How cloud formation affects the CH_4 abundance

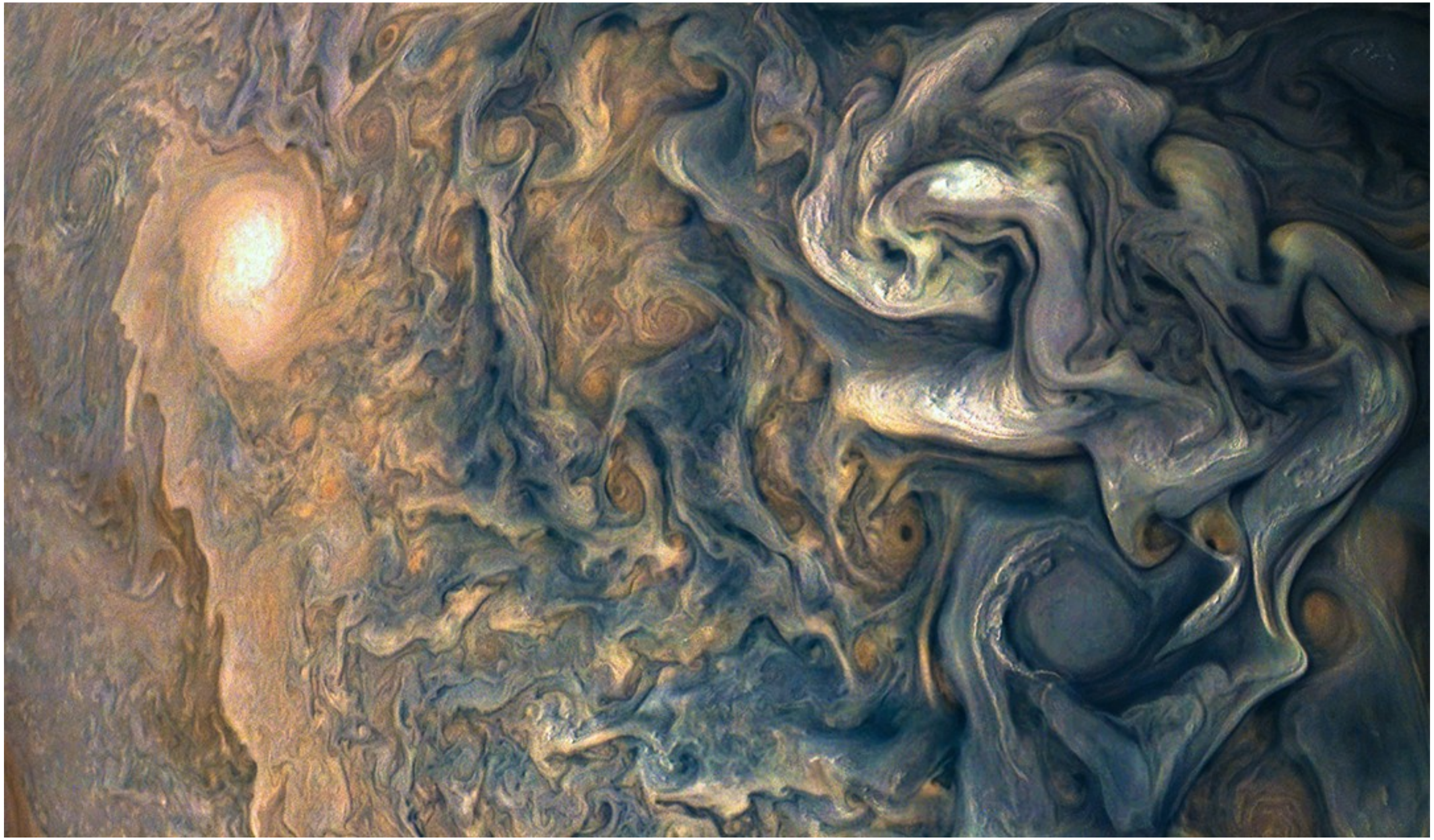
Sven Kiefer

KU Leuven, OEAW IWF, and TU Graz

H. Lecoq-Molinos, Ch. Helling, N. Bangera, L. Decin, L. X. Worutowicz

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860470.

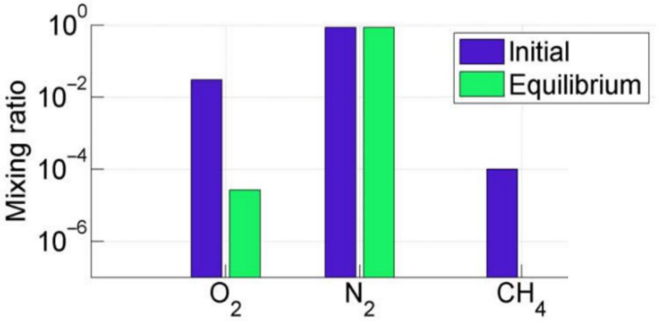
The importance of clouds in (exo)planets



SWRI/NASA

The importance of chemical disequilibrium

Biology



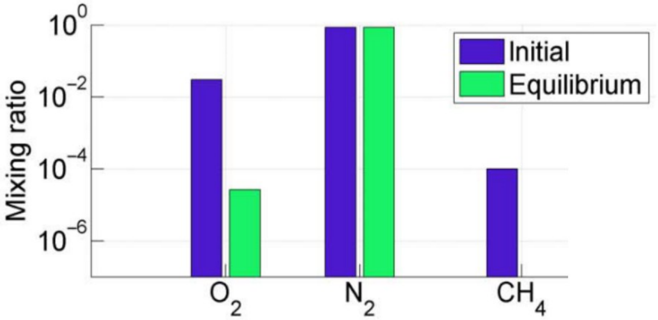
Krissansen-Totton et al. (2023)

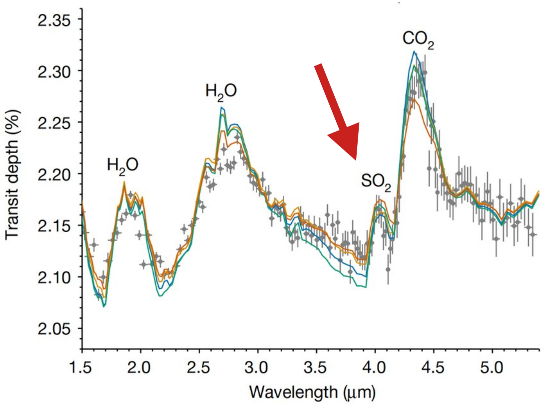
The importance of chemical disequilibrium

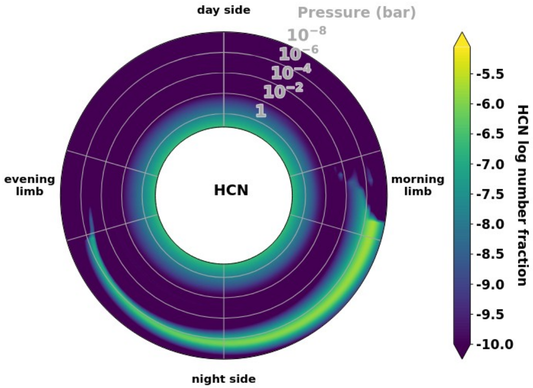
Biology

Photo-chemistry

Atmospheric dynamics







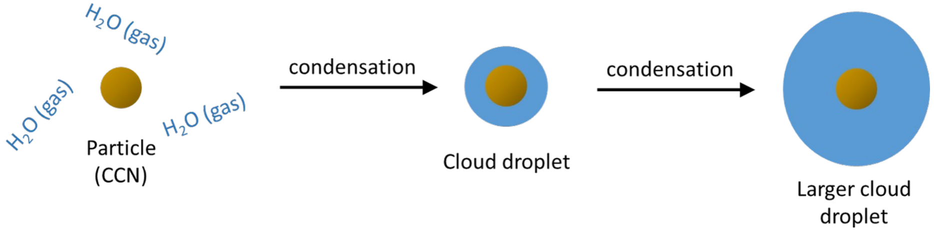
Krissansen-Totton et al. (2023)

Tsai et al. (2023)

Baeyens et al. (2023)

How do clouds form in gas-giants?

Cloud formation - Earth



Top Image: Aerosols Department Of Physics And Astronomy Uppsala
Bottom Image: BBC science focus, Alexandra Franklin-Cheung

Cloud formation – Hot Jupiter

Cloud formation – Hot Jupiter

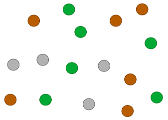
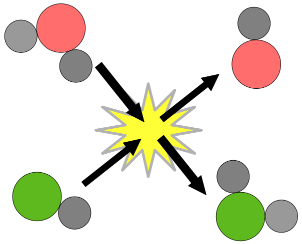


Image altered from Helling (2018)

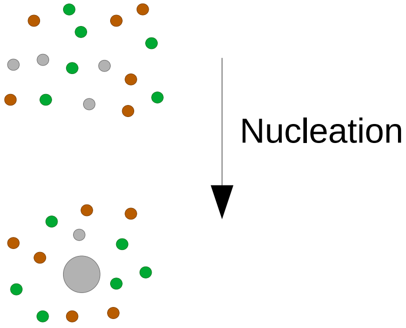
Kinetic Chemistry



For this study:

→ Elements: N, C, H, O
→ Additional: Ti, Si
→ 69 species
→ 780 reactions

Cloud formation – Hot Jupiter



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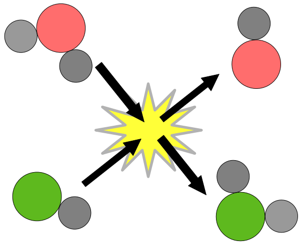
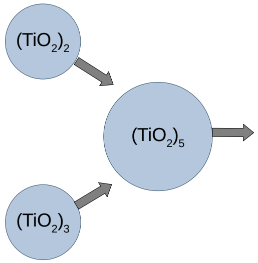
Kinetic Chemistry

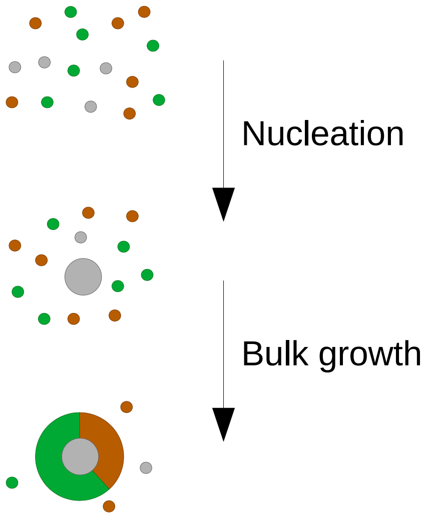


Kinetic nucleation



Nucleation:
→ kinetic polymer nucleation
→ Species: TiO_2[s]
→ Maximum size: $(TiO_2)_{15}$

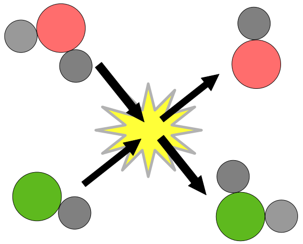
Cloud formation – Hot Jupiter


Nucleation

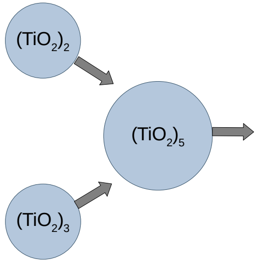
Bulk growth

Image altered from Helling (2018)

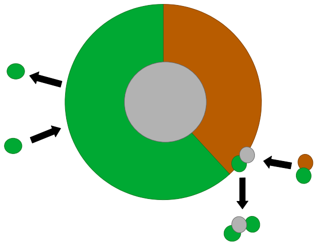
Kinetic Chemistry



Kinetic nucleation



Bulk growth



Cloud material

→ 9 Materials

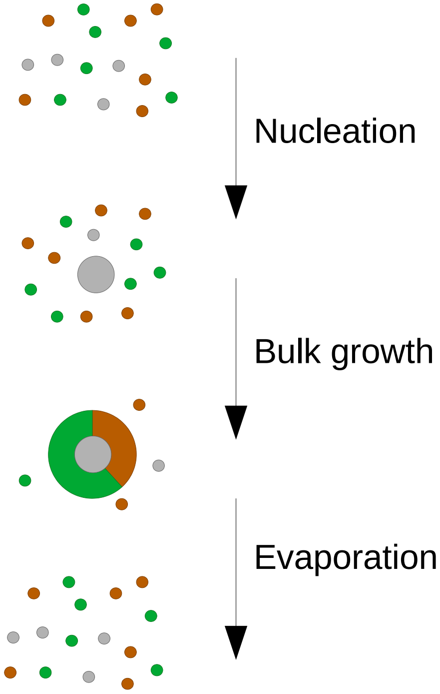
TiO_2 FeO Al_2O_3

Fe_2O_3SiO MgO SiO_2

Fe_2SiO_4 Mg_2SiO_4

→ 40 surface reactions

Cloud formation – Hot Jupiter



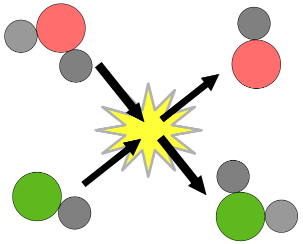
Nucleation

Bulk growth

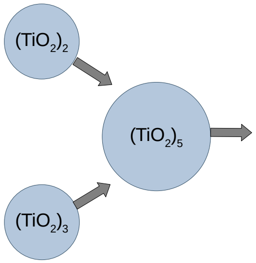
Evaporation

Image altered from Helling (2018)

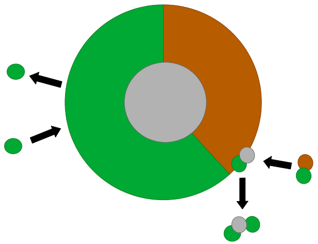
Kinetic Chemistry



Kinetic nucleation



Bulk growth



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Fe_2SiO_4	Mg_2SiO_4	

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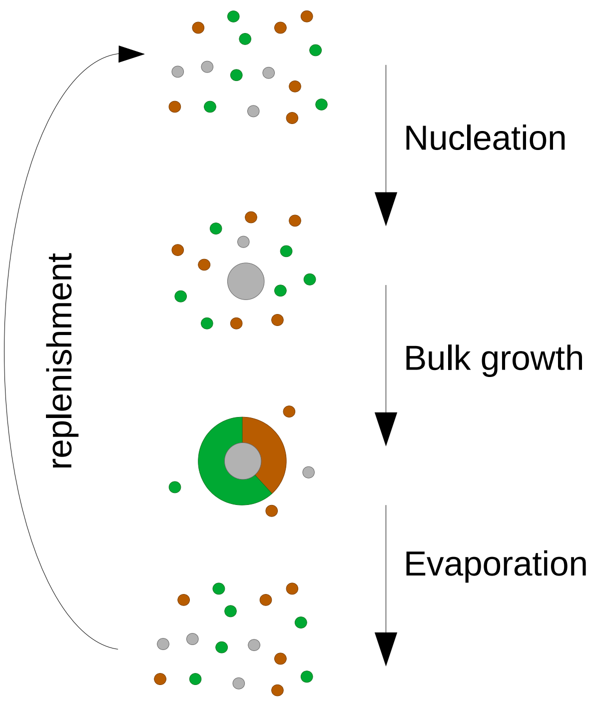

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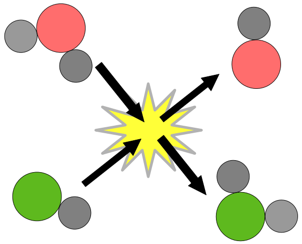

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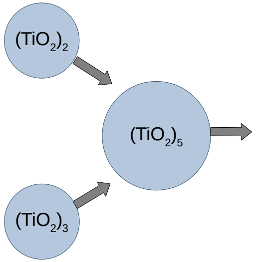
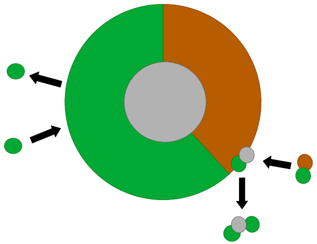


Bulk growth



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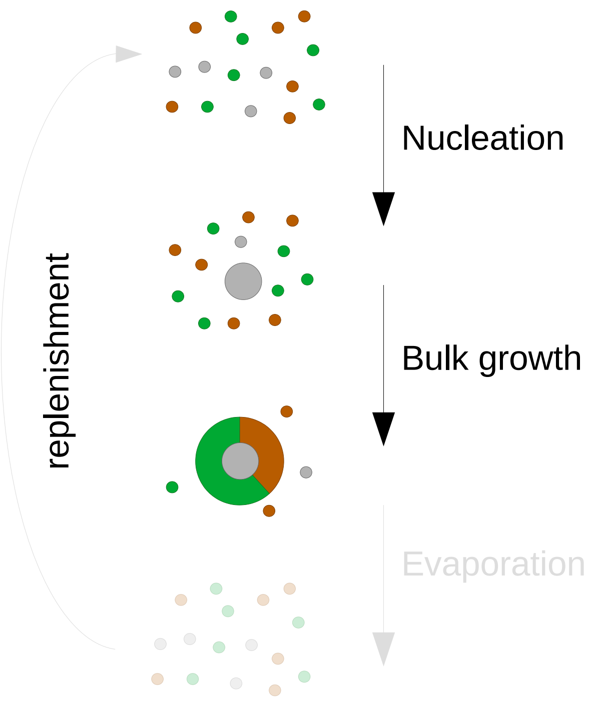

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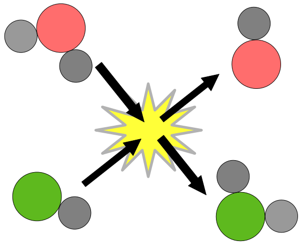
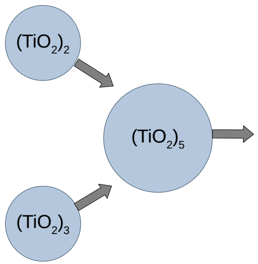
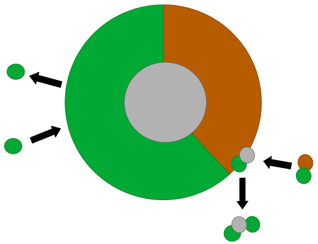
Kinetic Chemistry



Kinetic nucleation



Bulk growth



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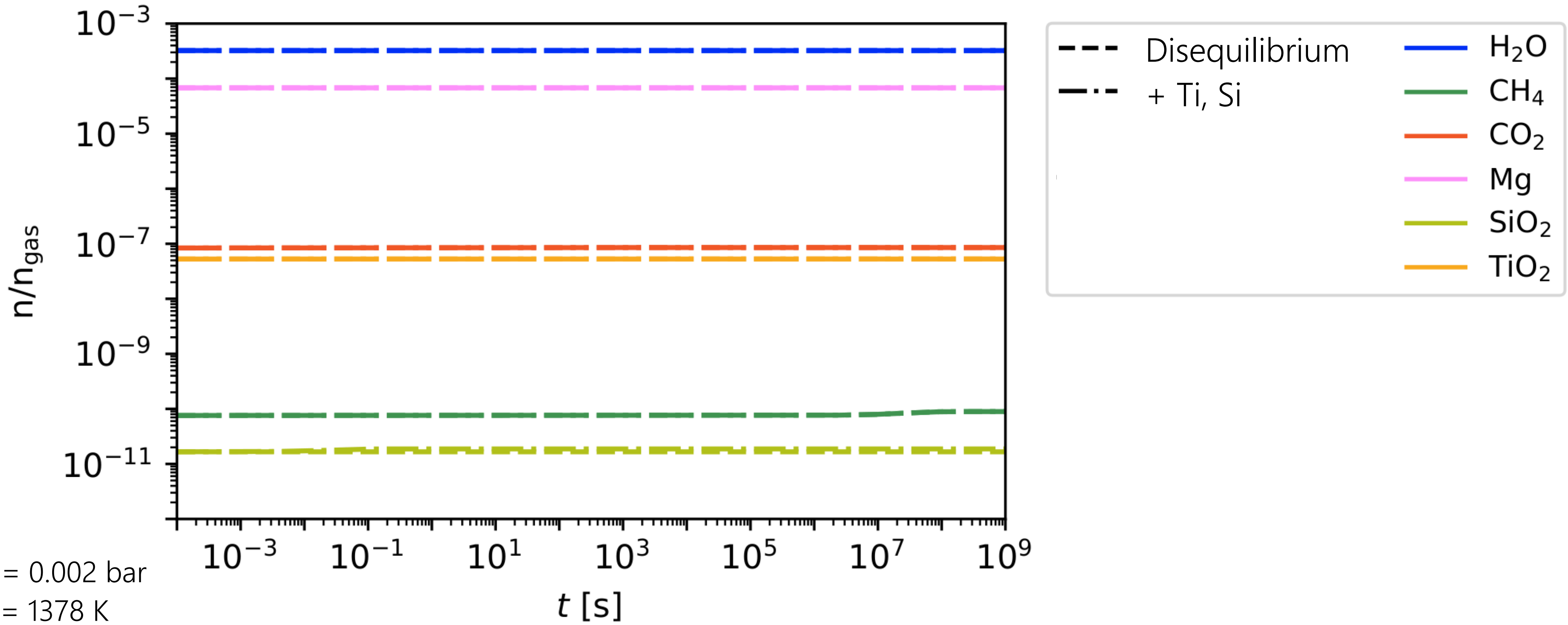
Fe_2SiO_4 Mg_2SiO_4

→ 40 surface reactions

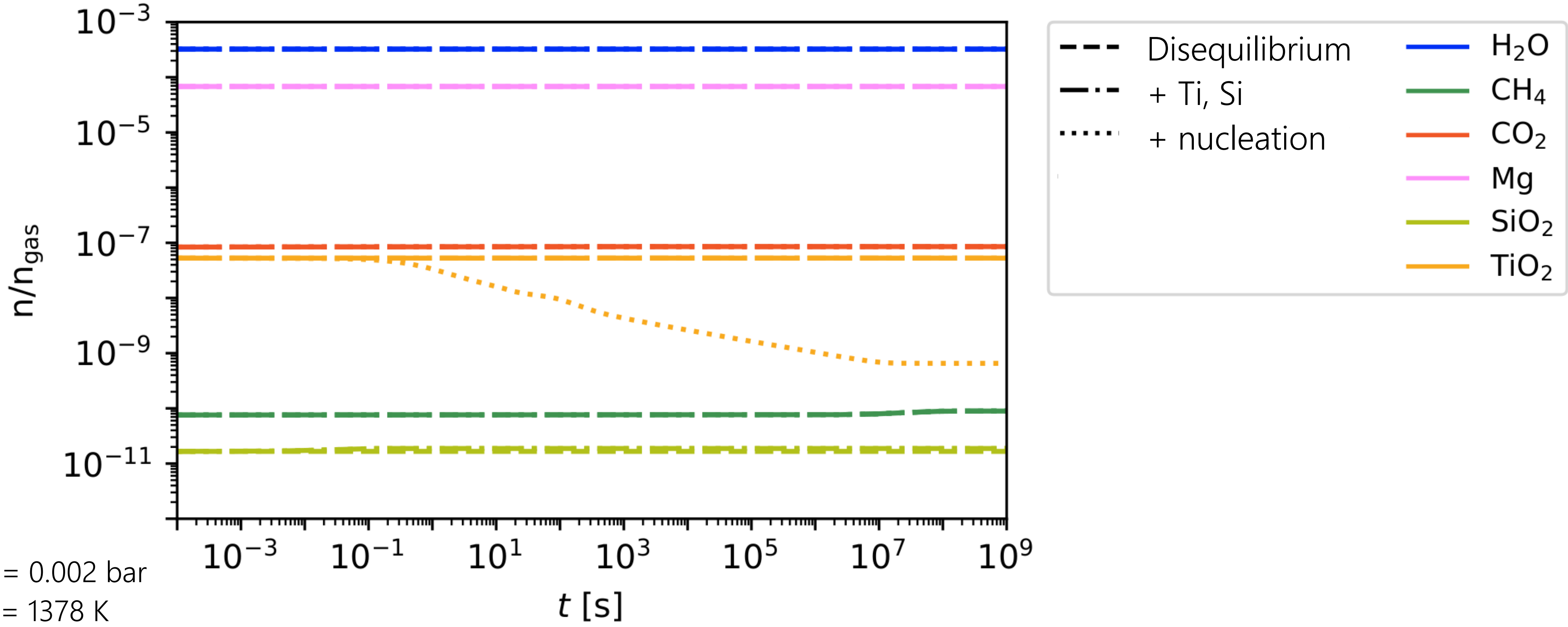
How do clouds affect the gas-phase?

Disequilibrium gas-phase



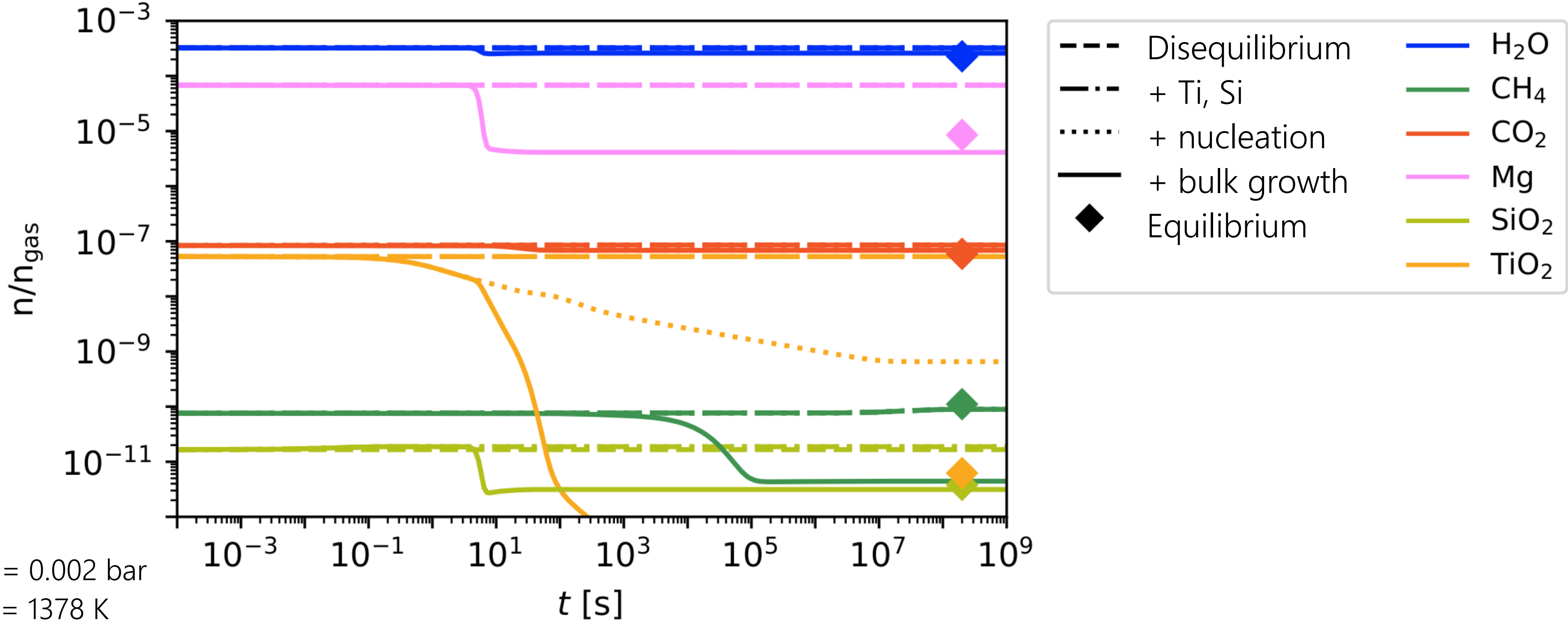
P = 0.002 bar
T = 1378 K

Disequilibrium gas-phase



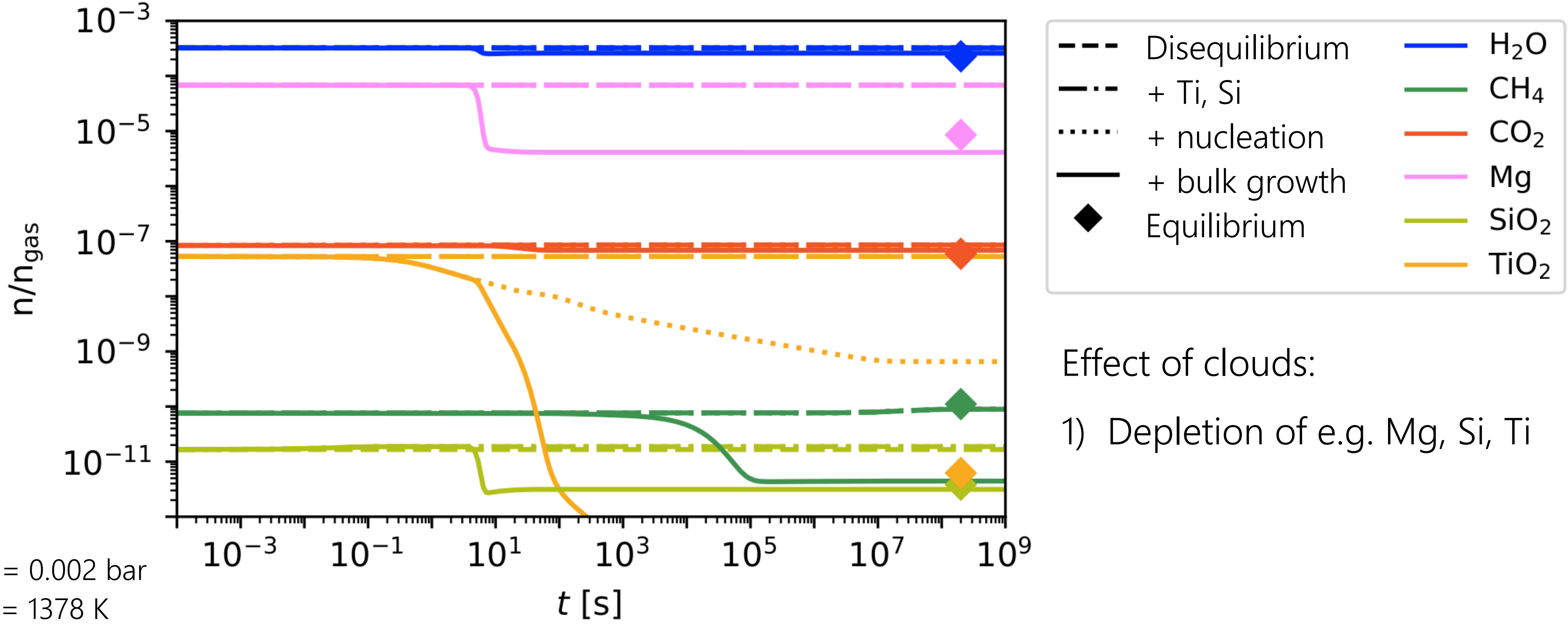
P = 0.002 bar
T = 1378 K

Disequilibrium gas-phase



P = 0.002 bar
T = 1378 K

Disequilibrium gas-phase

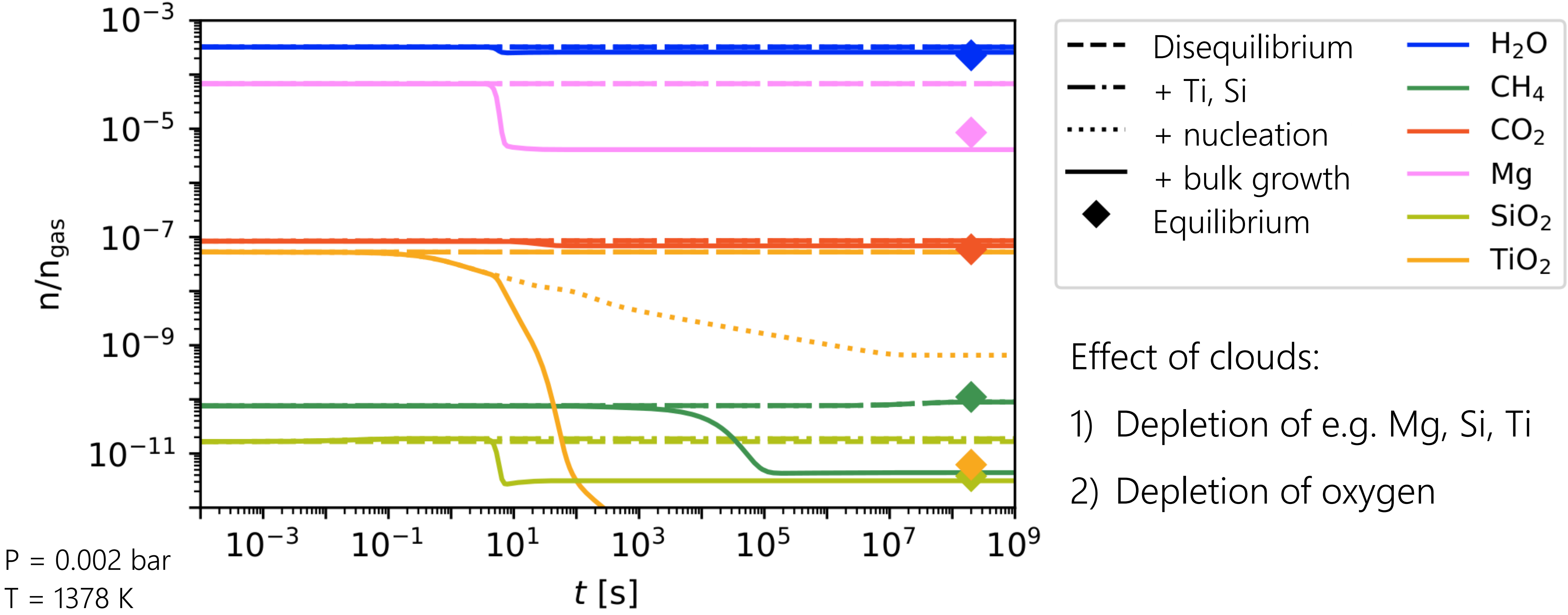


P = 0.002 bar
T = 1378 K

Effect of clouds:

1) Depletion of e.g. Mg, Si, Ti

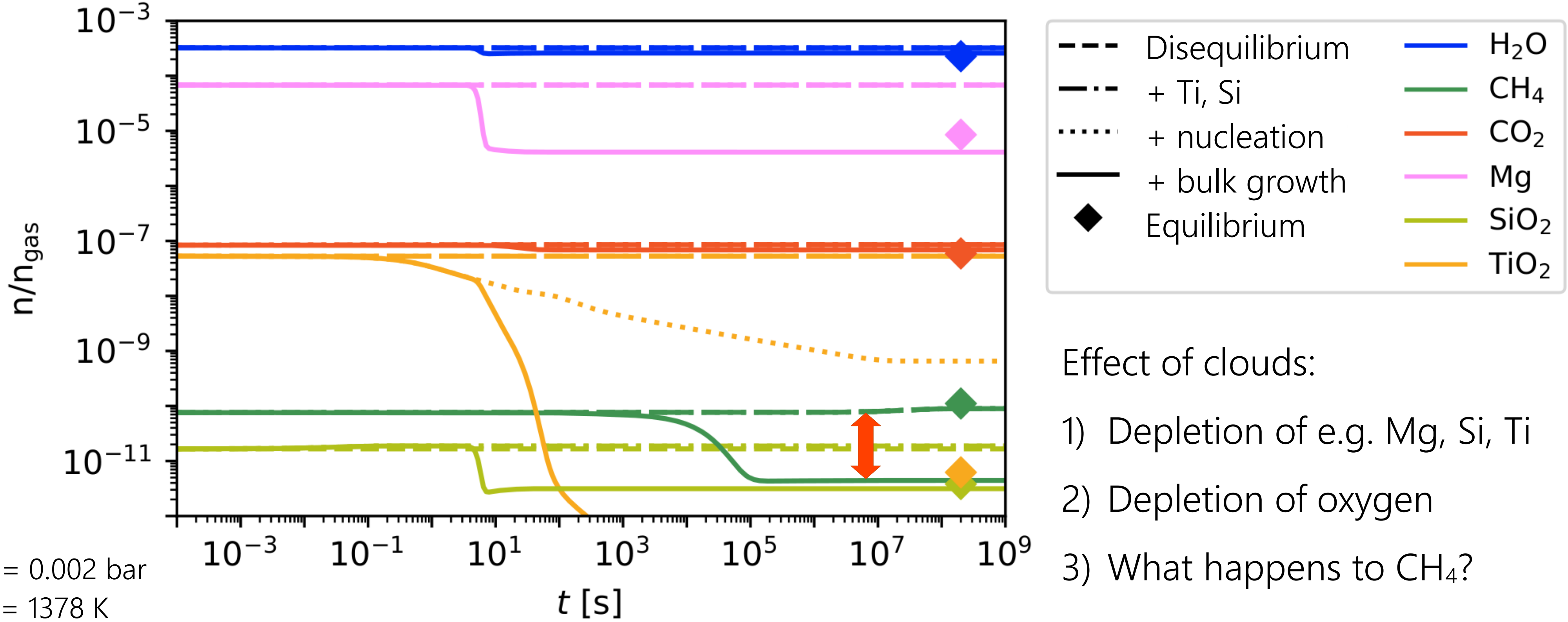
Disequilibrium gas-phase



Effect of clouds:

1) Depletion of e.g. Mg, Si, Ti
2) Depletion of oxygen

Disequilibrium gas-phase

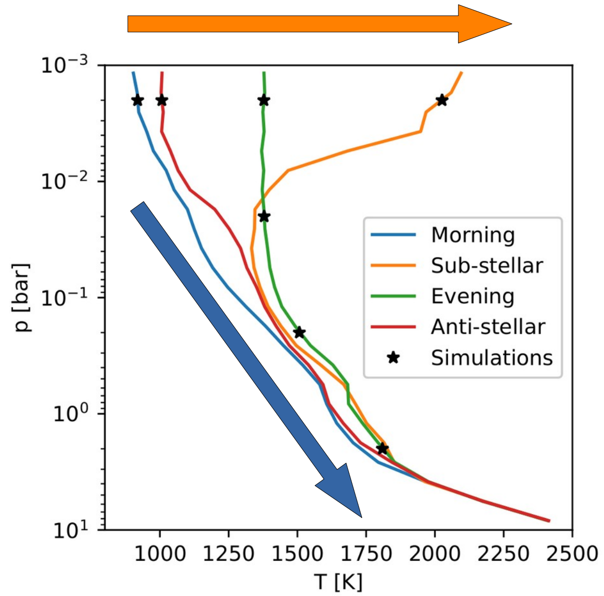


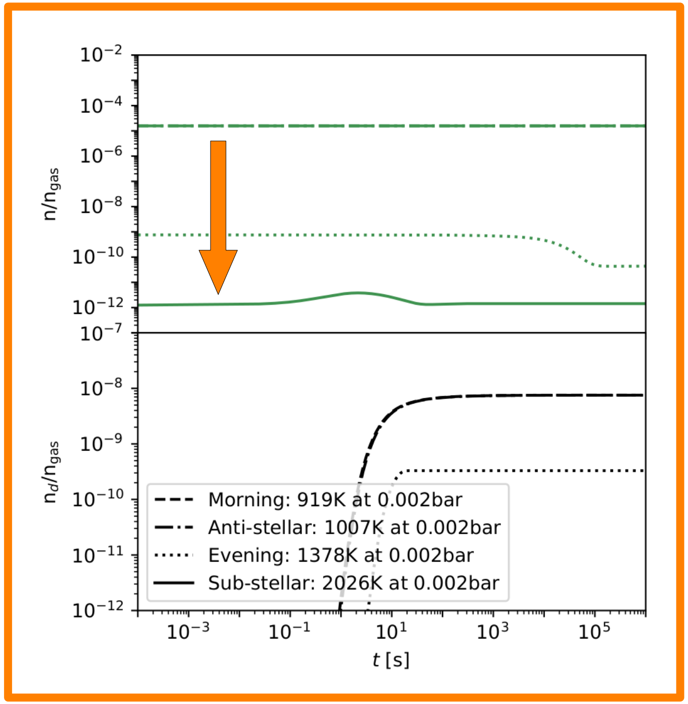
P = 0.002 bar
T = 1378 K

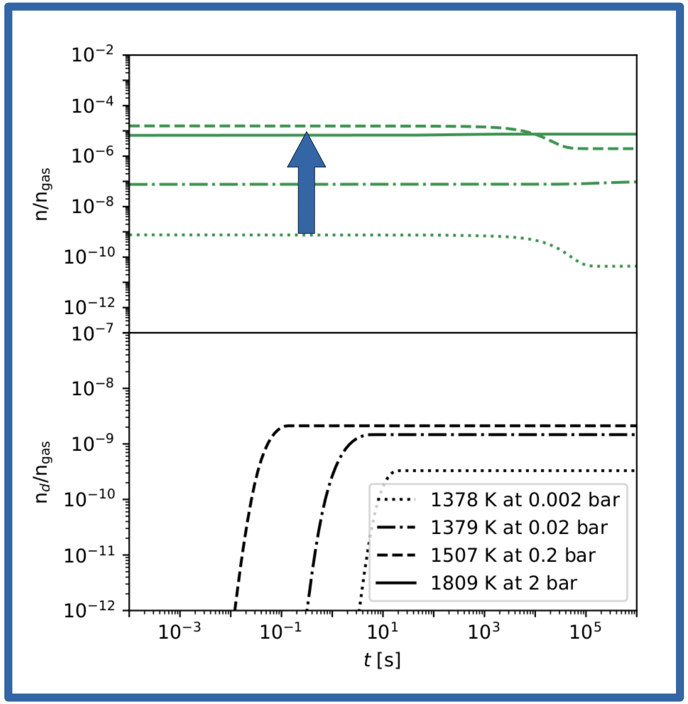
Effect of clouds:

1) Depletion of e.g. Mg, Si, Ti
2) Depletion of oxygen
3) What happens to CH_4?

A well known hot Jupiter: HD 209458 b







→ CH4 depletion depends on temperature and pressure

What happens to CH_4?

SiO-SiO_2 cycle

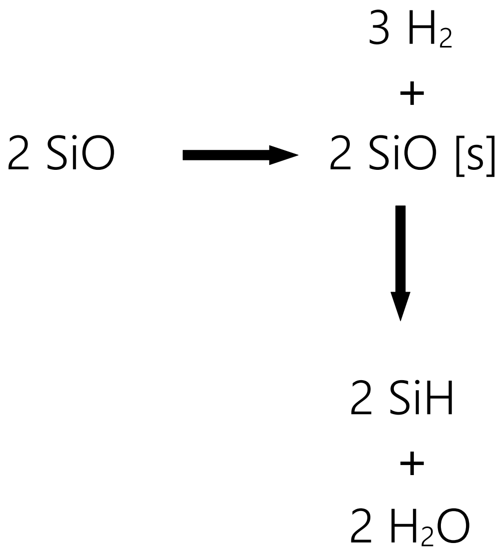
Nidhi Bangera

SiO-SiO$_2$ cycle

$$2\,\mathrm{SiO} \longrightarrow 2\,\mathrm{SiO}\,[s]$$

Nidhi Bangera

SiO-SiO_2 cycle



$3\ H_2$

+

$2\ SiO \longrightarrow 2\ SiO\ [s]$

$\downarrow$

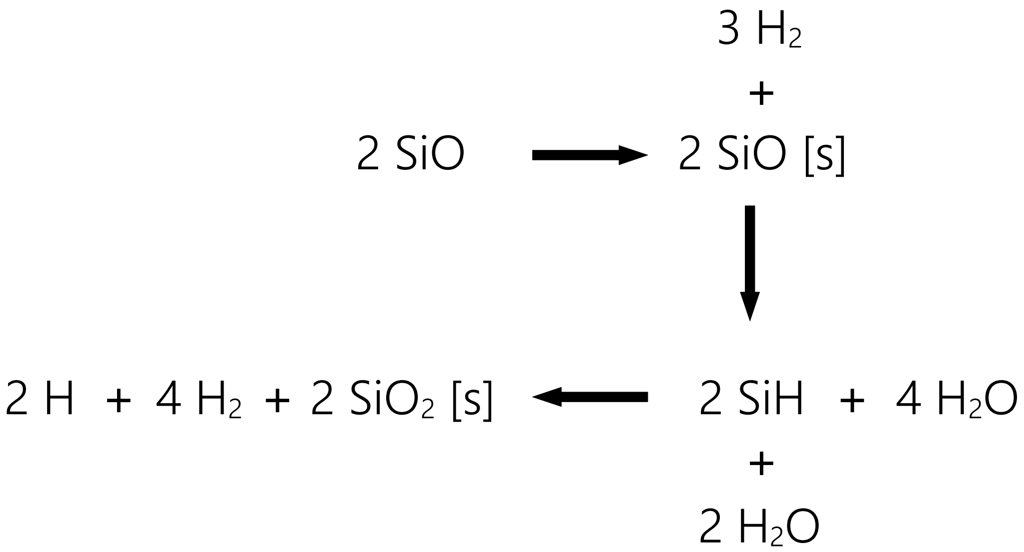
$2\ SiH$

+

$2\ H_2O$

Nidhi Bangera

SiO-SiO_2 cycle



$3\ H_2$

+

$2\ SiO \longrightarrow 2\ SiO\ [s]$

$\downarrow$

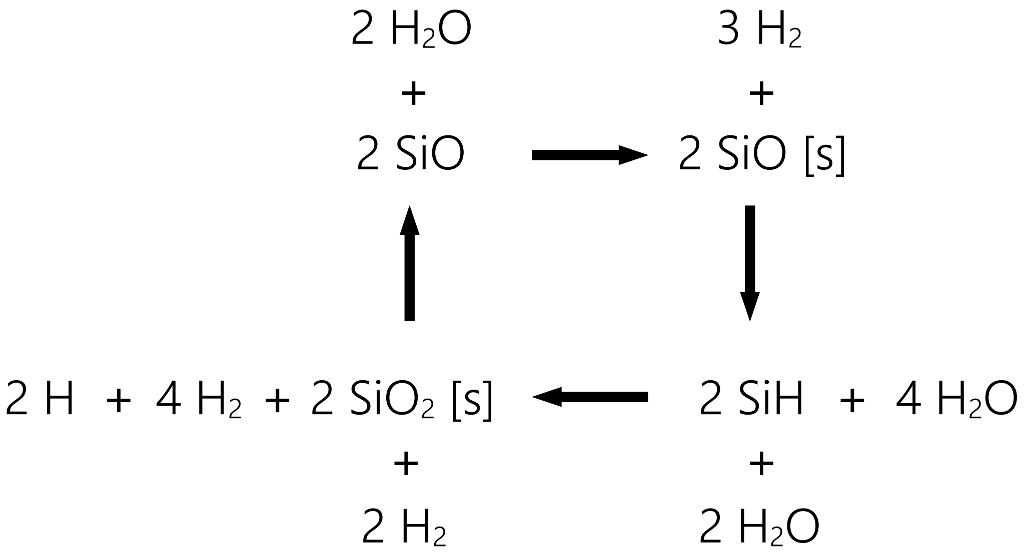
$2\ H + 4\ H_2 + 2\ SiO_2\ [s] \longleftarrow 2\ SiH + 4\ H_2O$

+

$2\ H_2O$

Nidhi Bangera

SiO-SiO_2 cycle



$2\ H_2O$

+

2 SiO

$3\ H_2$

+

2 SiO [s]

$2\ SiH + 4\ H_2O$

+

$2\ H_2O$

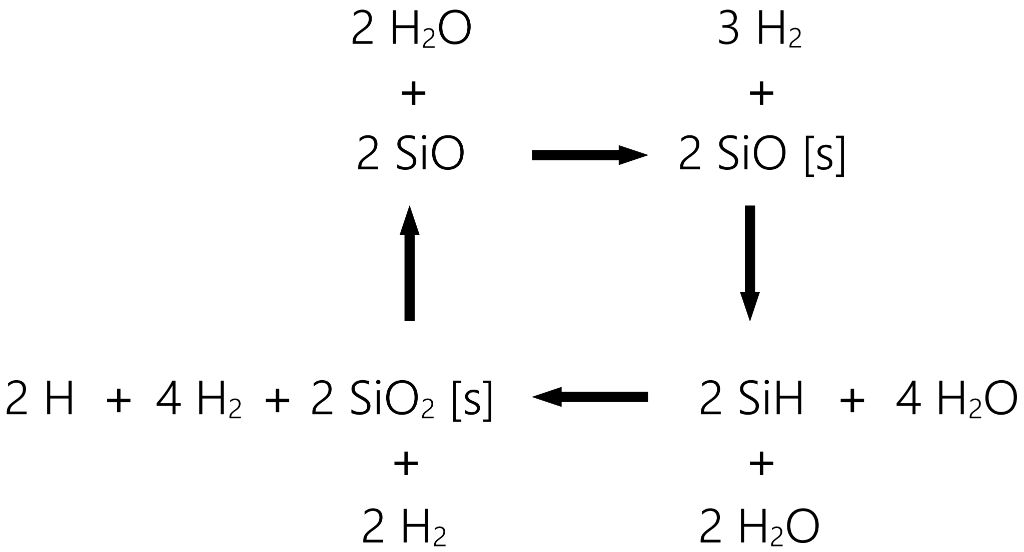
$2\ H + 4\ H_2 + 2\ SiO_2$ [s]

+

$2\ H_2$

Nidhi Bangera

SiO-SiO_2 cycle



$$\begin{tikzcd} 2\,H_2O + 2\,SiO \arrow[r] & 3\,H_2 + 2\,SiO\,[s] \arrow[d] \\ 2\,H + 4\,H_2 + 2\,SiO_2\,[s] + 2\,H_2 \arrow[u] & 2\,SiH + 4\,H_2O + 2\,H_2O \arrow[l] \end{tikzcd}$$

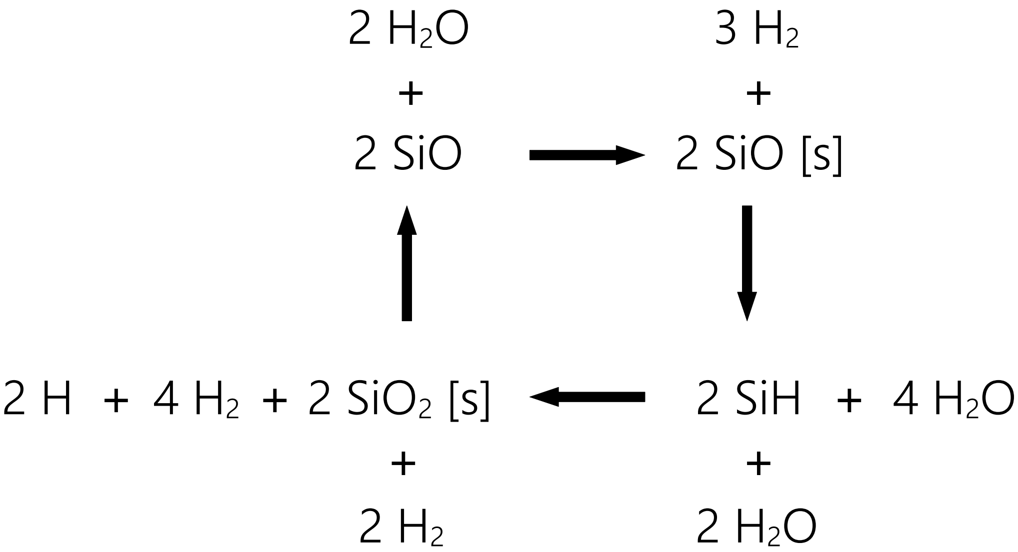
$$\boxed{H_2 \rightarrow 2\,H.}$$

Nidhi Bangera

SiO-SiO$_2$ cycle

$$\begin{aligned} CH_4 + H &\rightarrow CH_3 + H_2, \\ CH_3 + H &\rightarrow CH_2 + H_2, \\ CH_2 + H &\rightarrow CH + H_2. \end{aligned}$$

$$CH + H_2O \rightarrow H_2CO + H.$$



$2\ H_2O$ + $2\ SiO$

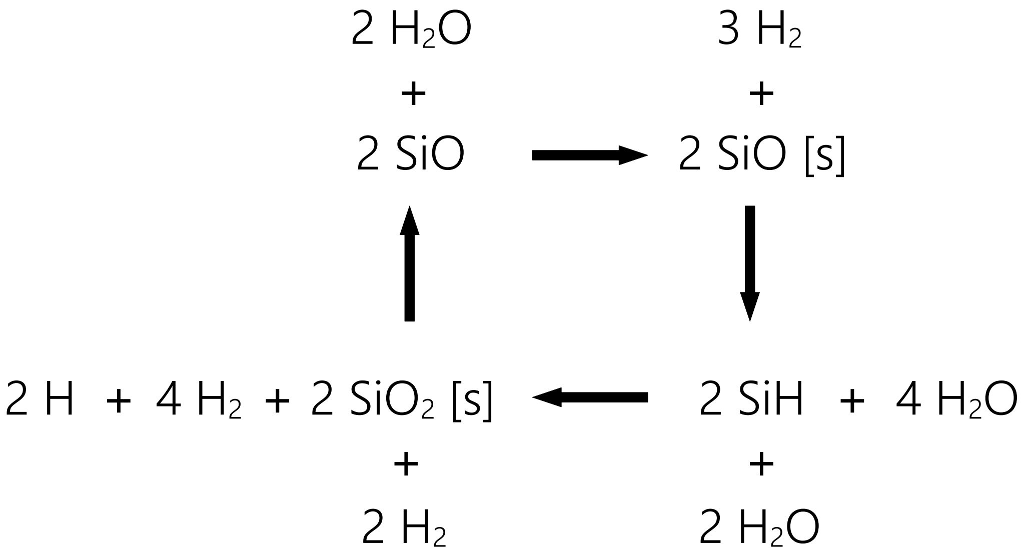
$3\ H_2$ + $2\ SiO\ [s]$

$2\ SiH$ + $4\ H_2O$ + $2\ H_2O$

$2\ H$ + $4\ H_2$ + $2\ SiO_2\ [s]$ + $2\ H_2$

$$\boxed{H_2 \rightarrow 2\ H.}$$

SiO-SiO$_2$ cycle



$2\ H_2O$ + $2\ SiO$ → $3\ H_2$ + $2\ SiO\ [s]$

↓

$2\ SiH$ + $4\ H_2O$ + $2\ H_2O$

←

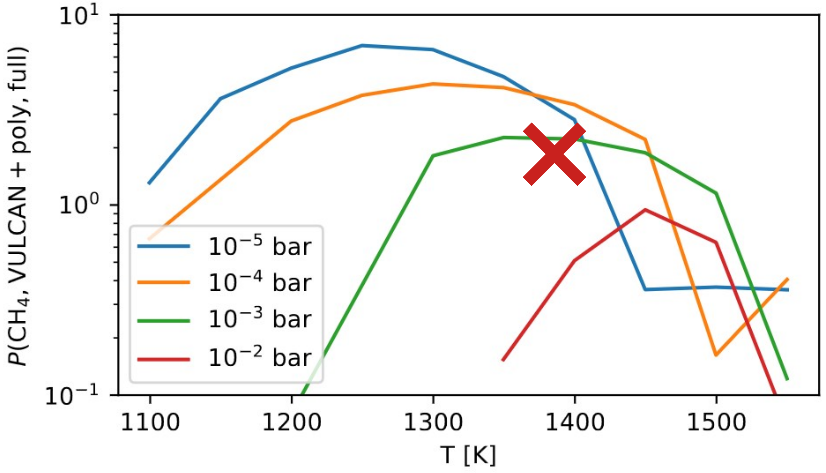
$2\ H$ + $4\ H_2$ + $2\ SiO_2\ [s]$ + $2\ H_2$

↑

$$\boxed{H_2 \rightarrow 2\ H.}$$

$$\boxed{\begin{aligned} CH_4 + H &\rightarrow CH_3 + H_2, \\ CH_3 + H &\rightarrow CH_2 + H_2, \\ CH_2 + H &\rightarrow CH + H_2. \end{aligned}}$$

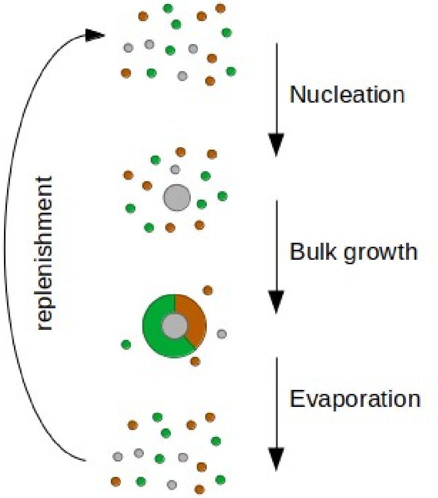
$$\boxed{CH + H_2O \rightarrow H_2CO + H.}$$



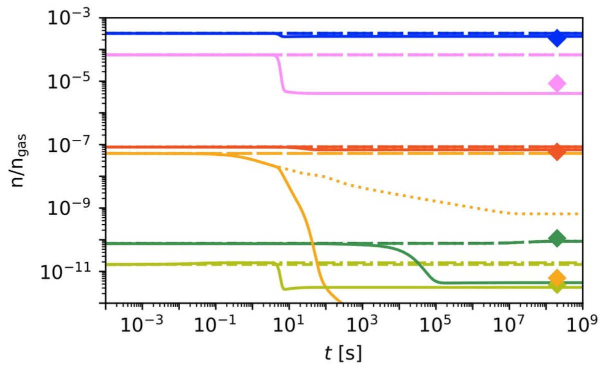
Summary

sven.kiefer@kuleuven.be
Kiefersv.github.io
@ExoSvenK

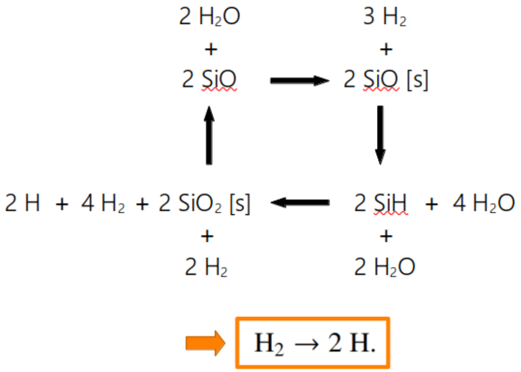
Clouds in hot Jupiters form from refractory materials



Clouds deplete the local gas-phase abundances



A catalytic SiO-SiO$_2$ cycle impacts CH$_4$ abundances



$2\ H_2O$ + $2\ SiO$ → $3\ H_2$ + $2\ SiO\ [s]$

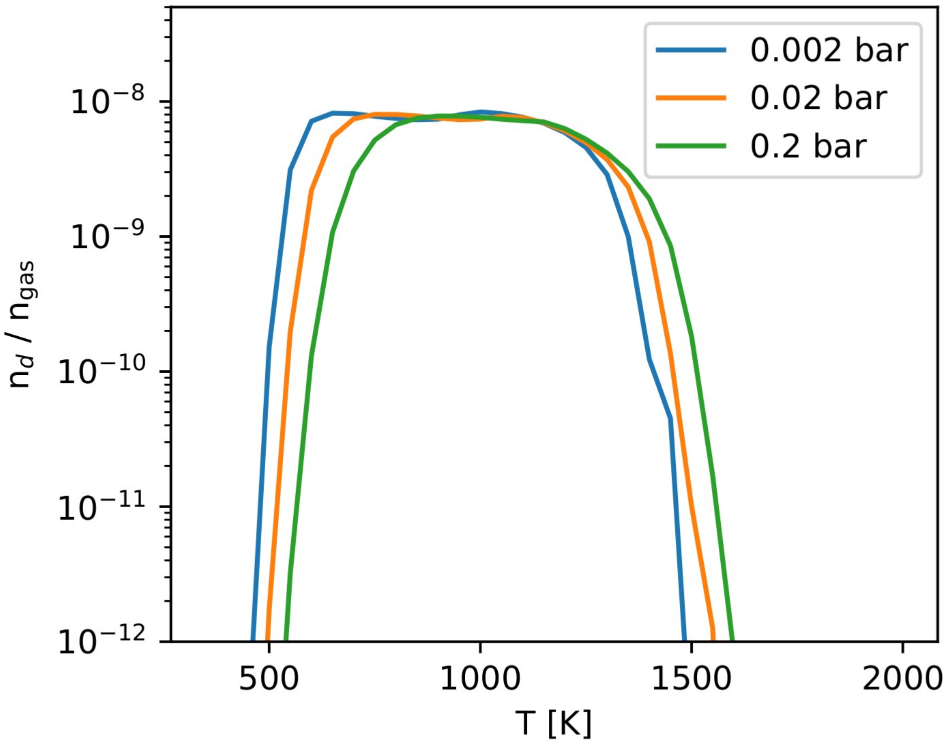
$2\ SiH + 4\ H_2O$ + $2\ H_2O$ ← $2\ H + 4\ H_2 + 2\ SiO_2\ [s]$ + $2\ H_2$

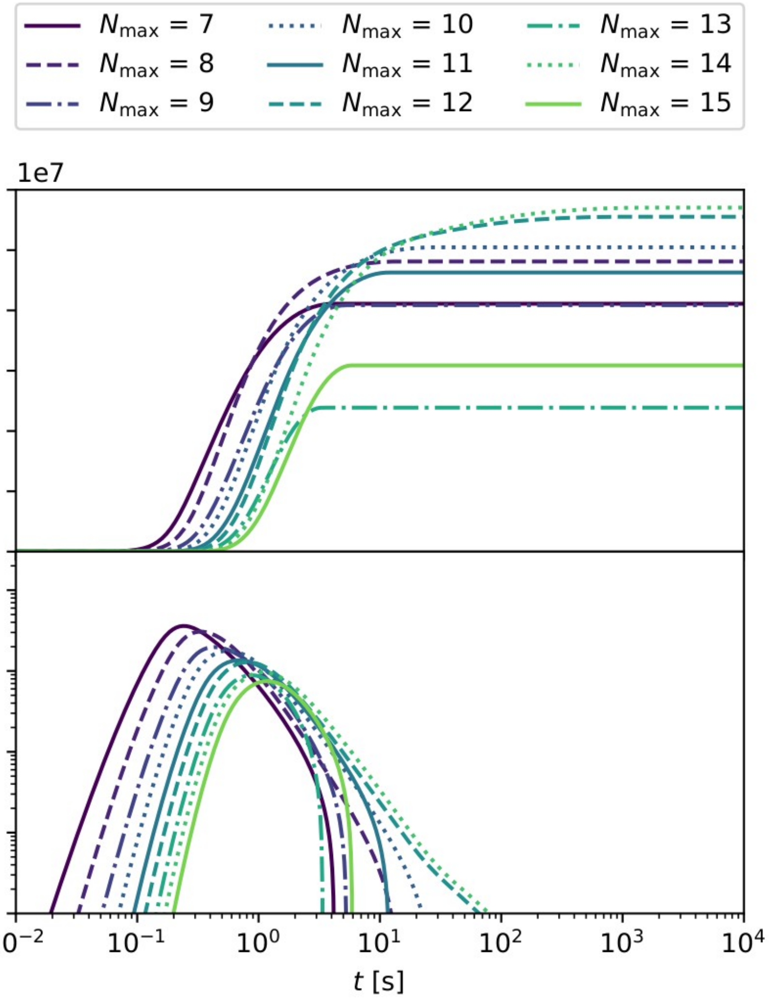
$H_2 \rightarrow 2\ H.$

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860470.

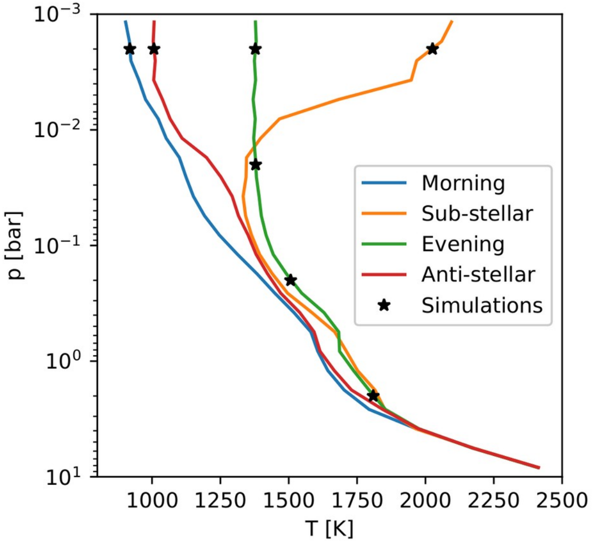
Additional Slides

Kinetic TiO_2 nucleation

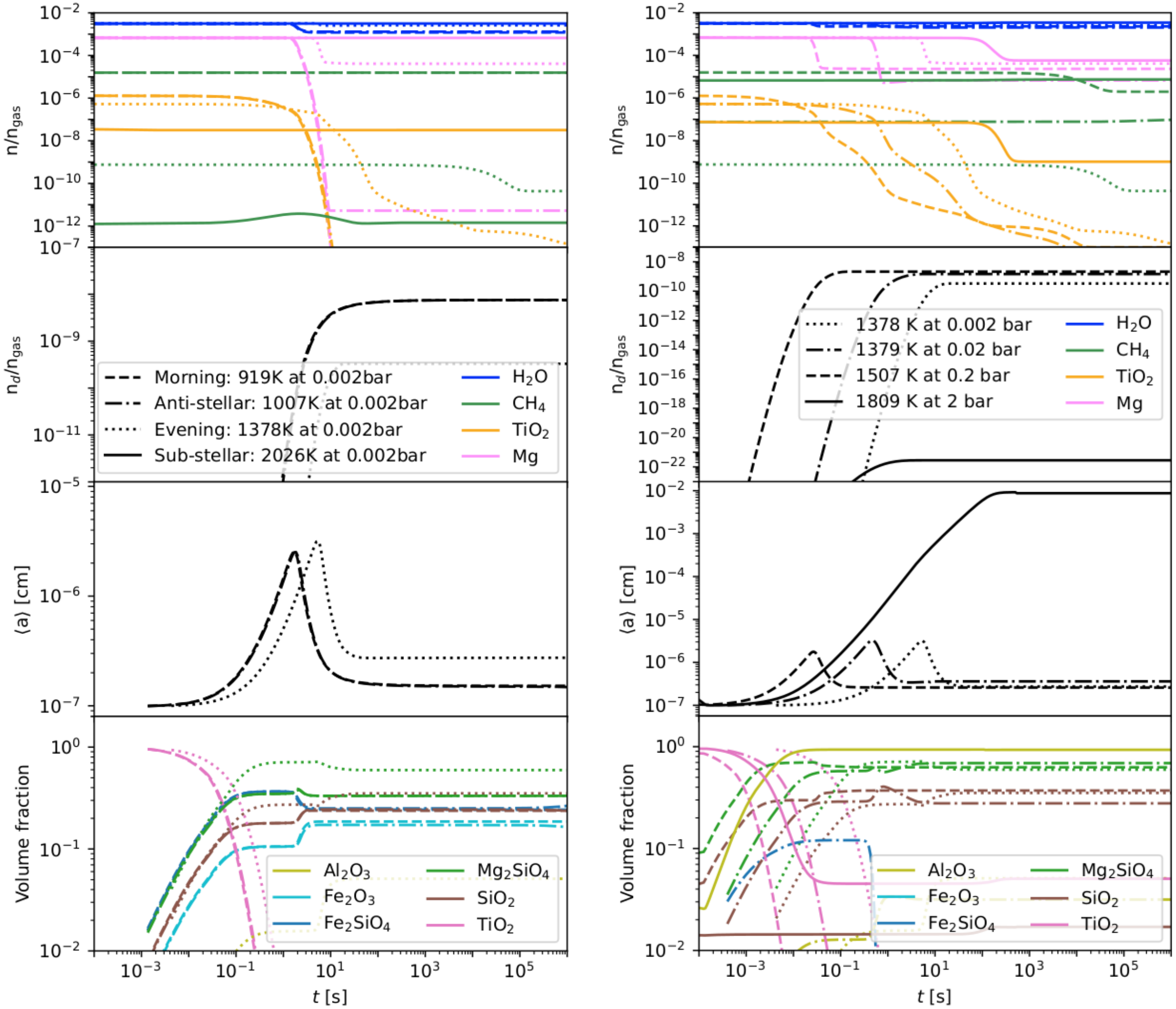




HD 209458 b

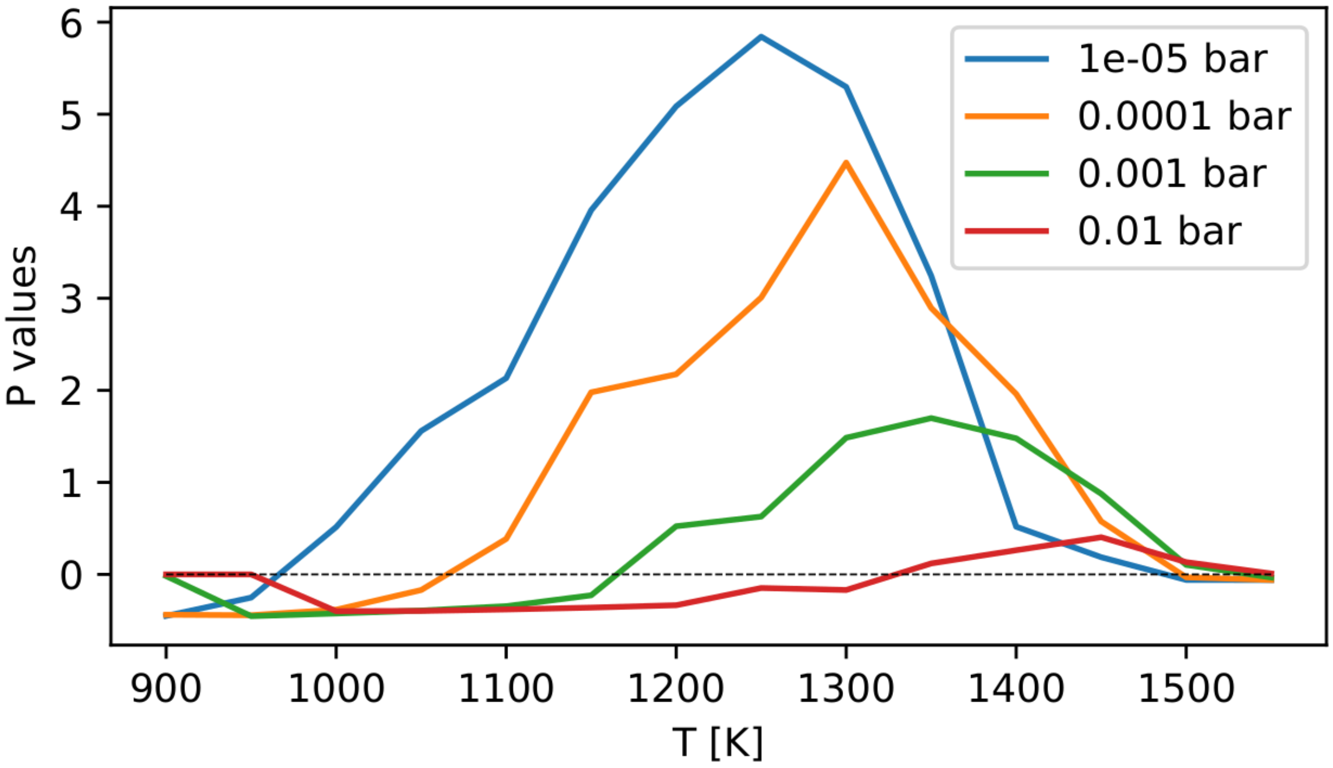


p [bar]
T [K]
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
1000
1250
1500
1750
2000
2250
2500
Morning
Sub-stellar
Evening
Anti-stellar
Simulations

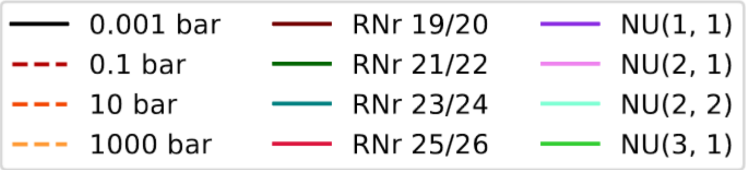


n/n_{gas}
n_d/n_{gas}
⟨a⟩ [cm]
Volume fraction
t [s]
Morning: 919K at 0.002bar
Anti-stellar: 1007K at 0.002bar
Evening: 1378K at 0.002bar
Sub-stellar: 2026K at 0.002bar
H_2O
CH_4
TiO_2
Mg
1378 K at 0.002 bar
1379 K at 0.02 bar
1507 K at 0.2 bar
1809 K at 2 bar
Al_2O_3
Fe_2O_3
Fe_2SiO_4
Mg_2SiO_4
SiO_2
TiO_2
10^{-3}
10^{-1}
10^{1}
10^{3}
10^{5}

SiO-SiO$_2$ cycle grid

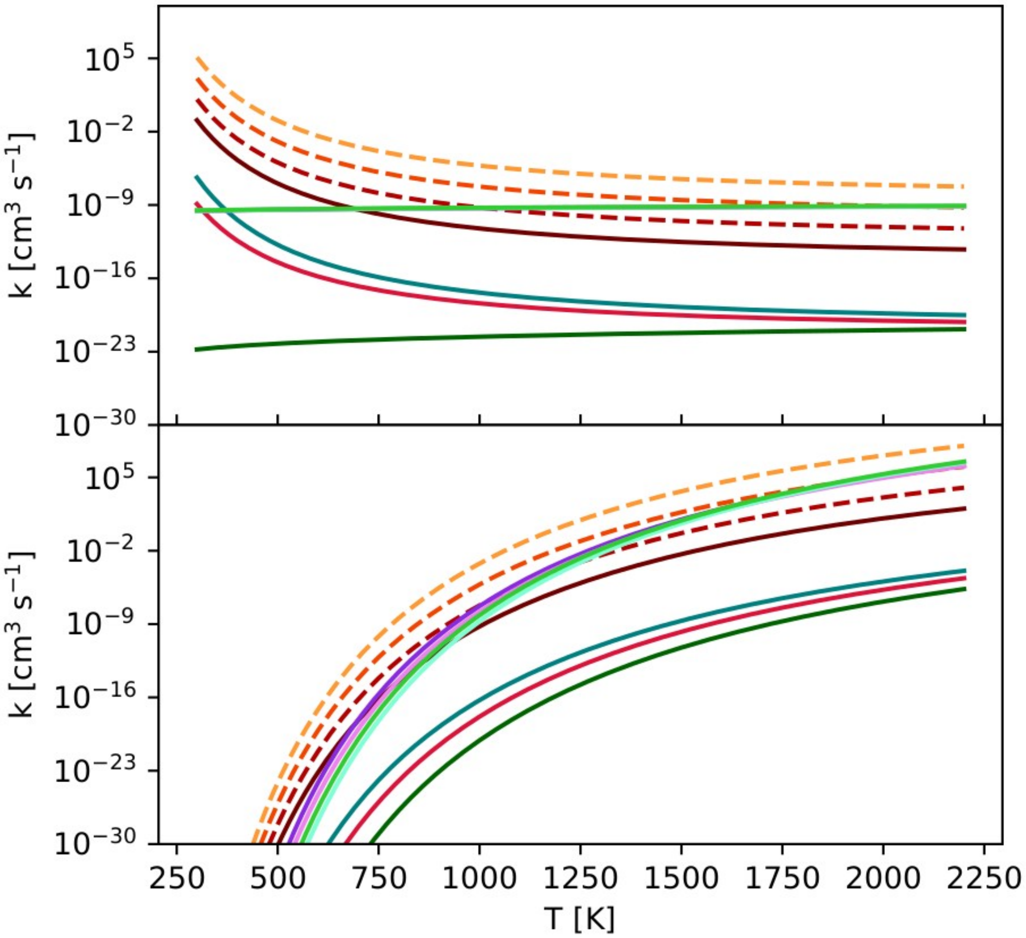


Three Body Reactions

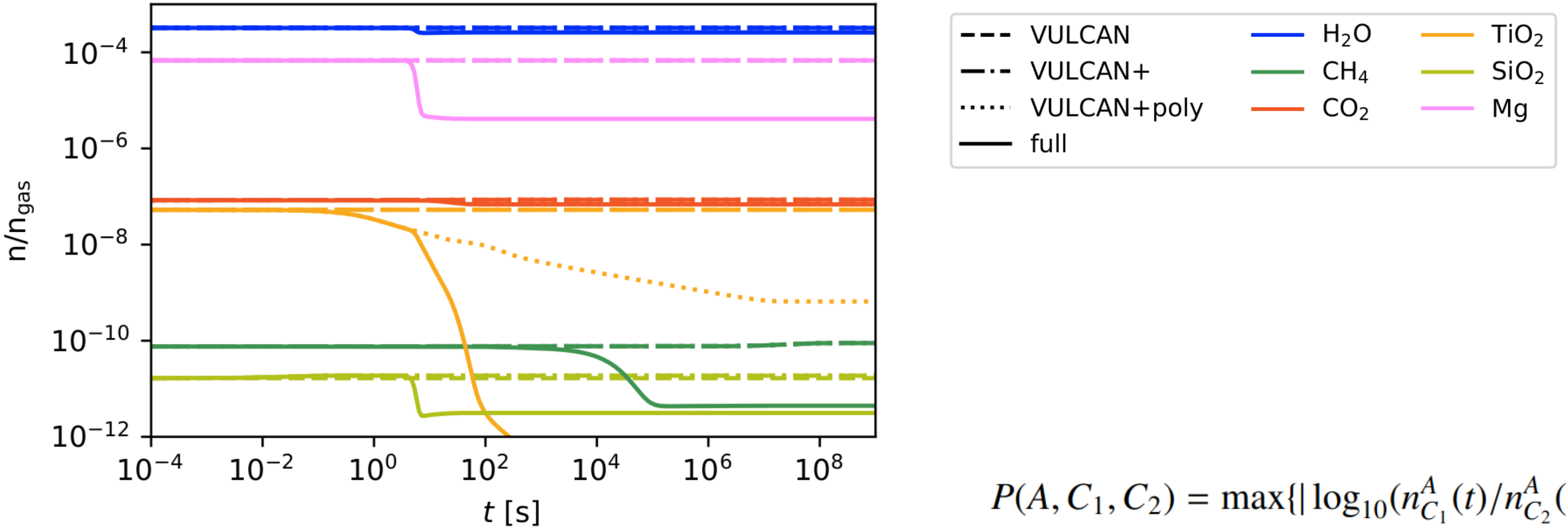


$$\mathrm{NU}(i, j) : (\mathrm{TiO_2})_i + (\mathrm{TiO_2})_i \leftrightarrow (\mathrm{TiO_2})_{(i+j)}$$

19 $(\mathrm{TiO_2})_2 + \mathrm{M} \rightarrow \mathrm{TiO_2} + \mathrm{TiO_2} + \mathrm{M}$
20 $\mathrm{TiO_2} + \mathrm{TiO_2} + \mathrm{M} \rightarrow (\mathrm{TiO_2})_2 + \mathrm{M}$
21 $(\mathrm{TiO_2})_3 + \mathrm{M} \rightarrow (\mathrm{TiO_2})_2 + \mathrm{TiO_2} + \mathrm{M}$
22 $(\mathrm{TiO_2})_2 + \mathrm{TiO_2} + \mathrm{M} \rightarrow (\mathrm{TiO_2})_3 + \mathrm{M}$
23 $(\mathrm{TiO_2})_4 + \mathrm{M} \rightarrow (\mathrm{TiO_2})_3 + \mathrm{TiO_2} + \mathrm{M}$
24 $(\mathrm{TiO_2})_3 + \mathrm{TiO_2} + \mathrm{M} \rightarrow (\mathrm{TiO_2})_4 + \mathrm{M}$
25 $(\mathrm{TiO_2})_4 + \mathrm{M} \rightarrow (\mathrm{TiO_2})_2 + (\mathrm{TiO_2})_2 + \mathrm{M}$
26 $(\mathrm{TiO_2})_2 + (\mathrm{TiO_2})_2 + \mathrm{M} \rightarrow (\mathrm{TiO_2})_4 + \mathrm{M}$



Network Test



$$P(A, C_1, C_2) = \max\{|\log_{10}(n^A_{C_1}(t)/n^A_{C_2}(t))|, \forall t \in [10^{-4}, 10^9]\}$$

	H_2	H_2O	CO_2	CH_4	TiO_2	SiO_2	Mg
$P(A, \text{Equilibrium, VULCAN})$	4.84e-05	7.35e-03	1.58e-02	6.35e-02	-	-	-
$P(A, \text{VULCAN, VULCAN+})$	5.66e-11	1.34e-07	1.16e-05	1.17e-07	7.43e-04	5.25e-02	-
$P(A, \text{VULCAN+, VULCAN+poly})$	1.14e-07	1.32e-04	1.36e-04	1.32e-04	1.907	1.32e-04	-
$P(A, \text{VULCAN+poly, full})$	1.35e-03	0.107	9.52e-02	1.304	4.847	0.837	1.218

Surface reaction

$$2\mathrm{Mg} + \mathrm{SiO} + 3\mathrm{H_2O} \leftrightarrow \mathrm{Mg_2SiO_4}[\mathrm{s}] + 3\mathrm{H_2}$$

Surface reaction

$$2Mg + SiO + 3H_2O \leftrightarrow Mg_2SiO_4[s] + 3H_2$$

$$R_f = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}$$

$$R_b = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}^{\circ}$$

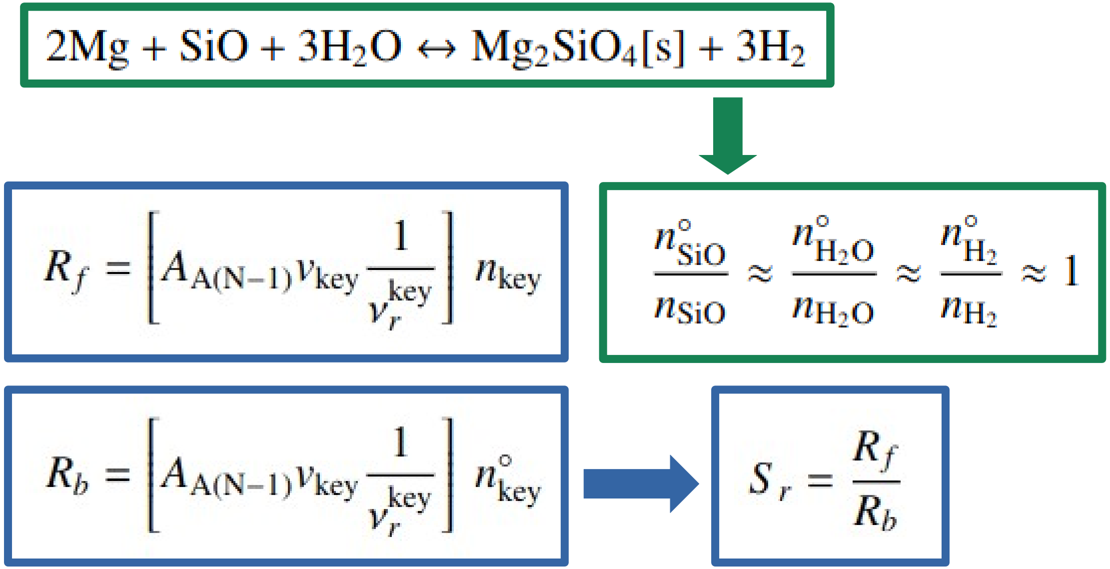
Surface reaction

$$2\mathrm{Mg} + \mathrm{SiO} + 3\mathrm{H_2O} \leftrightarrow \mathrm{Mg_2SiO_4[s]} + 3\mathrm{H_2}$$

$$R_f = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}$$

$$R_b = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n^{\circ}_{\mathrm{key}} \quad \longrightarrow \quad S_r = \frac{R_f}{R_b}$$

Surface reaction



$$2Mg + SiO + 3H_2O \leftrightarrow Mg_2SiO_4[s] + 3H_2$$

$$R_f = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}$$

$$\frac{n^{\circ}_{\mathrm{SiO}}}{n_{\mathrm{SiO}}} \approx \frac{n^{\circ}_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}}} \approx \frac{n^{\circ}_{\mathrm{H_2}}}{n_{\mathrm{H_2}}} \approx 1$$

$$R_b = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n^{\circ}_{\mathrm{key}}$$

$$S_r = \frac{R_f}{R_b}$$

Surface reaction

$$2\mathrm{Mg} + \mathrm{SiO} + 3\mathrm{H_2O} \leftrightarrow \mathrm{Mg_2SiO_4[s]} + 3\mathrm{H_2}$$

$$R_f = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}$$

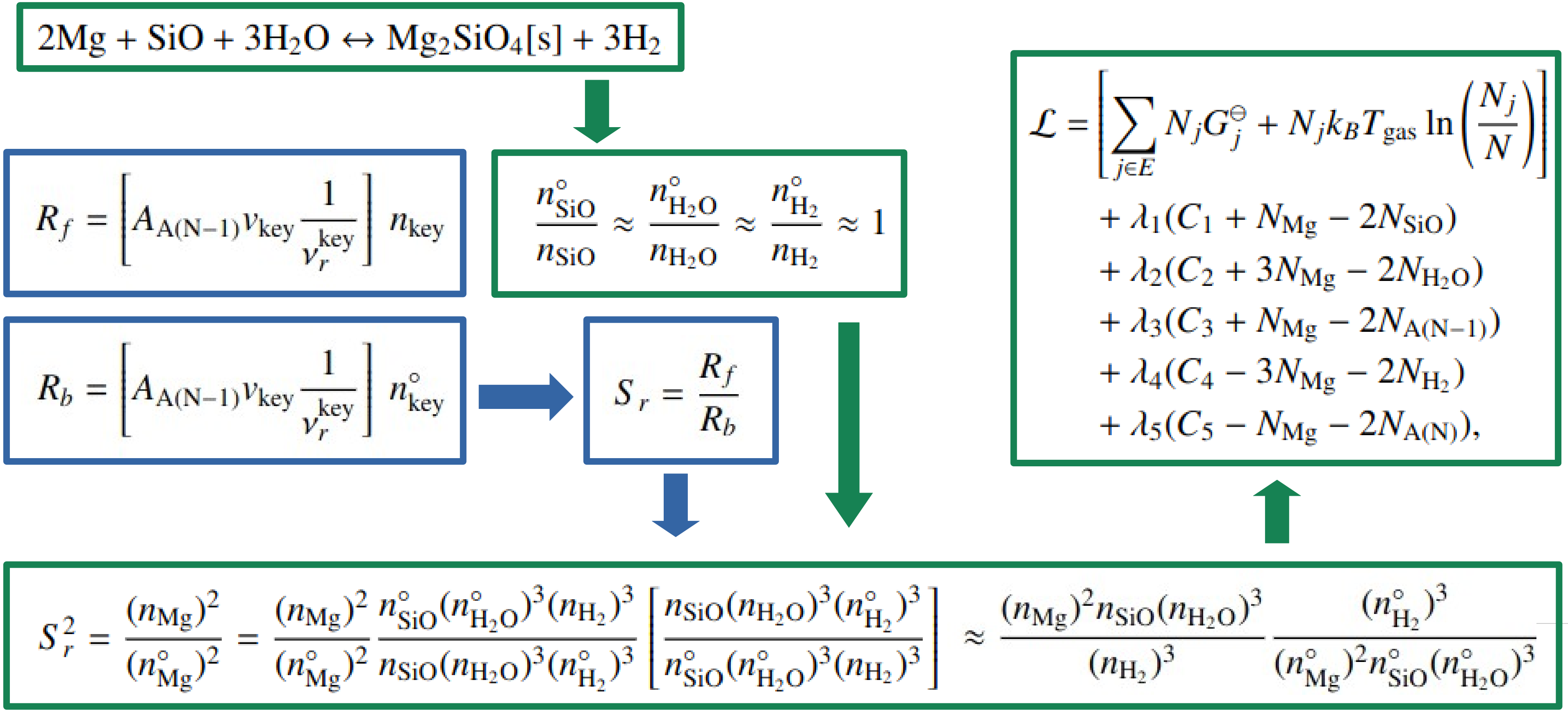
$$\frac{n^\circ_{\mathrm{SiO}}}{n_{\mathrm{SiO}}} \approx \frac{n^\circ_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}}} \approx \frac{n^\circ_{\mathrm{H_2}}}{n_{\mathrm{H_2}}} \approx 1$$

$$R_b = \left[A_{\mathrm{A(N-1)}} \nu_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n^\circ_{\mathrm{key}}$$

$$S_r = \frac{R_f}{R_b}$$

$$S_r^2 = \frac{(n_{\mathrm{Mg}})^2}{(n^\circ_{\mathrm{Mg}})^2} = \frac{(n_{\mathrm{Mg}})^2}{(n^\circ_{\mathrm{Mg}})^2} \frac{n^\circ_{\mathrm{SiO}} (n^\circ_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}})^3}{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n^\circ_{\mathrm{H_2}})^3} \left[\frac{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n^\circ_{\mathrm{H_2}})^3}{n^\circ_{\mathrm{SiO}} (n^\circ_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}})^3} \right] \approx \frac{(n_{\mathrm{Mg}})^2 n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3}{(n_{\mathrm{H_2}})^3} \frac{(n^\circ_{\mathrm{H_2}})^3}{(n^\circ_{\mathrm{Mg}})^2 n^\circ_{\mathrm{SiO}} (n^\circ_{\mathrm{H_2O}})^3}$$

Surface reaction



$$2\mathrm{Mg} + \mathrm{SiO} + 3\mathrm{H_2O} \leftrightarrow \mathrm{Mg_2SiO_4[s]} + 3\mathrm{H_2}$$

$$R_f = \left[A_{\mathrm{A(N-1)}} v_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n_{\mathrm{key}}$$

$$\frac{n^{\circ}_{\mathrm{SiO}}}{n_{\mathrm{SiO}}} \approx \frac{n^{\circ}_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}}} \approx \frac{n^{\circ}_{\mathrm{H_2}}}{n_{\mathrm{H_2}}} \approx 1$$

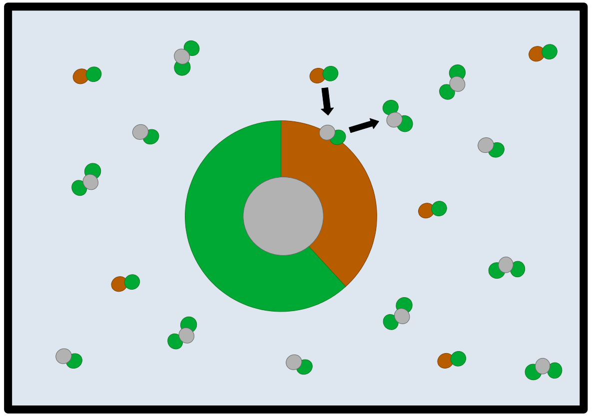
$$R_b = \left[A_{\mathrm{A(N-1)}} v_{\mathrm{key}} \frac{1}{\nu_r^{\mathrm{key}}} \right] n^{\circ}_{\mathrm{key}}$$

$$S_r = \frac{R_f}{R_b}$$

$$\begin{aligned} \mathcal{L} = & \left[\sum_{j \in E} N_j G_j^{\ominus} + N_j k_B T_{\mathrm{gas}} \ln \left(\frac{N_j}{N} \right) \right] \\ & + \lambda_1 (C_1 + N_{\mathrm{Mg}} - 2N_{\mathrm{SiO}}) \\ & + \lambda_2 (C_2 + 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2O}}) \\ & + \lambda_3 (C_3 + N_{\mathrm{Mg}} - 2N_{\mathrm{A(N-1)}}) \\ & + \lambda_4 (C_4 - 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2}}) \\ & + \lambda_5 (C_5 - N_{\mathrm{Mg}} - 2N_{\mathrm{A(N)}}), \end{aligned}$$

$$S_r^2 = \frac{(n_{\mathrm{Mg}})^2}{(n^{\circ}_{\mathrm{Mg}})^2} = \frac{(n_{\mathrm{Mg}})^2}{(n^{\circ}_{\mathrm{Mg}})^2} \frac{n^{\circ}_{\mathrm{SiO}} (n^{\circ}_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}})^3}{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n^{\circ}_{\mathrm{H_2}})^3} \left[\frac{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n^{\circ}_{\mathrm{H_2}})^3}{n^{\circ}_{\mathrm{SiO}} (n^{\circ}_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}})^3} \right] \approx \frac{(n_{\mathrm{Mg}})^2 n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3}{(n_{\mathrm{H_2}})^3} \frac{(n^{\circ}_{\mathrm{H_2}})^3}{(n^{\circ}_{\mathrm{Mg}})^2 n^{\circ}_{\mathrm{SiO}} (n^{\circ}_{\mathrm{H_2O}})^3}$$

Surface reaction



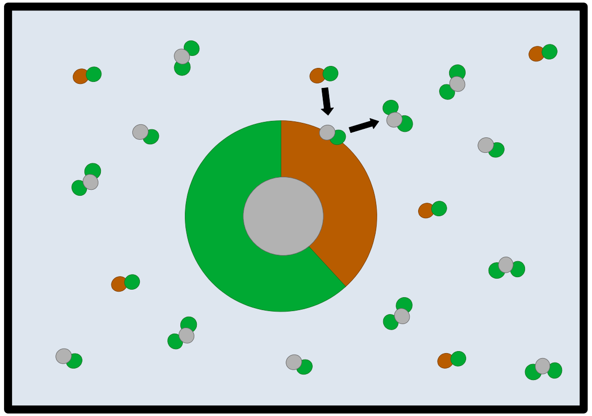
→ Box with given abundances
→ Only 1 surface reaction happens

$$\mathcal{L} = \left[\sum_{j\in E} N_j G_j^{\ominus} + N_j k_B T_{\mathrm{gas}} \ln\left(\frac{N_j}{N}\right)\right] + \lambda_1(C_1 + N_{\mathrm{Mg}} - 2N_{\mathrm{SiO}}) + \lambda_2(C_2 + 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2O}}) + \lambda_3(C_3 + N_{\mathrm{Mg}} - 2N_{\mathrm{A(N-1)}}) + \lambda_4(C_4 - 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2}}) + \lambda_5(C_5 - N_{\mathrm{Mg}} - 2N_{\mathrm{A(N)}}),$$

$$S_r^2 = \frac{(n_{\mathrm{Mg}})^2}{(n_{\mathrm{Mg}}^{\circ})^2} = \frac{(n_{\mathrm{Mg}})^2}{(n_{\mathrm{Mg}}^{\circ})^2}\frac{n_{\mathrm{SiO}}^{\circ}(n_{\mathrm{H_2O}}^{\circ})^3(n_{\mathrm{H_2}})^3}{n_{\mathrm{SiO}}(n_{\mathrm{H_2O}})^3(n_{\mathrm{H_2}}^{\circ})^3}\left[\frac{n_{\mathrm{SiO}}(n_{\mathrm{H_2O}})^3(n_{\mathrm{H_2}}^{\circ})^3}{n_{\mathrm{SiO}}^{\circ}(n_{\mathrm{H_2O}}^{\circ})^3(n_{\mathrm{H_2}})^3}\right] \approx \frac{(n_{\mathrm{Mg}})^2 n_{\mathrm{SiO}}(n_{\mathrm{H_2O}})^3}{(n_{\mathrm{H_2}})^3}\frac{(n_{\mathrm{H_2}}^{\circ})^3}{(n_{\mathrm{Mg}}^{\circ})^2 n_{\mathrm{SiO}}^{\circ}(n_{\mathrm{H_2O}}^{\circ})^3}$$

Surface reaction

$$S_r^{\nu_{\mathrm{key}}} = \frac{\Pi_{X\in F} n_X^{\nu_X}}{\Pi_{Y\in D} n_Y^{\nu_Y}} \left(\frac{p^{\ominus}}{k_B T_{\mathrm{gas}}}\right)^{l_Y - l_X} \exp\left(\frac{1}{k_B T_{\mathrm{gas}}}\left[G_{\mathrm{A}}^{\ominus} - \sum_{X\in F} \nu_X G_{\mathrm{X}}^{\ominus} + \sum_{Y\in D} \nu_Y G_{\mathrm{Y}}^{\ominus}\right]\right)$$



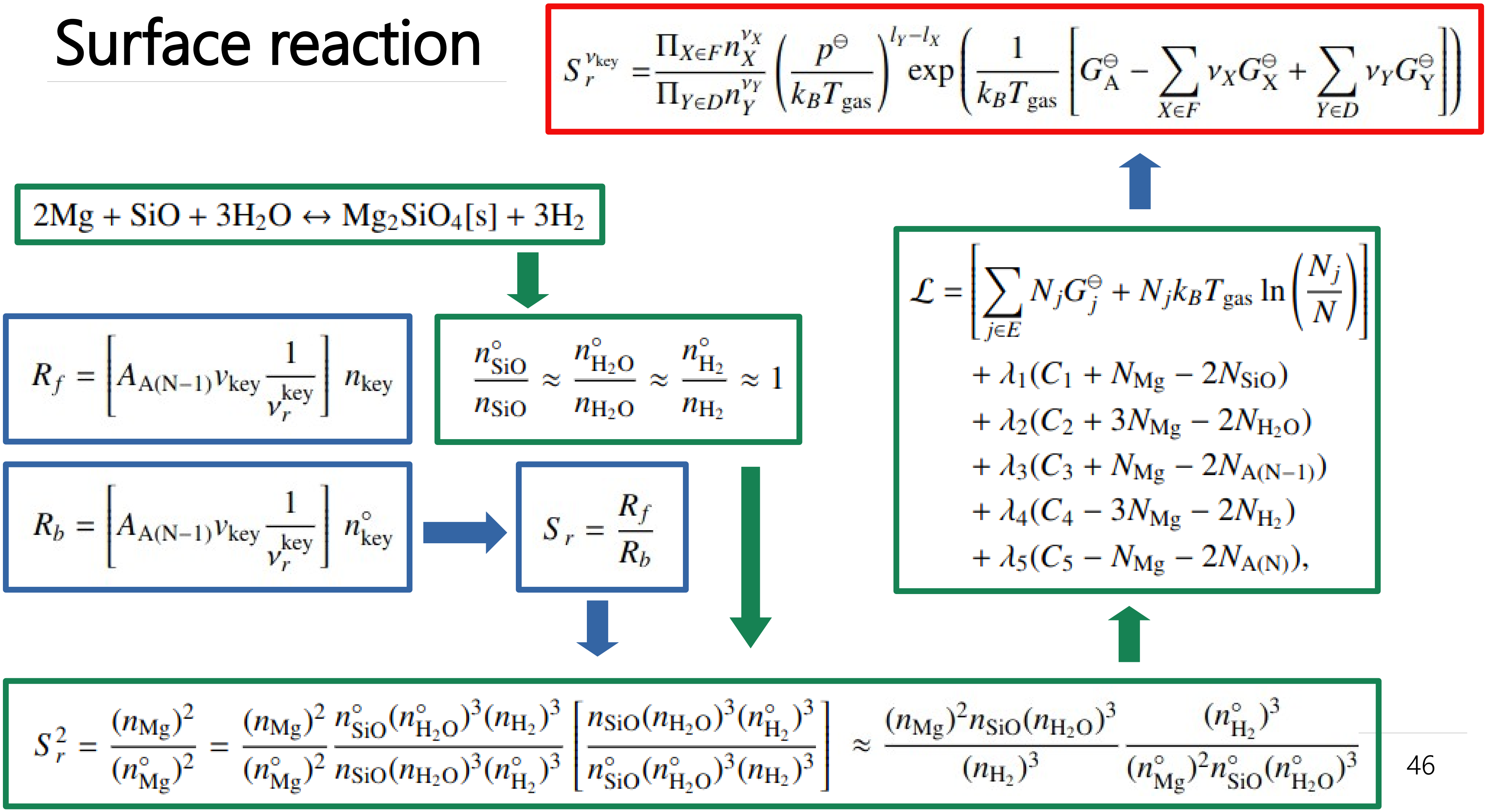
→ Box with given abundances

→ Only 1 surface reaction happens

$$\begin{aligned}\mathcal{L} = &\left[\sum_{j\in E} N_j G_j^{\ominus} + N_j k_B T_{\mathrm{gas}} \ln\left(\frac{N_j}{N}\right)\right] \\ &+ \lambda_1 (C_1 + N_{\mathrm{Mg}} - 2N_{\mathrm{SiO}}) \\ &+ \lambda_2 (C_2 + 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2O}}) \\ &+ \lambda_3 (C_3 + N_{\mathrm{Mg}} - 2N_{\mathrm{A(N-1)}}) \\ &+ \lambda_4 (C_4 - 3N_{\mathrm{Mg}} - 2N_{\mathrm{H_2}}) \\ &+ \lambda_5 (C_5 - N_{\mathrm{Mg}} - 2N_{\mathrm{A(N)}}),\end{aligned}$$

$$S_r^2 = \frac{(n_{\mathrm{Mg}})^2}{(n_{\mathrm{Mg}}^{\circ})^2} = \frac{(n_{\mathrm{Mg}})^2}{(n_{\mathrm{Mg}}^{\circ})^2} \frac{n_{\mathrm{SiO}}^{\circ} (n_{\mathrm{H_2O}}^{\circ})^3 (n_{\mathrm{H_2}})^3}{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}}^{\circ})^3} \left[\frac{n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3 (n_{\mathrm{H_2}}^{\circ})^3}{n_{\mathrm{SiO}}^{\circ} (n_{\mathrm{H_2O}}^{\circ})^3 (n_{\mathrm{H_2}})^3}\right] \approx \frac{(n_{\mathrm{Mg}})^2 n_{\mathrm{SiO}} (n_{\mathrm{H_2O}})^3}{(n_{\mathrm{H_2}})^3} \frac{(n_{\mathrm{H_2}}^{\circ})^3}{(n_{\mathrm{Mg}}^{\circ})^2 n_{\mathrm{SiO}}^{\circ} (n_{\mathrm{H_2O}}^{\circ})^3}$$

Surface reaction



$$2Mg + SiO + 3H_2O \leftrightarrow Mg_2SiO_4[s] + 3H_2$$

$$\frac{n^\circ_{SiO}}{n_{SiO}} \approx \frac{n^\circ_{H_2O}}{n_{H_2O}} \approx \frac{n^\circ_{H_2}}{n_{H_2}} \approx 1$$

$$R_f = \left[A_{A(N-1)}\nu_{key}\frac{1}{\nu_r^{key}}\right] n_{key}$$

$$R_b = \left[A_{A(N-1)}\nu_{key}\frac{1}{\nu_r^{key}}\right] n^\circ_{key}$$

$$S_r = \frac{R_f}{R_b}$$

$$S_r^2 = \frac{(n_{Mg})^2}{(n^\circ_{Mg})^2} = \frac{(n_{Mg})^2}{(n^\circ_{Mg})^2}\frac{n^\circ_{SiO}(n^\circ_{H_2O})^3(n_{H_2})^3}{n_{SiO}(n_{H_2O})^3(n^\circ_{H_2})^3}\left[\frac{n_{SiO}(n_{H_2O})^3(n^\circ_{H_2})^3}{n^\circ_{SiO}(n^\circ_{H_2O})^3(n_{H_2})^3}\right] \approx \frac{(n_{Mg})^2 n_{SiO}(n_{H_2O})^3}{(n_{H_2})^3}\frac{(n^\circ_{H_2})^3}{(n^\circ_{Mg})^2 n^\circ_{SiO}(n^\circ_{H_2O})^3}$$

$$\begin{aligned}\mathcal{L} = &\left[\sum_{j\in E} N_j G_j^\ominus + N_j k_B T_{gas}\ln\left(\frac{N_j}{N}\right)\right]\\ &+\lambda_1(C_1 + N_{Mg} - 2N_{SiO})\\ &+\lambda_2(C_2 + 3N_{Mg} - 2N_{H_2O})\\ &+\lambda_3(C_3 + N_{Mg} - 2N_{A(N-1)})\\ &+\lambda_4(C_4 - 3N_{Mg} - 2N_{H_2})\\ &+\lambda_5(C_5 - N_{Mg} - 2N_{A(N)}),\end{aligned}$$

$$S_r^{\nu_{key}} = \frac{\Pi_{X\in F}n_X^{\nu_X}}{\Pi_{Y\in D}n_Y^{\nu_Y}}\left(\frac{p^\ominus}{k_B T_{gas}}\right)^{l_Y - l_X}\exp\left(\frac{1}{k_B T_{gas}}\left[G_A^\ominus - \sum_{X\in F}\nu_X G_X^\ominus + \sum_{Y\in D}\nu_Y G_Y^\ominus\right]\right)$$