Modelling Equilibrium Chemistry

Peter Woitke & Christiane Helling

University of St Andrews, Scotland

EWASS 2018, Liverpool, Wed April 4th, 2018

Chemical Equilibrium

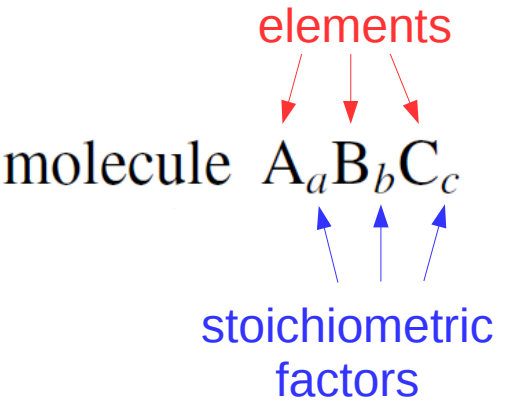
- part of **LTE** assumptions → ***molecular composition of the gas***
- widespread applications in astrophysics
  - cool stellar atmospheres & brown dwarfs
  - AGB stellar winds
  - planetary atmospheres

Two equivalent methods:

1) **minimisation of system Gibbs free energy**

2) **solution of Guldberg's law of mass action**

$$\frac{p_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c}}{p^{\ominus}} = \left(\frac{p_{\mathrm{A}}}{p^{\ominus}}\right)^a \left(\frac{p_{\mathrm{B}}}{p^{\ominus}}\right)^b \left(\frac{p_{\mathrm{C}}}{p^{\ominus}}\right)^c \exp\left(-\frac{\Delta G_{\mathrm{f}}^{\ominus}}{RT}\right)$$



Chemical Equilibrium

- part of **LTE** assumptions → ***molecular composition of the gas***
- widespread applications in astrophysics
  - cool stellar atmospheres & brown dwarfs
  - AGB stellar winds
  - planetary atmospheres

Two equivalent methods:

1) **minimisation of system Gibbs free energy**

2) **solution of Guldberg's law of mass action**

$$\frac{p_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c}}{p^\ominus} = \left(\frac{p_\mathrm{A}}{p^\ominus}\right)^a \left(\frac{p_\mathrm{B}}{p^\ominus}\right)^b \left(\frac{p_\mathrm{C}}{p^\ominus}\right)^c \exp\left(-\frac{\Delta G_\mathrm{f}^\ominus}{RT}\right)$$

atom partial pressures

elements

molecule $\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c$

stoichiometric factors

change of ***Gibbs free energy***

$$\Delta G_\mathrm{f}^\ominus = G^\ominus(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T) - a\,G^\ominus(\mathrm{A}, T) - b\,G^\ominus(\mathrm{B}, T) - c\,G^\ominus(\mathrm{C}, T)$$

equilibrium constant

$$k_p(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T) = (p^\ominus)^{1-a-b-c} \exp\left(-\frac{\Delta G_\mathrm{f}^\ominus}{RT}\right)$$

$$p_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c} = k_p(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T)\; p_\mathrm{A}^a\, p_\mathrm{B}^b\, p_\mathrm{C}^c$$

Chemical Equilibrium

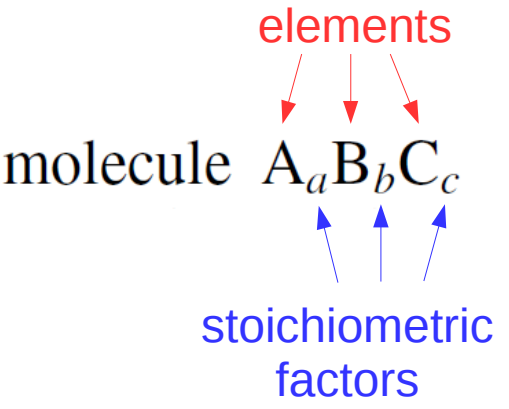
- part of **LTE** assumptions → ***molecular composition of the gas***
- widespread applications in astrophysics
  - cool stellar atmospheres & brown dwarfs
  - AGB stellar winds

White+1958, Eriksson 1971, Sharp & Huebner 1990, Allard+1997, Gordon & McBride 1994 (*CEA-code*), Lodders & Fegley 2002, Blecic 2016 (TEA-code), ...

1) minimisation of system Gibbs free energy

2) solution of Guldberg's law of mass action

Gustafsson 1971, Tsuji 1973, Gail & Sedlmayr 1986, Helling & Woitke 2004 – today, Heng+2016, ...



change of ***Gibbs free energy***

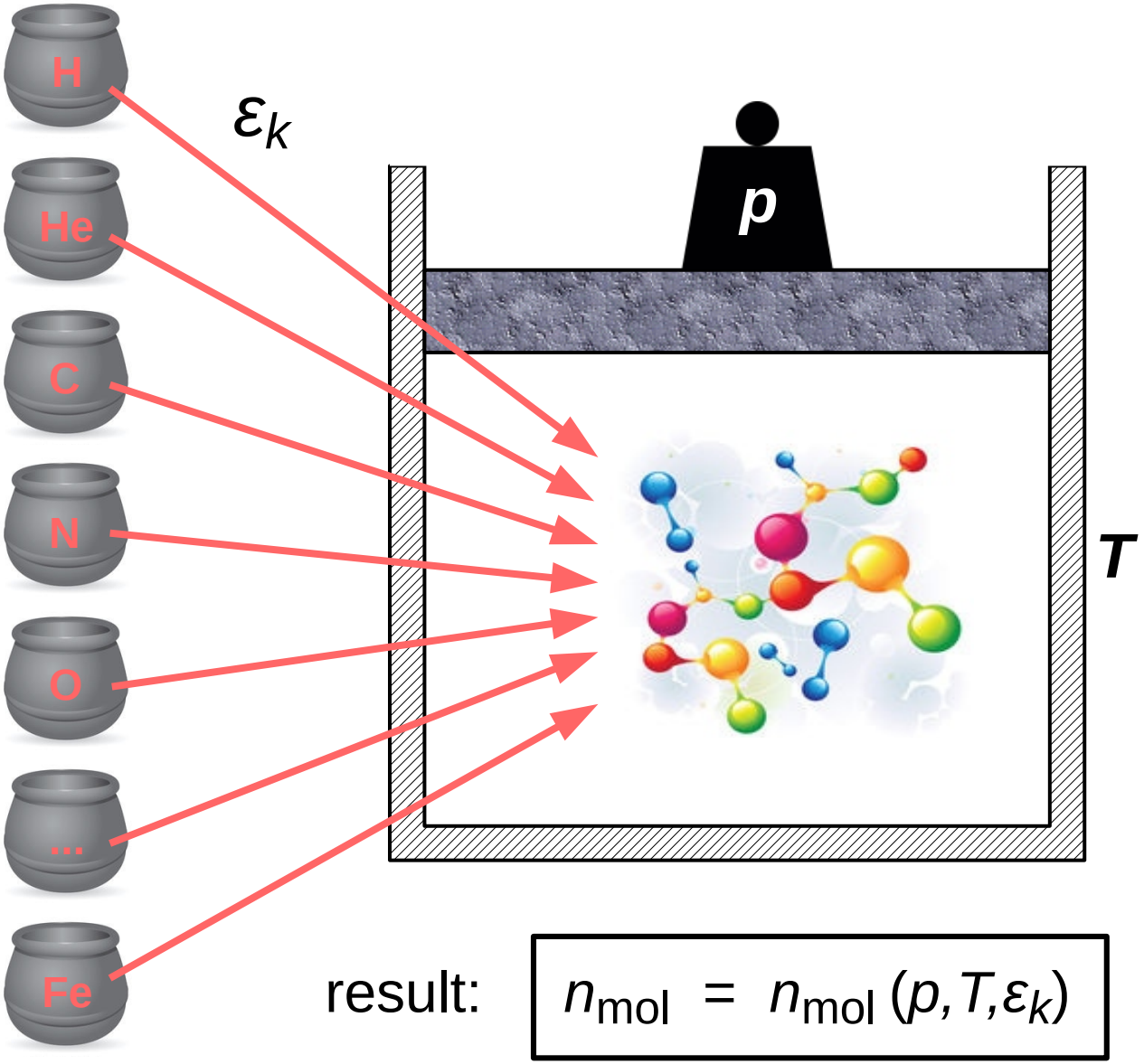
$$\Delta G_\mathrm{f}^\ominus = G^\ominus(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T) - a\,G^\ominus(\mathrm{A}, T) - b\,G^\ominus(\mathrm{B}, T) - c\,G^\ominus(\mathrm{C}, T)$$

equilibrium constant

$$k_p(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T) = (p^\ominus)^{1-a-b-c} \exp\left(-\frac{\Delta G_\mathrm{f}^\ominus}{RT}\right)$$

$$p_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c} = k_p(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c, T)\; p_\mathrm{A}^a\, p_\mathrm{B}^b\, p_\mathrm{C}^c$$

Chemical Equilibrium in the Gas Phase



result: $n_{\mathrm{mol}} = n_{\mathrm{mol}}(p, T, \varepsilon_k)$

method 1:

solve for

$$F = \sum F_i^2(\boldsymbol{x}) \rightarrow \min$$

$x_i = p_i$

$F_i \leftarrow$ *Gibbs free energy* of species *i*

method 2:

solve for

$$\boldsymbol{F}(\boldsymbol{x}) = 0$$

$x_k = p^{\mathrm{at}}{}_k$

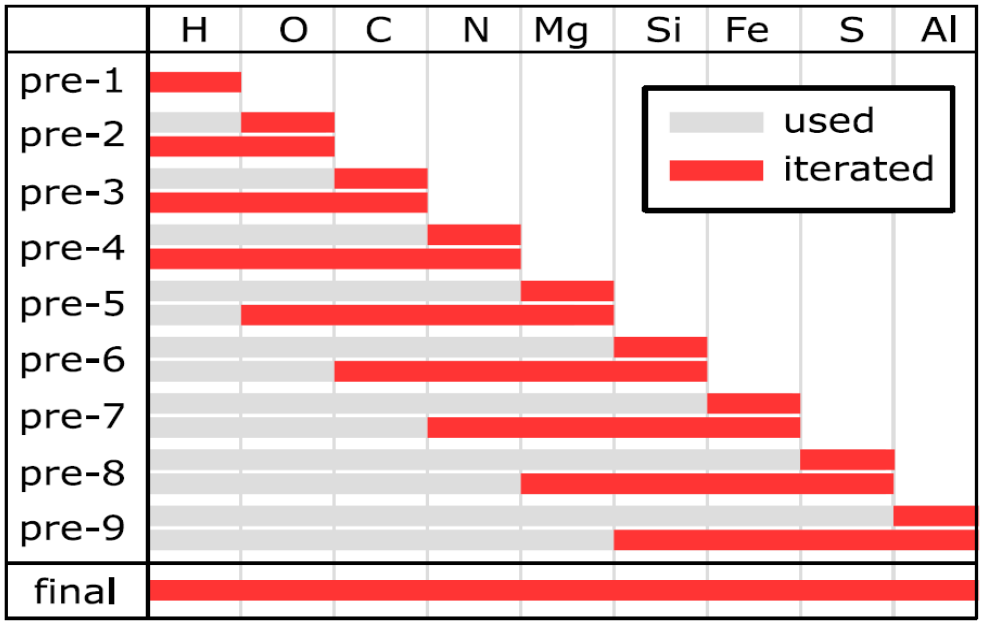
$F_k \leftarrow$ conservation of element *k*

The problems with method 2 for T→100 K ...

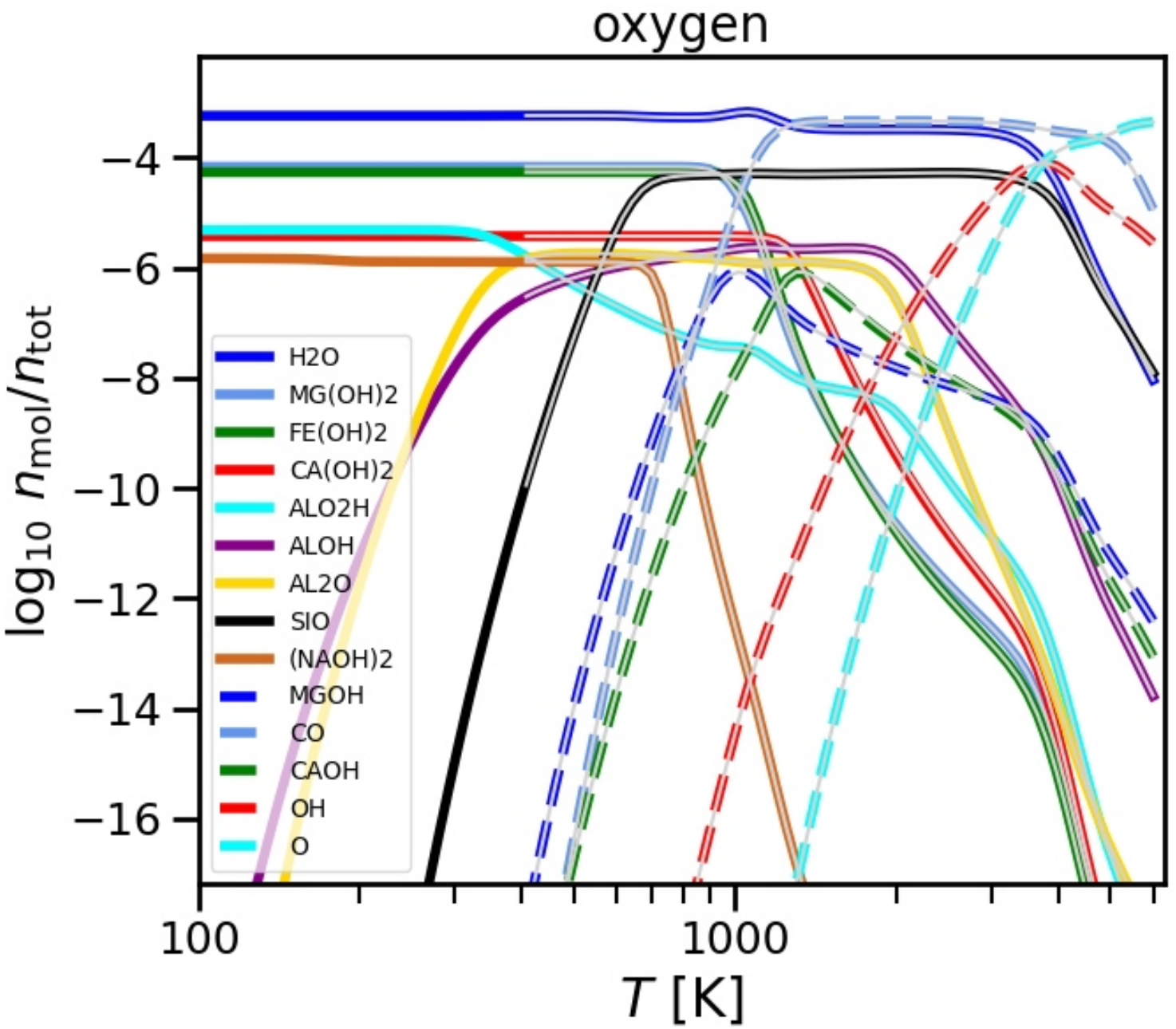
- atom partial pressures → $10^{-\text{several 100}}$
- equilibrium constants → $10^{+\text{several 100}}$ … $10^{+\text{several 1000}}$
- conditional number of Jacobi matrix → large
- solutions become very → “pure”

… but one can solve all these problems one by one …

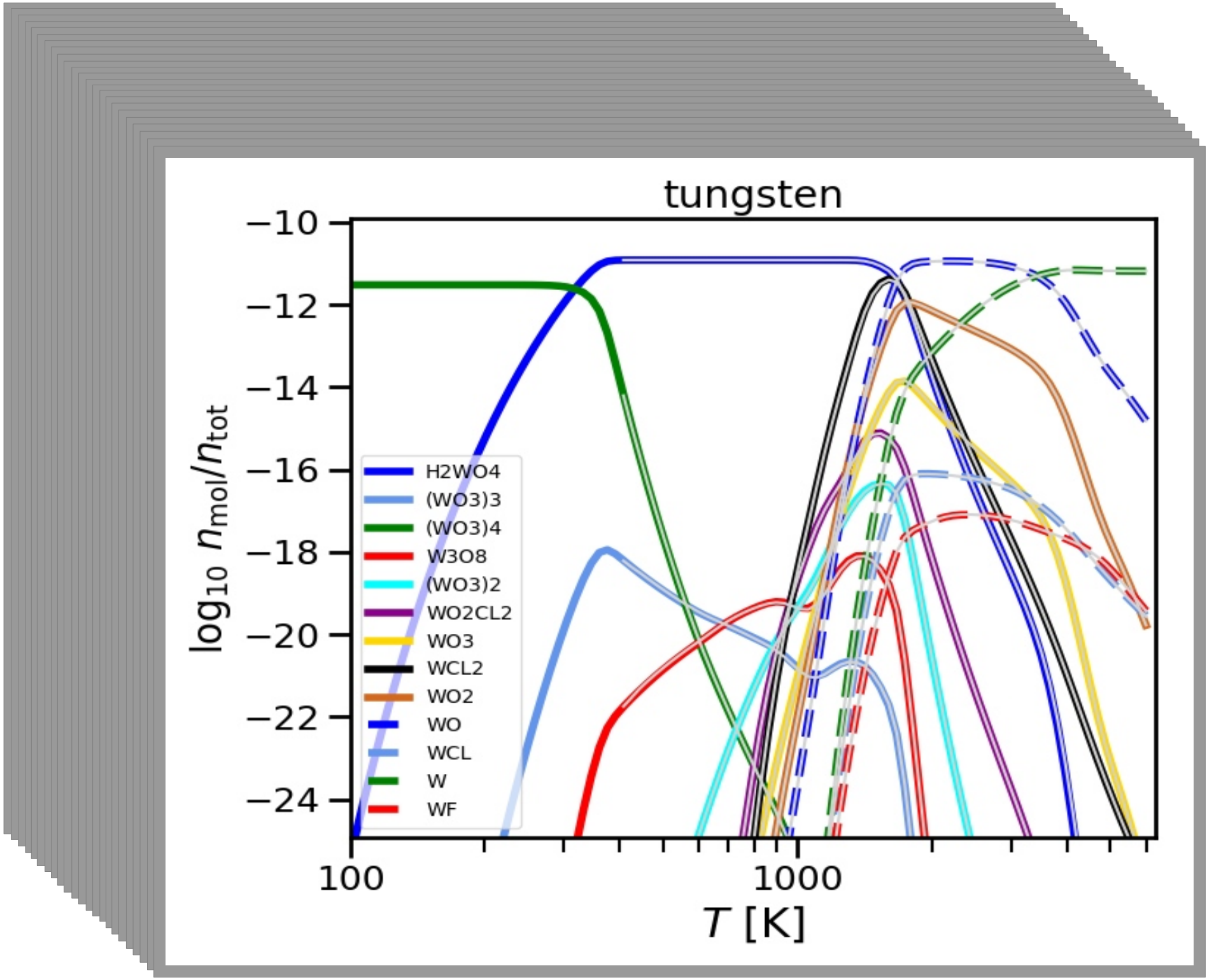
- quadrupole precision code
- careful pre-iterations, exploiting hierarchy of elements



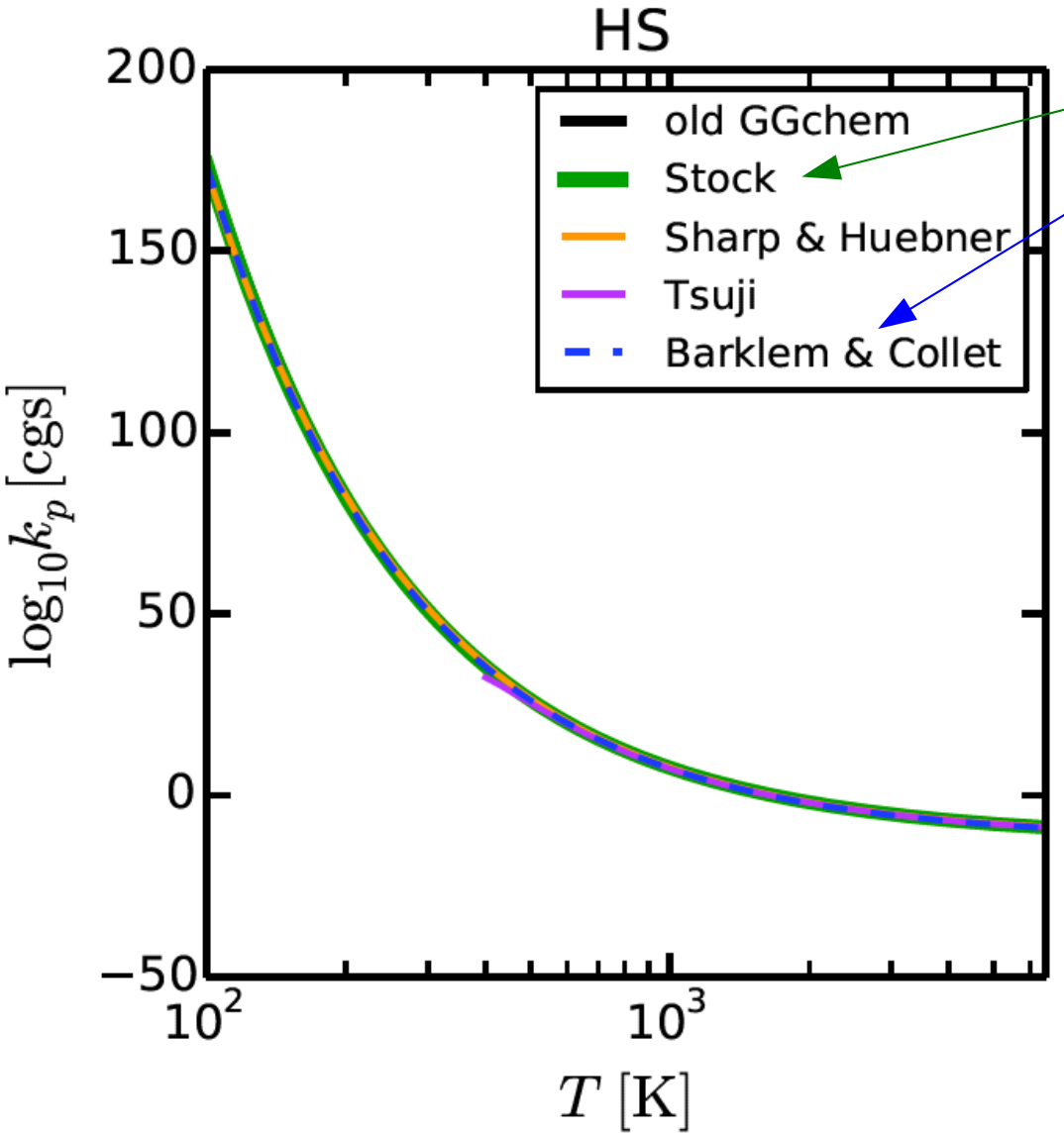
GGchem (Woitke+2017) benchmark against TEA (Blecic+2016)



- **24 elements**: H, He, Li, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zr, W
- **no ions / cations**
- all available molecules
  TEA: 400 (NIST-JANAF)
  GGchem: 445
- ***T*: 6000K → as low as possible**
- p = 1 bar

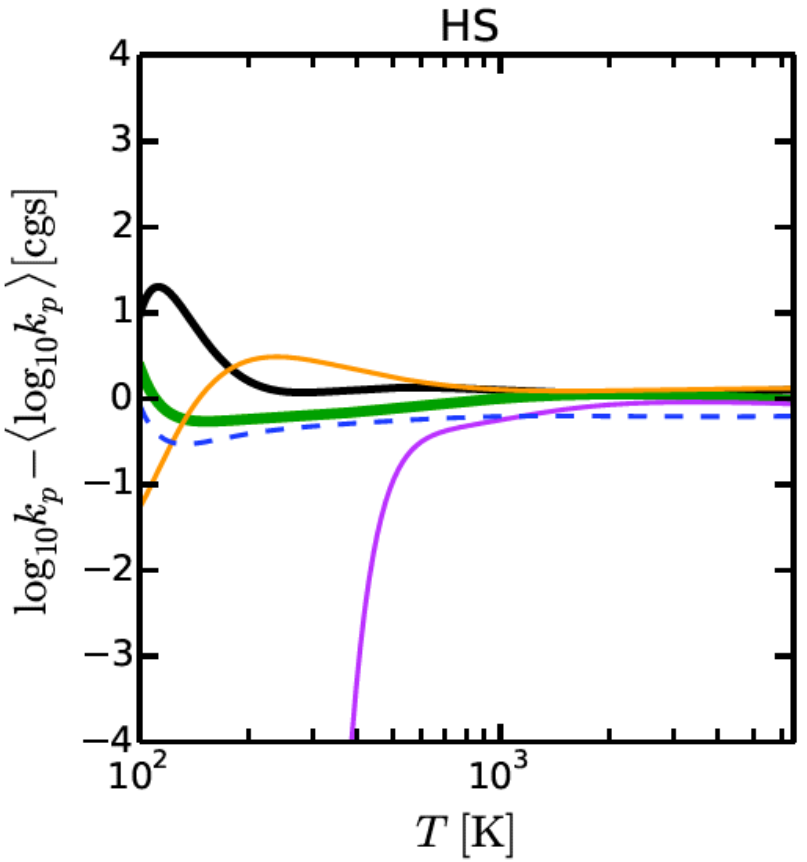

tungsten
−10
−12
−14
−16
−18
−20
−22
−24
$\log_{10} n_{\mathrm{mol}}/n_{\mathrm{tot}}$
H2WO4
(WO3)3
(WO3)4
W3O8
(WO3)2
WO2CL2
WO3
WCL2
WO2
WO
WCL
W
WF
100
1000
T [K]

Uncertainties in Thermo-Chemical Data



J. Stock 2008 (diploma thesis, Berlin)

Barklem & Collet (2016)



Uncertainties in Thermo-Chemical data

$$\theta = 5040/T$$

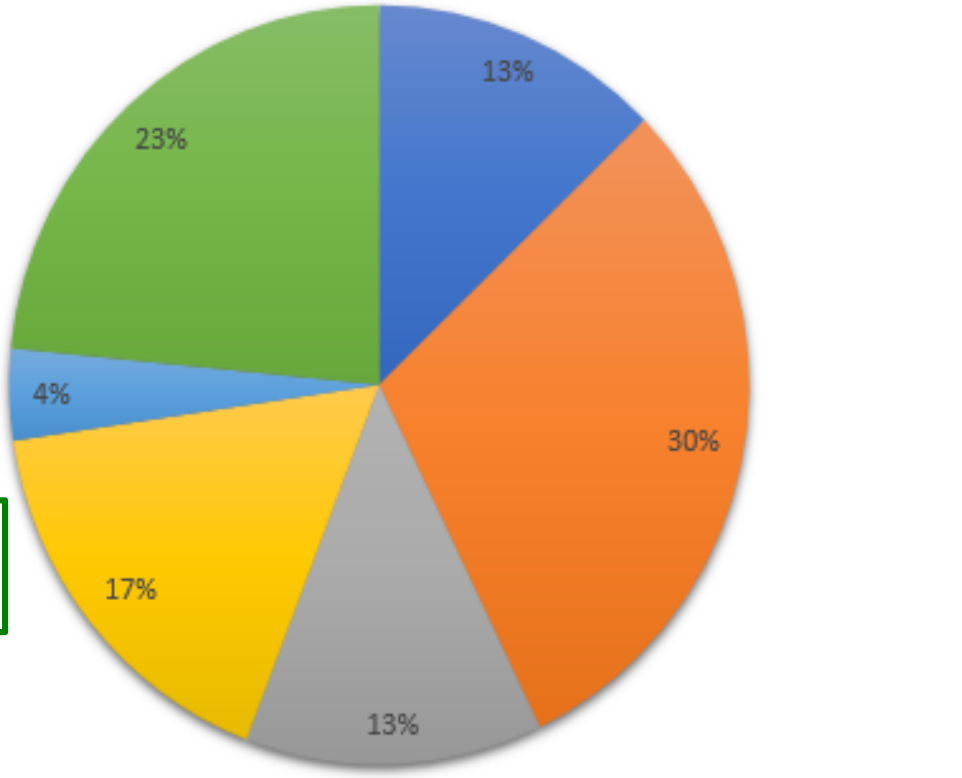
$$\log_{10} k_p^{\mathrm{Tsu}}(T) = -a_0 - a_1\theta - a_2\theta^2 - a_3\theta^3 - a_4\theta^4$$

$$\ln k_p^{\mathrm{Gail}}(T) = a_0 + a_1\theta + a_2\theta^2 + a_3\theta^3 + a_4\theta^4$$

$$\ln k_p^{\mathrm{S\&H}} = (1-n)\ln p^{\ominus} - \frac{a_0/T + a_1 + a_2\,T + a_3\,T^2 + a_4\,T^3}{R_{\mathrm{cal}}T}$$

$$\ln k_p^{\mathrm{St}} = (1-n)\ln p^{\ominus} + \left(\frac{a_0}{T} + a_1\,\ln T + a_2 + a_3\,T + a_4\,T^2\right)$$

J. Stock 2008 (diploma thesis, Berlin)



→ see our comparison catalogue:

Worters, Millard, Hunter, Helling, Woitke (2017)

	$\sigma[\log k_p(200\,\mathrm{K})]$	$\sigma[\log k_p(3000\,\mathrm{K})]$
data agrees well	< 0.1	< 0.05
data agrees	< 0.4	< 0.1
data disagrees at low T	> 0.4	< 0.1
data disagrees at high T	< 0.4	> 0.1
data disagrees	> 0.4	> 0.1

Phase Equilibrium

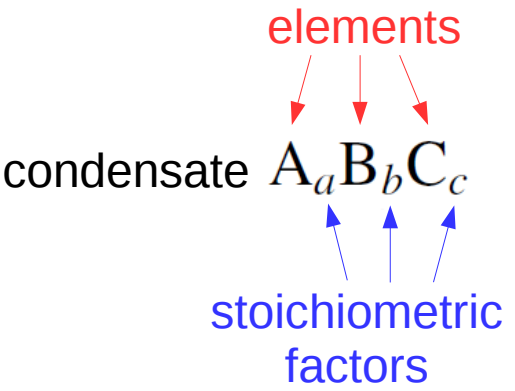
- part of **LTE** assumptions → ***molecular/condensed composition***

Two equivalent methods:

1) **minimisation of system Gibbs free energy**

2) **computation of supersaturation ratios**

$$S_j \begin{cases} < 1 & \text{condensate is unstable and not present,} \\ = 1 & \text{condensate is stable and present,} \end{cases}$$



species stable as free molecule

$$S_j = \frac{p_j}{p_j^{\mathrm{vap}}(T)}$$

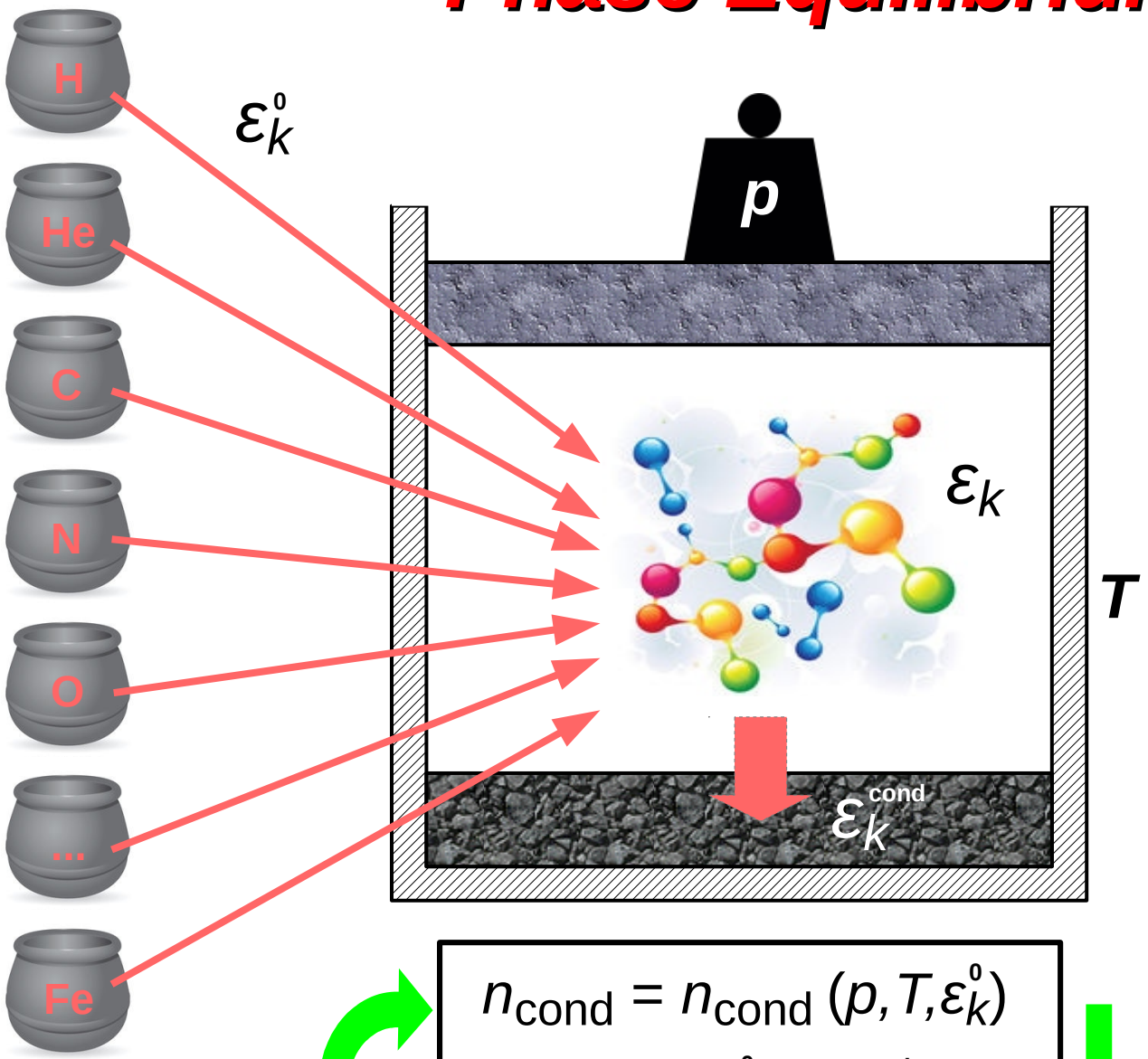
$$p_j^{\mathrm{vap}}(T) = p^{\ominus} \exp\left(\frac{G^{\ominus}(j[\mathrm{cond}],T) - G^{\ominus}(j,T)}{RT}\right)$$

not stable

$$S_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c} = \left(\frac{p_{\mathrm{A}}}{p^{\ominus}}\right)^a \left(\frac{p_{\mathrm{B}}}{p^{\ominus}}\right)^b \left(\frac{p_{\mathrm{C}}}{p^{\ominus}}\right)^c \exp\left(-\frac{\Delta G_{\mathrm{f}}^{\ominus}}{RT}\right)$$

$$\begin{aligned} \Delta G_{\mathrm{f}}^{\ominus} &= G^{\ominus}(\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c[\mathrm{cond}],T) \\ &\quad - a\,G^{\ominus}(\mathrm{A},T) - b\,G^{\ominus}(\mathrm{B},T) - c\,G^{\ominus}(\mathrm{C},T) \end{aligned}$$

Phase Equilibrium



$$n_{cond} = n_{cond}(p, T, \varepsilon_k^0)$$
$$\varepsilon_k = \varepsilon_k^0 - \varepsilon_k^{cond}$$
$$n_{mol} = n_{mol}(p, T, \varepsilon_k)$$

some properties of phase equilibrium:

(1) *no stoichiometric linear combinations of condensates!*

(2) $N \leq K$

N number of condensates
K number of elements in the condensates

(3) *can add arbitrary amounts of condensed elements without changing the gas solution*

$$\varepsilon_k^0 \rightarrow \varepsilon_k^0 + X\,\varepsilon_k^{cond}$$

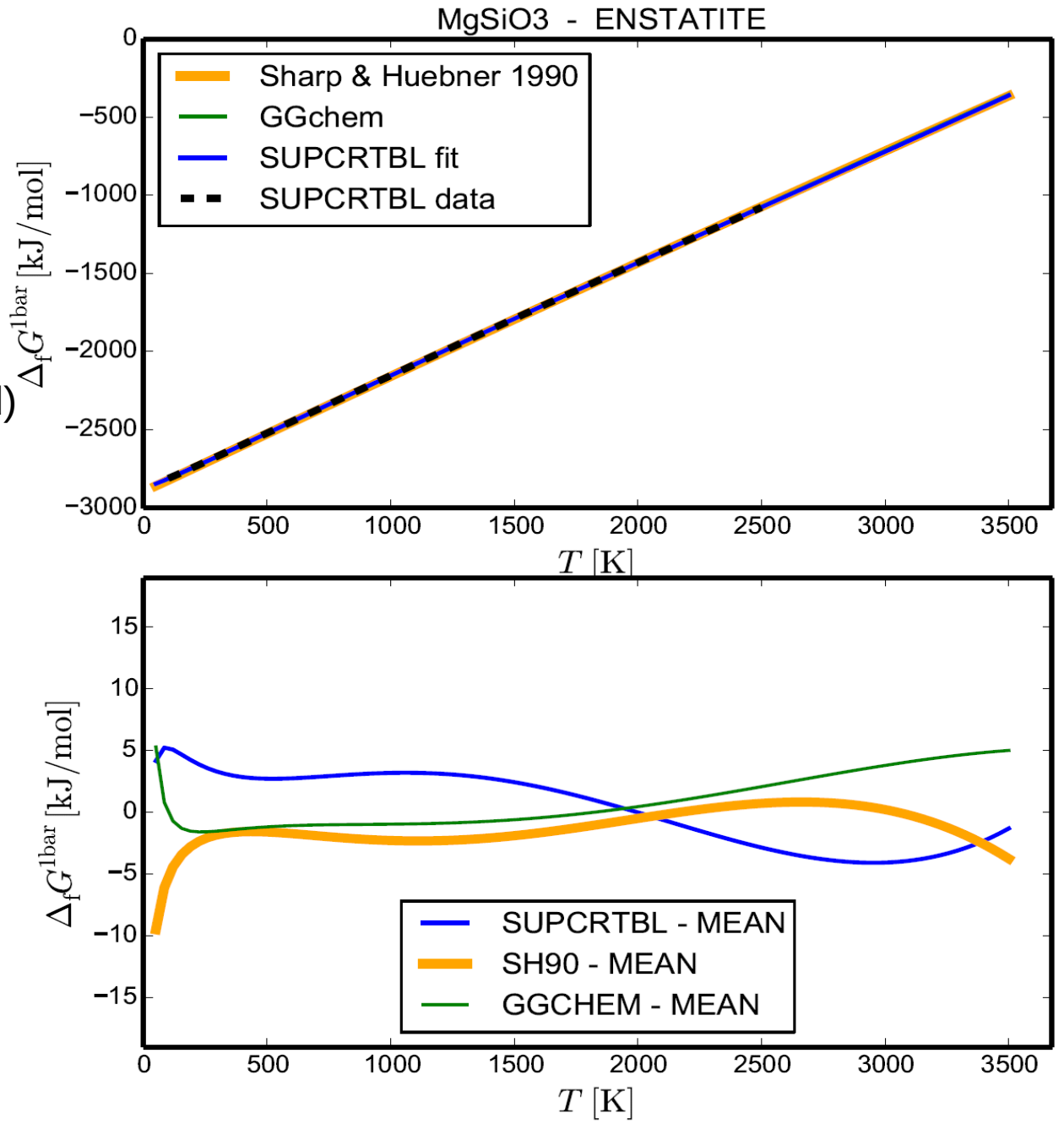
Uncertainties in Thermo-Chemical data II

condensed phase data:

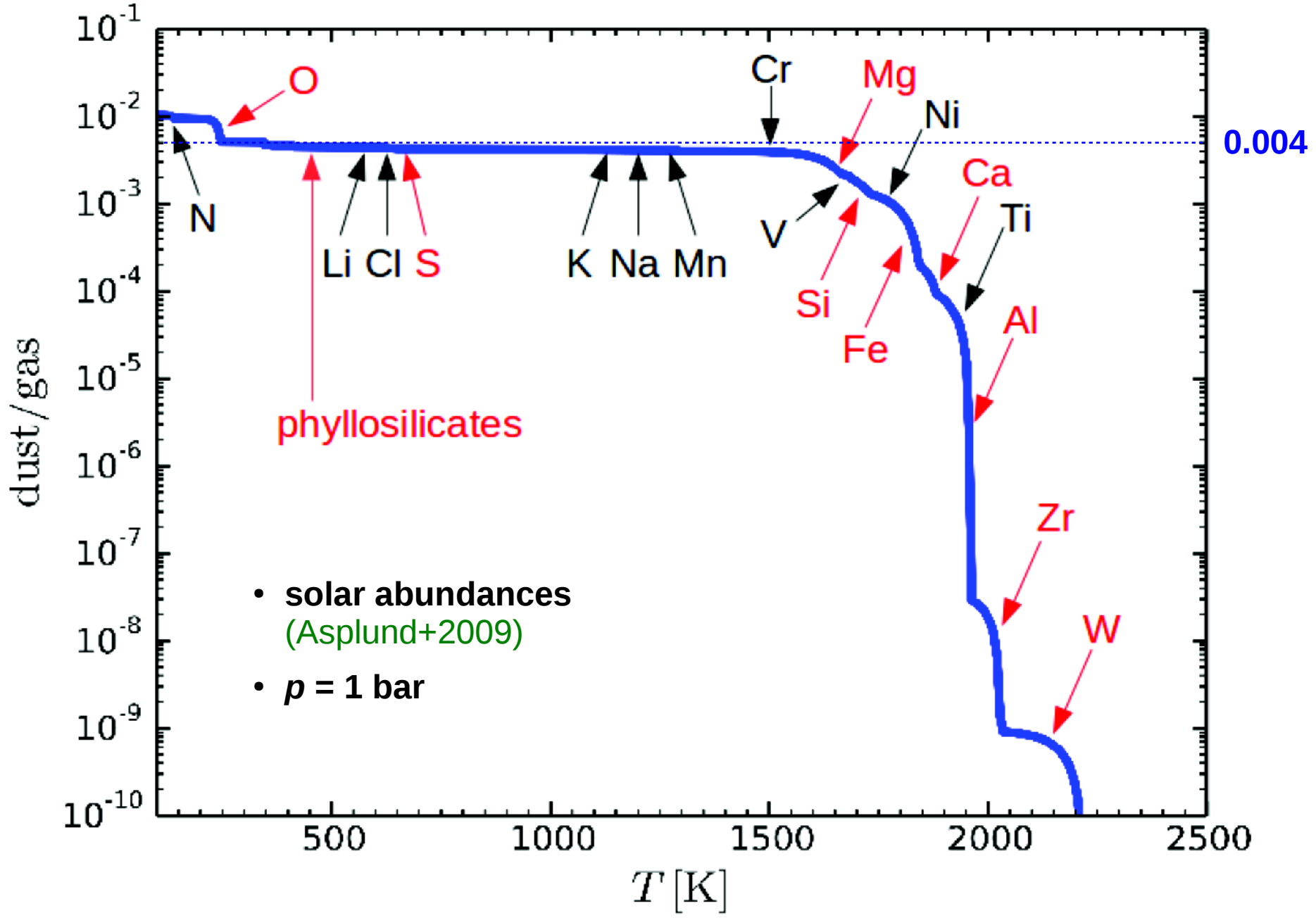
(1) **NIST-JANAF**
(103 solids/fluids extracted)
(Chase et al. 1986)

(2) **SUPCRTBL**
(geophysical database)
(121 minerals extracted)
(Zimmer et al. 2016)

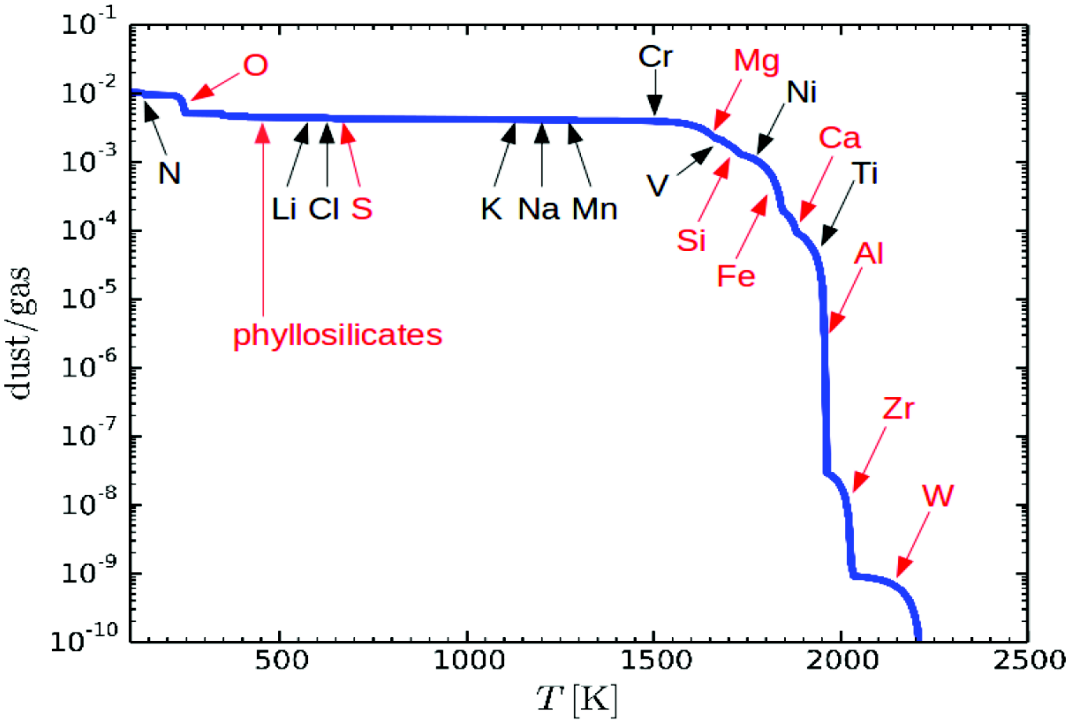
(3) **Sharp & Huebner (1990)**
(67 solids)

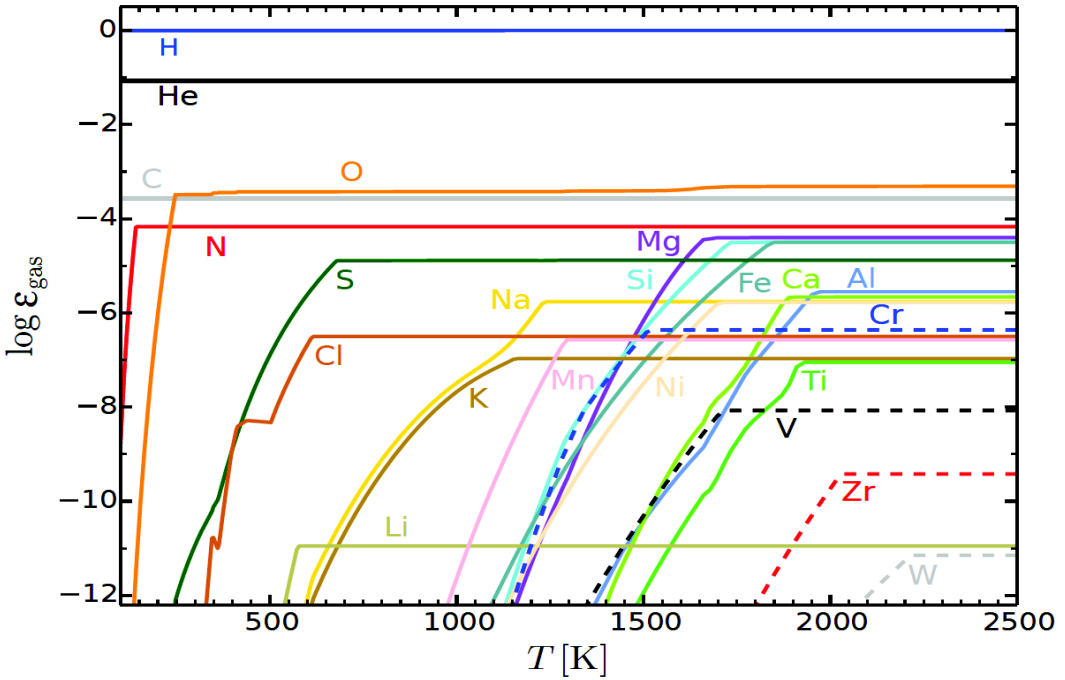


The condensation of the elements



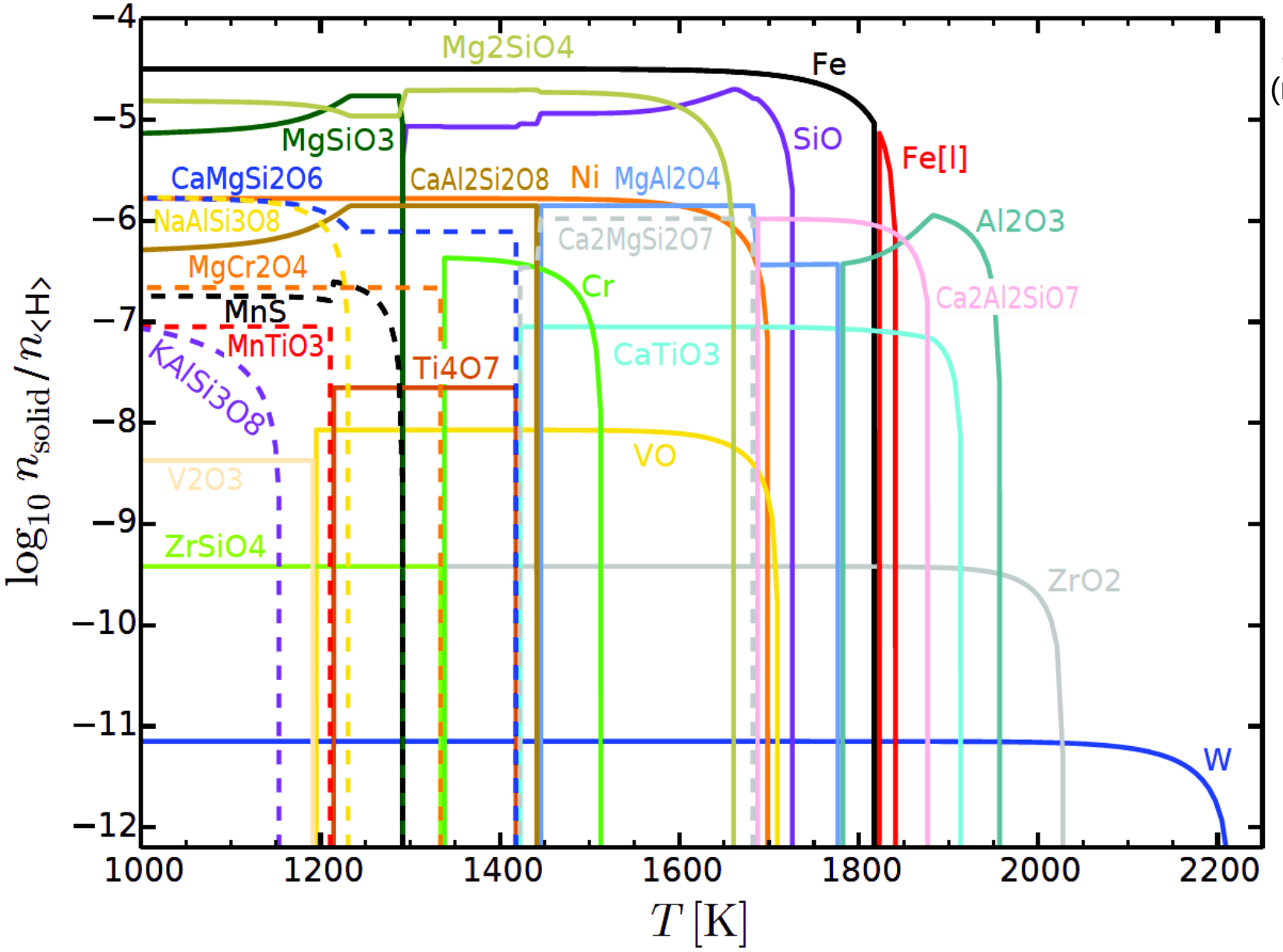
The condensation of the elements





- **solar abundances** (Asplund+2009)
- ***p* = 1 bar**

The condensation of the elements



stability sequence
(not formation sequence)

type I and II phase transitions

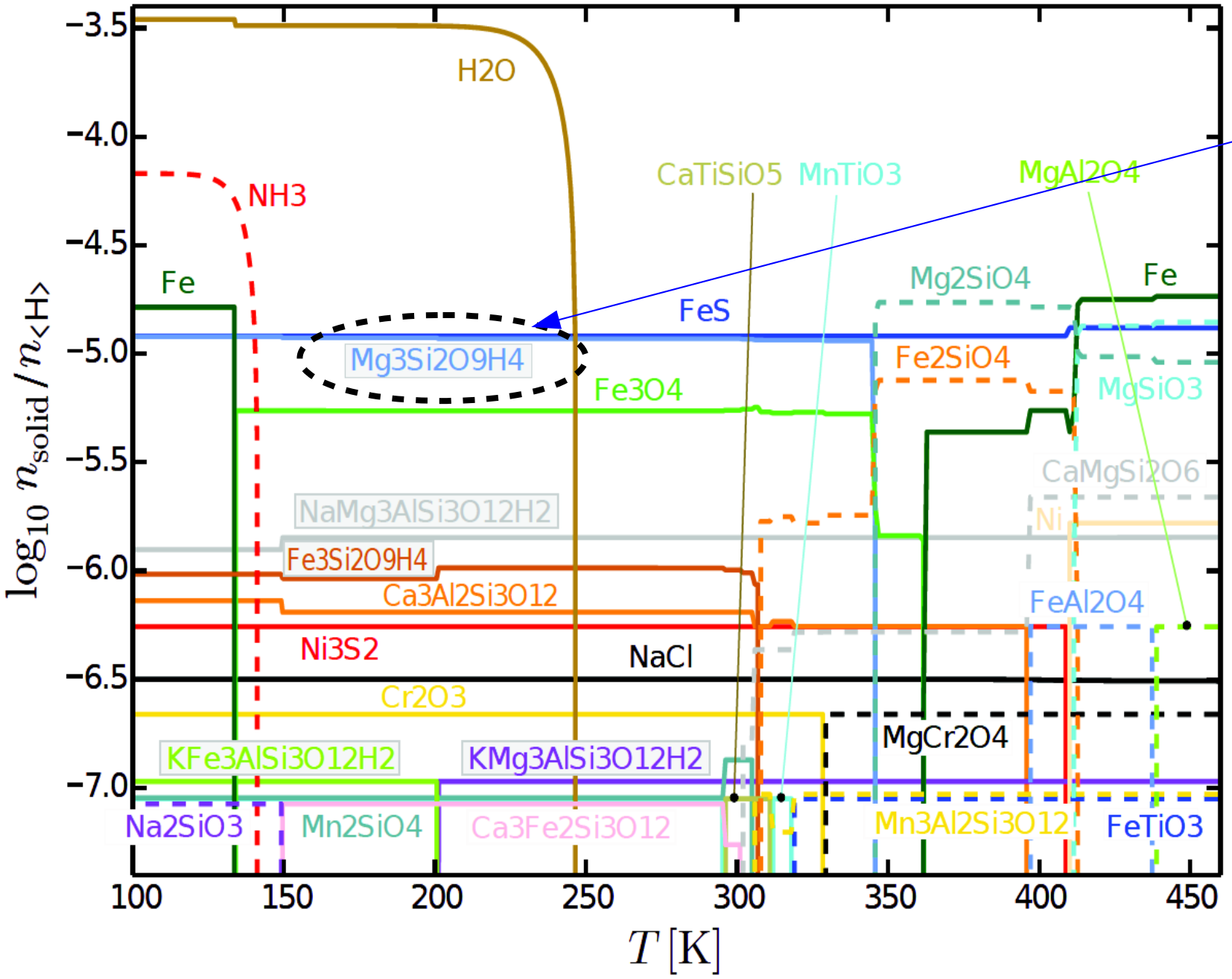
$Ca_2Al_2SiO_7$ (*gehlenite*)

$MgAl_2O_4$ (*spinel*)

$CaAl_2Si_2O_8$ (*anorthite*)
$NaAlSi_3O_8$ (*albite*)
$KAlSi_3O_8$ (*microcline*)

} *feldspar → basalt* (common rock)

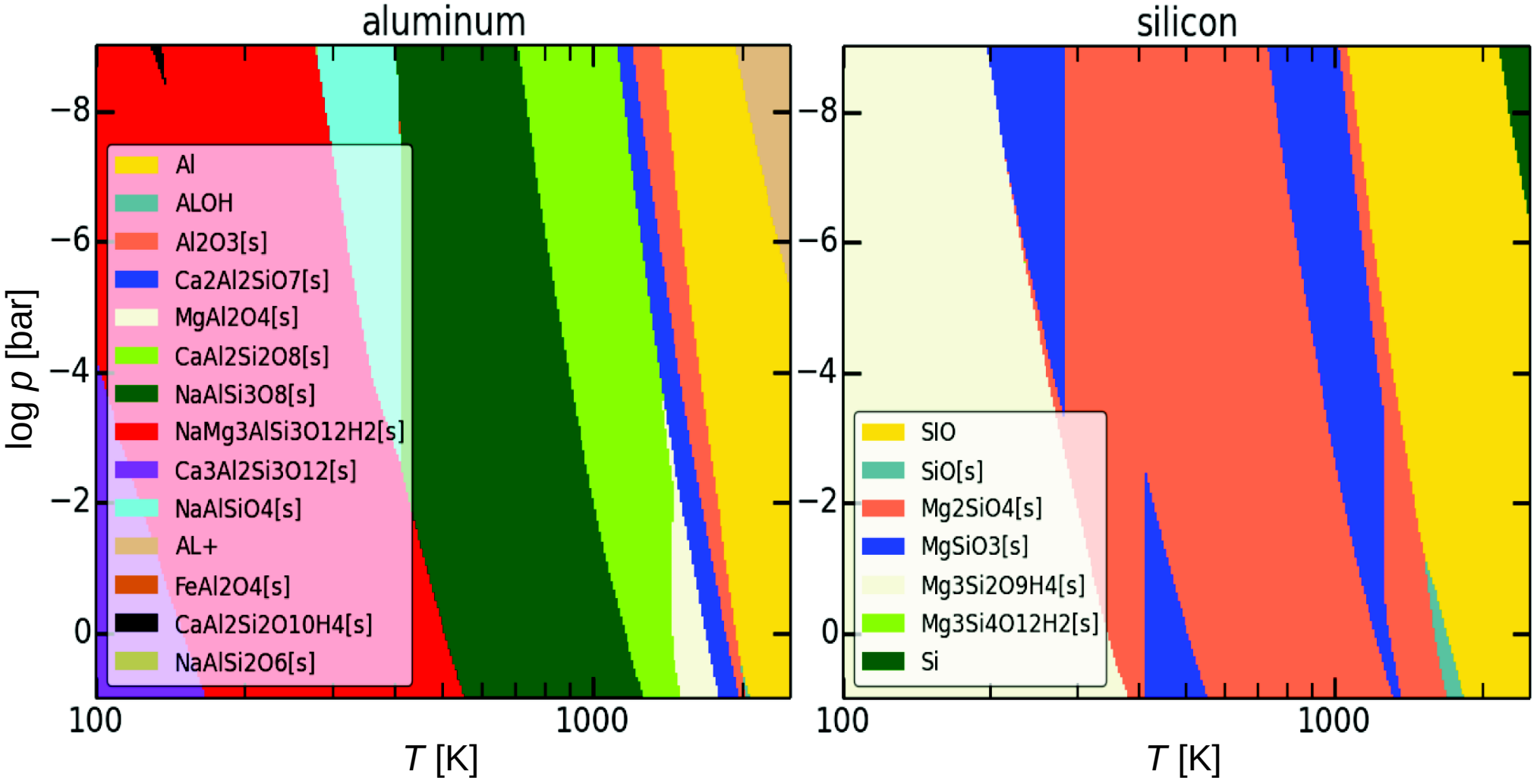
phyllosilicates



"***lizardite***" ($Mg_3Si_2O_9H_4$) most abundant Mg-Silicate below ~ 350 K

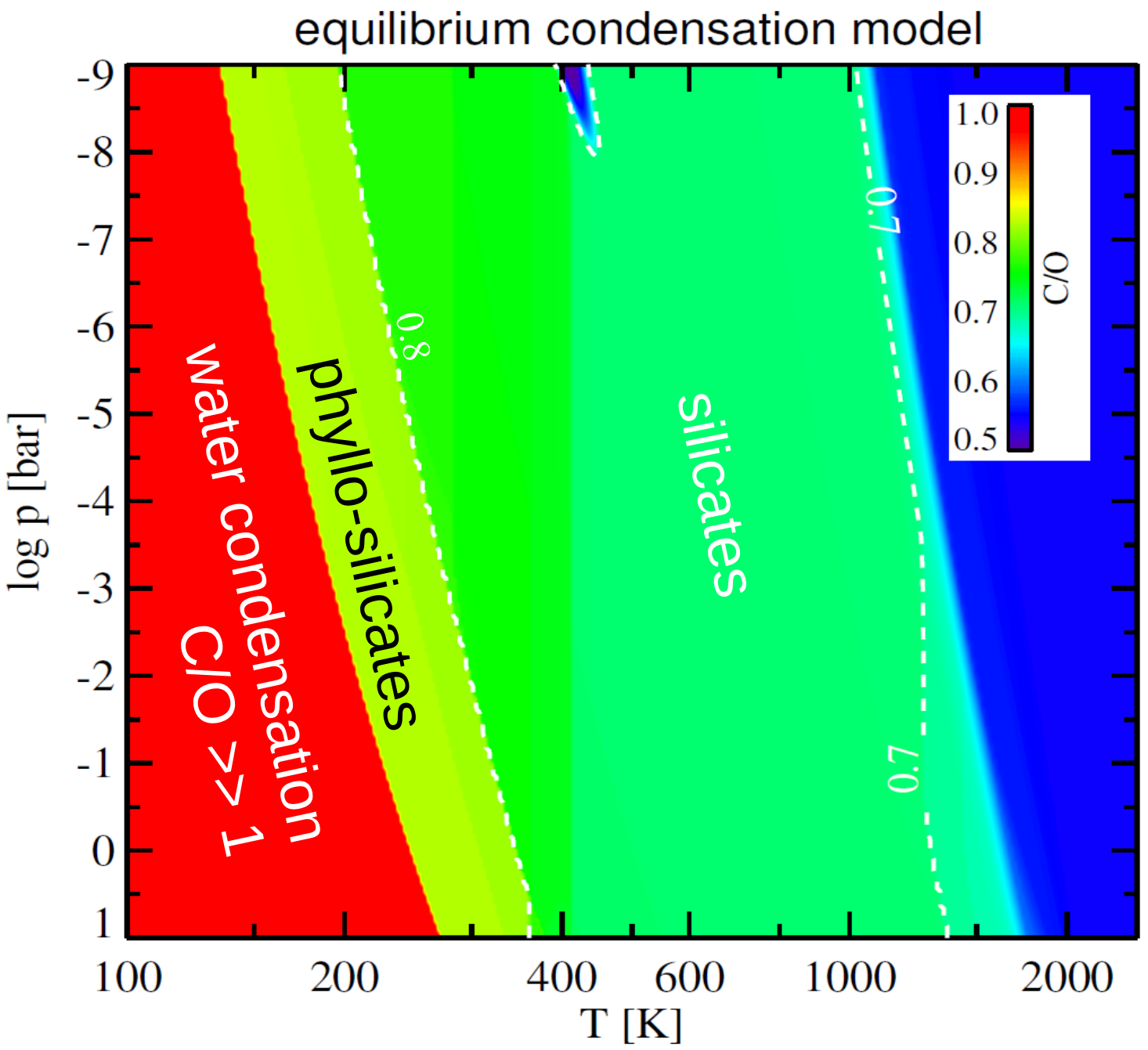
Mg, Si, Na, Al, K in phyllosilicates

Phase diagrams of the elements



- solar element abundances (Asplund+2009)

effective C/O ratio



- solar element abundances C/O ~ 0.55 (Asplund+2009)
- condensation: every Si atom consumes 3-4 O-atoms

  => C/O ~ 0.7 in gas phase (!)
- phyllosilicates => C/O ~ 0.8 in gas phase (!)

$\varepsilon_C = 2.7 \times 10^{-4}$

$\varepsilon_{Si} = 3.2 \times 10^{-5} \sim 8\ \varepsilon_C$

The GGchem code

- up to **40 elements** (H, … , Zr, and W)
- up to **1155 molecules**
- up to **200 condensates** (solids & liquids) from **NIST-JANAF** and **SUPCRTBL**
- **customised selection** of elements, molecules, and condensates
- thermo-chemical data **down to 100 K** carefully checked
- **ultra-fast Fortran-90 code**, about 40 ms / call for K=24 elements, scales ~ K^3
  - stable iterative solution scheme based on Newton-Raphson
  - fast real*8 (T > 1000 K) and stable real*16 (T → 100 K)
- **benchmarked** against TEA code (Blecic 2016)
- optionally include **ions and free electrons**
- specify gas density (ρ,T) or gas pressure (p,T)

→ Woitke, Helling, Hunter, Millard, Turner, Worters, Blecic, Stock (2017), **A&A in press**

→ ***public code:*** **https://github.com/pw31/GGchem**

> git clone https://github.com/pw31/GGchem

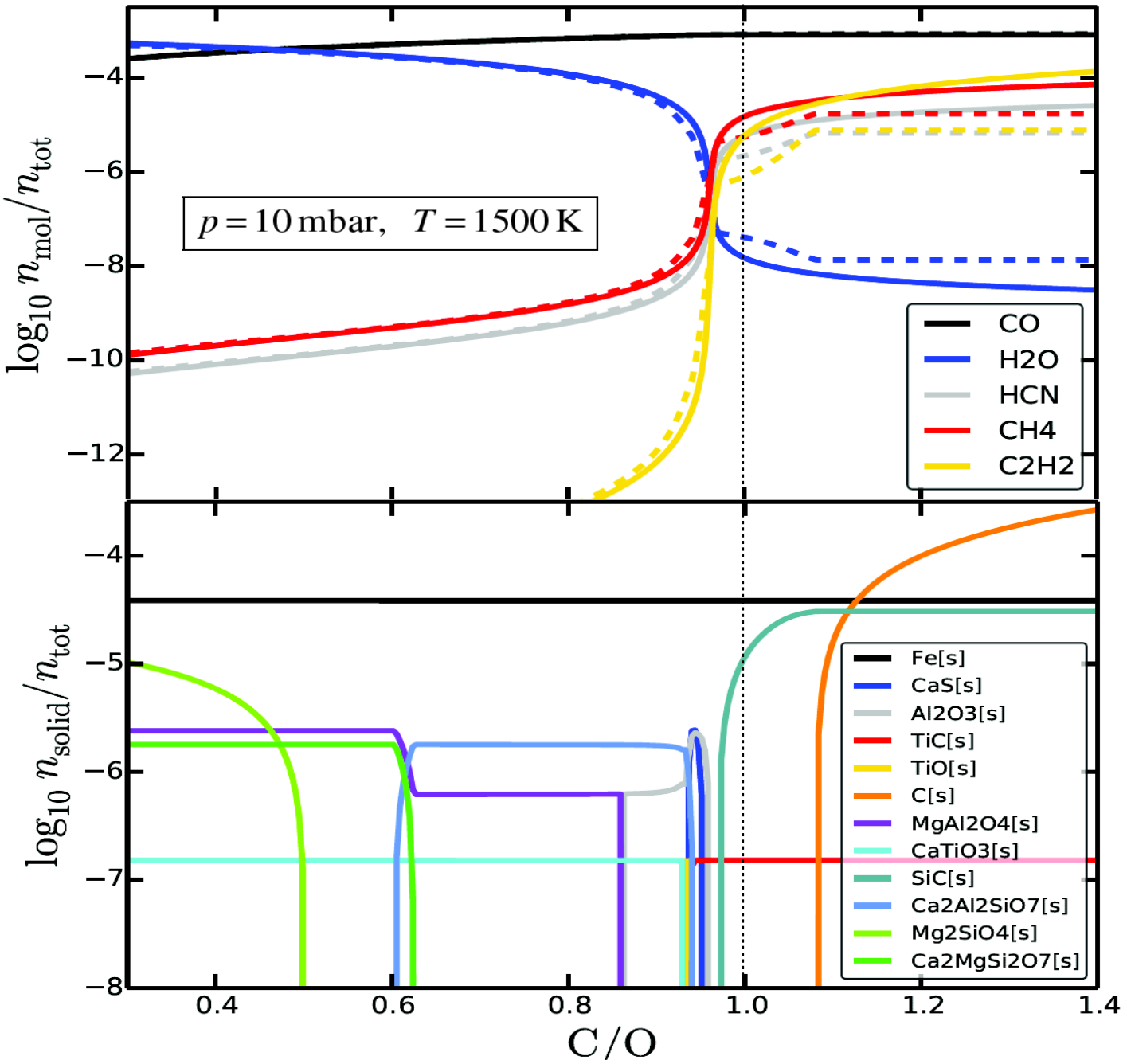
(includes all thermo-chemical data)

Summary

- 0.5 dex **uncertainties** in equilibrium constants $T \rightarrow 100$ K
- **metal hydrides** (CaH, FeH, TiH …) important astrophysical molecules, missing in NIST-JANAF, but available via (Barklem & Collet 2016)
- **geophysical database SUPCRTBL** (Zimmer+2016) for mineral thermo-chemical data
- expected standard **dust/gas ratio** should be 0.004 (not 0.01)
- **condensation lowers C/O** in the gas phase
- **metallic tungsten** (W) first condensate in space?
- **phyllosilicates** stable below about 500 K, lizardite ($Mg_3Si_2O_9H_4$) most abundant Mg-Silicate below 300 K
- ***public*** and ***easy-to-use*** chemical equilibrium code ***GGchem***

→ ***google for "GGchem github"***

CO blocking



- full = pure gas phase
  dashed = eq. cond.
- solar element abundances (Asplund+2009), but varying carbon (at fixed oxygen)