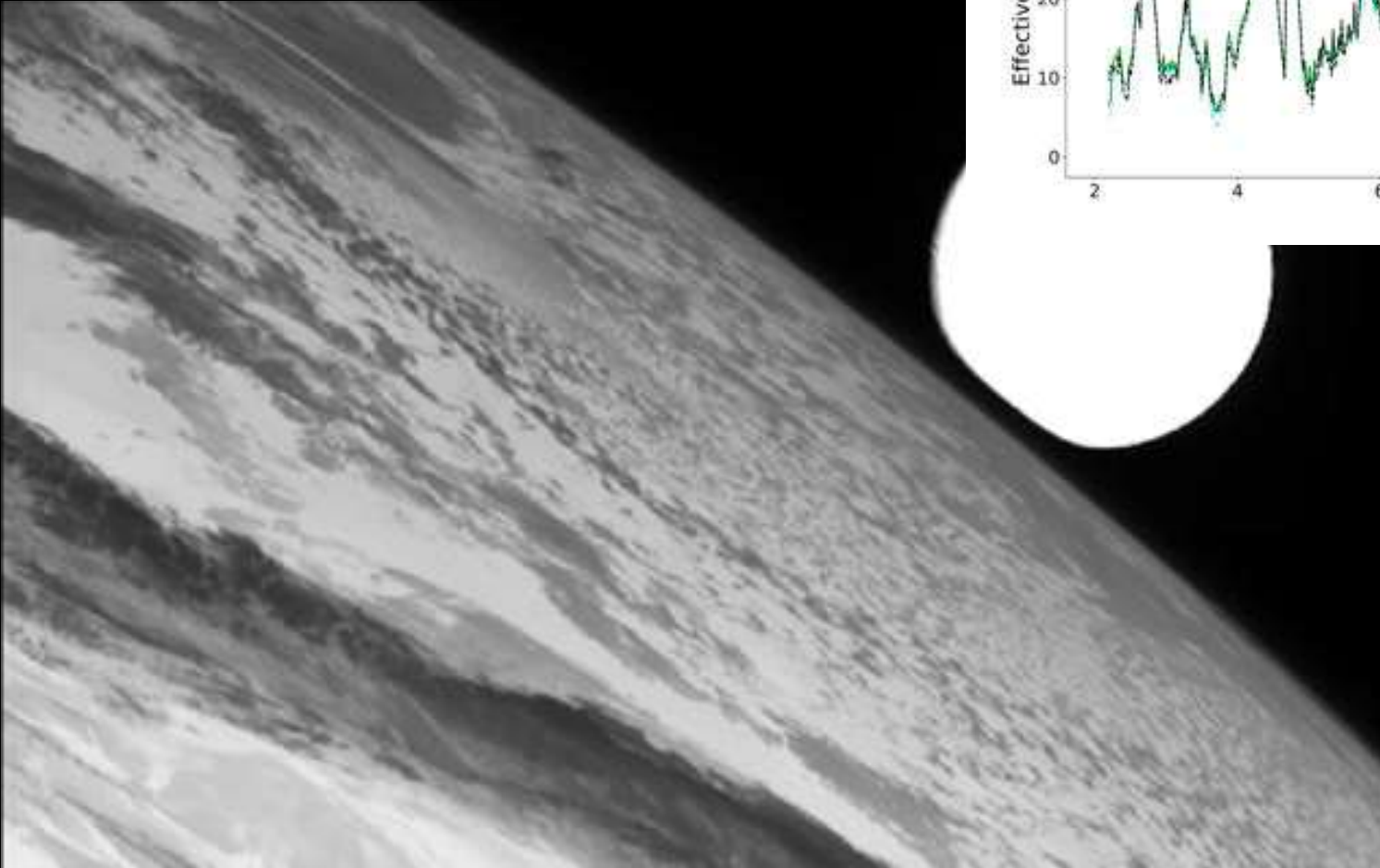
*Macdonald & Cowan (2019)*

## Real color



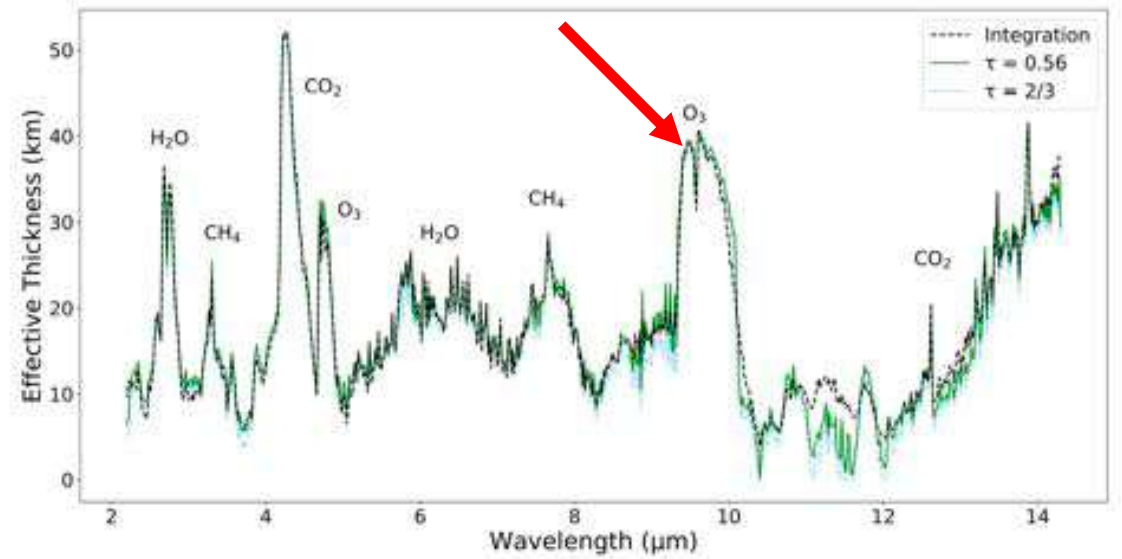
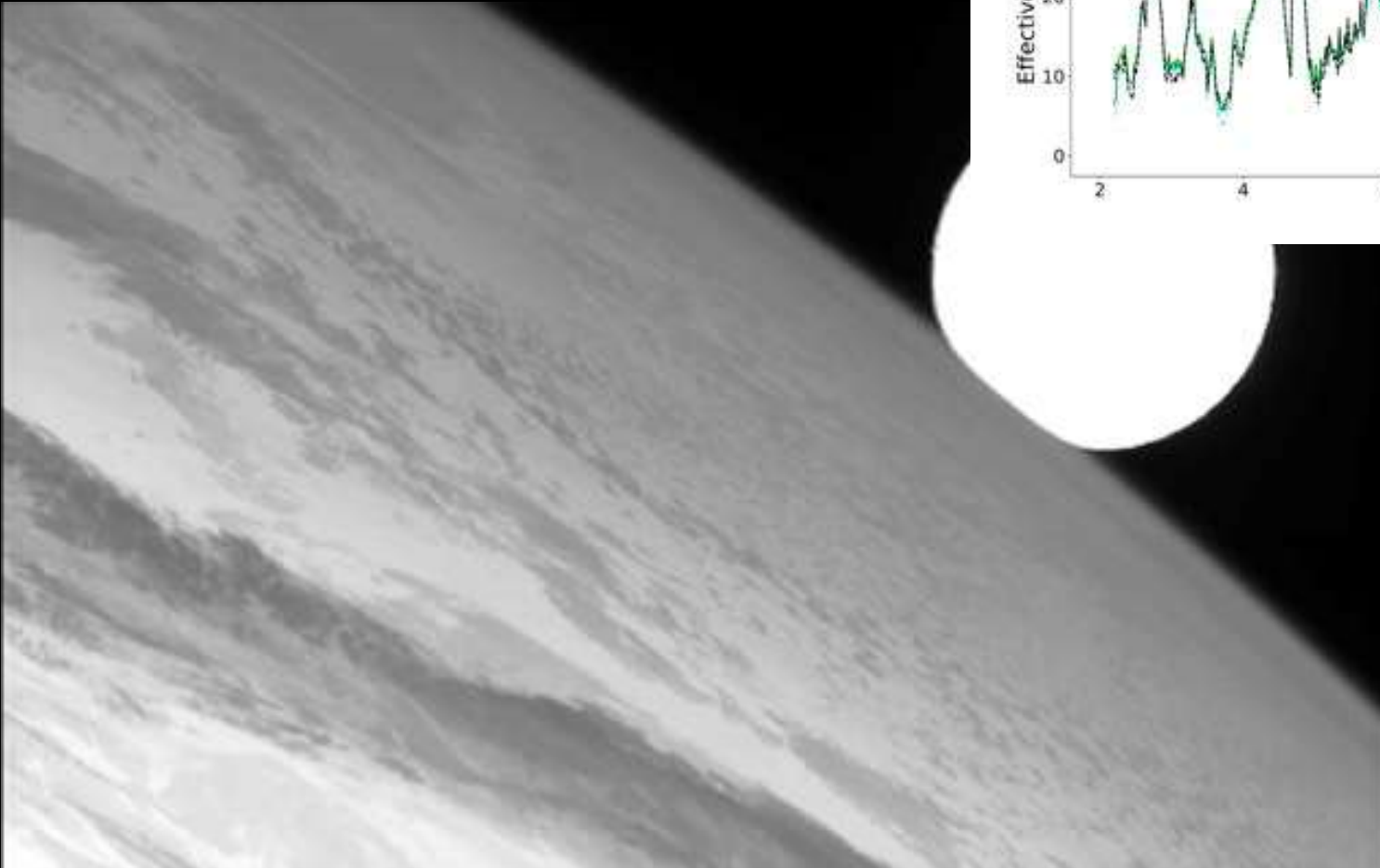
Credit: Himawary/Simon Proud/Vivien Parmentier

## 8.6 microns spectral window (15 km)



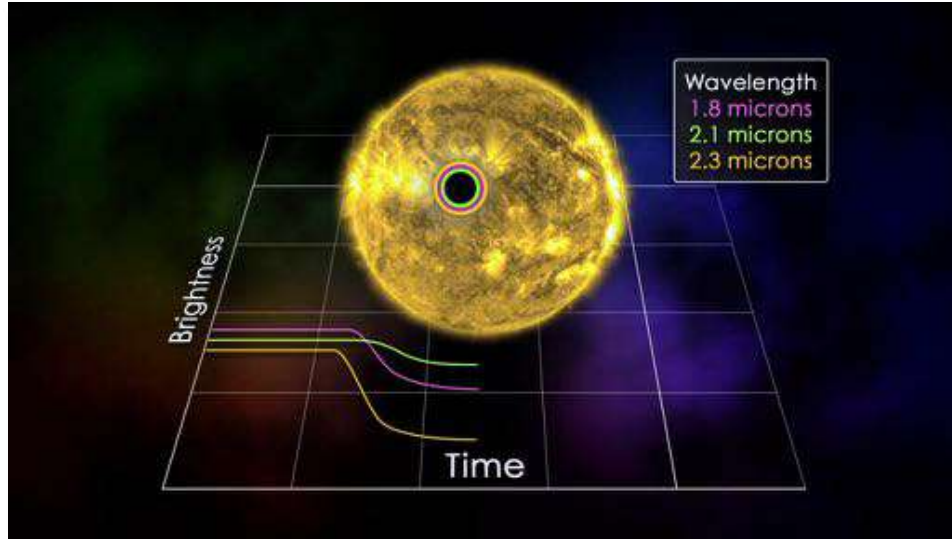


**9.6 microns  
O<sub>3</sub> band (40 km)**

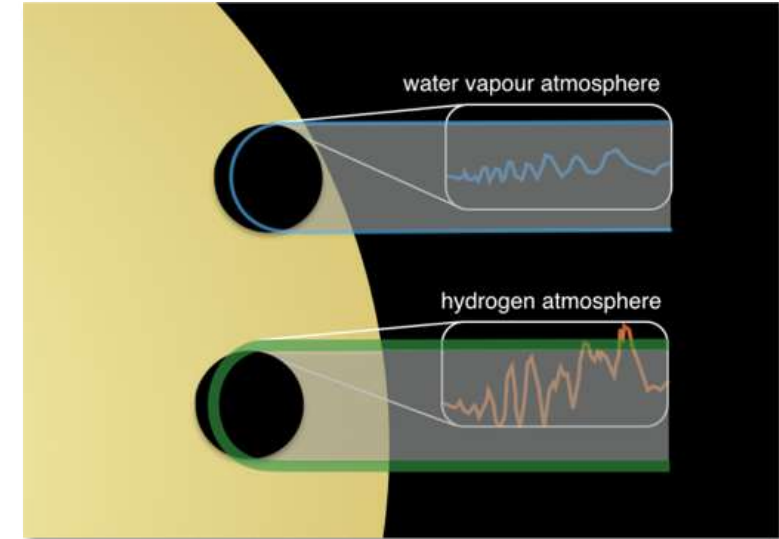


# Observations of clouds & haze in exoplanets

## Transit spectroscopy



## Effect of mean molecular weight



Variation of transit depth:

$$\Delta\delta_{tra} = \frac{\pi(R_p + N_H H)^2}{\pi R_*^2} - \frac{\pi R_p^2}{\pi R_*^2} \approx \frac{2N_H R_p H}{R_*^2}$$

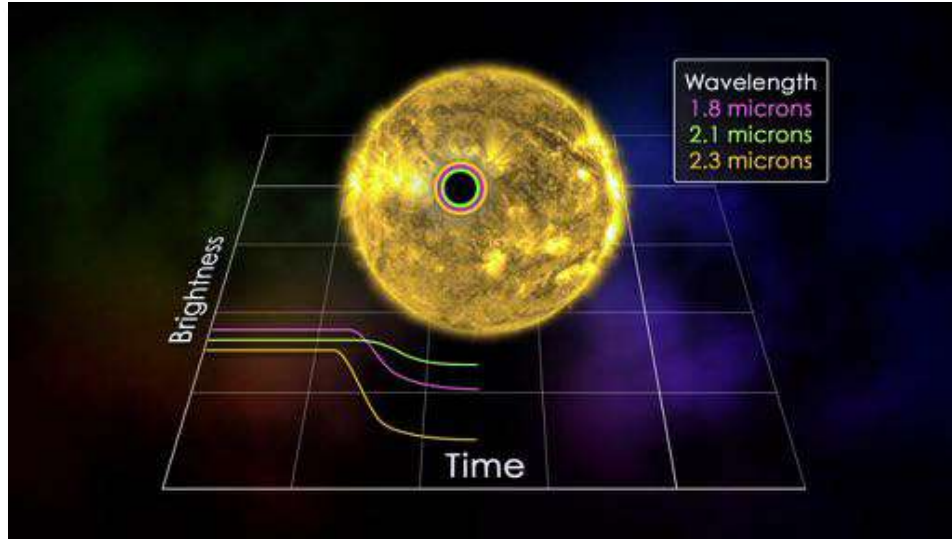
Scale height:  $H = \frac{RT}{Mg}$ ; Number of scale heights:  $N_H \approx 5$  (for low resolution)

For an Sun-like star:

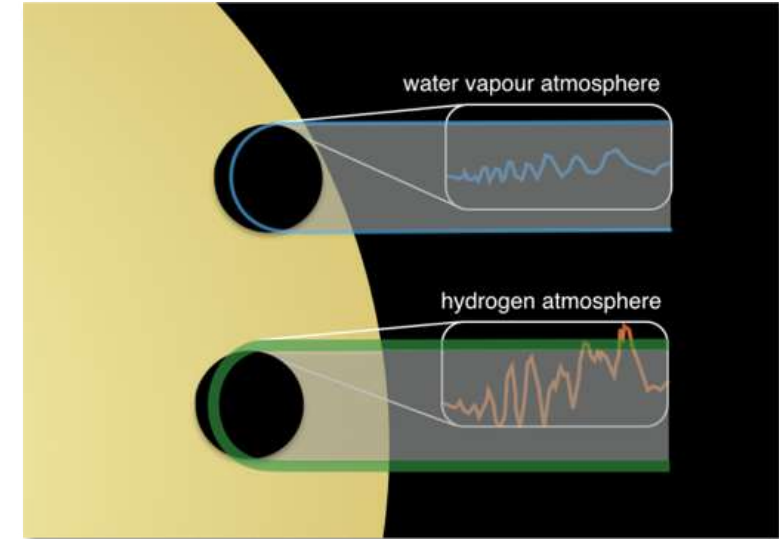
- Hot Jupiter ( $T=1300$  K,  $g=25$  m s<sup>-2</sup>,  $M=2.3$  g/mol):  $\delta_{tra} \approx 0.01$ ,  $\Delta\delta_{tra} \approx 4 \cdot 10^{-4}$
- Earth-like planet ( $T=280$  K,  $g=10$  m s<sup>-2</sup>,  $M=28$  g/mol):  $\delta_{tra} \approx 10^{-4}$ ,  $\Delta\delta_{tra} \approx 2 \cdot 10^{-6}$

# Observations of clouds & haze in exoplanets

## Transit spectroscopy



## Effect of mean molecular weight



Variation of transit depth:

$$\Delta\delta_{tra} = \frac{\pi(R_p + N_H H)^2}{\pi R_*^2} - \frac{\pi R_p^2}{\pi R_*^2} \approx \frac{2N_H R_p H}{R_*^2}$$

Scale height:  $H = \frac{RT}{Mg}$  ; Number of scale heights:  $N_H \approx 5$  (for low resolution)

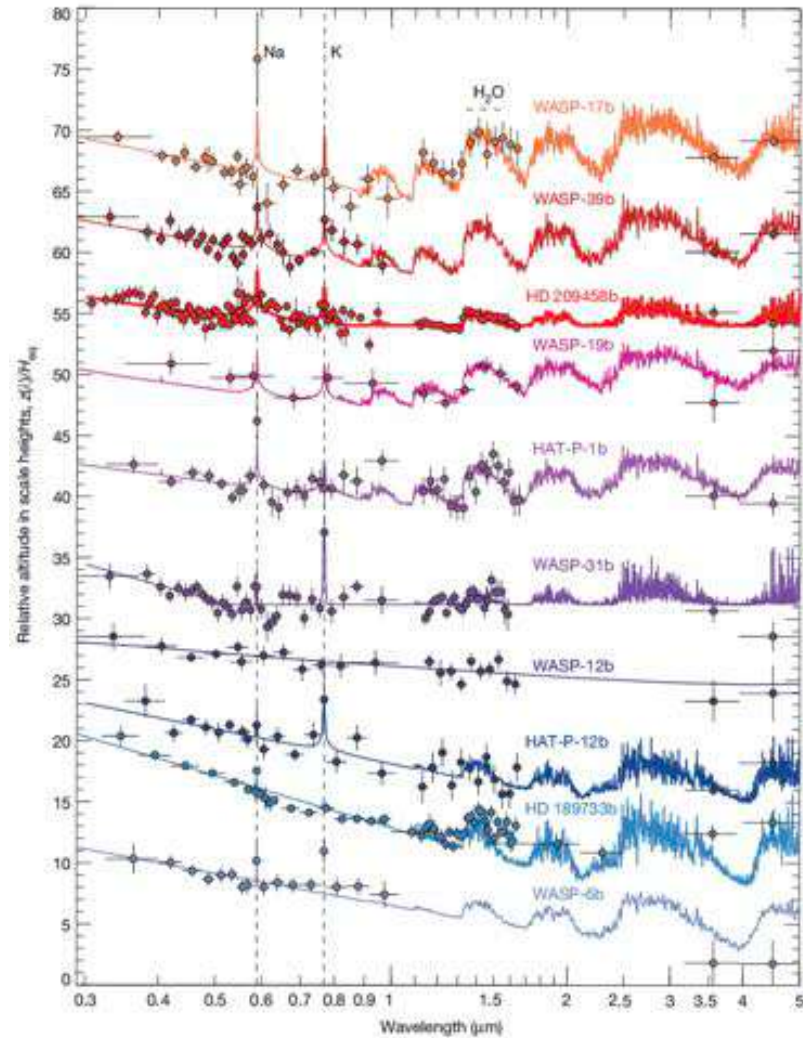
For Trappist-1 (0.015  $R_s$ ):

- Hot Jupiter ( $T=1300$  K,  $g=25$  m s<sup>-2</sup>,  $M=2.3$  g/mol):  $\delta_{tra} \approx 0.7$ ,  $\Delta\delta_{tra} \approx 2 \cdot 10^{-2}$

- Earth-like planet ( $T=280$  K,  $g=10$  m s<sup>-2</sup>,  $M=28$  g/mol):  $\delta_{tra} \approx 6 \cdot 10^{-3}$ ,  $\Delta\delta_{tra} \approx 10^{-4}$

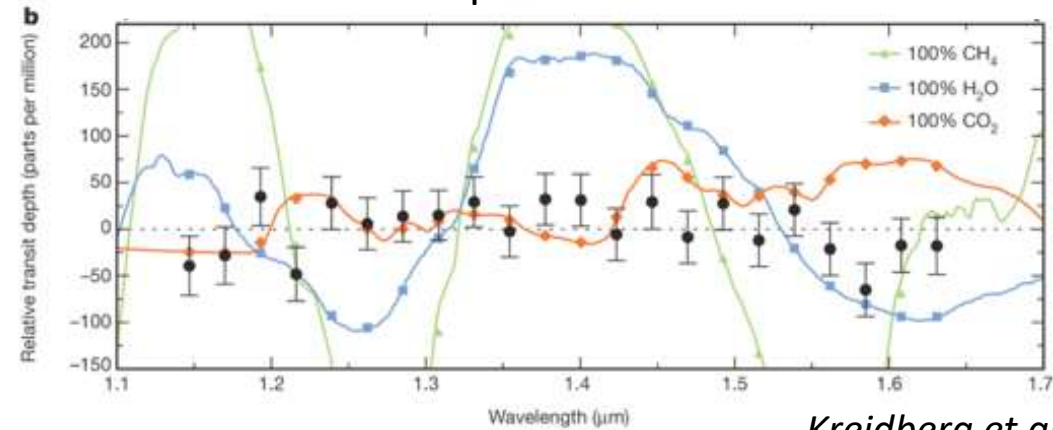
# Observations of clouds & haze in exoplanets

A continuum from cloudy to cloud-free planets by transit observations



*Sing et al. (2015)*

Flat transit spectrum of GJ 1214 b



*Kreidberg et al. (2014)*

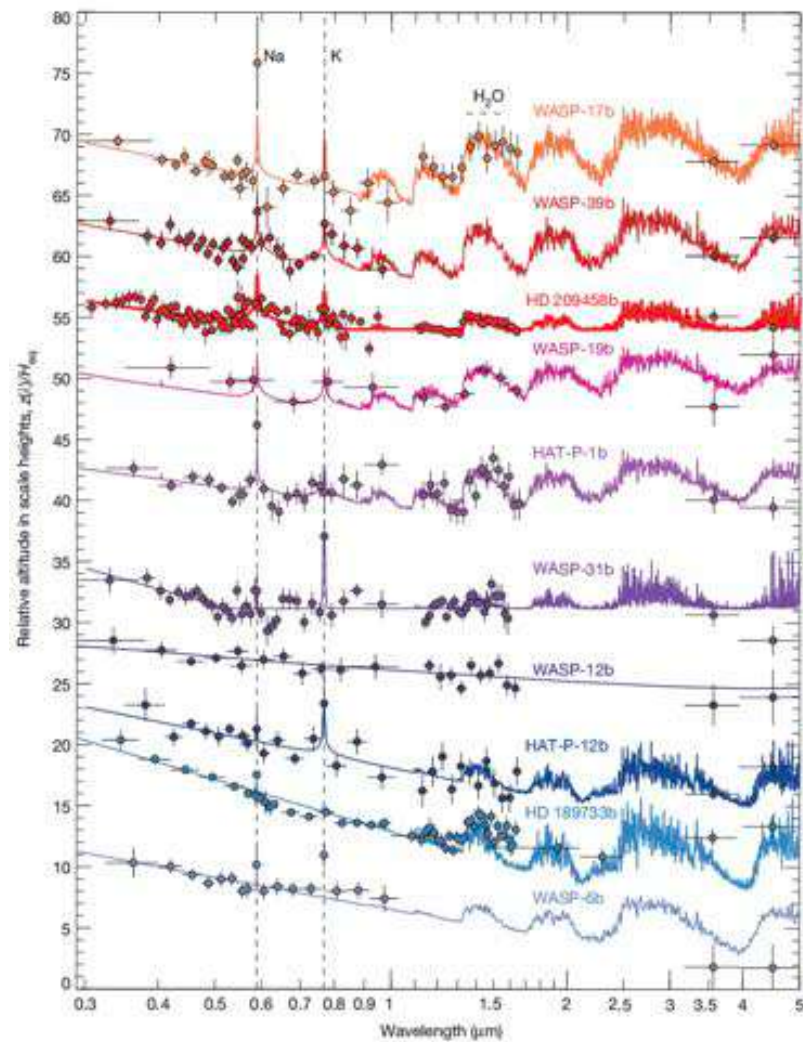
From transit observations:

→ Flat transit spectrum

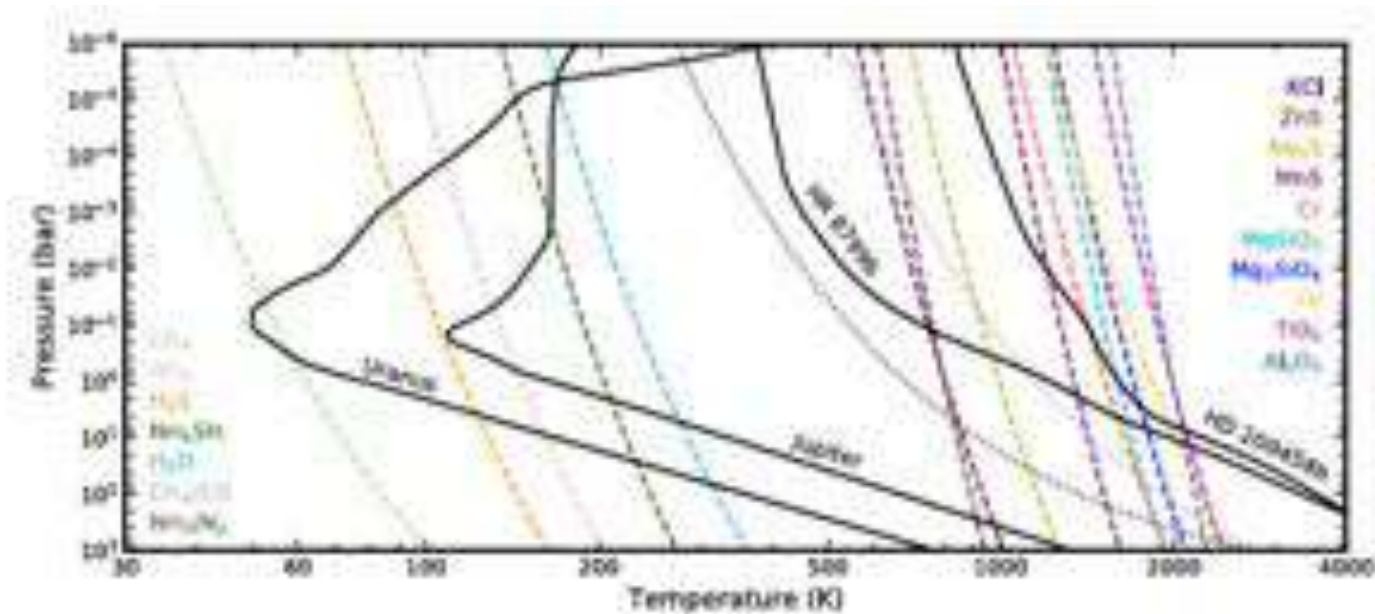
→ Mie/Rayleigh-scattering slope

# Observations of clouds & haze in exoplanets

A continuum from cloudy to cloud-free planets by transit observations



Sing et al. (2015)

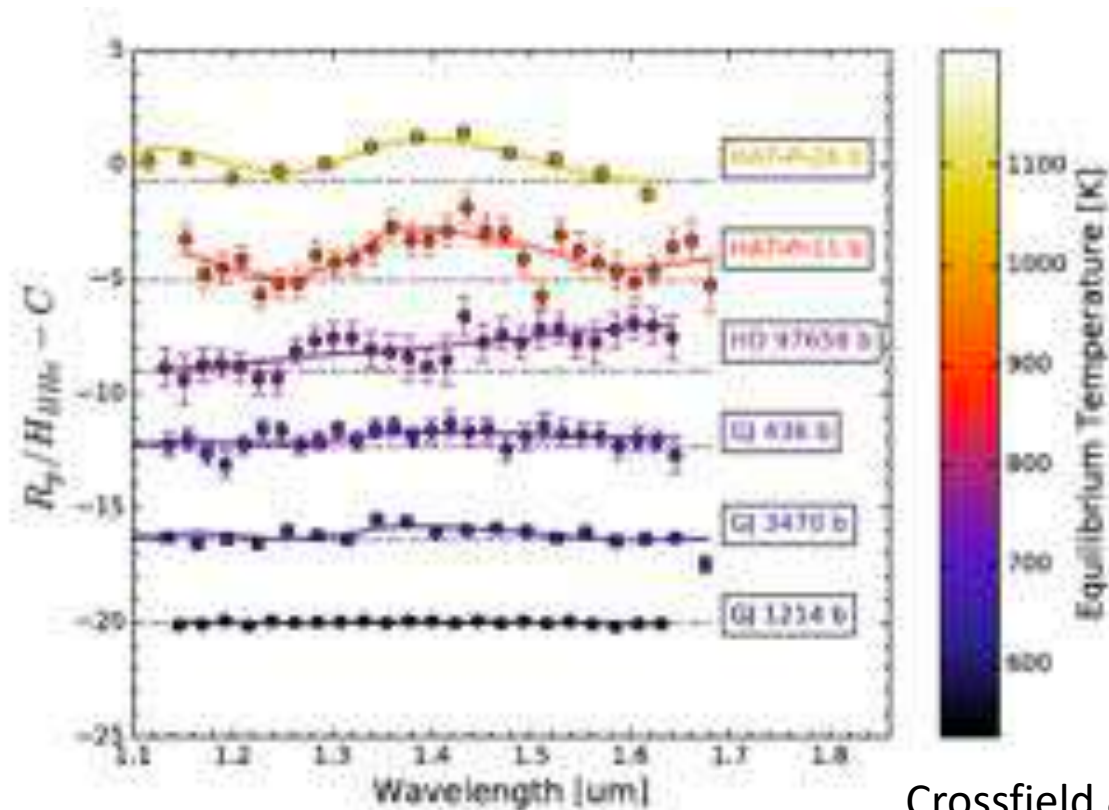


Gao et al. 2021

# Observations of clouds & haze in exoplanets

A photometric diagnostic for clouds/haze

The depth of the 1.4  $\mu\text{m}$  water band from HST-WFC3 = number of scale heights (assuming solar metallicity)

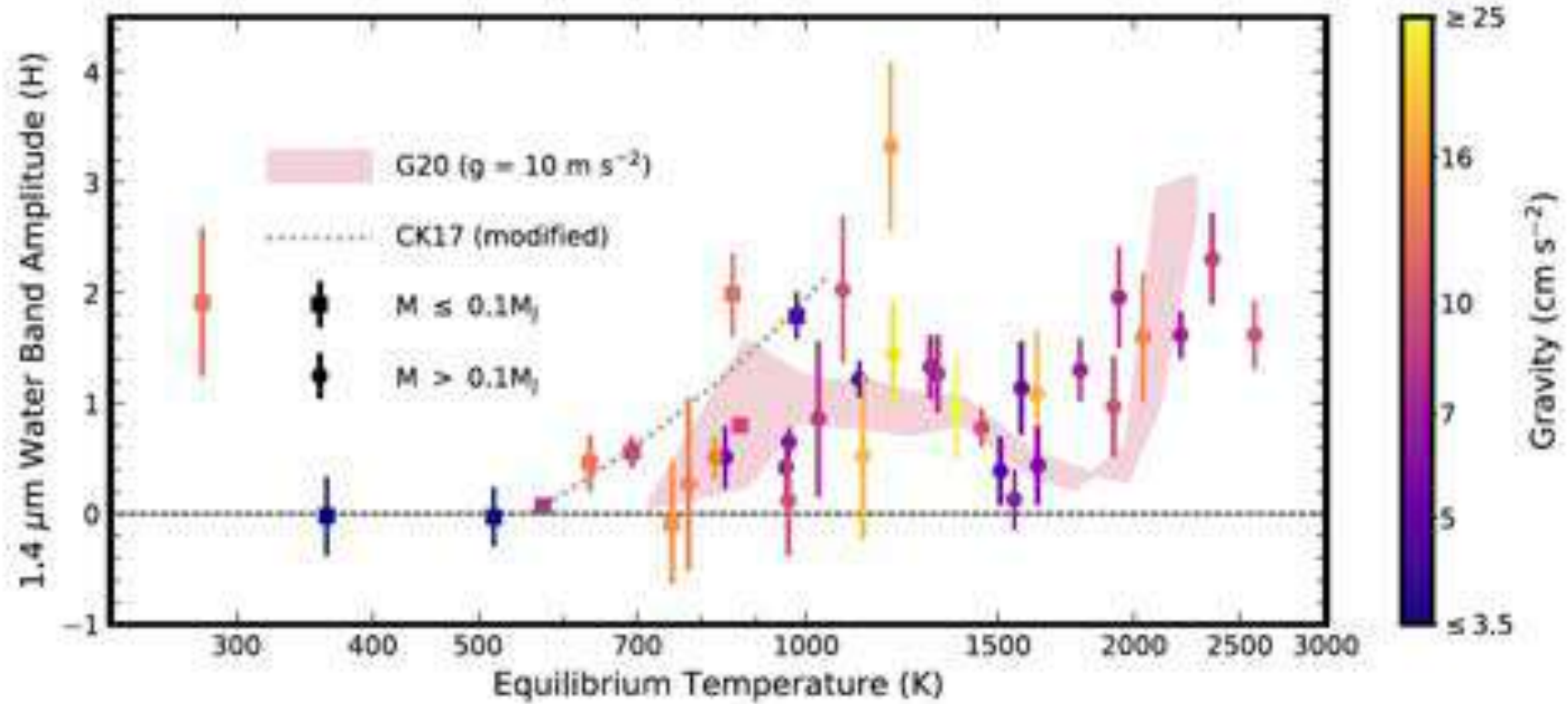


$$A_{H_2O} = \frac{\bar{X}_{[1.35-1.45\mu\text{m}]} - \bar{X}_{[1.22-1.29\mu\text{m}]}}{2R_p H / R_\star^2}$$

Crossfield & Kreidberg 2017

# Observations of clouds & haze in exoplanets

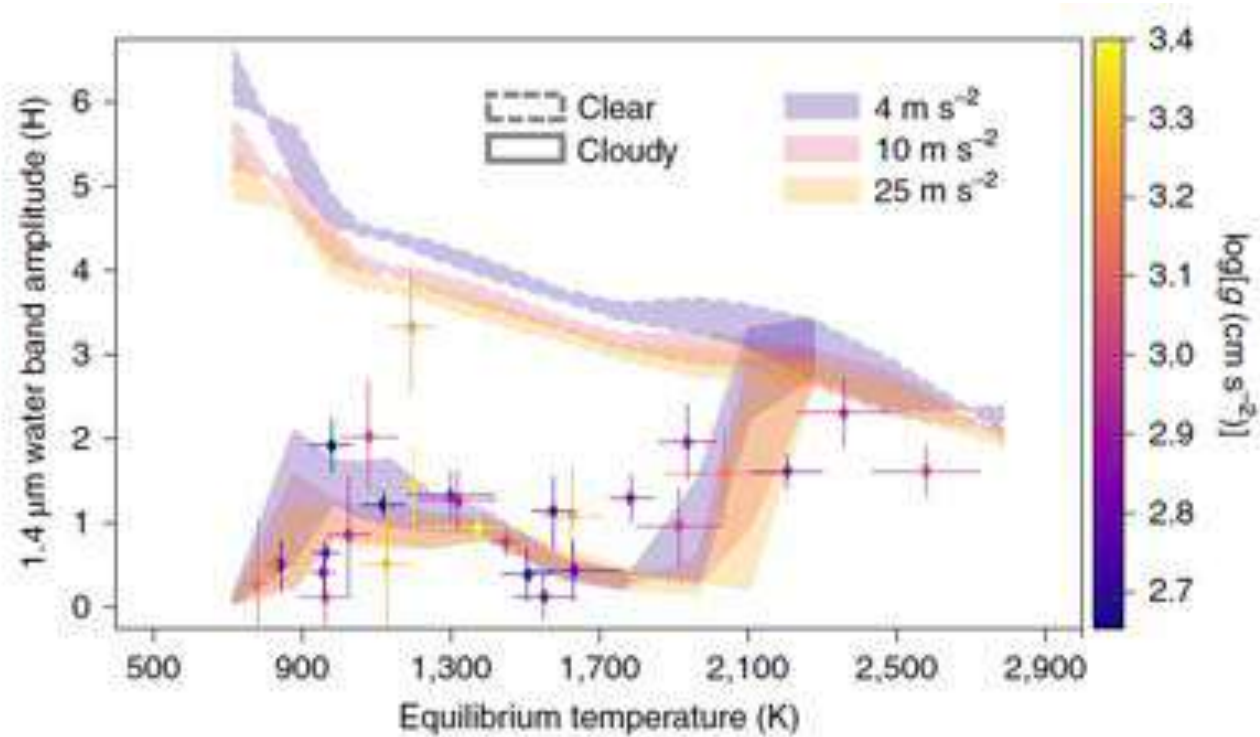
## Temperature trends in transit spectra



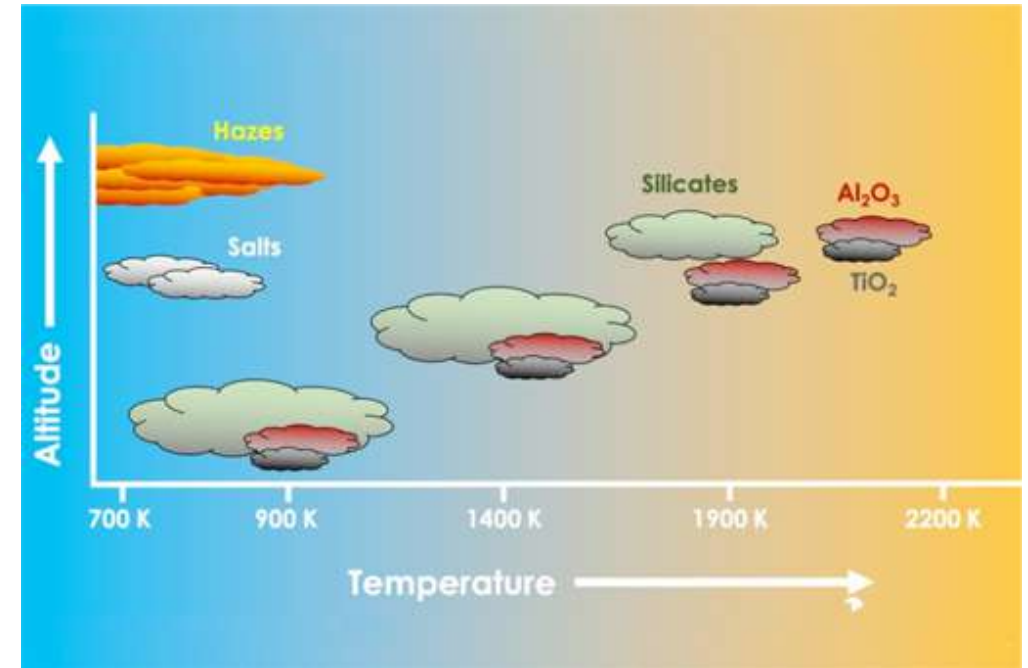
Gao et al. 2021

# Observations of clouds & haze in exoplanets

## Temperature trends in transit spectra for hot Jupiters



Gao et al. 2020



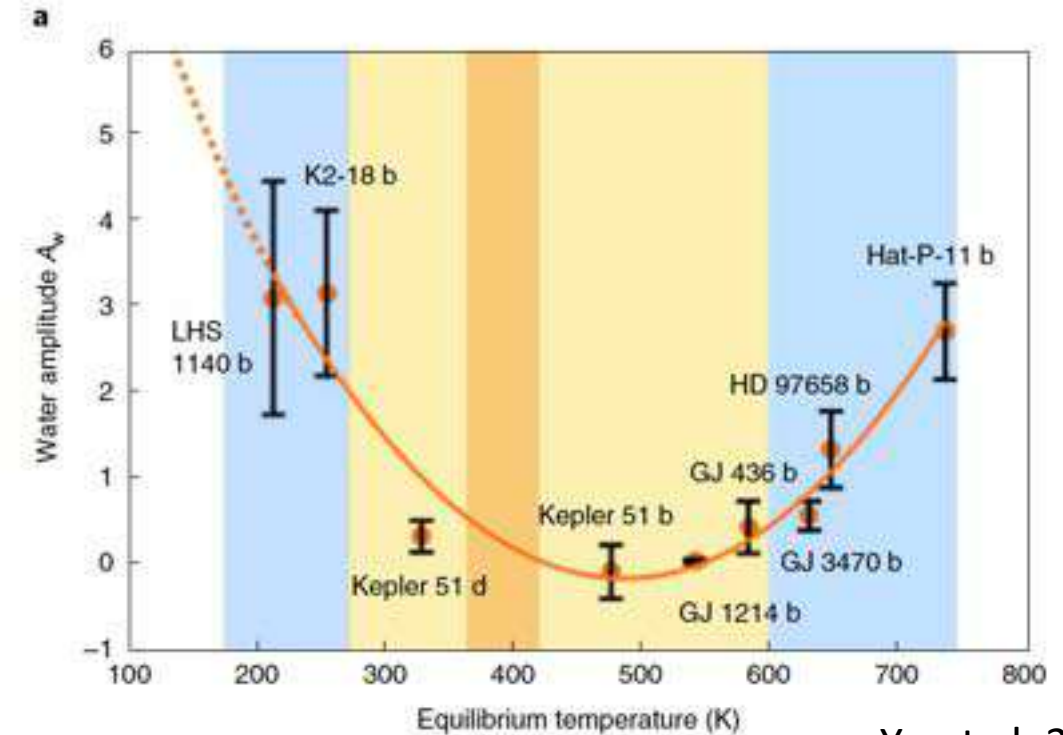
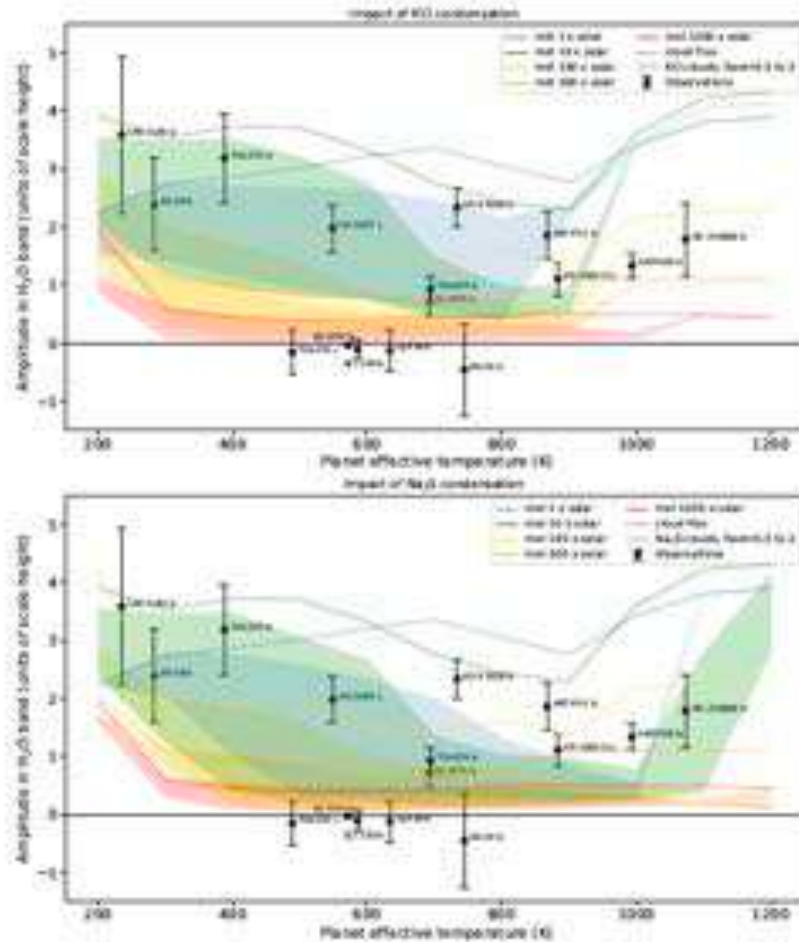
Main transitions:

- $T < 900$  K: Haze and salts
- $1200 < T < 2000$  K : silicates
- $T > 2000$  K: clear atmosphere +  $H_2$  dissociation



# Observations of clouds & haze in exoplanets

## Temperature trends in transit spectra for warm/temperate planets



Yu et al. 2021

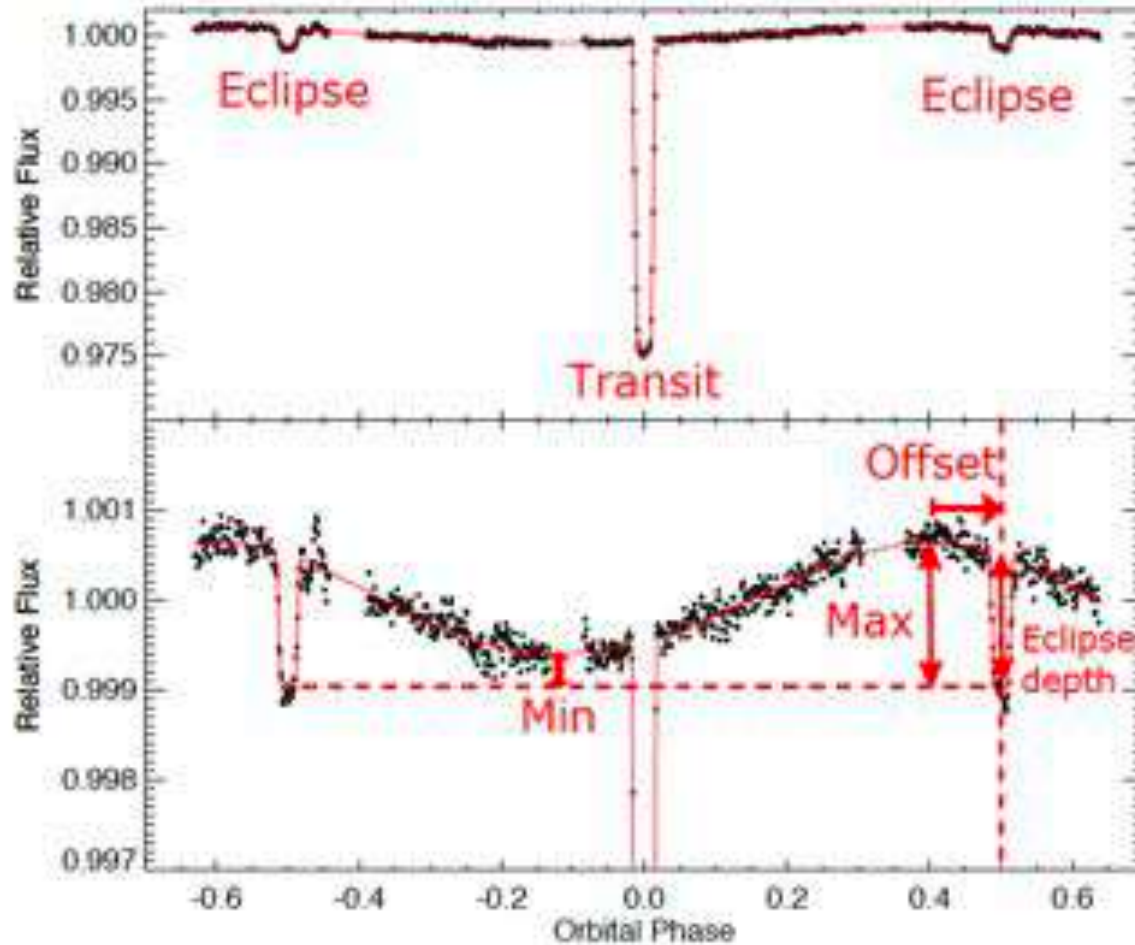
Planets with  $T_{eq}$  between 300 and 600 K are very cloudy/hazy.  
 Less haze below 300 K => wet deposition  
 But measurements could be biased by the high metallicity of these planets

Gressier et al. in rev

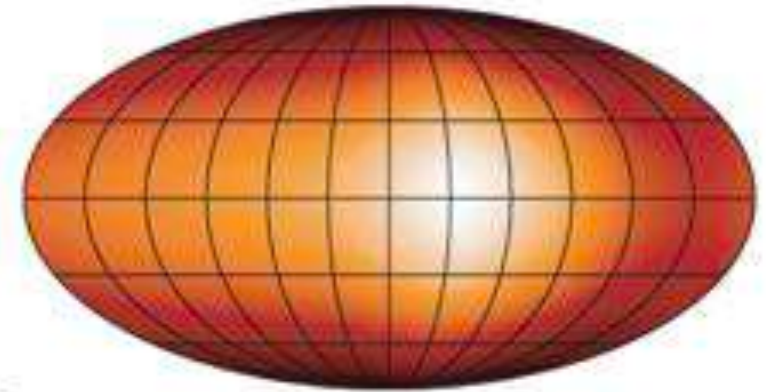
# Observations of clouds & haze in exoplanets

## Inhomogeneous cloud cover from phase curves

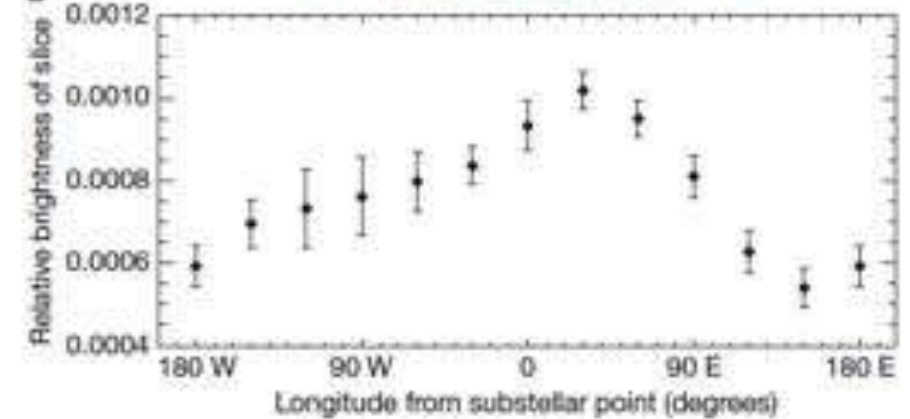
HD 189733 b



a



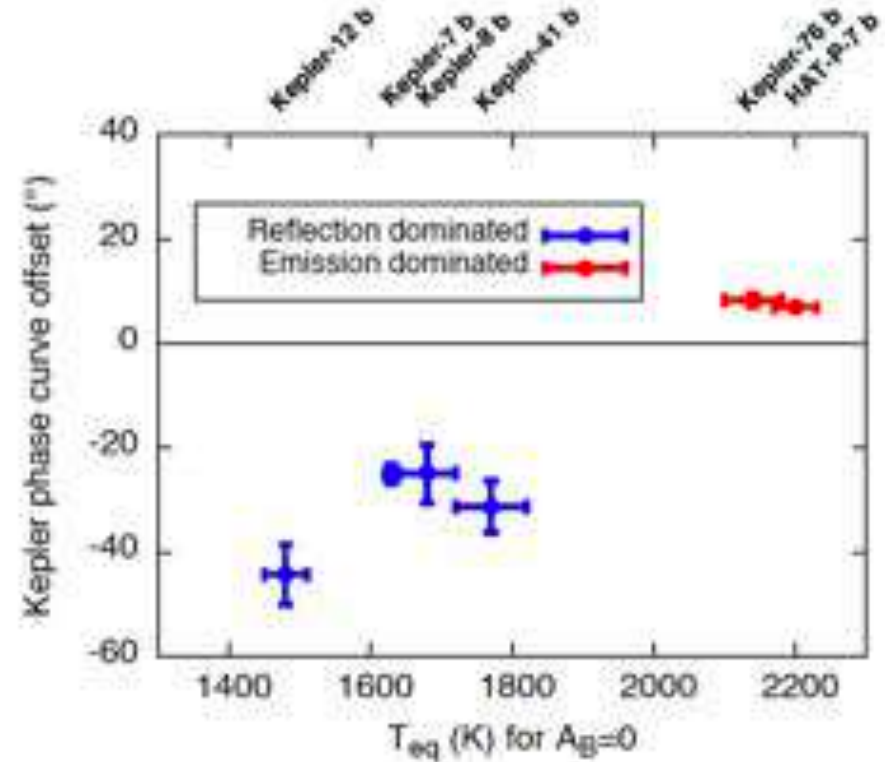
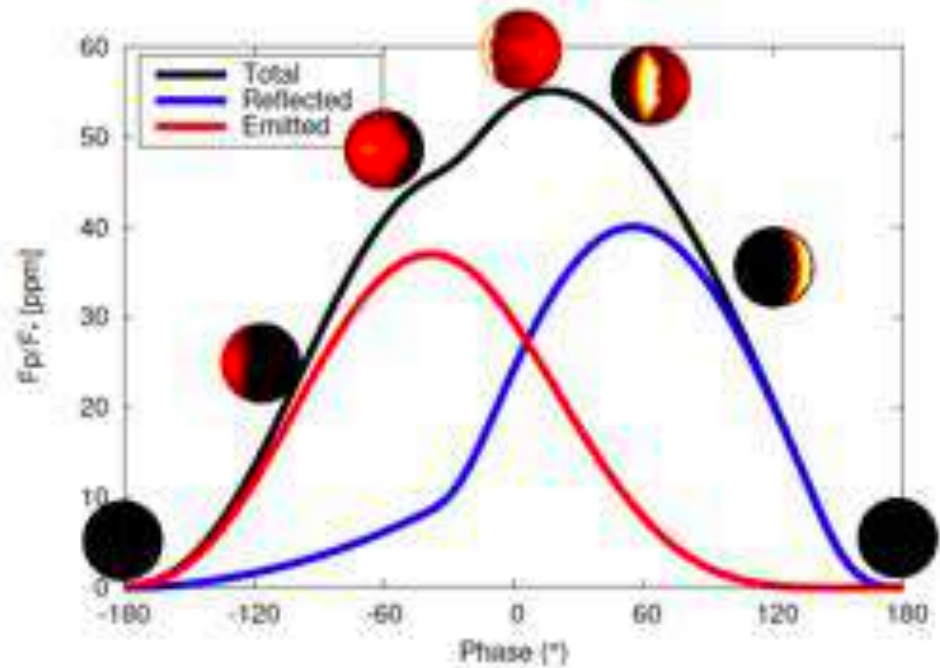
b



Knutson et al. 2007, 2012

# Observations of clouds & haze in exoplanets

## Inhomogeneous cloud cover from phase curves

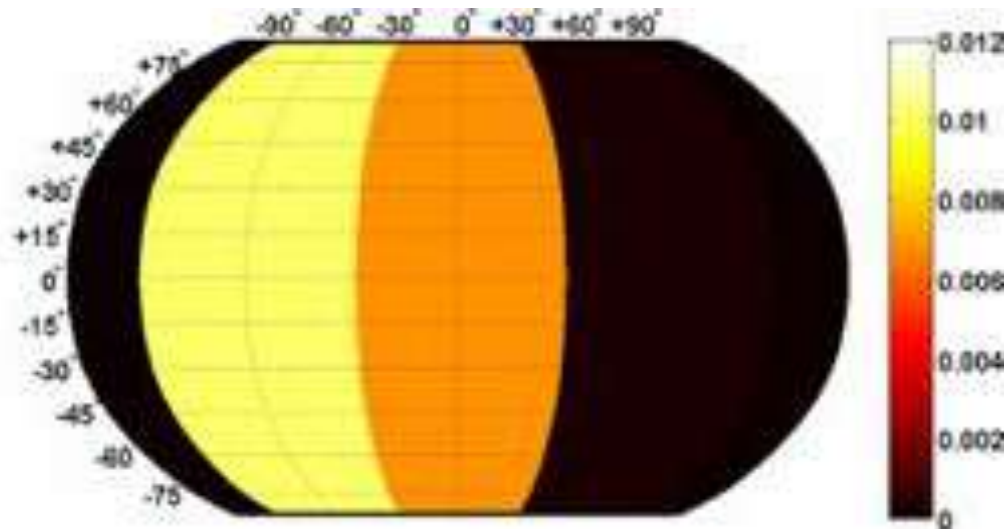


Parmentier et al. 2016

# Observations of clouds & haze in exoplanets

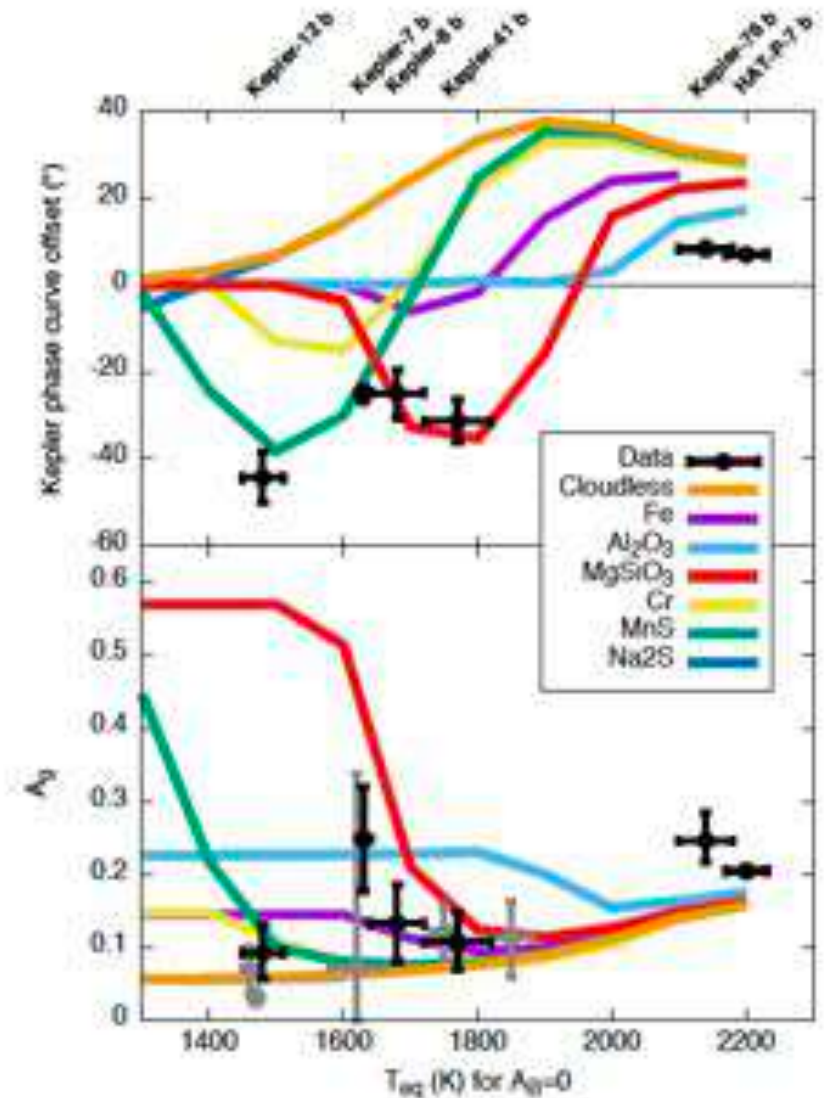
## Inhomogeneous cloud cover from phase curves

Albedo map of Kepler 7b



Demory et al. (2013)

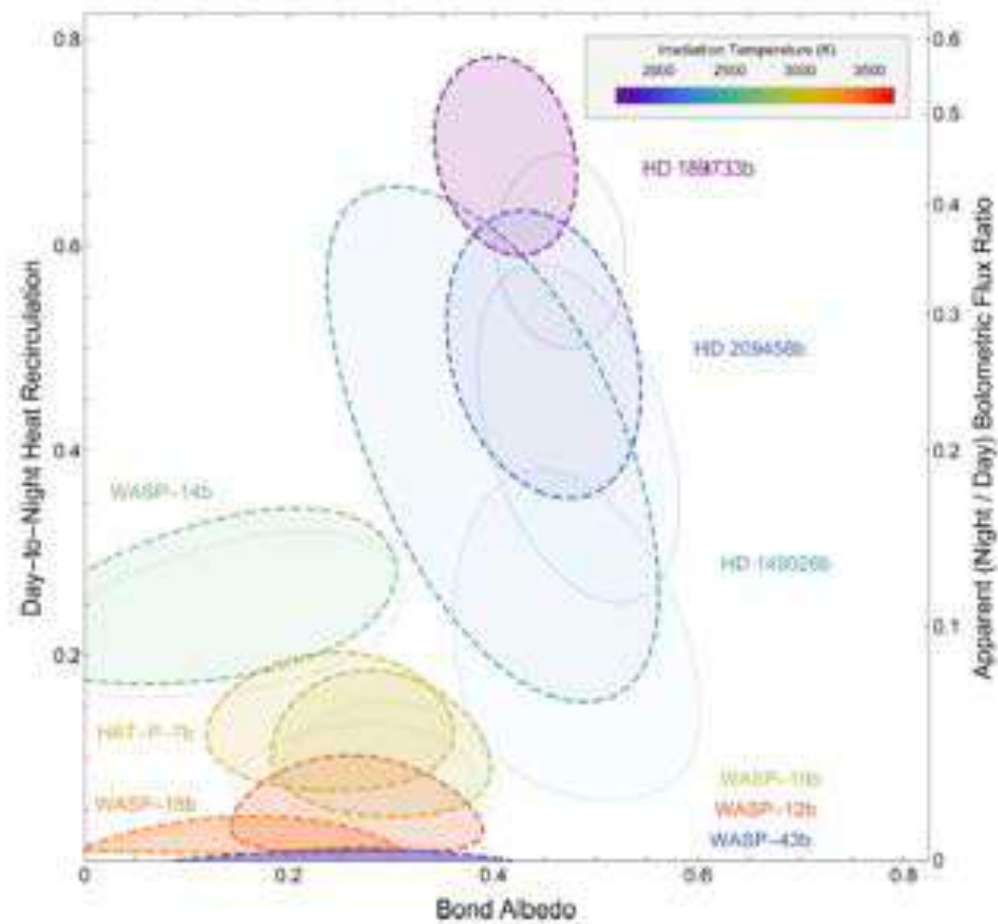
From visible phase curves:  
→ Relatively low geometric albedo  
→ Inhomogeneous cloud cover



Parmentier et al. 2016

# Observations of clouds & haze in exoplanets

## The albedo problem for exoplanets

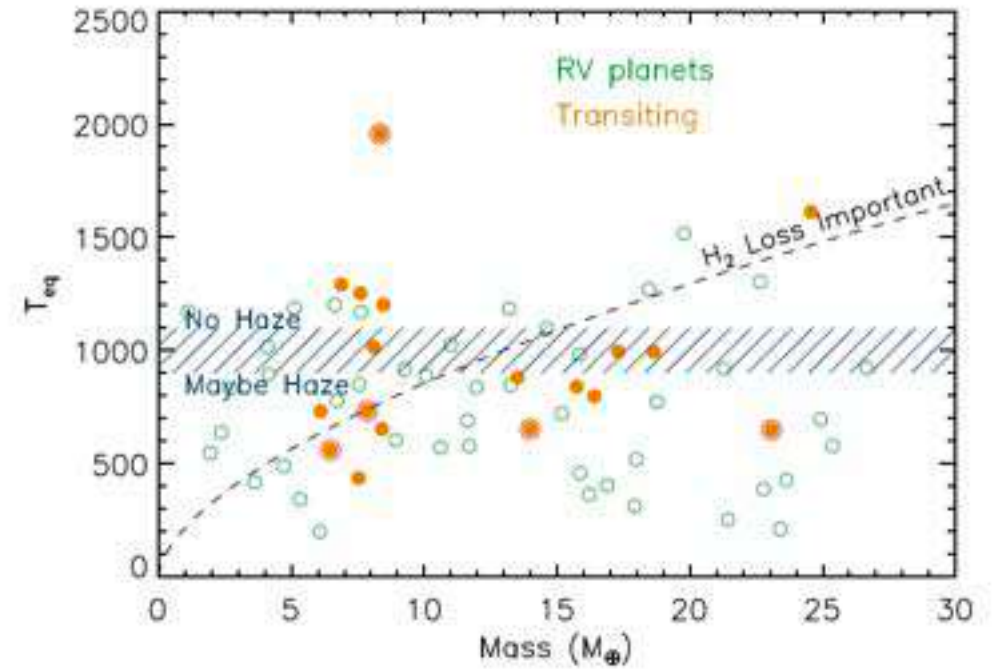
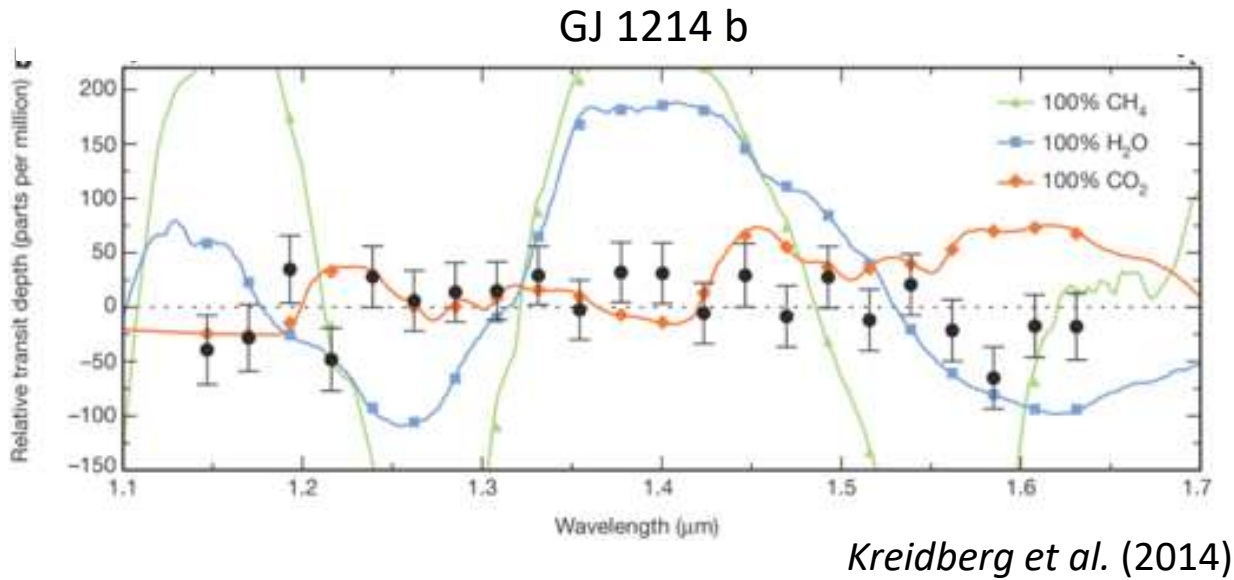


Schwartz 2017

- Bond albedo from Spitzer phase curve is significantly higher than geometric albedo from Kepler
- Potential high reflectivity in near-IR

# Observations of clouds & haze in exoplanets

Evidence for photochemical haze on warm sub-Neptunes ?



Fortney et al. 2013

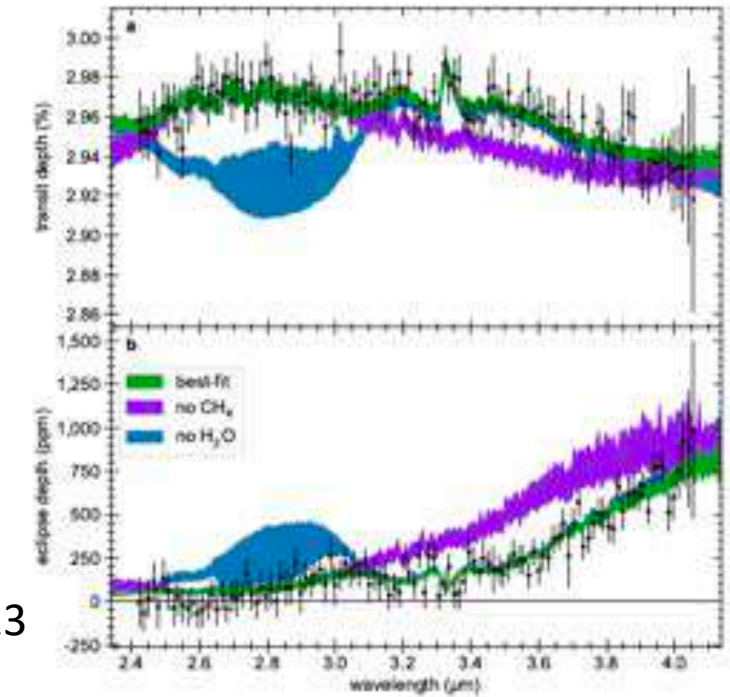
# Observations of clouds & haze in exoplanets

## Methane depletion on warm sub-Neptunes/Neptunes

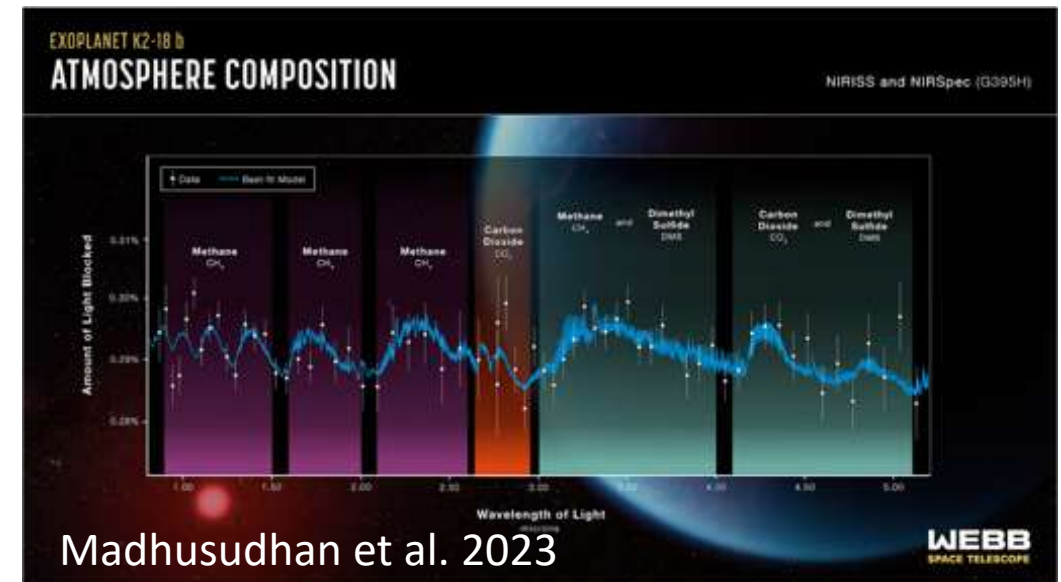
Planet	H <sub>2</sub> O	CH <sub>4</sub>	CO	CO <sub>2</sub>	NH <sub>3</sub>	HCN	reference <sup>1</sup>
Keck-e							T15a
GJ 436 b							
GJ 1132 b							
GJ 1254 b							
GJ 3470 b							H19a, E22
HAT-P-11 b							F14, E22
HAT-P-26 b							W17, MD19, E22
HD 8167 c							G20, M20a, E22
HD 97658 b							E22
HD 106815 c							G20, K20, E22
HD 219666 b							
HIP 41378 b							
K2-18 b							T19, H19b, E22
K2-24 b							
LHS 1140 b							E22
LTT 9759 b							
TOI 370 c							
TOI 370 d							E22
TOI 679 b							E22, E22
TRAPPIST-1 b							
TRAPPIST-1 c							
TRAPPIST-1 d							
TRAPPIST-1 e							
TRAPPIST-1 f							
TRAPPIST-1 g							
TRAPPIST-1 h							

Gressier et al. (2022)

WASP-80 b



Bell et al. 2023



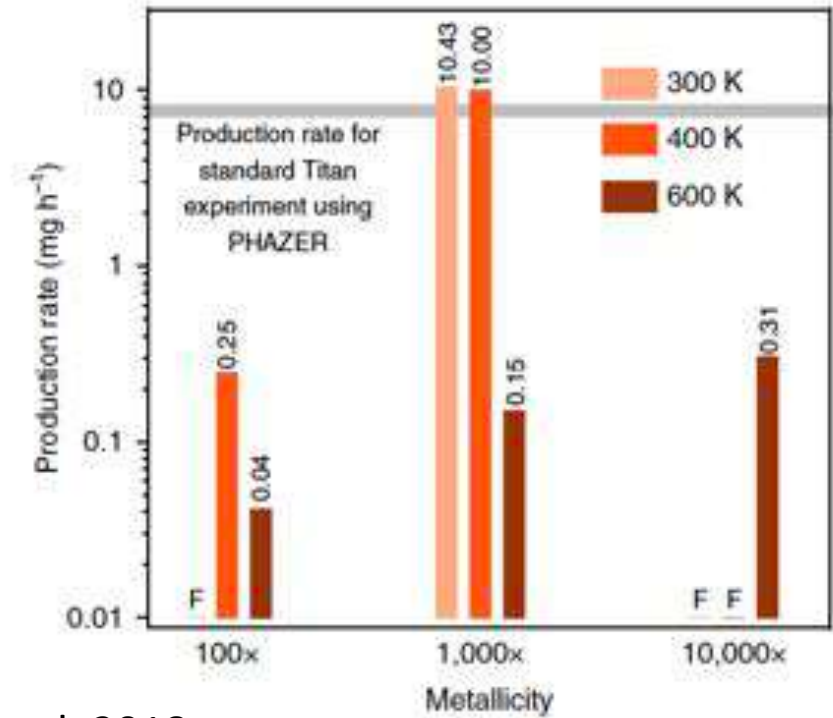
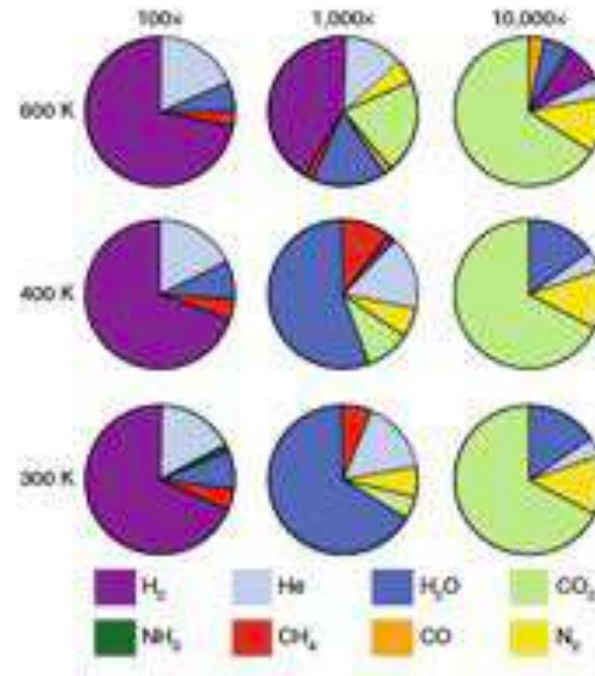
Madhusudhan et al. 2023

WEBB  
SPACE TELESCOPE

# Observations of clouds & haze in exoplanets

## Lab experiments of haze formation

PHAZER



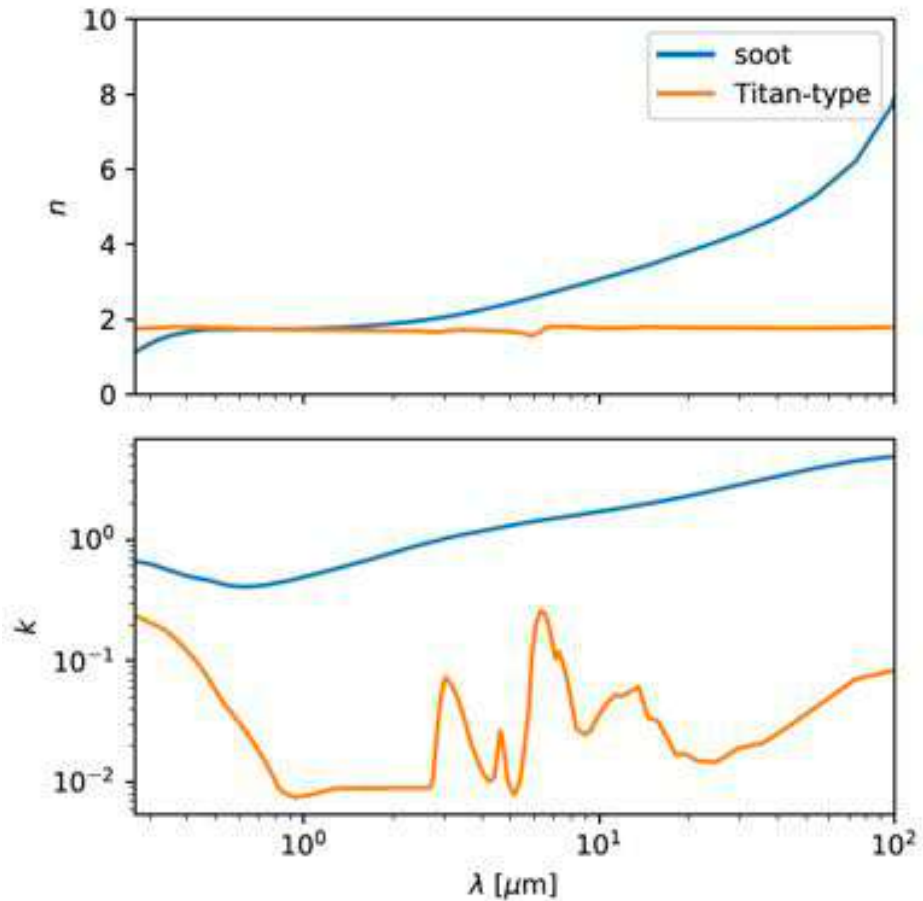
Hörst et al. 2018

Great diversity of haze production rate for sub-Neptunes  
Haze production without CH<sub>4</sub>

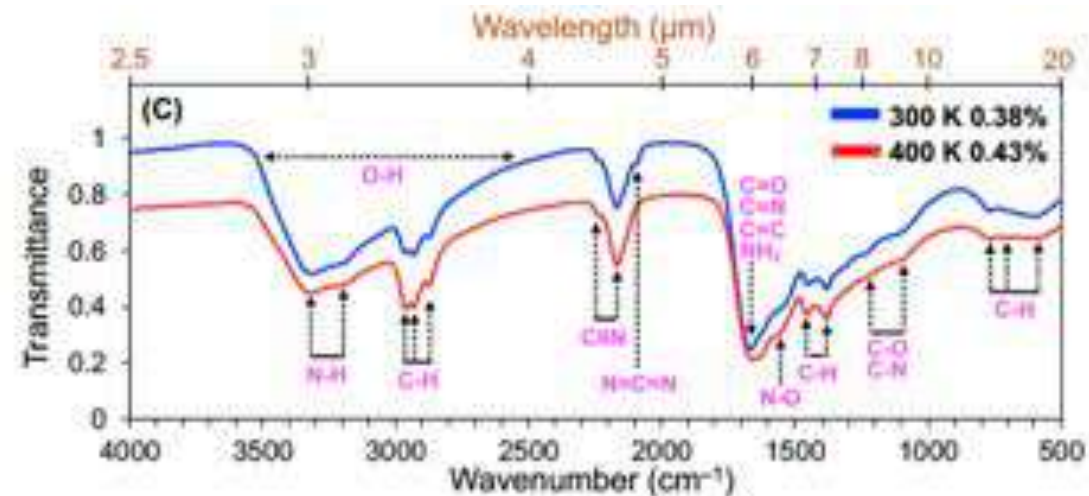
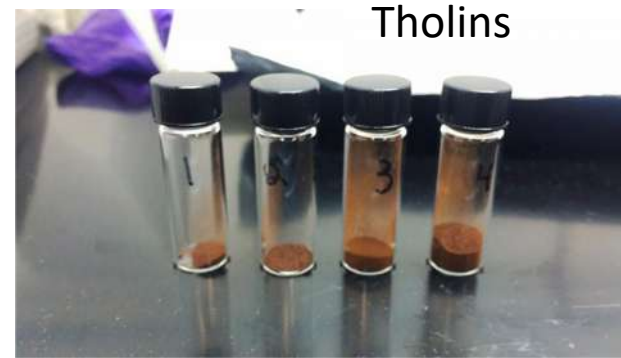


# Observations of clouds & haze in exoplanets

## Lab experiments of haze formation



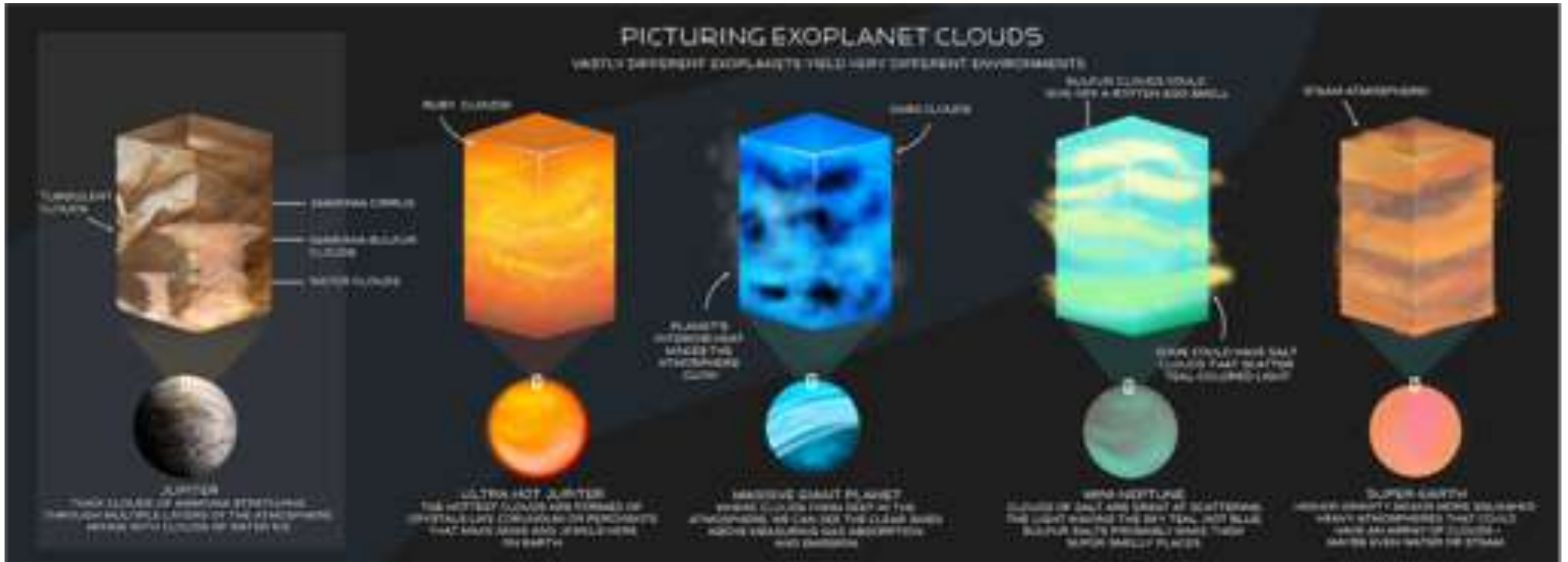
Steinrueck et al. 2023



He et al., 2023

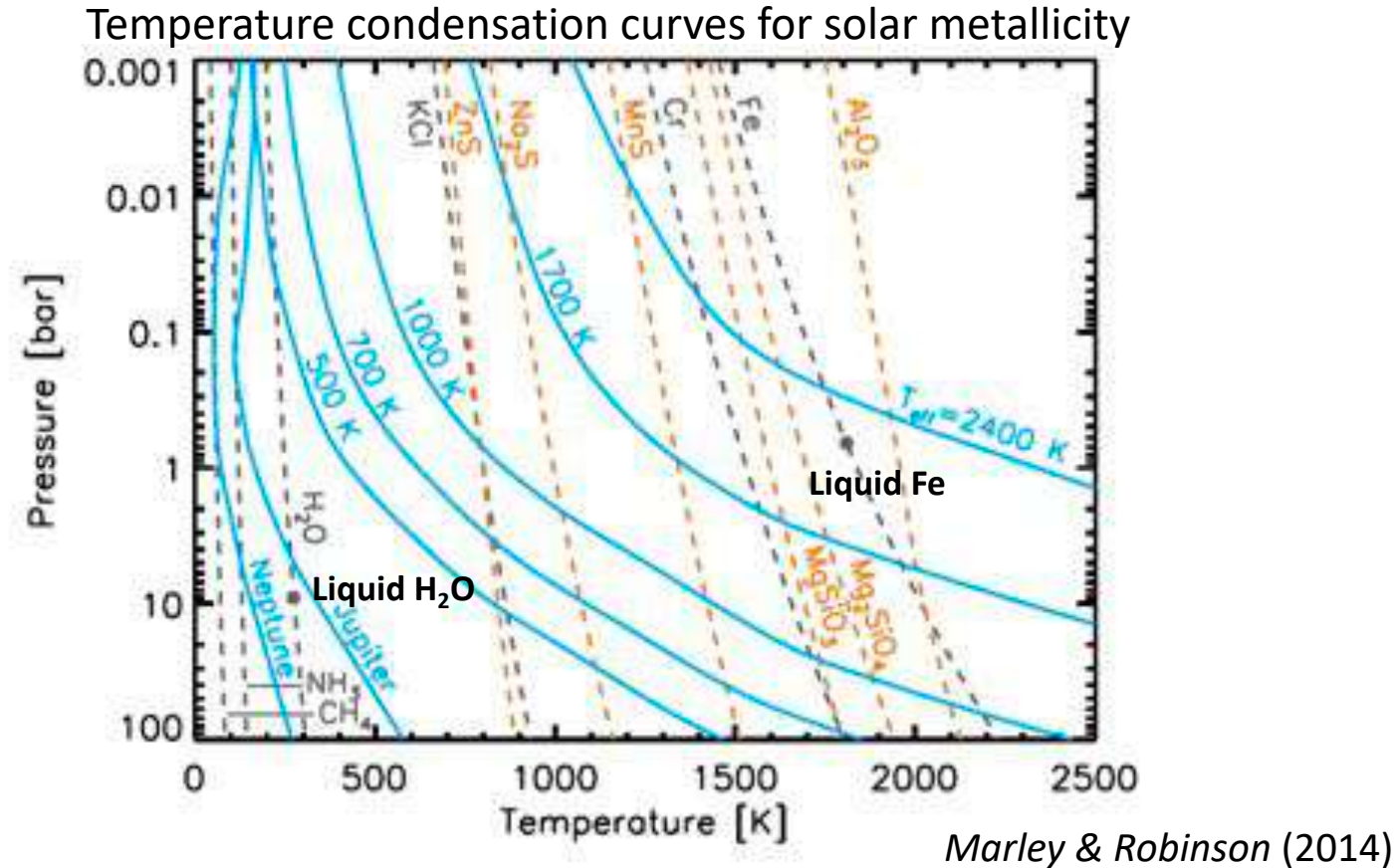
Haze features are related to specific chemical bonds

# How to model clouds/haze in exoplanetary atmospheres ?



# Modeling clouds & haze

## Condensation curves



Elemental abundances from *Lodders et al.* (2003)

Temperature condensation curves from *Visscher et al.* (2006, 2010)

Clausius-Clapeyron relation:

$$P_{sat} = P_{sat}(T_0) e^{-\frac{L}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)}$$

# Modeling clouds & haze

## 1D Cloud models

### 1) Model with $f_{sed}$ from Ackerman & Marley 2001

At equilibrium :

$$\frac{\partial q_c}{\partial z} = -\frac{\partial q_s}{\partial z} - \frac{V_{sed}}{K_{zz}} q_c$$

- $q_c$  = mass mixing ratio of condensate
- $q_s$  = mass mixing ratio of vapor at saturation
- $V_{sed}$  = sedimentation speed
- $K_{zz}$  = eddy diffusion coefficient

Mixing length theory:

$$K_{zz} = \frac{H}{3} \left(\frac{L}{H}\right)^{4/3} \left(\frac{rF_{conv}}{c_p \rho_a}\right)^{1/3}$$

Ackerman & Marley 2001: Mixing length:  $L=H$

**Assumption:**  $f_{sed} = \frac{HV_{sed}}{K_{zz}} = \text{constant}$  (generally  $f_{sed} = 1-5$ )

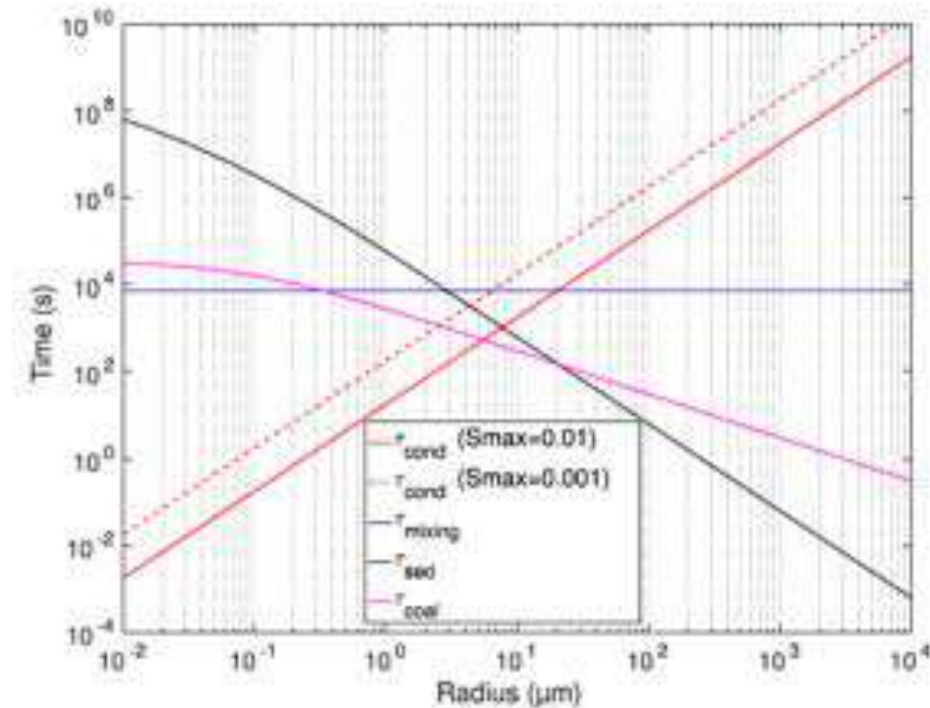
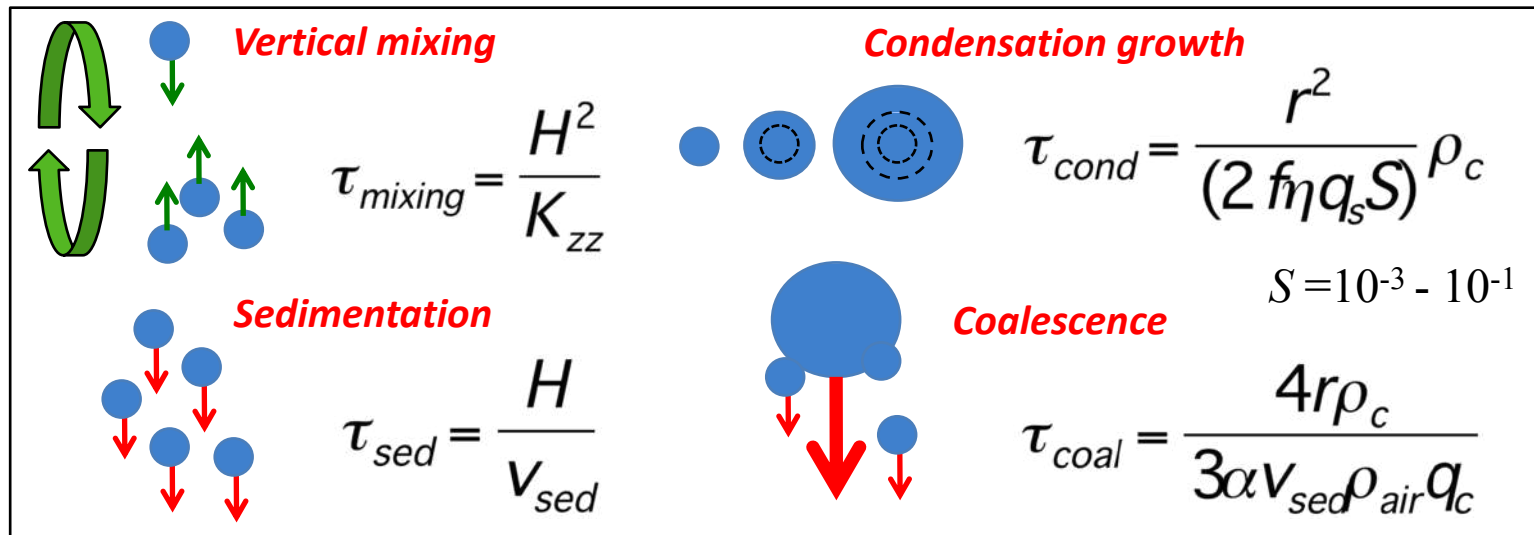
Above condensation:  $q_c = qc_0 \left(\frac{P}{P_0}\right)^{f_{sed}}$

# Modeling clouds & haze

## 1D Cloud models

### 2) Model with simple microphysics using timescales from Rossow 1978

e.g. BT-Settl (*Allard et al. 2001*) and Exo-REM (*Charnay et al. 2018*)

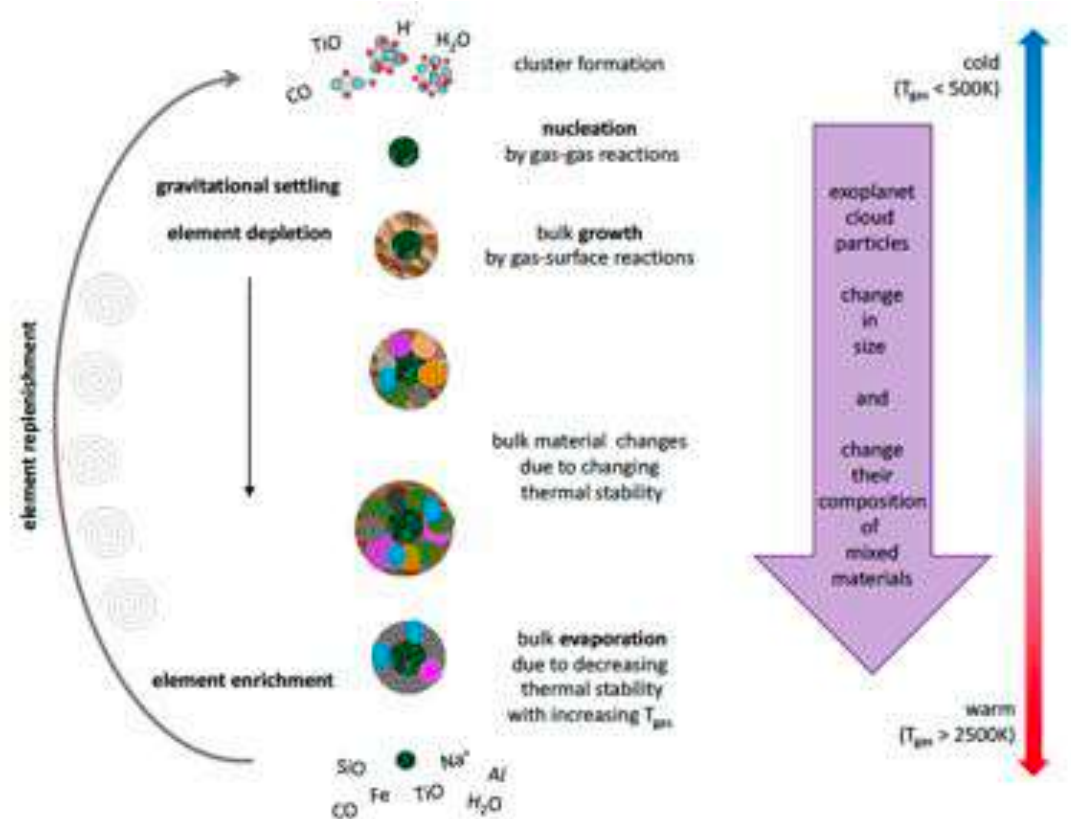


# Modeling clouds & haze

## 1D Cloud models

### 3) Models with full microphysics

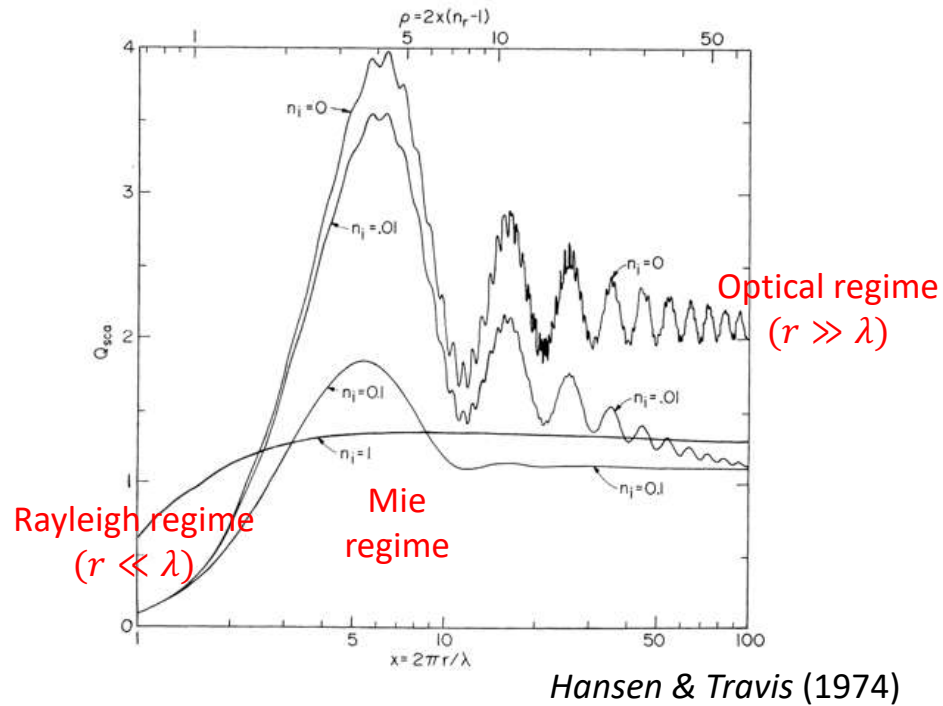
e.g. Drift-Phoenix (*Woitke & Helling 2003*)



# Modeling clouds & haze

## Opacity

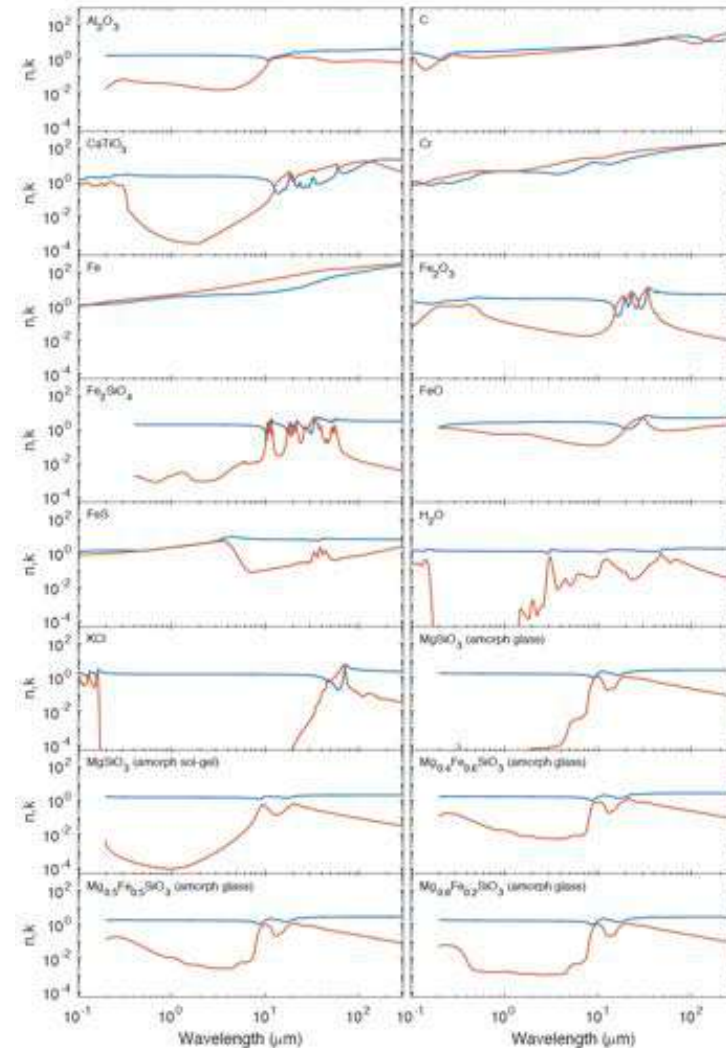
We usually compute aerosol optical properties ( $Q_{\text{ext}} = \sigma_{\text{ext}} / \pi r^2$ ,  $\omega_0$ ,  $g$ ) from Mie Theory with optical indexes and assuming spherical particules



Cloud optical depth:  $\tau_c = \frac{3 Q_{\text{ext}} w}{4 \rho r_e}$

$w$ : mass column  
 $\rho$ : volumic mass  
 $r_e$ : effective radius

Optical indexes  
 ( $n$ =real=scattering,  $k$ =imaginary=absorption)

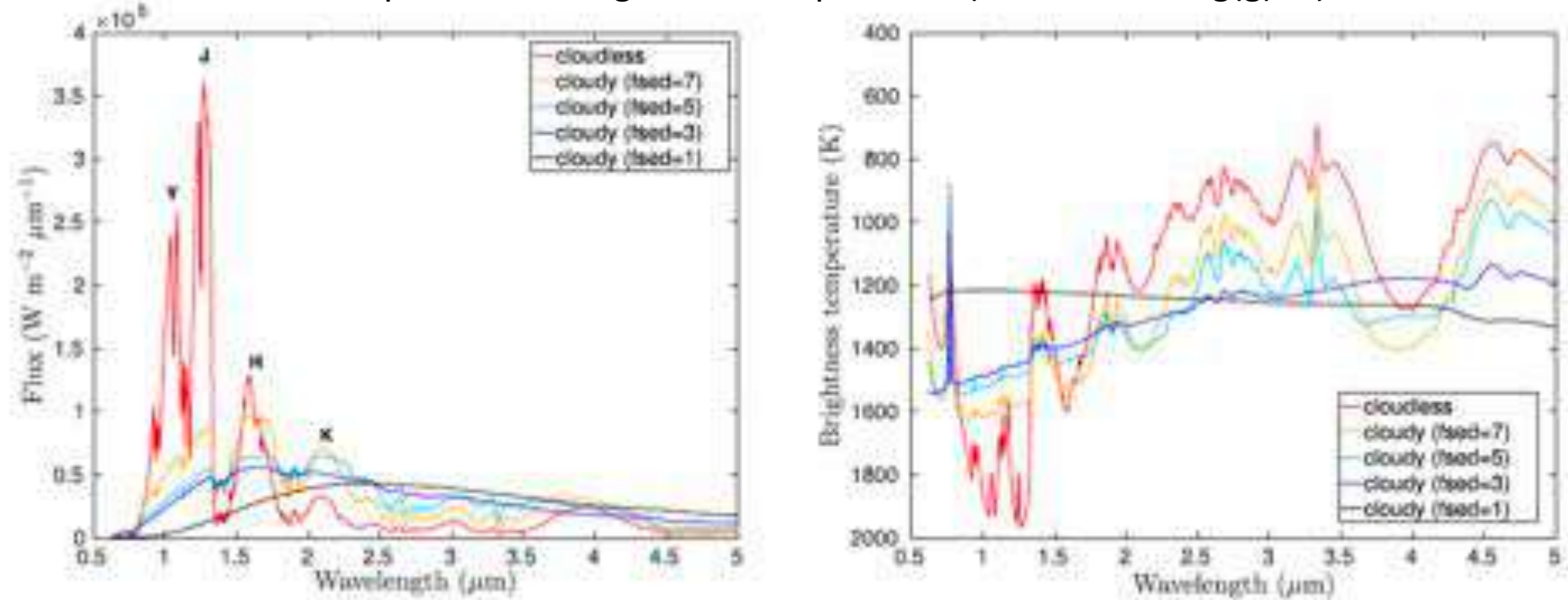


*Kitzmann et al. 2017*

# Modeling clouds & haze

## Radiative effects: absorption/emission of thermal radiation

Emission spectra and brightness temperature ( $T_{\text{eff}}=1300\text{K}$ ,  $\log(g)=5$ )



*Charnay et al. (2018)*

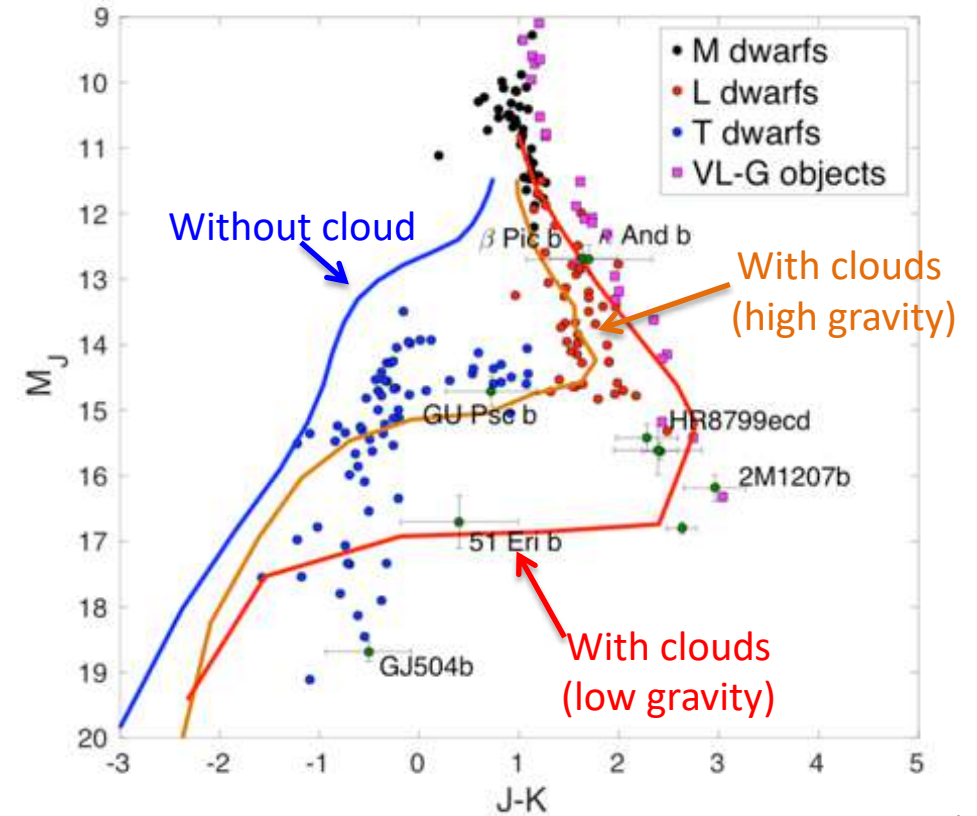
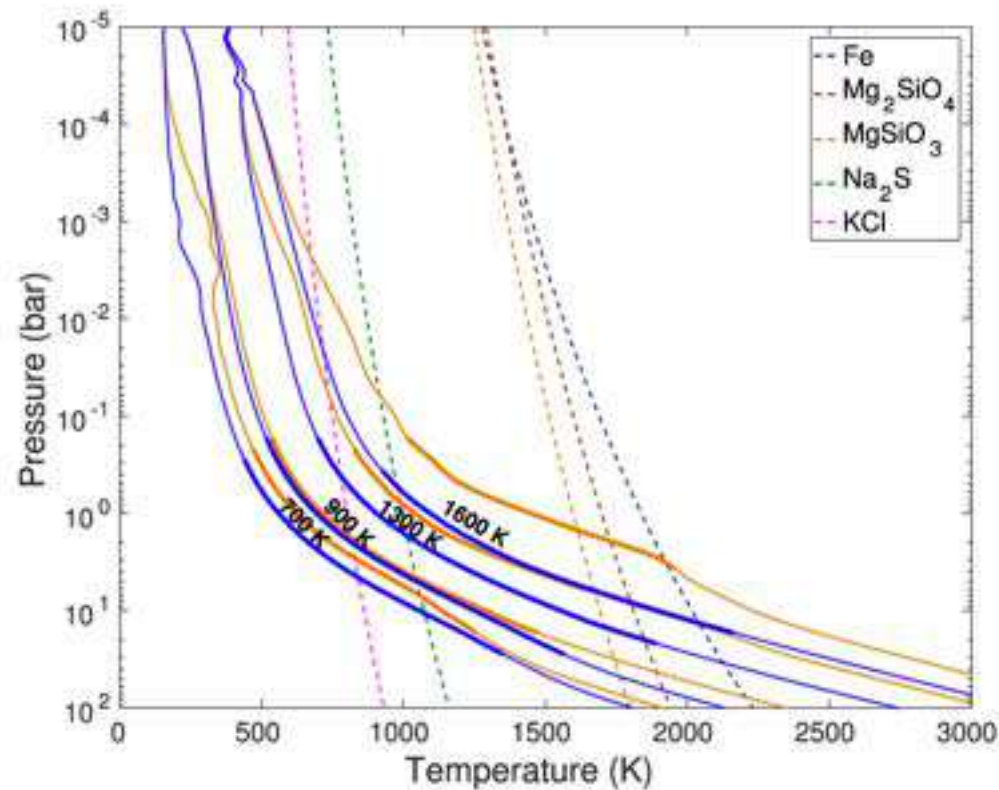


- Clouds produce a decrease of flux in spectral windows and an increase in spectral bands (greenhouse warming).
- With thick clouds, spectrum close to a blackbody



# Modeling clouds & haze

## Radiative effects: thermal structure and L-T transition



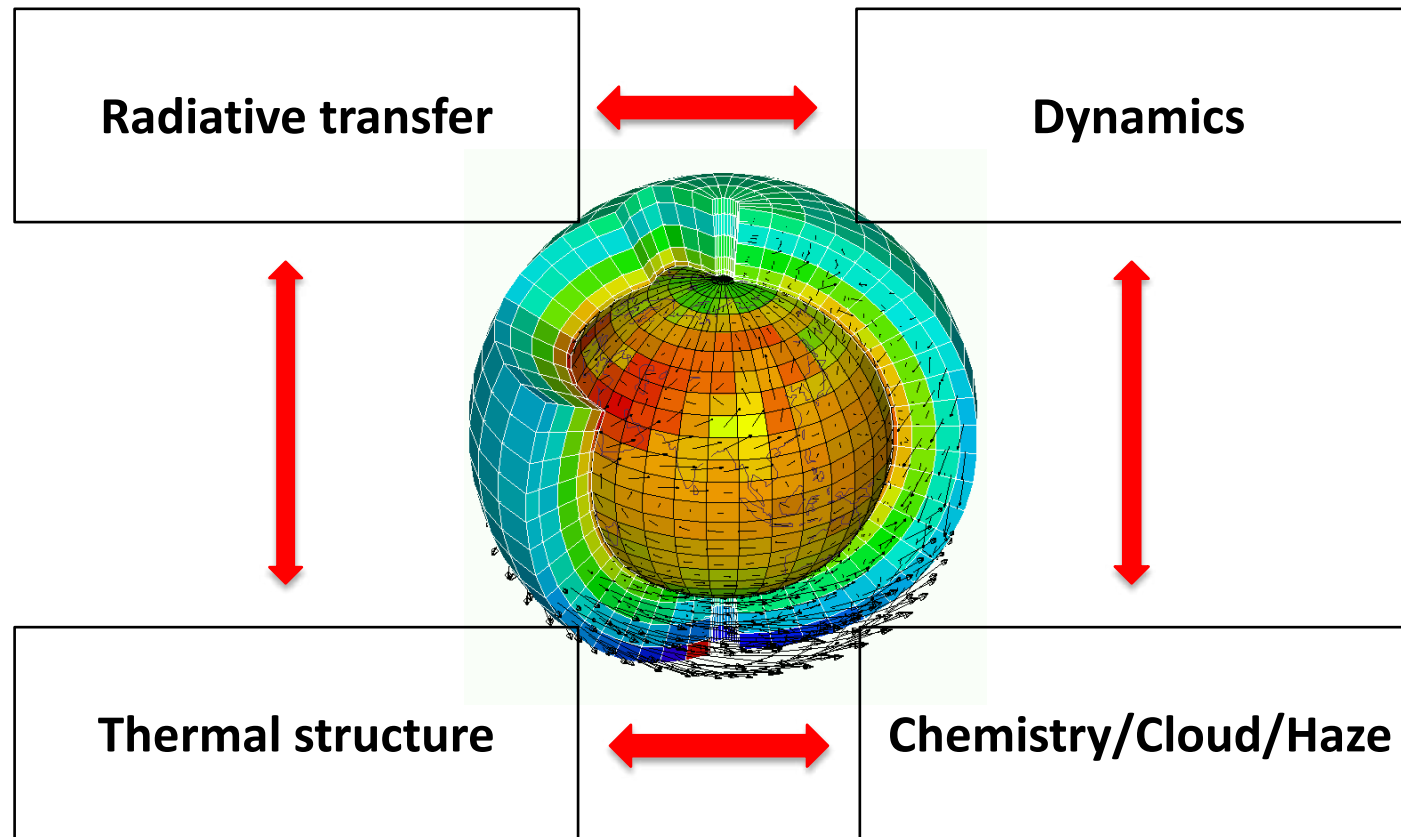
Charnay et al. (2018)

Clouds below photosphere ( $\tau \sim 1$ ) for  $T_{\text{eff}} < 1300$  K  
 $\Rightarrow$  LT transition

# Modeling clouds & haze

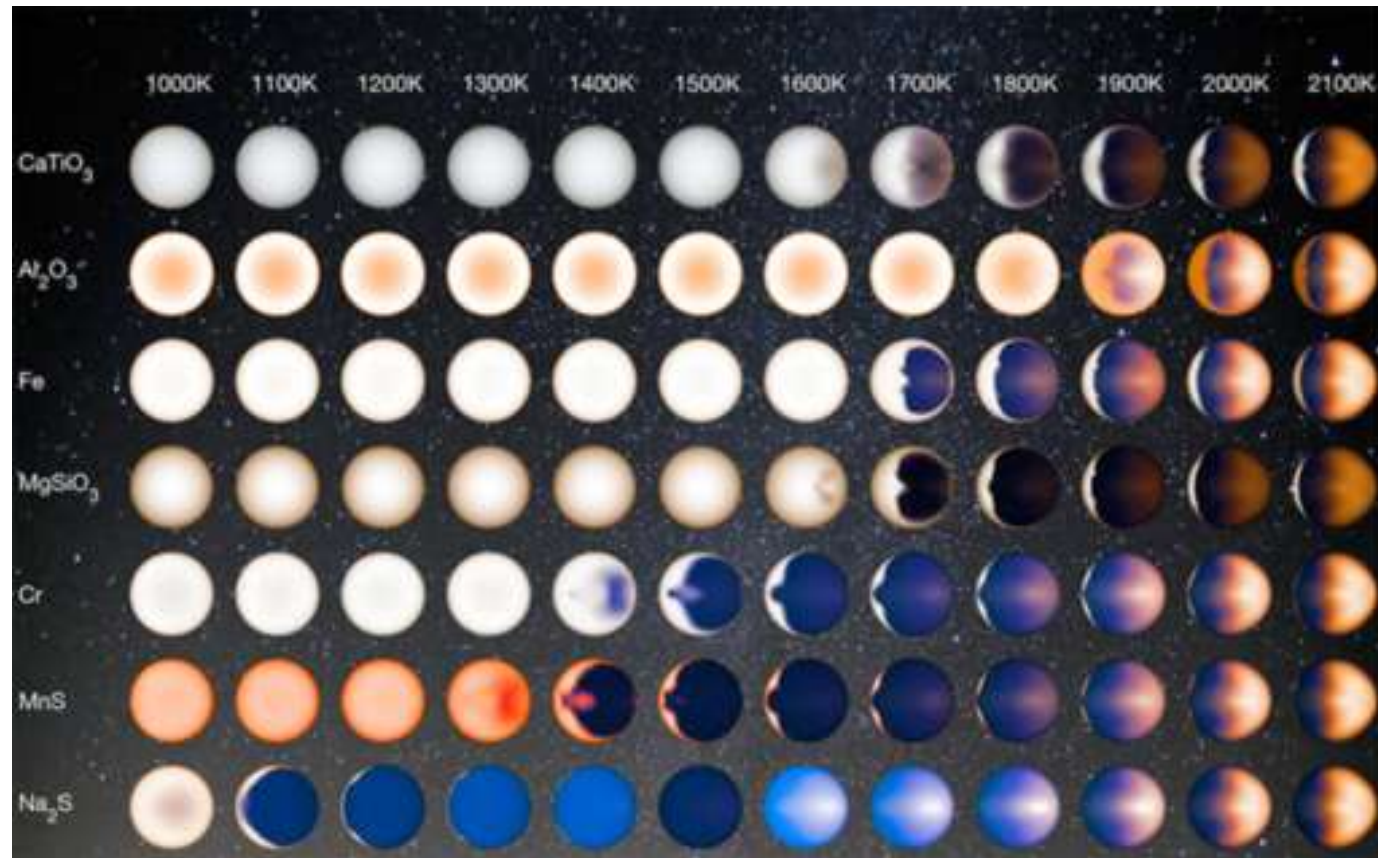
## 3D models

For strongly irradiated exoplanets, we need 3D GCM !



# Modeling clouds & haze

## 3D models



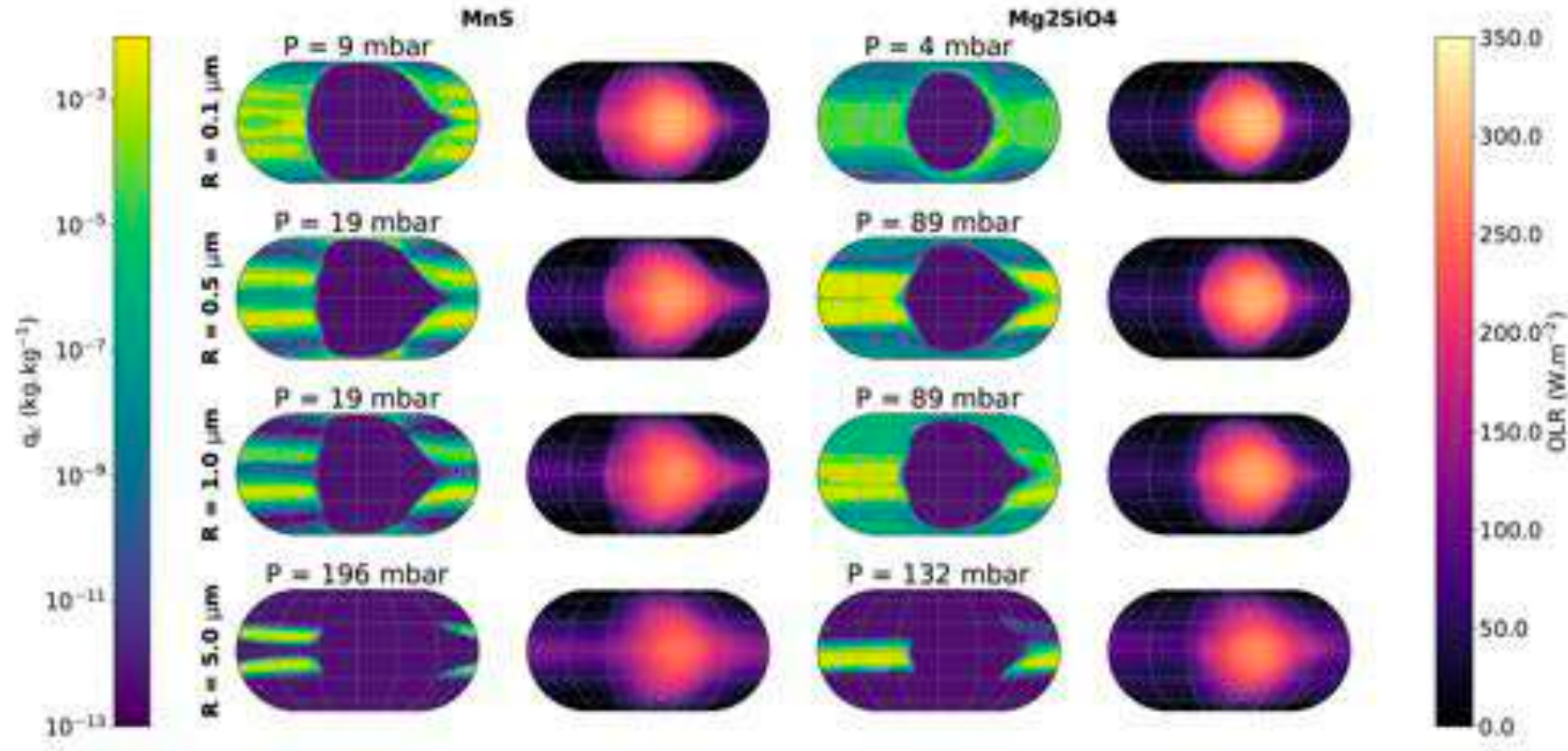
Parmentier et al. 2016

Numerous GCMs are used to simulate clouds with different complexity:

- Post-treatment
- Fixed clouds (e.g. MIT-GCM, THOR)
- Advection of cloud tracers (i.e. Generic PCM)
- Fully coupled to microphysics

# Modeling clouds & haze

## Nightside clouds on hot Jupiters



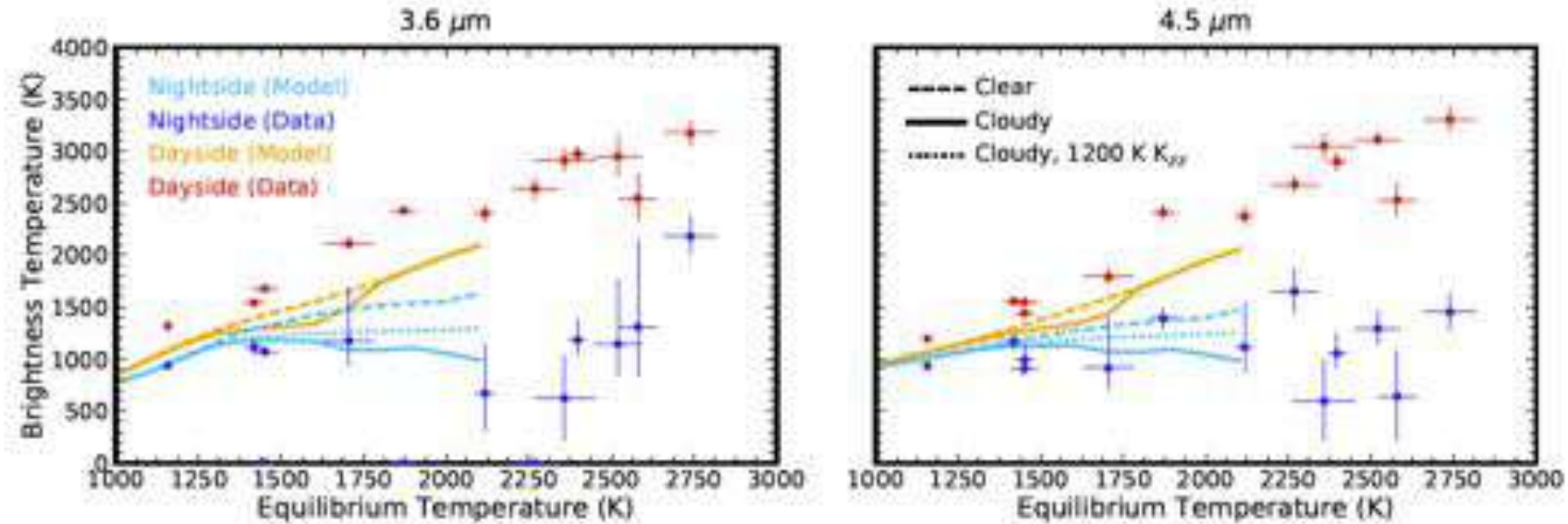
Teinturier et al. in rev.

**Silicate and salt clouds form on the nightside**  
**The west (evening) limb is cloudier than the east (morning) limb**  
**Nightside clouds produce a greenhouse effect (positive radiative forcing)**

# Modeling clouds & haze

## Nightside clouds on hot Jupiters

Spitzer observations of hot Jupiters



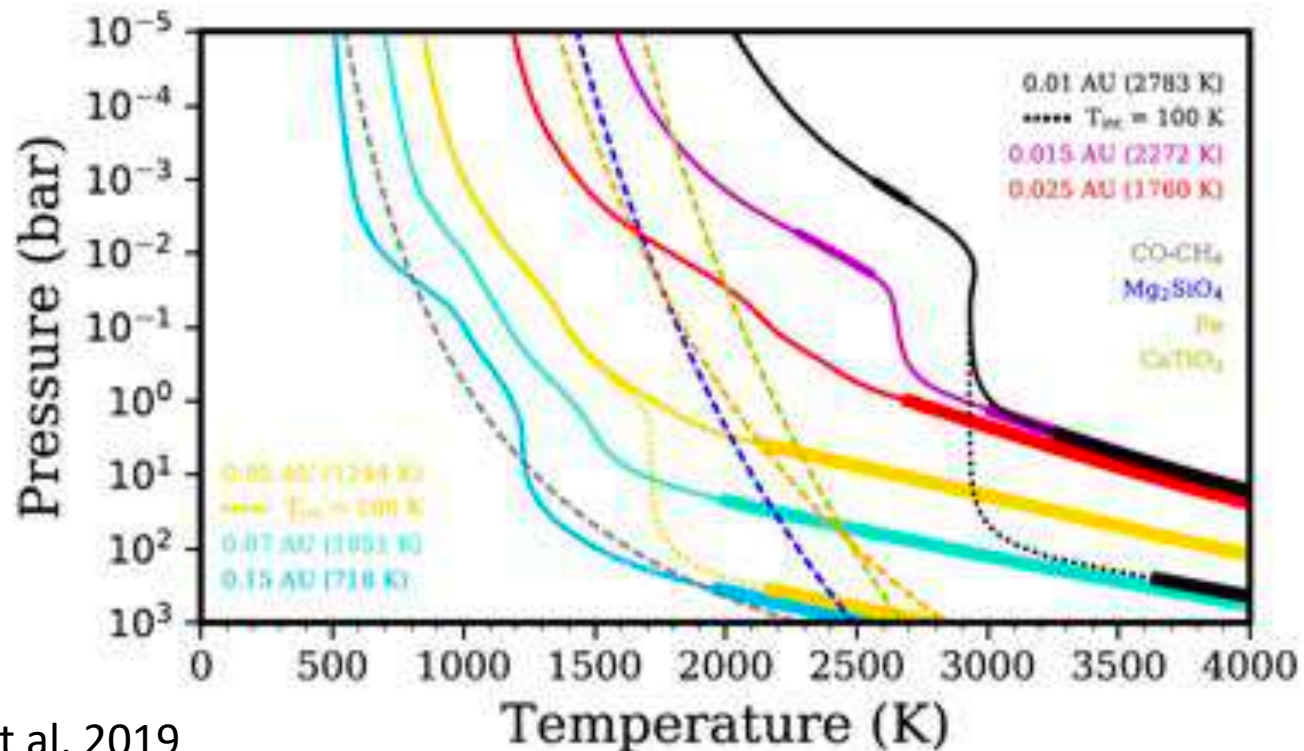
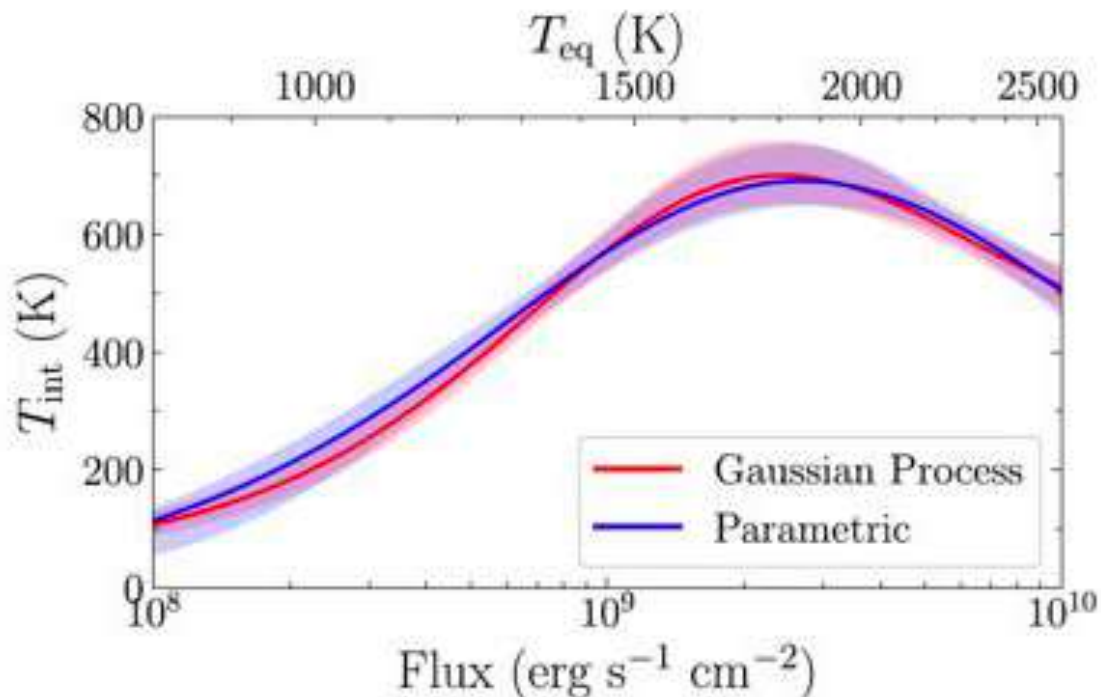
Gao et al. (2020)

**From thermal phase curves:**

- High thermal emission from the dayside
- Low thermal emission from the nightside
- consistent with prediction from GCMs

# Modeling clouds & haze

A challenge for 3D models: the deep interior conditions

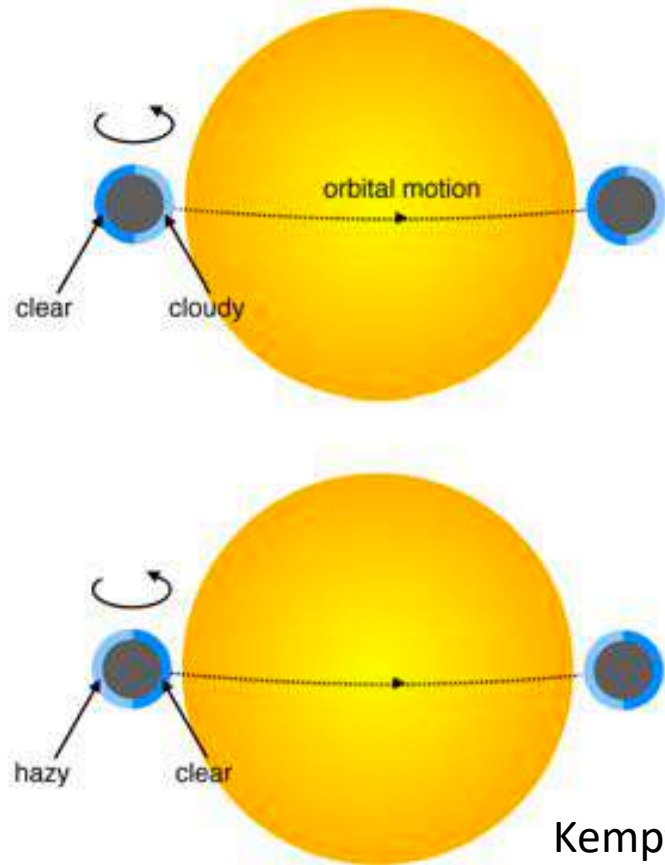


Thorngreen et al. 2019

The deep interior temperature strongly affects cloud formation higher in the atmosphere  
The radius inflation of hot Jupiters suggests high intrinsic temperature, limiting the cold trapping

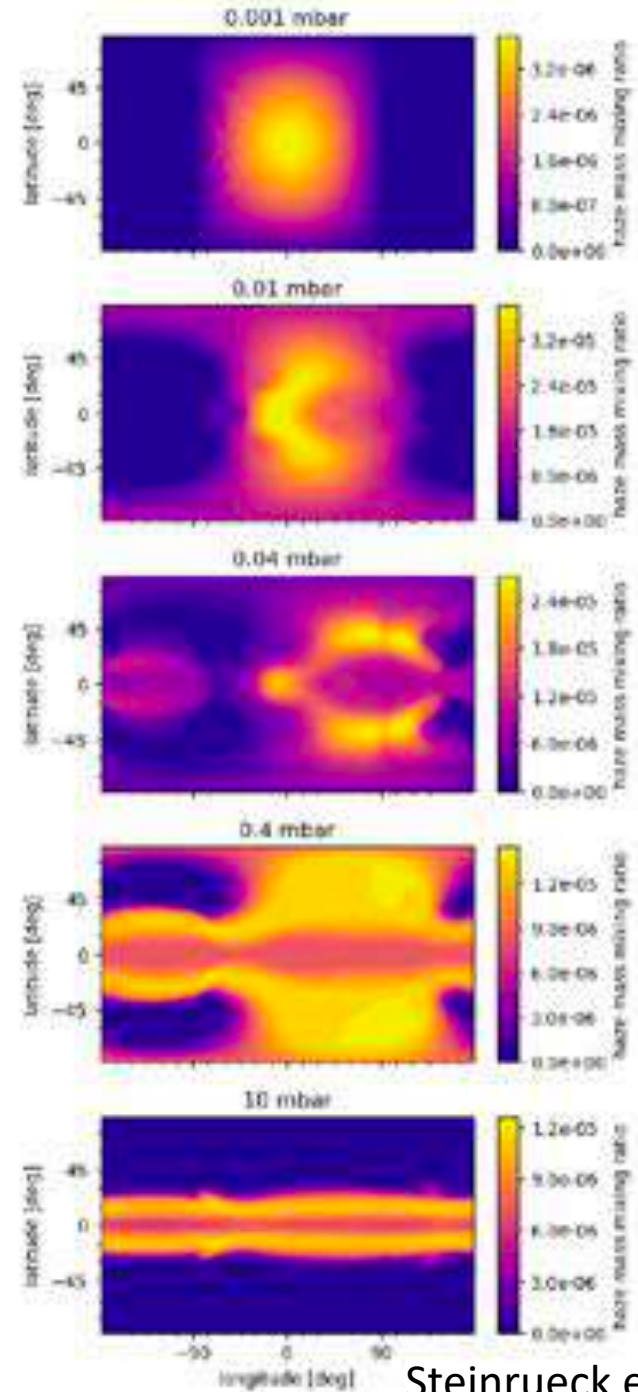
# Modeling clouds & haze

## Photochemical haze on hot Jupiters



Kempton et al. 2017

The east (morning) limb is hazier than the west (evening) limb  
=> Potential diagnostic between clouds and haze



Steinrueck et al. 2020

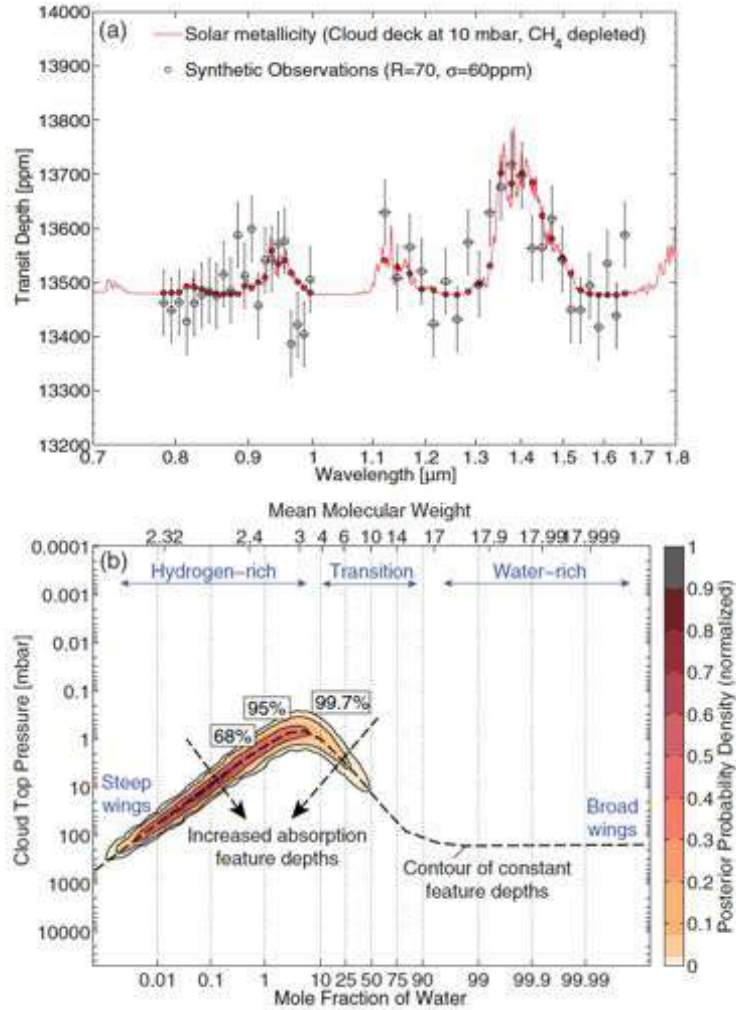
# How to probe cloudy atmospheres ?



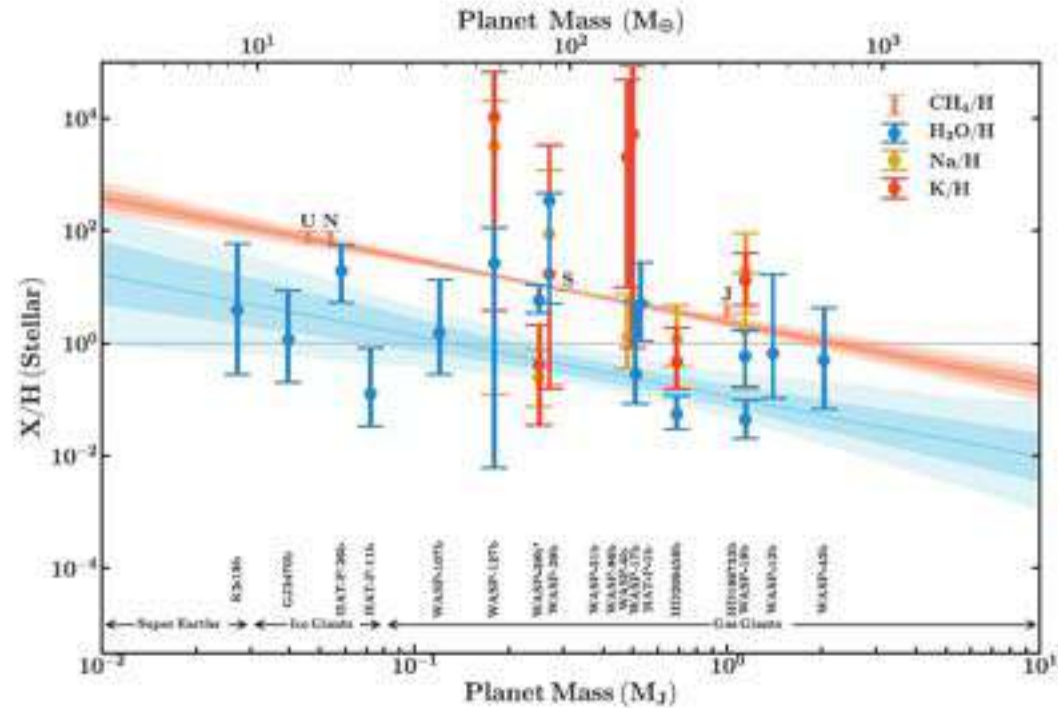


# Probing cloudy atmosphere

Problem: degeneracy between metallicity and clouds



Line & Seager 2013



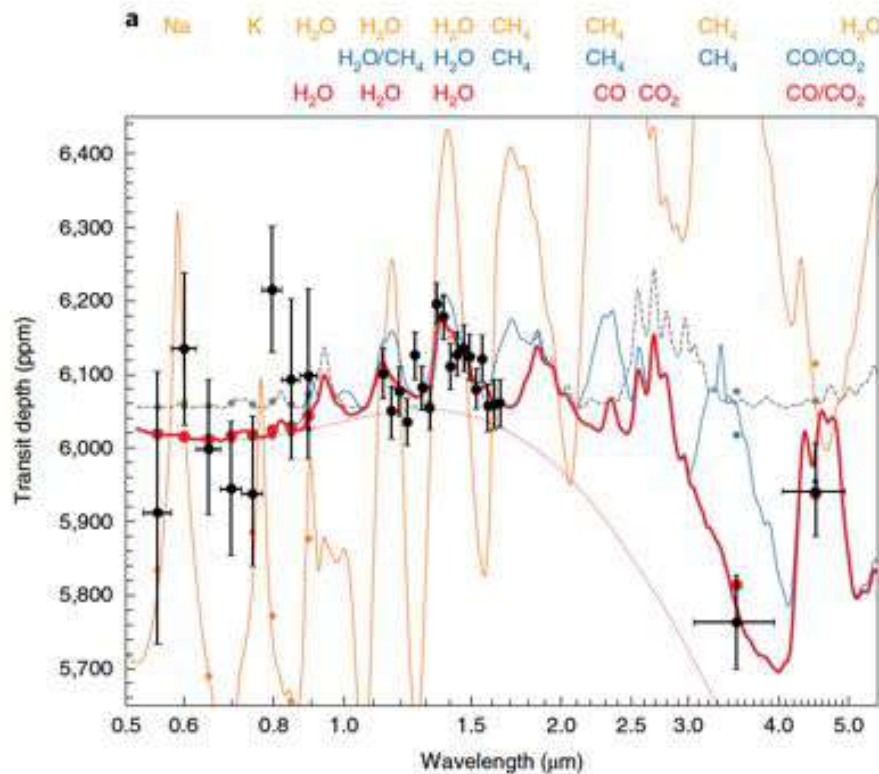
Fortney et al. 2022

Strong biases between metallicity and clouds in atmospheric retrieval

# Probing cloudy atmosphere

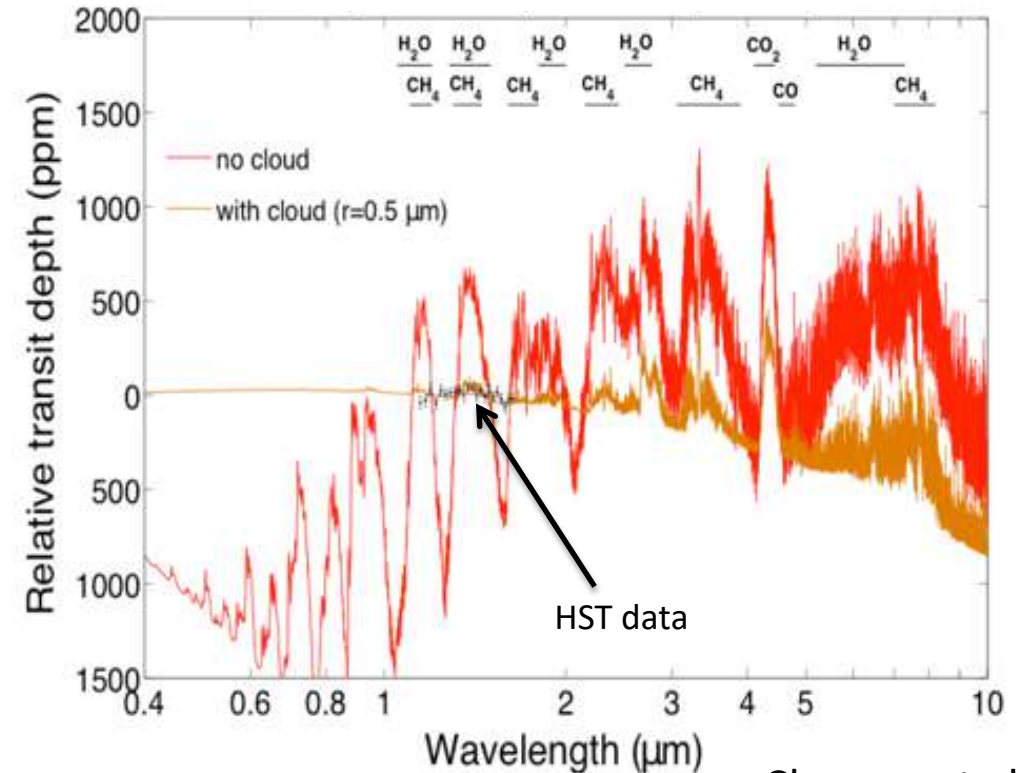
## 1) Large spectral coverage (JWST, Ariel)

HST+Spitzer spectrum of GJ 3470 b



Benneke et al. 2018

HST+model spectra of GJ 1214 b



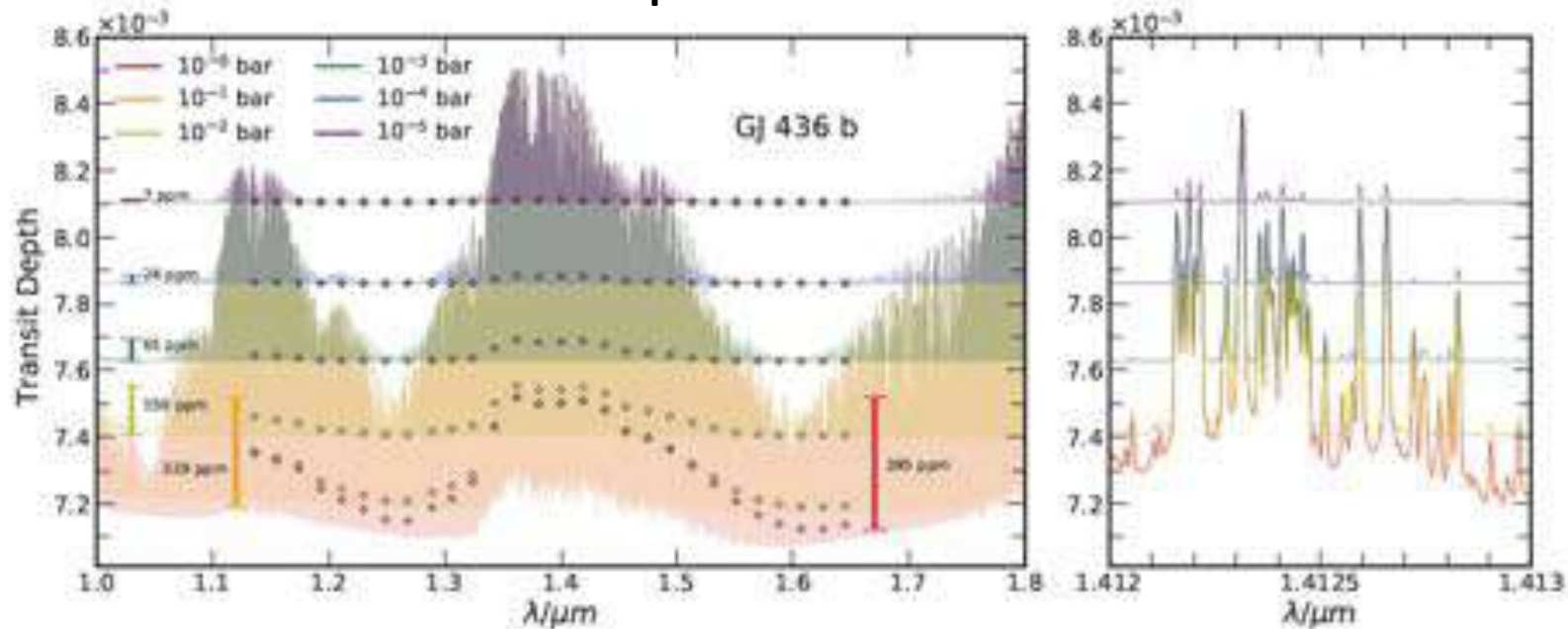
Charnay et al. 2015

**Clouds/haze should be optically thinner at long wavelengths  
where molecular features are stronger**

# Probing cloudy atmosphere

## 2) High-resolution spectroscopy (VLT-CRIRES, SPIRou, ELT-ANDES, GMT)

HR spectrum of GJ 436b

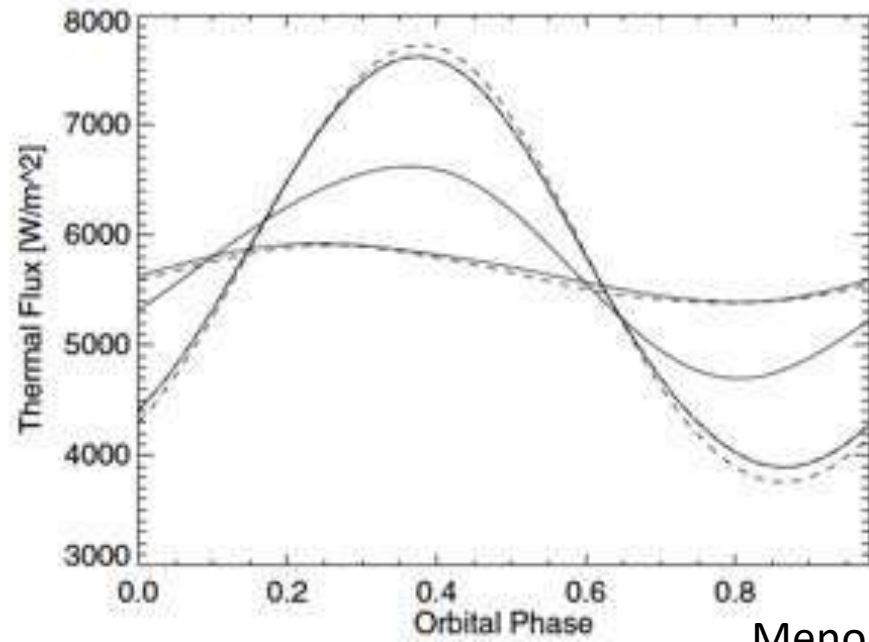


Gandhi et al. 2020

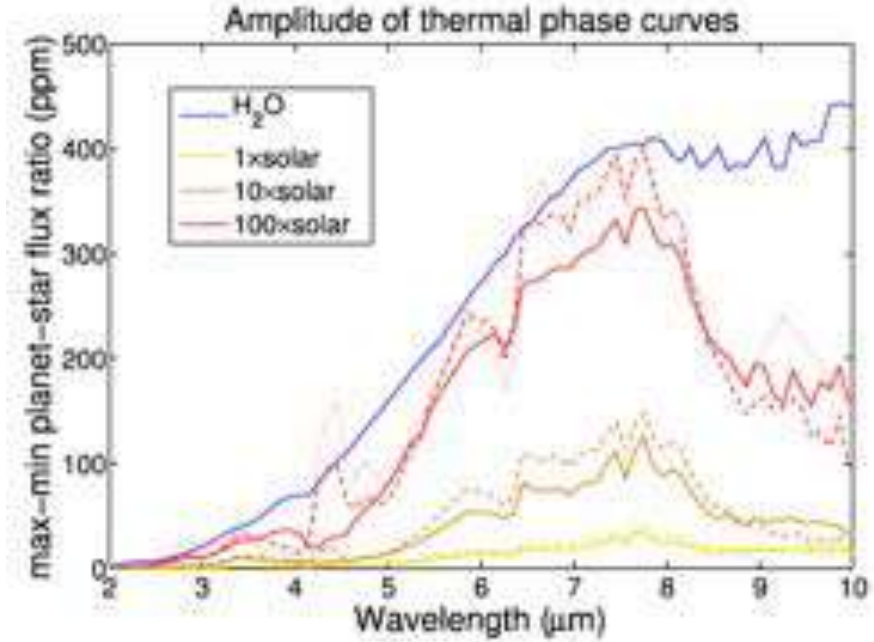
High spectral resolution can probe above clouds for low mean molecular weight

# Probing cloudy atmosphere

## 3) Thermal phase curves (JWST, Ariel)



Menou 2012



Charnay et al. 2015

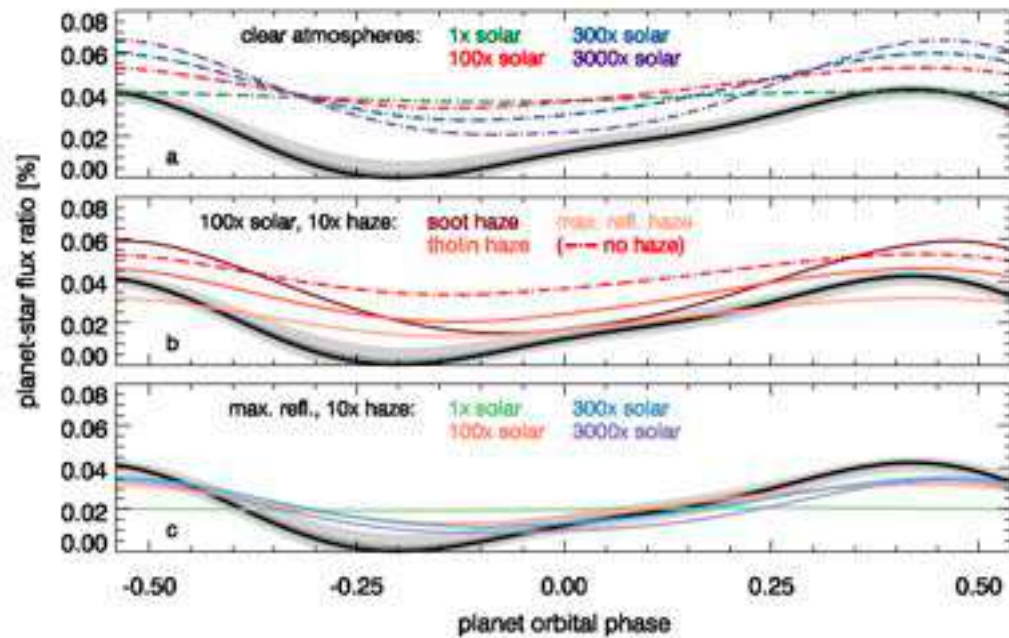
$$\tau_{rad} \sim \frac{c_p P_{phot}}{g \sigma T^3}$$

The amplitude of thermal phase curve increases with metallicity

# Probing cloudy atmosphere

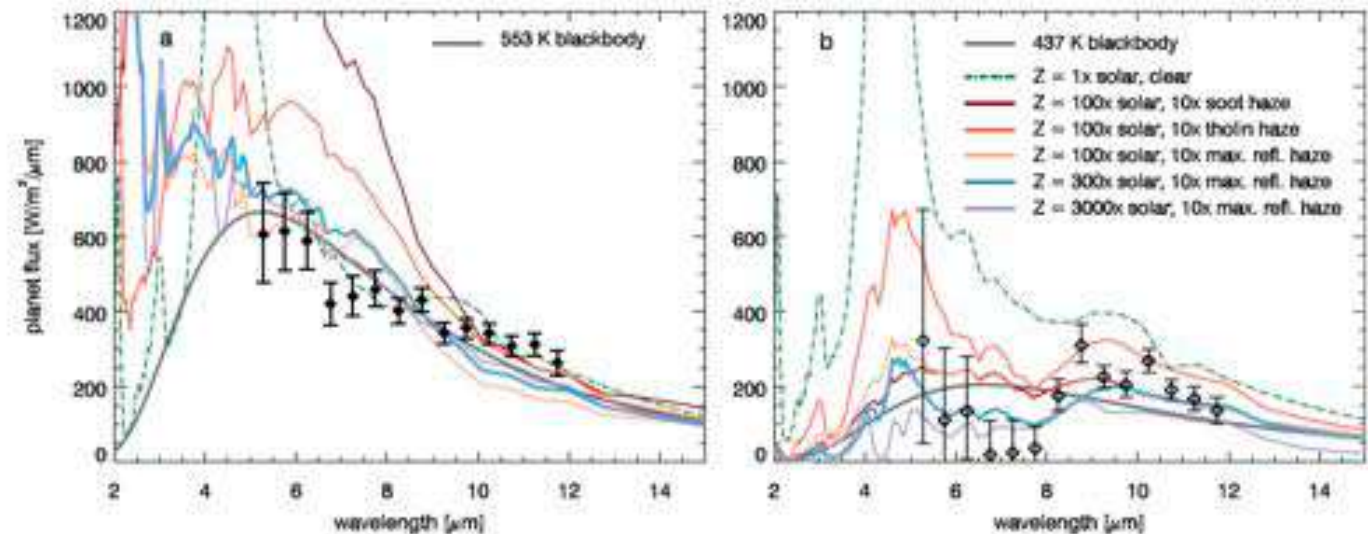
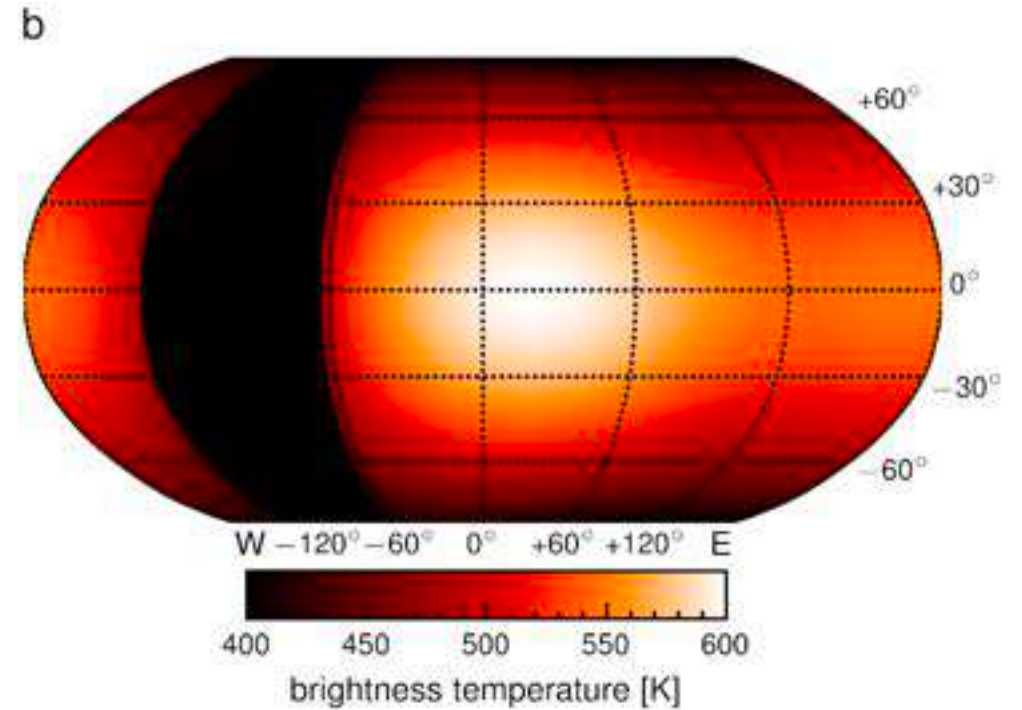
## 3) Thermal phase curves (JWST, Ariel)

### MIRI phase curve of GJ 1214 b (Kempton et al. 2023)



### Evidence for:

- A high metallicity (>100 xsolar)
- Water vapour
- Highly reflective clouds/haze ( $A_B \sim 0.5$ )



# Colors of GJ1214b

Potassium chloride (KCl)



Zinc sulfide (ZnS)



Organic haze



Charnay et al. (2015)

© Manchu & Fossé







# Cloud identification



*Cumulus*

# Cloud identification



*Cirrostratus*

# Observations of clouds & haze in exoplanets

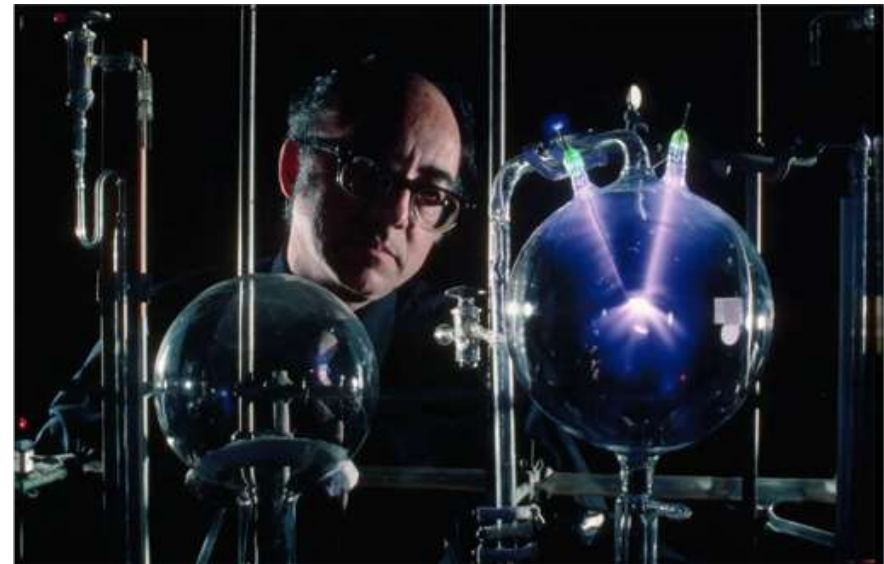
## Lab experiments of haze formation

**Table 8**  
Molecular Formulae Detected from the TRAPPIST-1 Mission: A Summary

Mass (m/z) ± Δ ppm	Detection	Formula	Parent Molecule	Reference
86.0317 ± 4.3	—	C <sub>2</sub> H <sub>2</sub>	Oxymethylene	Minerals/haze
135.0941 ± 5.8	—	C <sub>2</sub> N <sub>2</sub>	Adonite	Nucleobase base
137.0671 ± 5.8	—	C <sub>2</sub> H <sub>2</sub> O	Hydroxyacetylene	Non-protogenic amino acid
141.0426 ± 4.8	—	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub>	Acetonitrile dinitrile	Biological amino acid nucleobase
151.0884 ± 4.8	+/-	C <sub>2</sub> N <sub>2</sub> O	Quinone	Nucleobase base
151.0823 ± 4.7	—	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub>	1,2-dicyanoglyoxime	Non-protogenic amino acid
173.0426 ± 3.8	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	peroxyacetylene acid	Acetic/benzoic acid
173.0796 ± 5.4	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Diperoxide	Non-protogenic amino acid
155.0893 ± 4.4	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Hydroxy	Biological amino acid
159.0847 ± 5.1	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	L, L, 4-hydroxy-2-pyrrolidone	Non-protogenic amino acid
177.0779 ± 4.9	—	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O	Formamide	Non-protogenic amino acid
180.0884 ± 4.6	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Diperoxide glycol	Nucleobase base derivative
185.0790 ± 4.7	—	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O	Phenylamine	Non-protogenic amino acid
187.0825 ± 5.4	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1,2-dicyanoglyoxime	Non-protogenic amino acid
189.0851 ± 4.8	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1,2-dicyanoglyoxime	Non-protogenic amino acid
171.0644 ± 3.3	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Hydroxyacetylene	Non-protogenic amino acid
174.0846 ± 3.7	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Phenylglyoxal, m-cyan	Non-protogenic amino acid
179.0846 ± 4.5	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Heterophenylamine	Non-protogenic amino acid
181.0779 ± 3.7	+/-	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O	Formamide	Biological amino acid
183.0864 ± 3.3	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Hydroxy	Non-protogenic amino acid
193.0739 ± 5.1	+	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O	Phenylglyoxal, m-acetyl	Non-protogenic amino acid
185.0871 ± 3.4	+/-	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O	Formamide, O-methyl	Non-protogenic amino acid
190.0884 ± 3.4	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Phenylglyoxal, m-acetyl	Non-protogenic amino acid
190.0849 ± 2.6	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Phenylglyoxal, m-acetyl	Non-protogenic amino acid
204.0899 ± 3.0	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Hydroxy	Biological amino acid
205.0851 ± 4.4	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Hydroxy	Non-protogenic amino acid
206.0904 ± 3.3	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Non-protogenic amino acid
208.0862 ± 3.3	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Phenylglyoxal	Non-protogenic amino acid
210.0841 ± 3.7	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	peroxyacetylene	Non-protogenic amino acid
211.0825 ± 3.1	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Formamide, O-methyl	Non-protogenic amino acid
220.0849 ± 3.9	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1,2-dicyanoglyoxime	Biological amino acid derivative
224.0797 ± 4.3	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1,2-dicyanoglyoxime	Biological amino acid derivative
226.0866 ± 3.7	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Biological amino acid derivative
246.0884 ± 4.1	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Biological amino acid derivative
248.0776 ± 3.2	+	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Non-protogenic amino acid
267.0219 ± 4.0	+/-	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Non-protogenic amino acid
276.0231 ± 4.8	—	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Acetylacetylene	Biological amino acid derivative

Note: Detection reference indicates energy balance and detection priority. Flashes (+) positive ion, (-) negative ion and +/- (±) positive ion, n negative ion. We report the smaller Δ ppm between measured m/z and exact m/z when a detection was made to have the most conservative result.

Experiment of Miller-Urey



Moran et al. 2020

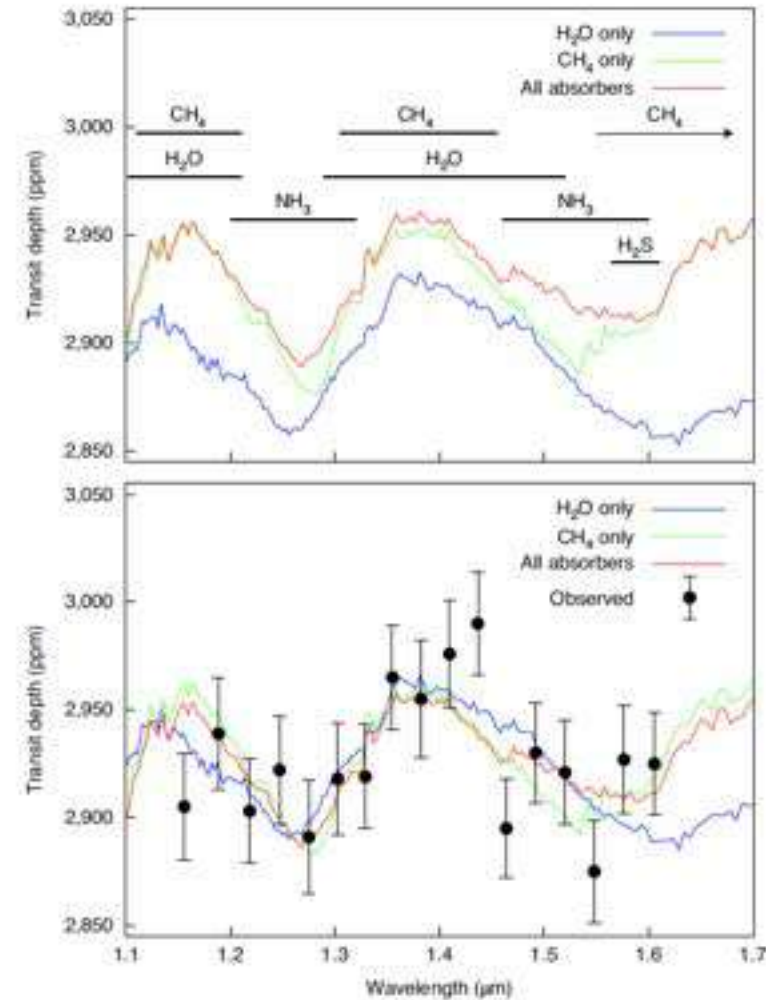
Formation of amino acids and nucleobases with exoplanet haze.  
Interest for prebiotic chemistry

# Observations of clouds & haze in exoplanets

## Methane depletion on warm sub-Neptunes/Neptunes

Planet	H <sub>2</sub> O	CH <sub>4</sub>	CO	CO <sub>2</sub>	NH <sub>3</sub>	HCN	reference <sup>1</sup>
Keck-9					■		T15a
GJ 436 b							
GJ 1132 b							
GJ 1214 b	■						
GJ 3470 b	■						B19a, E22
HAT-P-11 b	■						F14, E22
HAT-P-26 b	■						W17, MD19, E22
HD 8167 c	■			■			G20, M20a, E22
HD 97658 b	■				■		E22
HD 106815 c	■				■		G20, K20, E22
HD 219666 b	■						
HIP 41378 b	■						
K2-18 b	■						T19, B19b, E22
K2-24 b	■						
LHS 1140 b	■						E22
LTT 9759 b							
TOI 270 c				■			
TOI 270 d	■						E22
TOI 674 b	■				■		E22, E22
TRAPPIST-1 b							
TRAPPIST-1 c							
TRAPPIST-1 d							
TRAPPIST-1 e							
TRAPPIST-1 f							
TRAPPIST-1 g							
TRAPPIST-1 h							

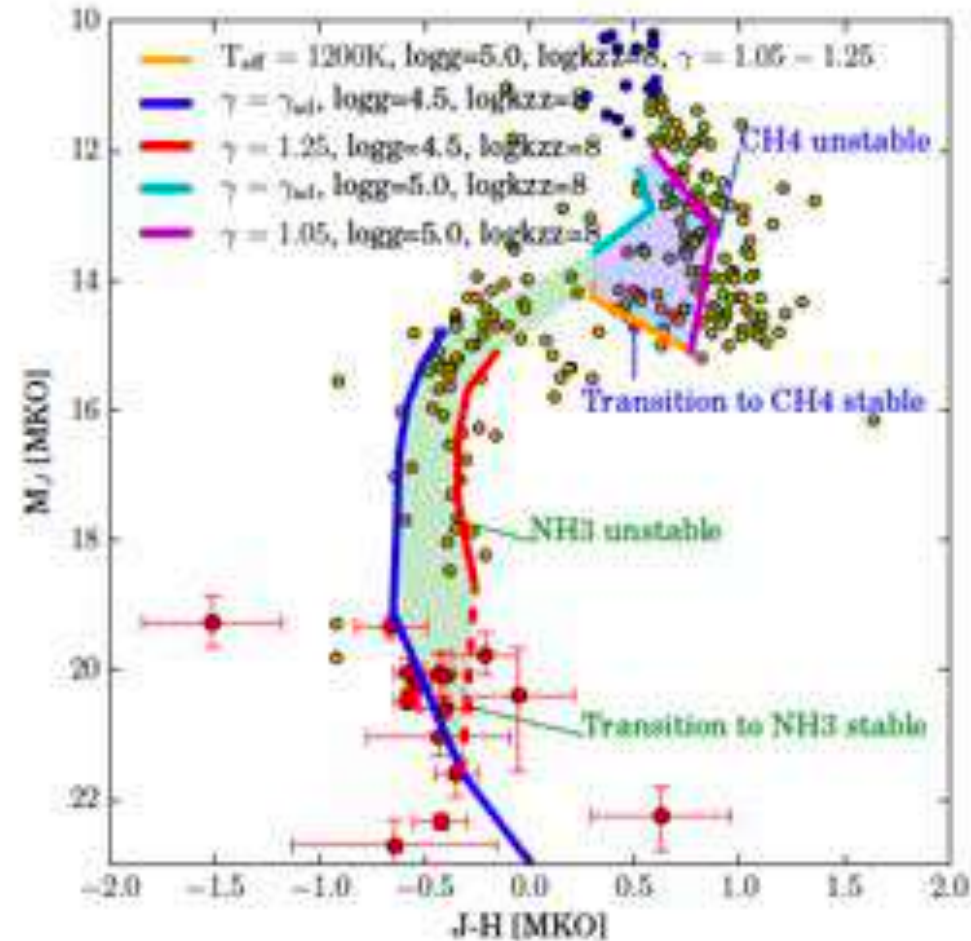
Gressier et al. (2022)



Bézard, Charnay & Blain 2021

# Observations of clouds in brown dwarfs

## Fingering convection as the driver of the LT-transition



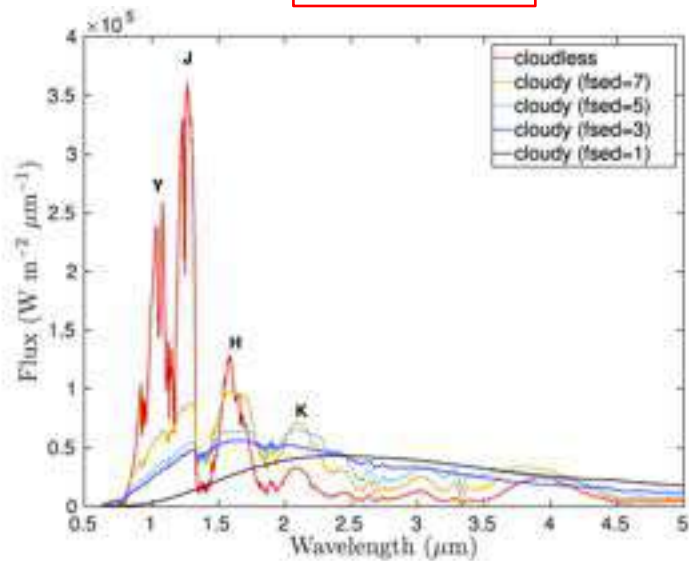
Tremblin et al. 2015, 2016, 2017

# Probing cloudy atmosphere

## Biases: isothermal/clouds

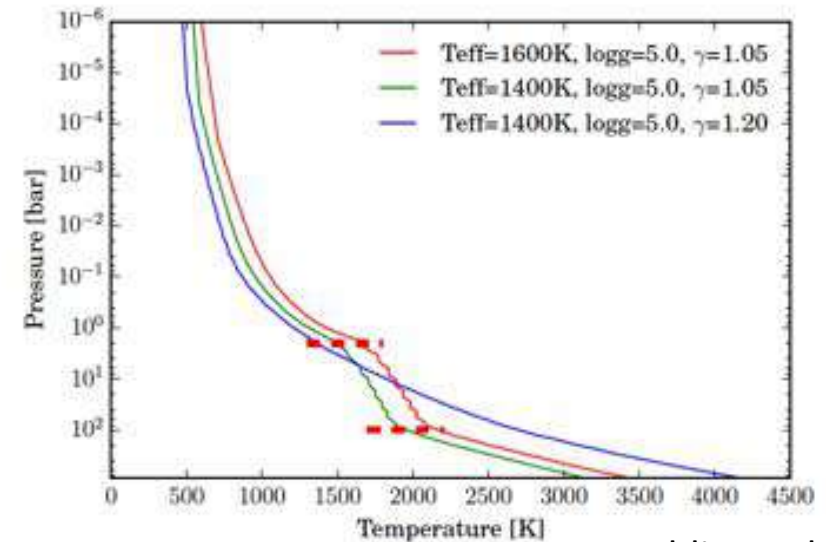
How to reduce spectral features in emission spectra ?

**Clouds**



Charnay et al. (2018)

**Reduced thermal gradient**

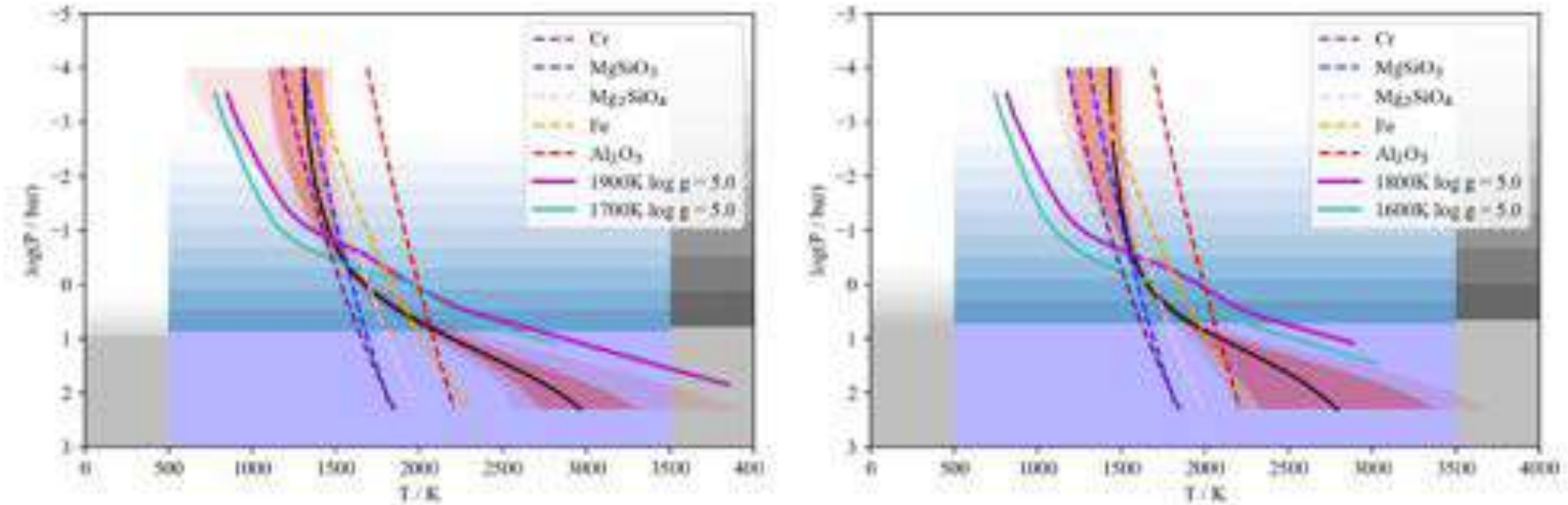


Tremblin et al. (2017)

# Probing cloudy atmosphere

## 4) Biases: isothermal/clouds

Atmospheric retrieval of two L dwarfs by Burningham et al. (2017):



Both clouds + reduced thermal gradient ! 😬

But the retrieval might be biased by its relatively simple cloud model

# Probing cloudy atmosphere

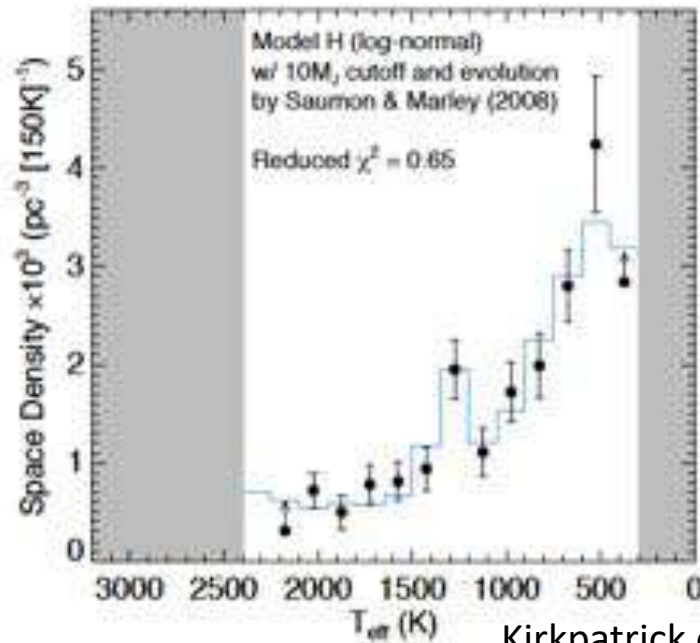
## 4) Biases: isothermal/clouds

How to break degeneracy between clouds and reduced thermal gradient ?

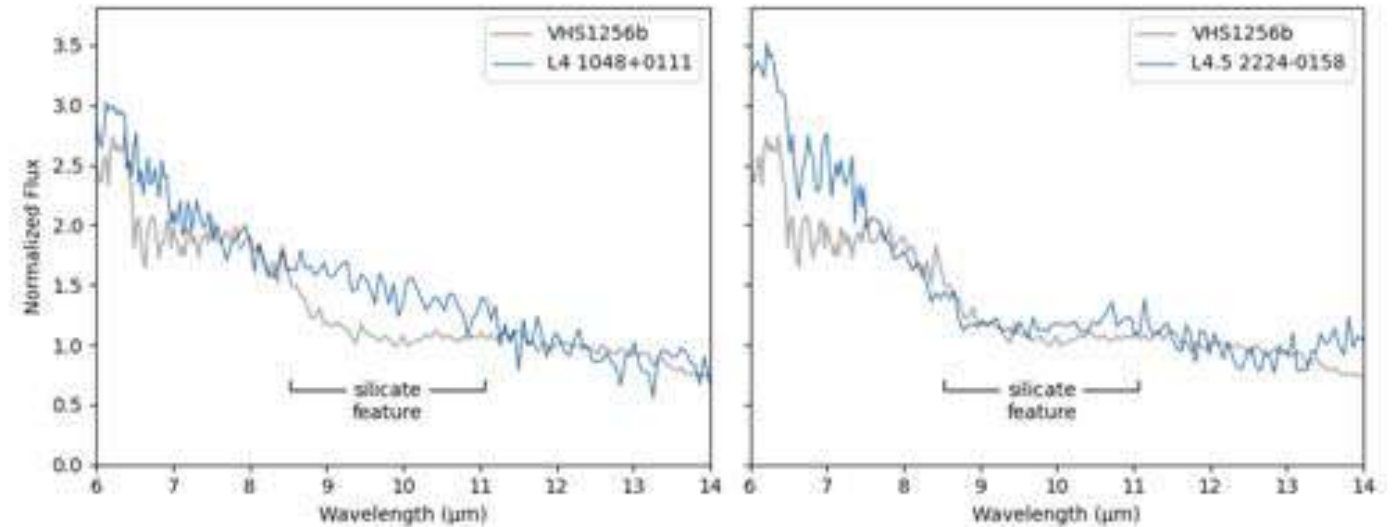
1) Cloud absorption features

2) Thermal evolution

Excess of BD at the LT transition



Silicate feature on VHS 1256 b



Miles et al. (2022)

But:

- 1) Clouds can be a mixture of species (e.g. Jupiter's clouds)
- 2) Best et al. 2020 found a minimum of BD at the LT transition

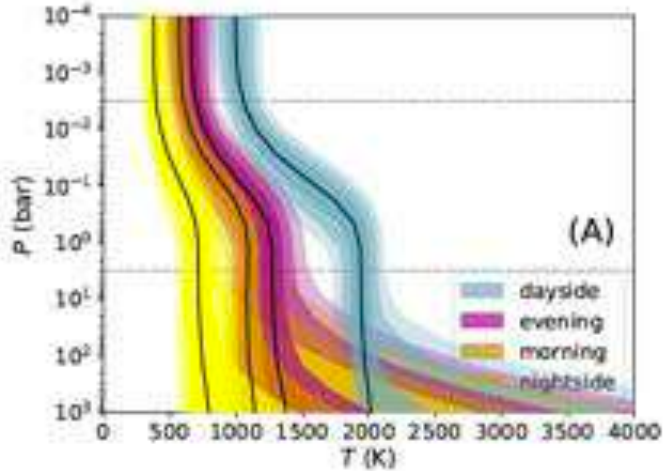


# Lessons from models and retrieval

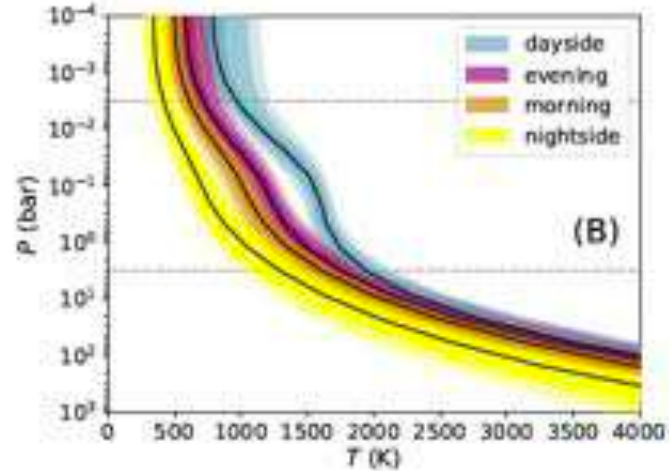
## 5) Biases: 3D structure

Improvement with global/2D retrieval  
(e.g. Chubb & Min 2022, Irwin et al. 2019, Changeat et al. 2021)

Without cloud

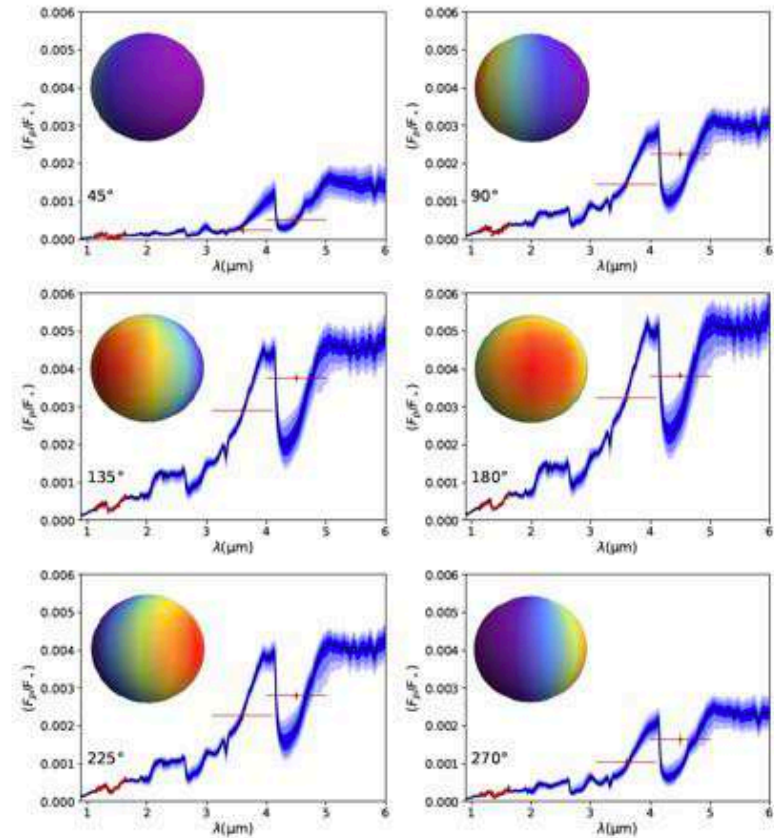


With clouds



Chubb & Min (2019)

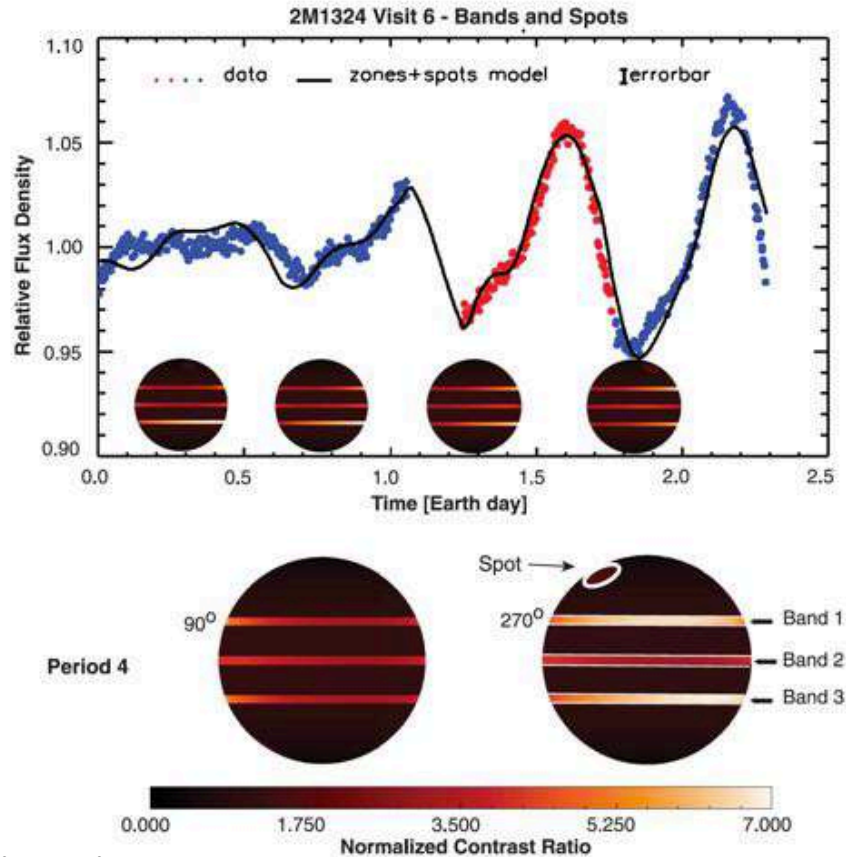
Without clouds



# Lessons from models and retrieval

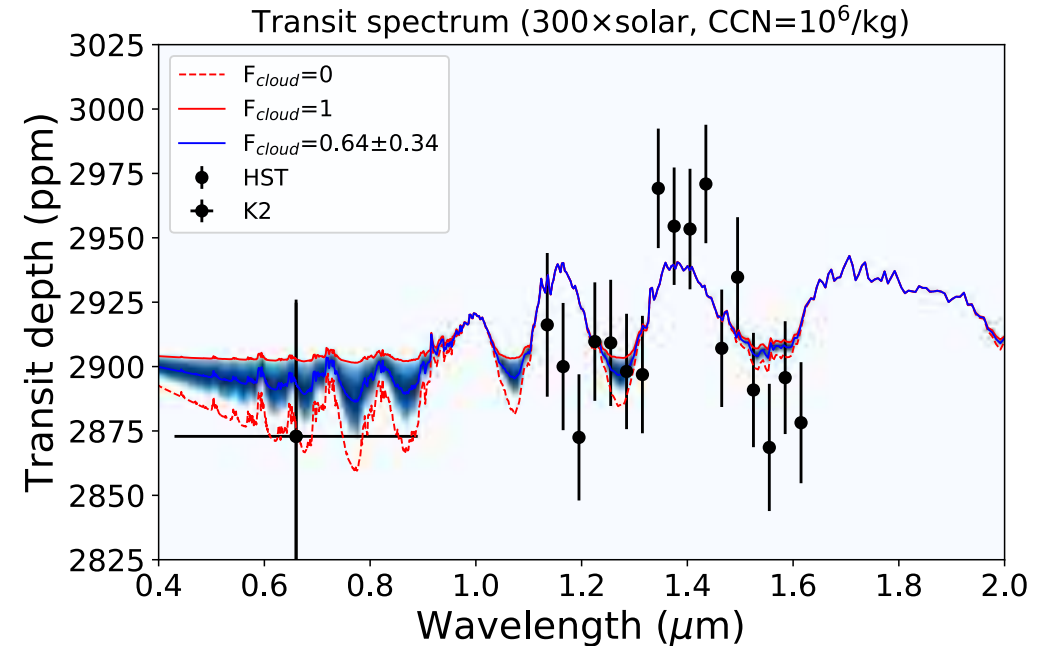
## 6) Biases: time-variability

Variability of a brown dwarf with Spitzer



Apai et al. (2017)

3D simulation of K2-18 b with water clouds

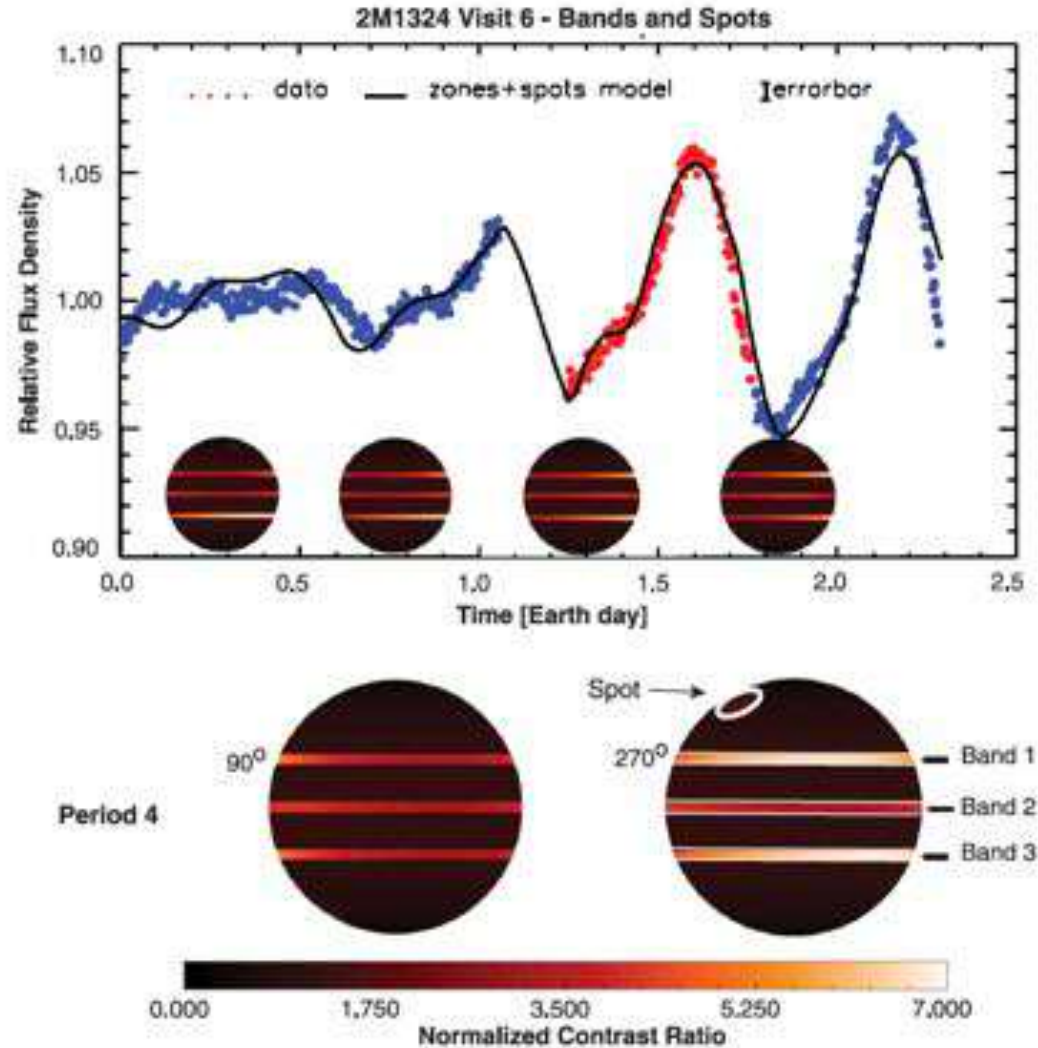


Charnay et al. (2021)

Possible variability of cloudiness and spectra

# Observations of clouds in brown dwarfs

## Variability of brown dwarf at the LT transition



# Observations of clouds in brown dwarfs

## Measurement of rotational period

