Chemistry of Silicate Vapor and Steam Atmospheres during Formation of the Earth and Moon

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(1) Silicate Vapor Atmospheric Chemistry and Chemical Constraints on Formation of the Moon

Summary - I

- Oxygen is the major element in rocky material
- Recognized by Victor Goldschmidt in 1928
- Oxygen is 62 atom % of Earth's crust
- Oxygen is 58 atom % of Bulk Silicate Earth
- Oxygen is 58 atom % of Bulk Silicate Moon
- (based on current BSM models by others)

- **Hot silicate vapor is O_2 – rich and is**
- **Orders of magnitude more oxidizing than solar composition gas**

Summary - II

- 1970s – 1990s Experiments, analyses of meteorite samples, and thermodynamics show unique trace element abundances produced by vaporization / condensation of silicates at high oxygen fugacity (partial pressure)
- We apply this knowledge to formation of the Moon
- Presence or absence of analogous signatures constrains the P and T for gas – condensed phase separation (when equilibrium stops) in an open system
- Heavy isotope enrichments for Cl, Ga, K, Rb, Zn indicate loss of hot silicate vapor during lunar formation (Moynier, Sharp, Wang & Jacobsen) – an open system

Summary - III

- Geochemical data show
- No Ce depletion in bulk silicate Moon
- Lunar Lu/Hf, Hf/W, Nd/Sm, Th/U $\simeq$ BSE
- Lunar Rb/Sr, K/U < BSE values
- Can set T_{max} and T_{min} values at each pressure
- Can constrain geochemically realistic lunar formation models

Summary - IV

- But:
- Some key element ratios uncertain, e.g., Hf/W, Th/U for bulk silicate Moon
- Use P,T constraints from our modeling and/or K isotopes to predict these key ratios from chemical equilibrium calculations

(2) Steam Atmosphere Chemistry on the early Earth.

Summary -1

- Reducing gases produced by outgassing of chemically reduced material, either chondritic (H, L, LL, EH, EL, CV) or achondritic (Eucrite) see
- Bukvic 1979 MSc Thesis, MIT, Advisor John S. Lewis
- Schaefer & Fegley 2007 Icarus 186, 462-483
- Schaefer & Fegley 2010 Icarus 208, 438-448
- Zahnle, et al 2010 The Origins of Life pp. 49-66
- Fegley & Schaefer 2014 Treatise on Geochemistry 2nd ed
- Schaefer & Fegley 2017 ApJ 843:120)
- Steam Atmosphere not necessarily steam-rich
- Depends on the unknown redox state of planetary embryo, planetesimal, rocky planet, early Earth, etc.

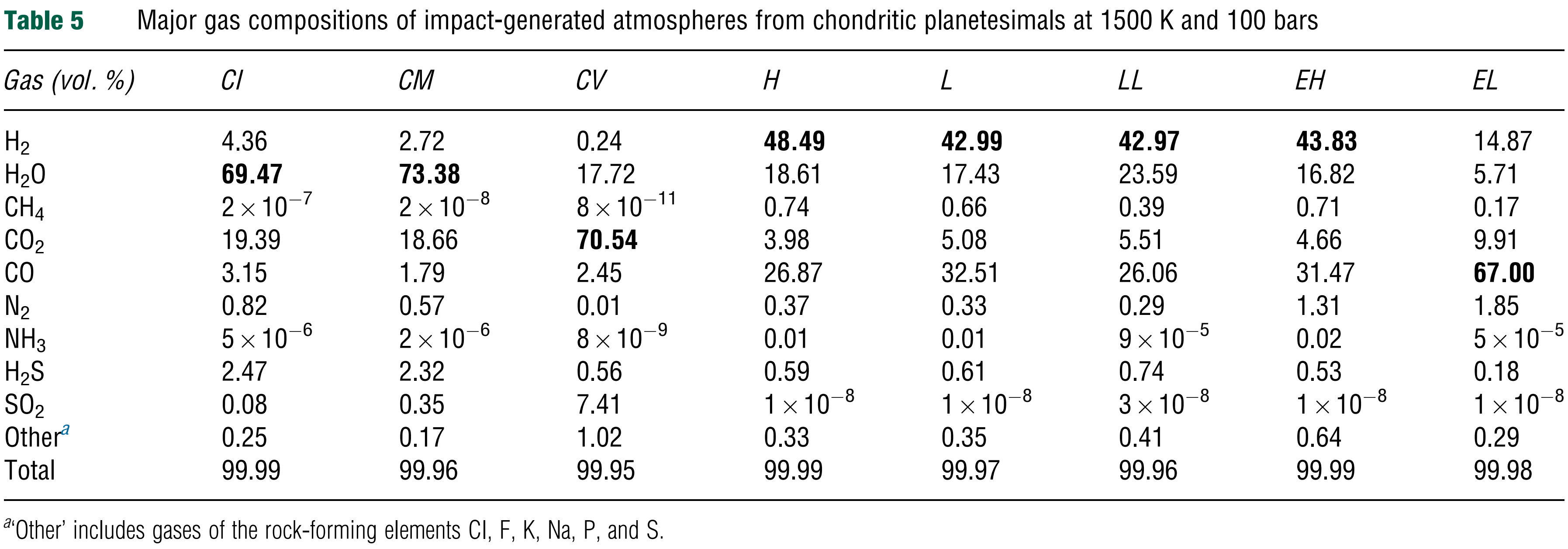


Table 5 Major gas compositions of impact-generated atmospheres from chondritic planetesimals at 1500 K and 100 bars

Gas (vol. %)	*CI*	*CM*	*CV*	*H*	*L*	*LL*	*EH*	*EL*
H_2	4.36	2.72	0.24	**48.49**	**42.99**	**42.97**	**43.83**	14.87
H_2O	**69.47**	**73.38**	17.72	18.61	17.43	23.59	16.82	5.71
CH_4	2×10^{-7}	2×10^{-8}	8×10^{-11}	0.74	0.66	0.39	0.71	0.17
CO_2	19.39	18.66	**70.54**	3.98	5.08	5.51	4.66	9.91
CO	3.15	1.79	2.45	26.87	32.51	26.06	31.47	**67.00**
N_2	0.82	0.57	0.01	0.37	0.33	0.29	1.31	1.85
NH_3	5×10^{-6}	2×10^{-6}	8×10^{-9}	0.01	0.01	9×10^{-5}	0.02	5×10^{-5}
H_2S	2.47	2.32	0.56	0.59	0.61	0.74	0.53	0.18
SO_2	0.08	0.35	7.41	1×10^{-8}	1×10^{-8}	3×10^{-8}	1×10^{-8}	1×10^{-8}
Other[a]	0.25	0.17	1.02	0.33	0.35	0.41	0.64	0.29
Total	99.99	99.96	99.95	99.99	99.97	99.96	99.99	99.98

[a] ‘Other’ includes gases of the rock-forming elements Cl, F, K, Na, P, and S.

From: Schaefer & Fegley 2010 Icarus 208, 438-448.

Summary -2

- **If steam atmosphere is steam rich, Nominal case here**
- Silica and many other oxides dissolve in steam
- Greatly different solubility for different oxides
- If steam atmosphere is lost the steam soluble element inventory is changed
- This is potentially important for bulk composition, density, heat balance, interior structure, volatile element inventory
- Spectroscopically active gases in steam atmosphere
- Fegley et al 2016 ApJ 824:103

Summary -3

- Astronomical observations show atmospheric escape from some exoplanets – one of which is a hot rocky planet (55 Cancri-e)
- Recent modeling (Zahnle and Catling, 2017; Lopez, 2018; Owen and Wu, 2017; Owen, 2019) shows stellar EUV-driven photo-evaporative mass loss is important for the evolution of hot rocky exoplanets.
- Atmospheric loss from early Earth needs to be seriously considered by cosmochemists

(1) Silicate Vapor Atmospheric Chemistry and Chemical Constraints on Formation of the Moon

Background

- Cl, Ga, K, Rb, Zn isotopic anomalies indicate lunar material formed at high temperatures from ejecta after a giant impact on the early Earth
- Giant impact models predict high T silicate melt – vapor system
- We show chemical equilibrium calculations for a **bulk silicate Earth (BSE)** composition system over a wide P – T range can constrain lunar formation conditions
- We do <u>not</u> say BSM = BSE, this is a model composition

Introduction & Background - 2

- High temperature vaporization/condensation at high O_2 partial pressure produces **unique trace element abundance patterns** (Fegley & Cameron 1987 EPSL 82, 207-222)
- Lanthanides (Ce/LREE, Nd/Sm)
- Actinides (Th/U)
- Lithophiles (Lu/Hf, Rb/Sr, K/U)
- Hafnium – Tungsten

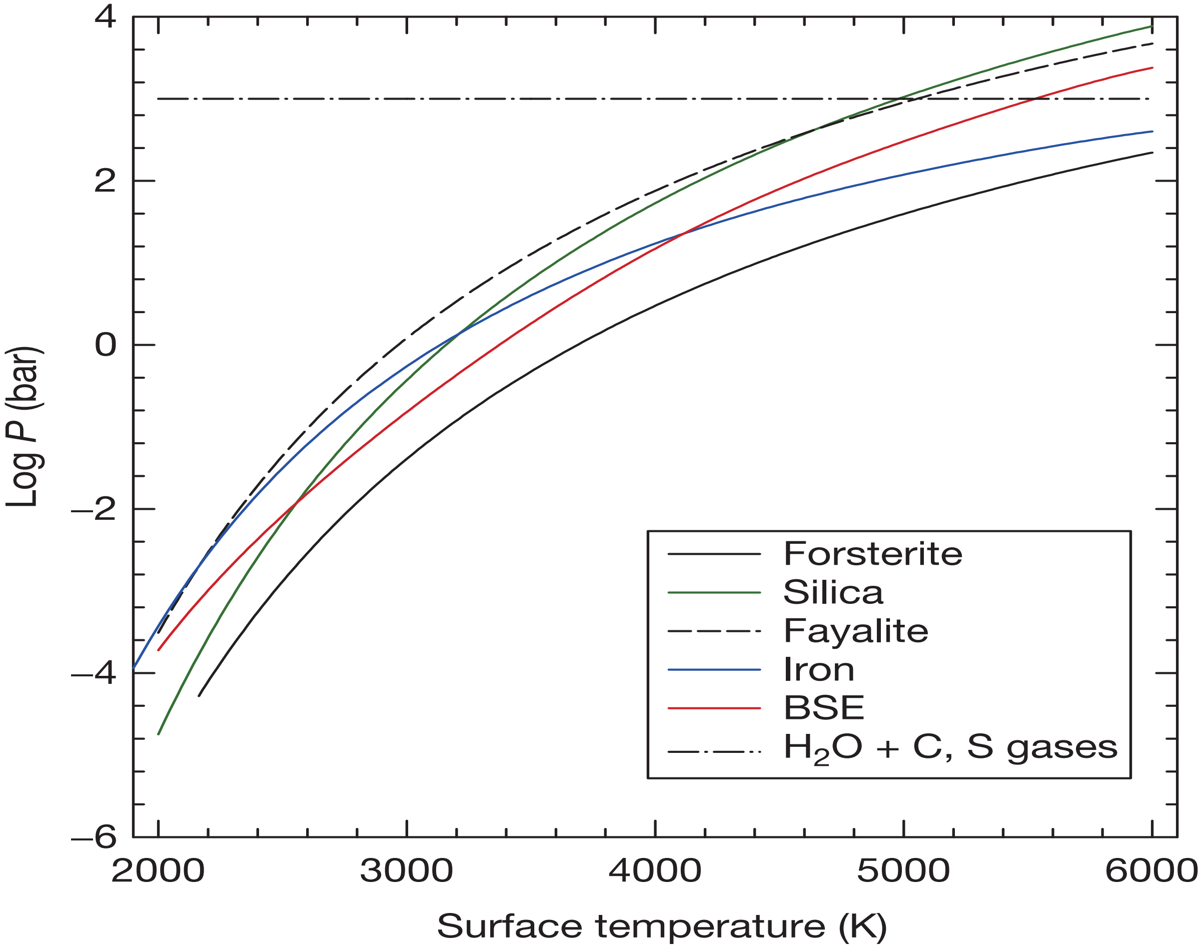
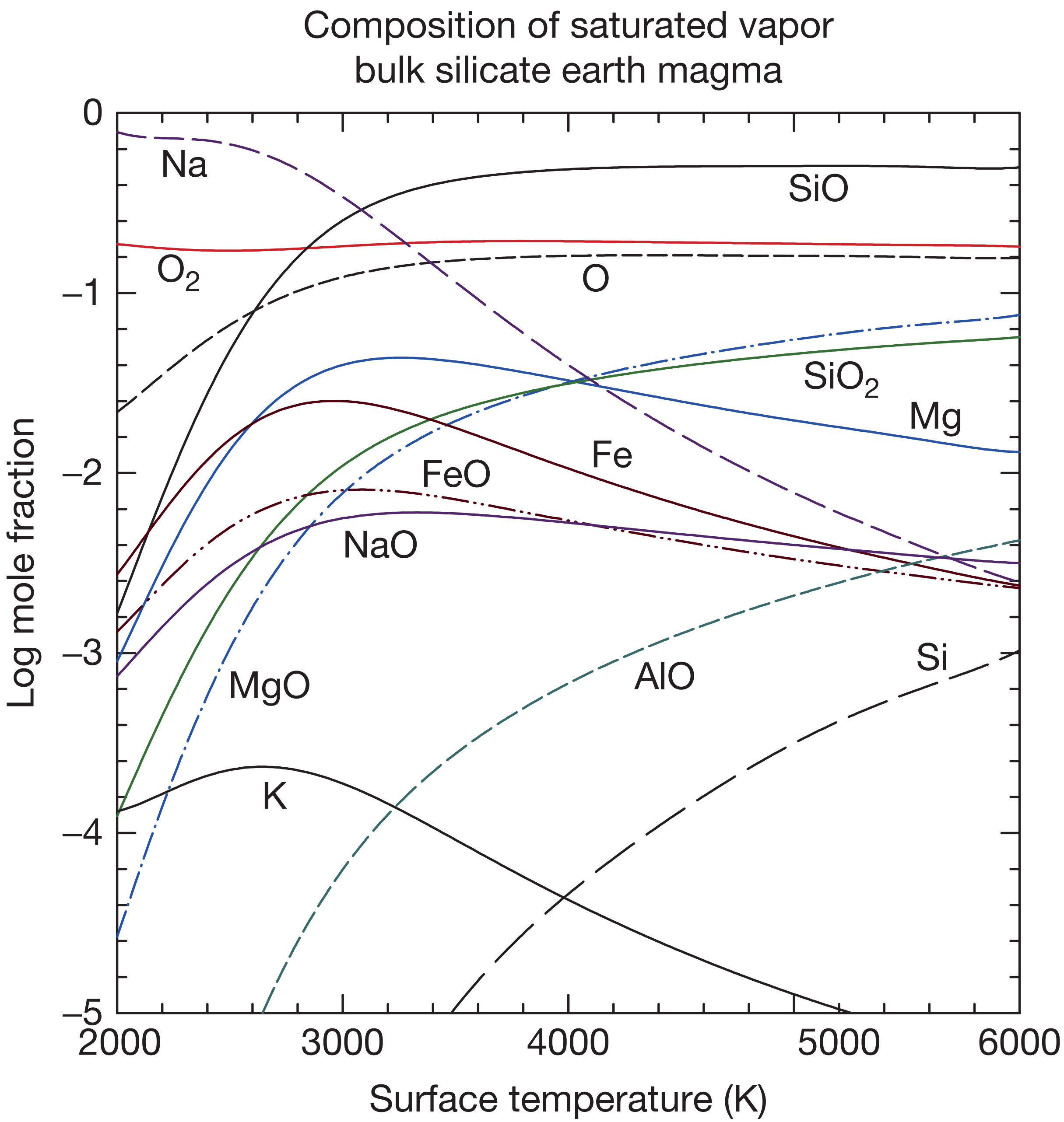


Figure 3 Temperature-dependent vapor pressures of iron metal, forsterite, fayalite, silica, and bulk silicate Earth magma are compared to the total partial pressure of $H_2O + C$, S gases corresponding to the BSE inventory of these volatiles.

From: Fegley & Schaefer 2014 Treatise on Geochemistry 2nd ed



From: Fegley & Schaefer 2014 Treatise on Geochemistry 2nd ed

Oxygen fugacity of silicate vapor

- **Look at two examples:**
- Knudsen effusion mass spectrometry (KEMS) of pure silica (Kazenas et al 1985)

- Calculated fO_2 of BSE vapor along liquid – vapor saturation curve (Visscher & Fegley 2013 Astrophys J 767, L12)

☞Shown on next two slides

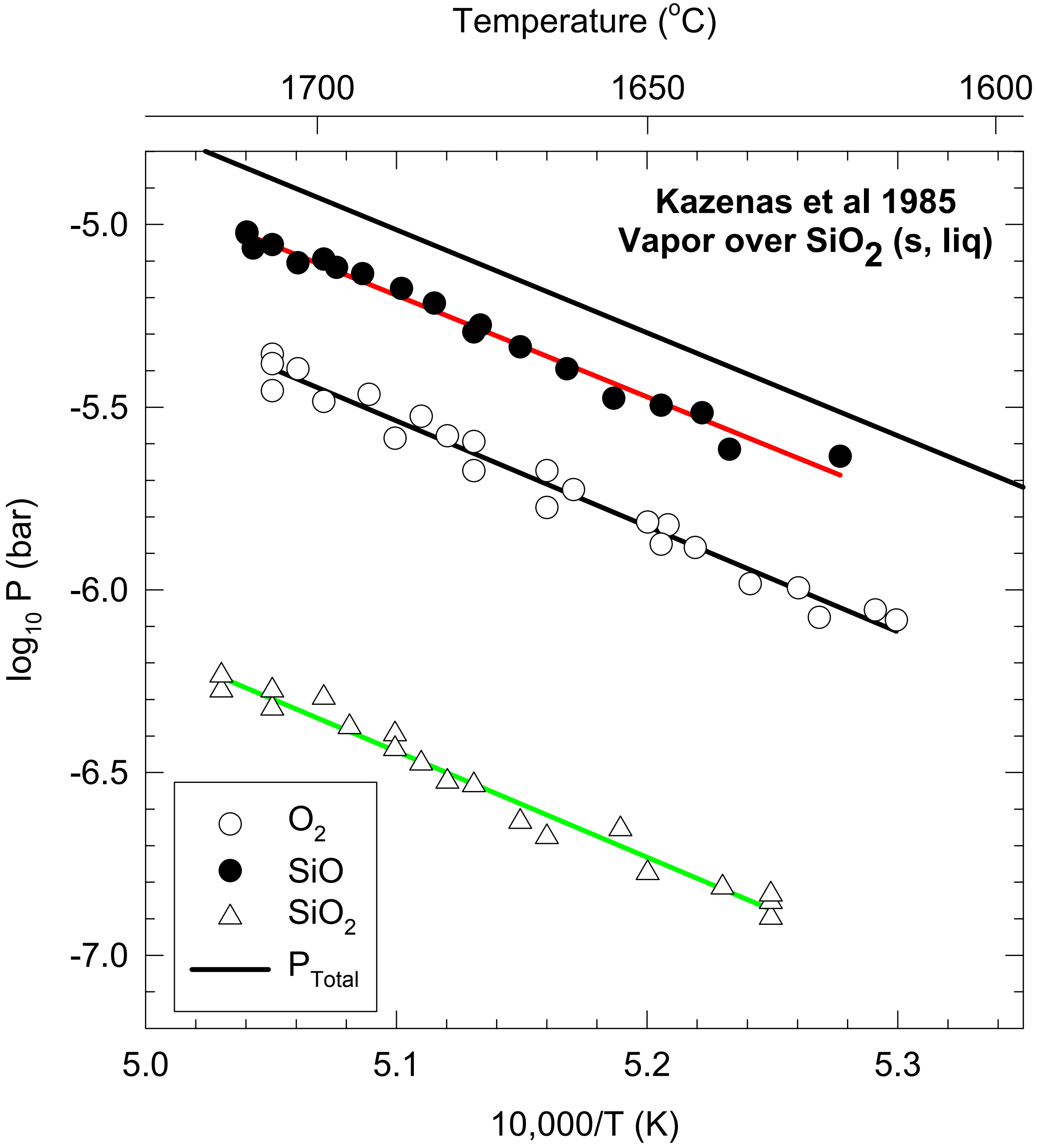
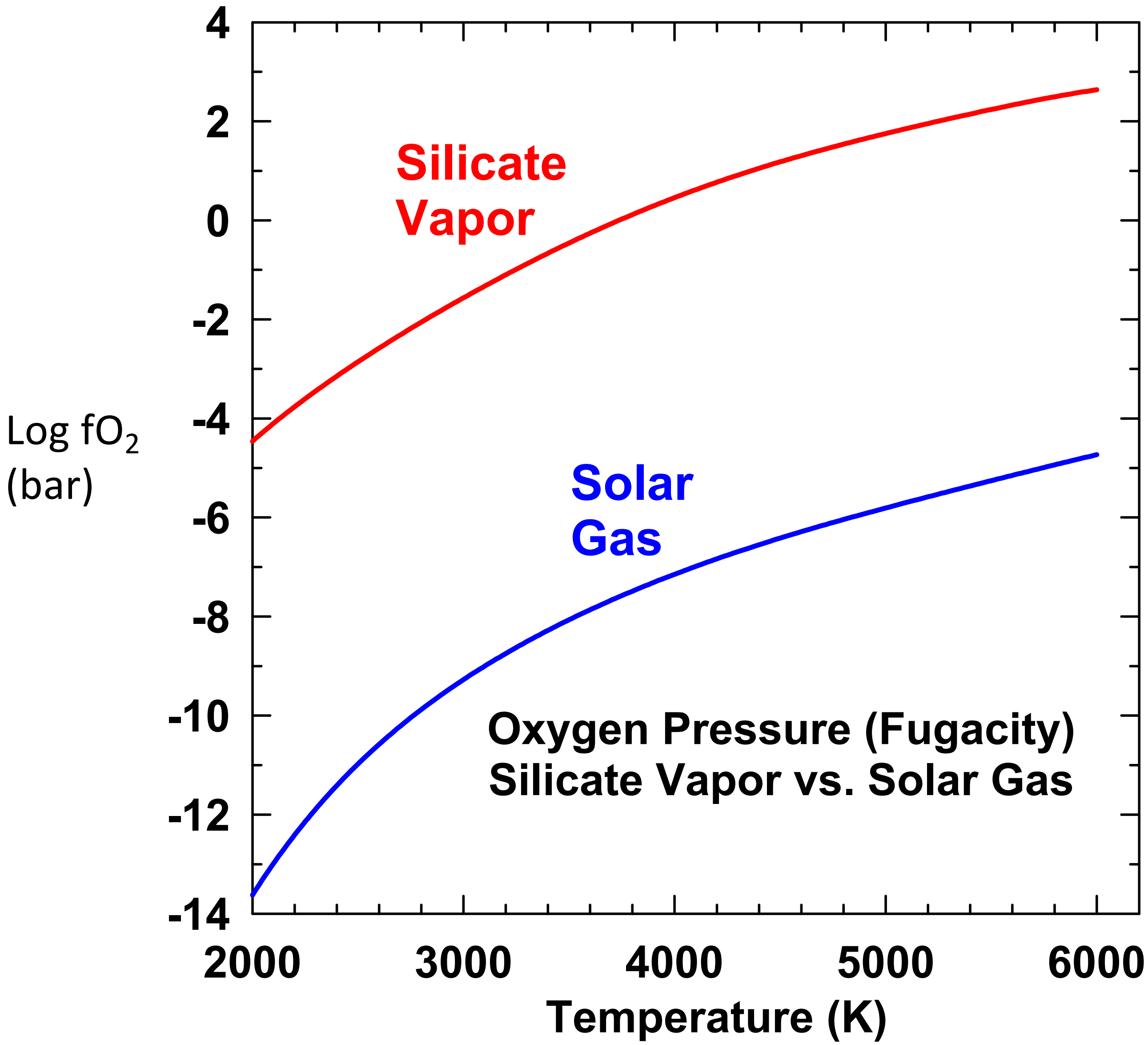


Figure 7-9, Fegley & Osborne, *Practical Chemical Thermodynamics for Geoscientists*



From: Visscher & Fegley 2013 Astrophys J 767, L12

Chemistry at high O_2 partial pressure in silicate vapor

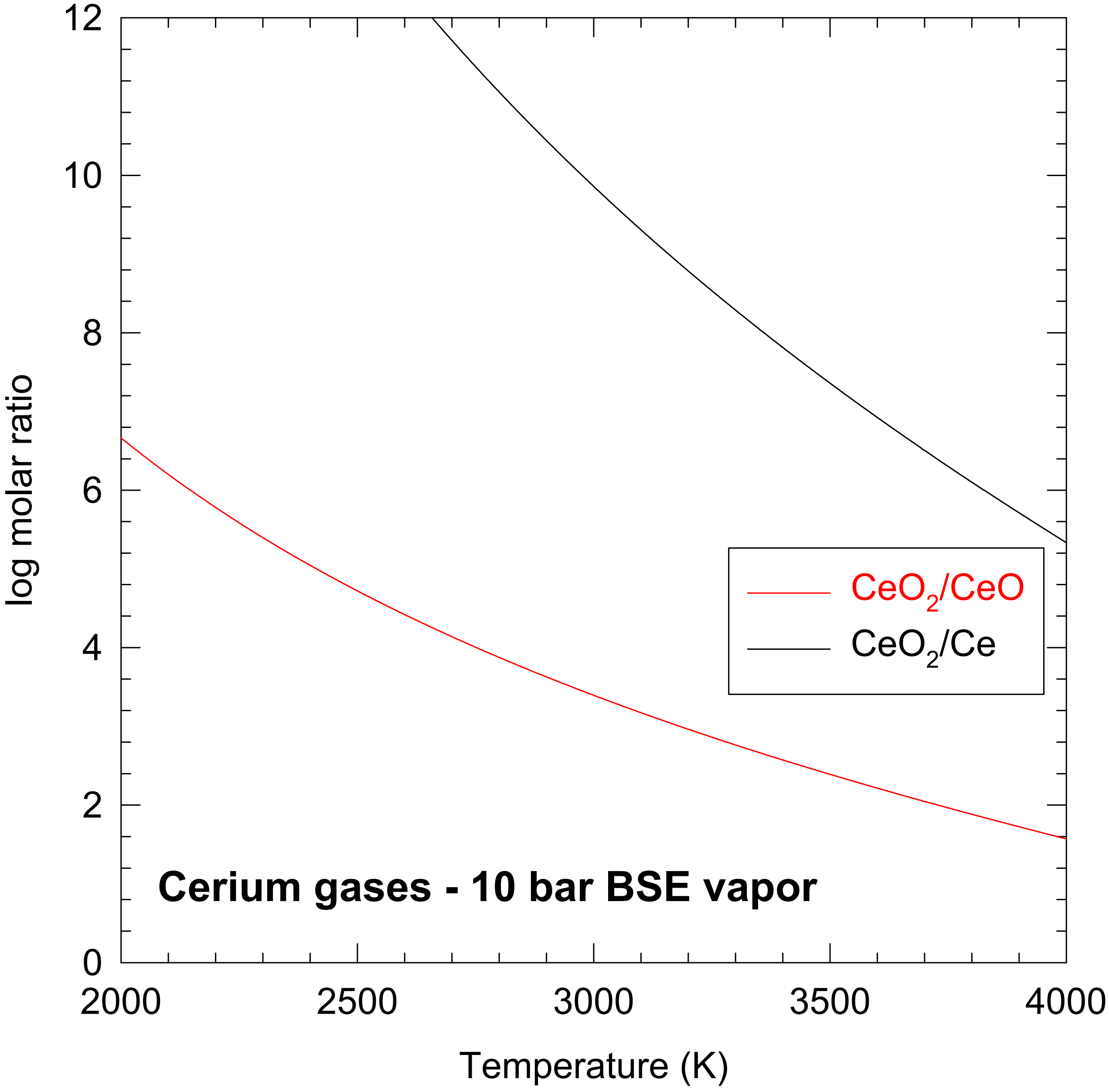
- R – stands for a Rare Earth Element
- Major gases of most REE in astronomical systems are
- Monoxides – RO
- Monatomic gas – R
- Relevant condensation chemistry at high T is
- $2\ RO\ (gas) + \frac{1}{2}\ O_2\ (gas) \rightarrow R_2O_3\ (melt)$
- $2\ R\ (gas) + 3/2\ O_2\ (gas) \rightarrow R_2O_3\ (melt)$
- **High $P(O_2)$ drives condensation of most REE**

REE Condensation Chemistry - 2

- Differences in REE abundance patterns due to
- ΔG° of condensation/vaporization reaction
- MO/M ratio in gas phase (next slide)
- Different activity coefficients for each R_2O_3
- See papers about REE condensation chemistry applied to Ca,Al-rich inclusions
- Boynton 1975 GCA 39, 569-584
- Davis & Grossman 1979 GCA 43, 1611-1632
- Kornacki & Fegley 1986 EPSL 79, 217-234

Cerium Chemistry

- Cerium is notable exception
- Three Ce-bearing gases CeO_2, CeO, Ce
- At high fO_2 CeO_2 is major gas
- Condensation reaction is
- 2 CeO_2 (gas) $\leftarrow$ Ce_2O_3 (melt) + ½ O_2 (gas)
- Higher fO_2 makes Ce more volatile
- (Boynton 1978 LPS IX, 120-122)



From: Fegley & Lodders 2017 Chemical constraints on the origin of the Moon. #6227, LPI Contribution No. 1987, 80th annual meeting of the Meteoritical Society, Santa Fe, NM.

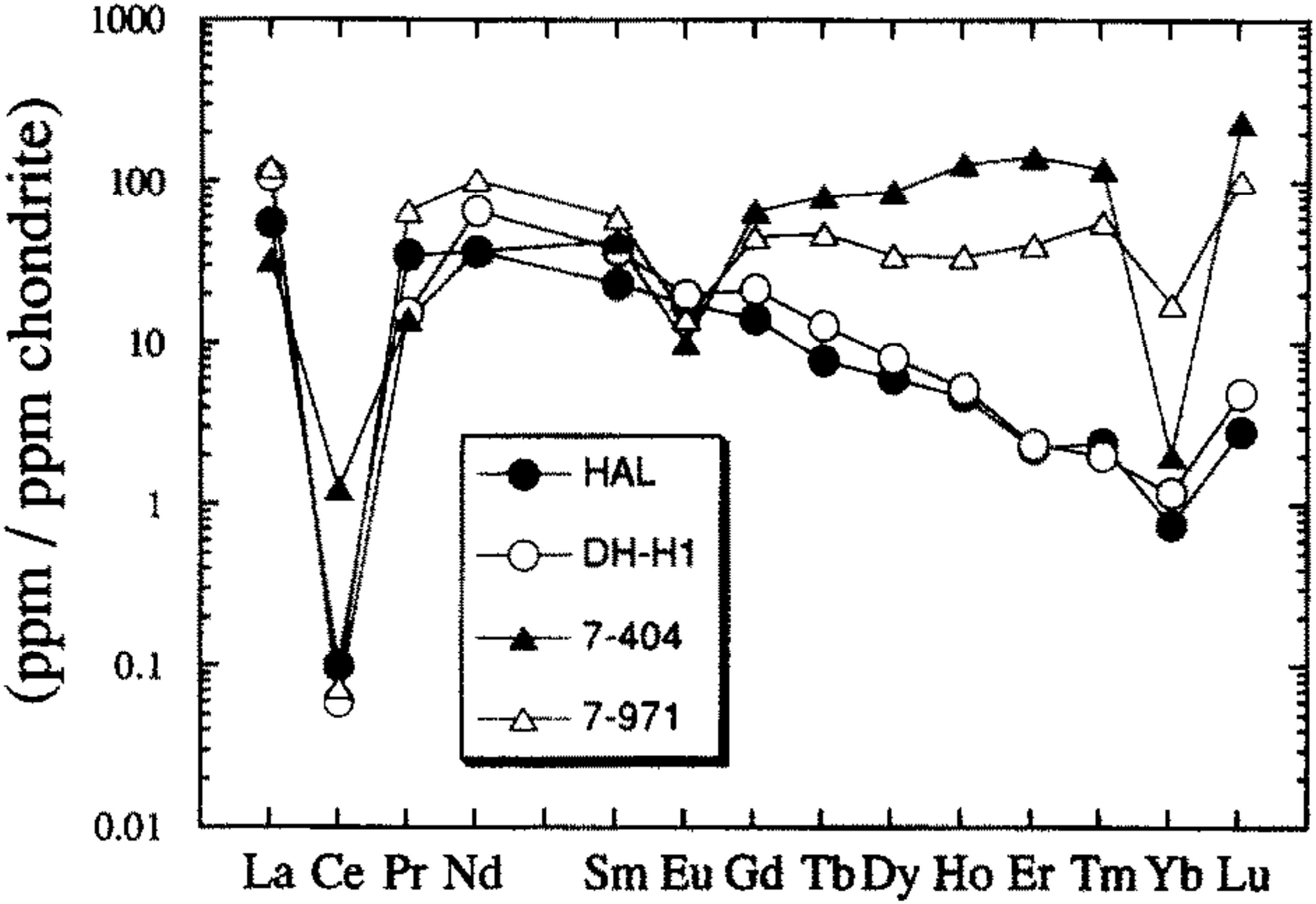
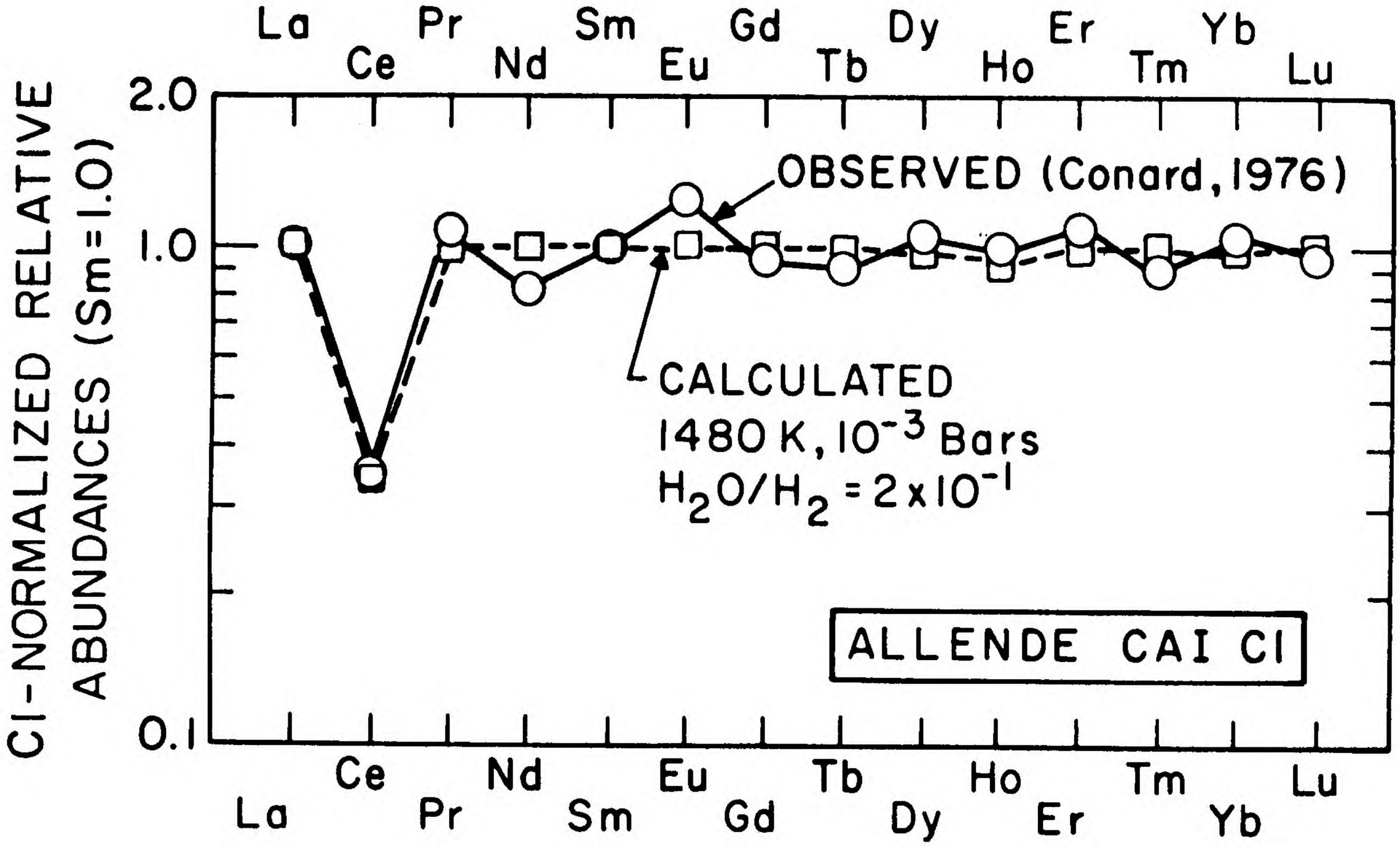


FIG. 8. Trace-element abundances in four HAL-type inclusions show distinctive Ce depletions. Ytterbium is also depleted in all four inclusions, while Pr and Eu are depleted in DH-H1, 7-404, and 7-971. REEs in HAL and DH-H1 are fractionated according to ionic radius, with depleted HREEs indicating melt partitioning. Data are from HINTON et al. (1988) and IRELAND et al. (1988).



From: Fegley 1986 Lunar Planet Sci 18, pp. 220-221.

☞Come back to this later when discussing W/Hf fractionations

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Evidence for distillation in the formation of HAL and related hibonite inclusions

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Cerium Depletions

- Next slide shows REE abundance patterns in melt for isobaric cooling at 10 bar pressure
- **Smaller Ce depletions at lower temperature**
- **No Ce depletion in bulk silicate Moon**
- Ringwood 1979 Origin of the Earth & Moon
- Korotev 2005 Chem Erde 65, 297-346
- **Temperature at which depletion disappears gives T_{max} for lunar formation at that total pressure**
- This is $\lesssim$ 3300 K at 10 bars

From: Fegley & Lodders 2017 Chemical constraints on the origin of the Moon. #6227,
LPI Contribution No. 1987, 80th annual meeting of the Meteoritical Society, Santa Fe, NM.

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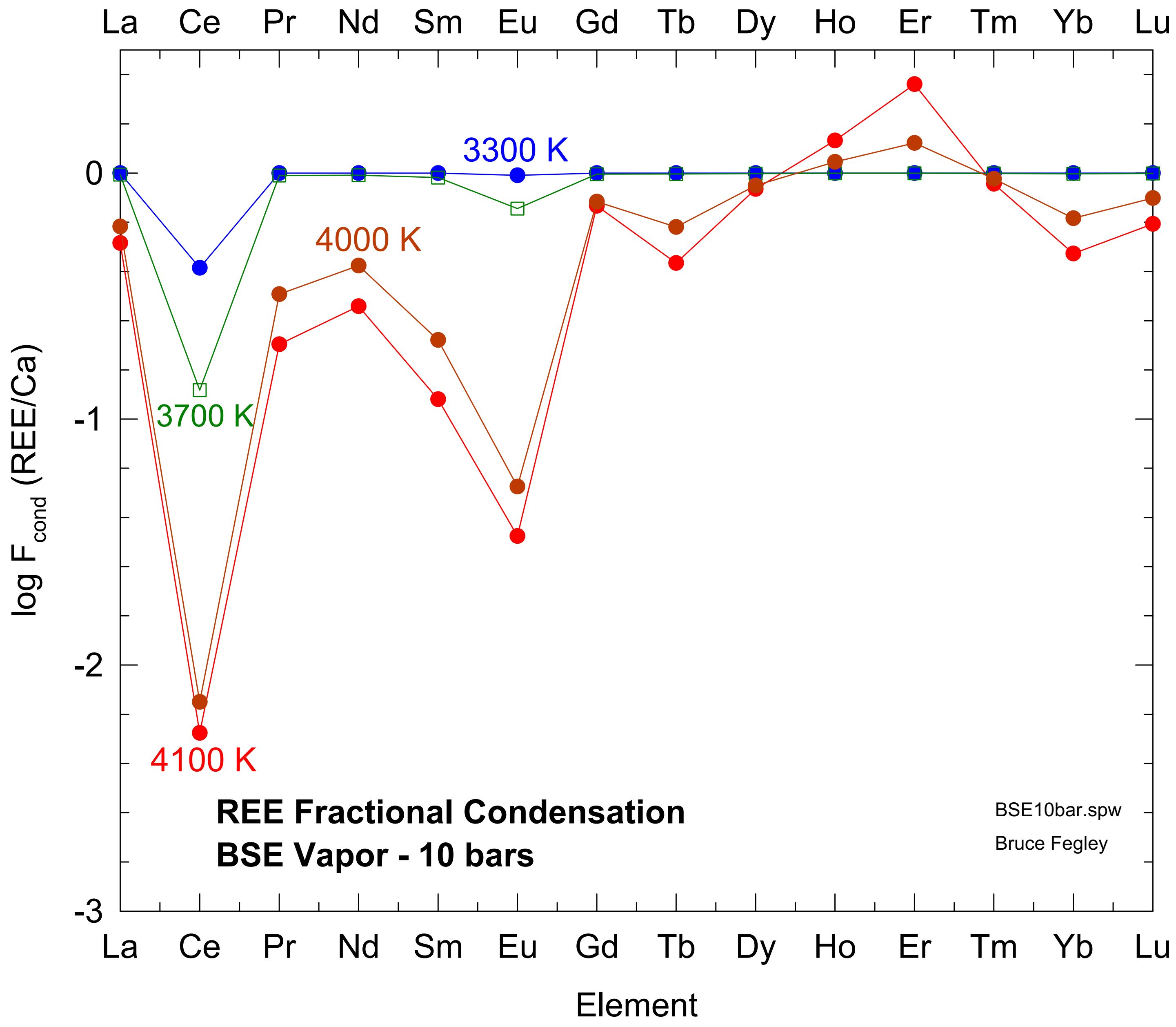


fO_2 and Th/U Fractionation

- UO_3 (gas) ← UO_2 (melt) + ½ O_2 (gas)
- **Higher fO_2 makes Uranium more volatile**
- ThO (gas) + ½ O_2 (gas) → ThO_2 (melt)
- **Higher fO_2 makes Thorium more refractory**
- BSE-normalized atomic Th/U ~ 2.4 at 3300 K, 10 bars BSE vapor (should be unity if unfractionated from BSE model composition)

P(O_2) and W/Hf Fractionation

- **Higher fO_2 makes W more volatile**
  Fegley & Palme 1985 EPSL 72, 311-326
- WO_3 (gas) ← W (metal) + 3/2 O_2 (gas)
- **Higher P(O_2) makes Hf more refractory**
- Fegley et al 2012 Bull Am Astron Soc 44
- HfO (gas) + ½ O_2 (gas) = HfO_2 (melt)
- BSE-normalized W/Hf ~ 1 at 3300 K, 10 bars BSE vapor (assuming WO_3 condenses in silicate melt)
- BSE-normalized W/Hf << 1 at 3300 K if WO_3 does not condense in silicate melt)

W Depletion – CAI C1

- CAI C1 – depleted in W and also in Ce
- Same fO_2 gives both depletions
- (2nd & 3rd slides after this one)
- This fO_2 slightly lower than predicted for proto-lunar disk (next slide)
- Visscher & Fegley 2013 ApJ 767, L12

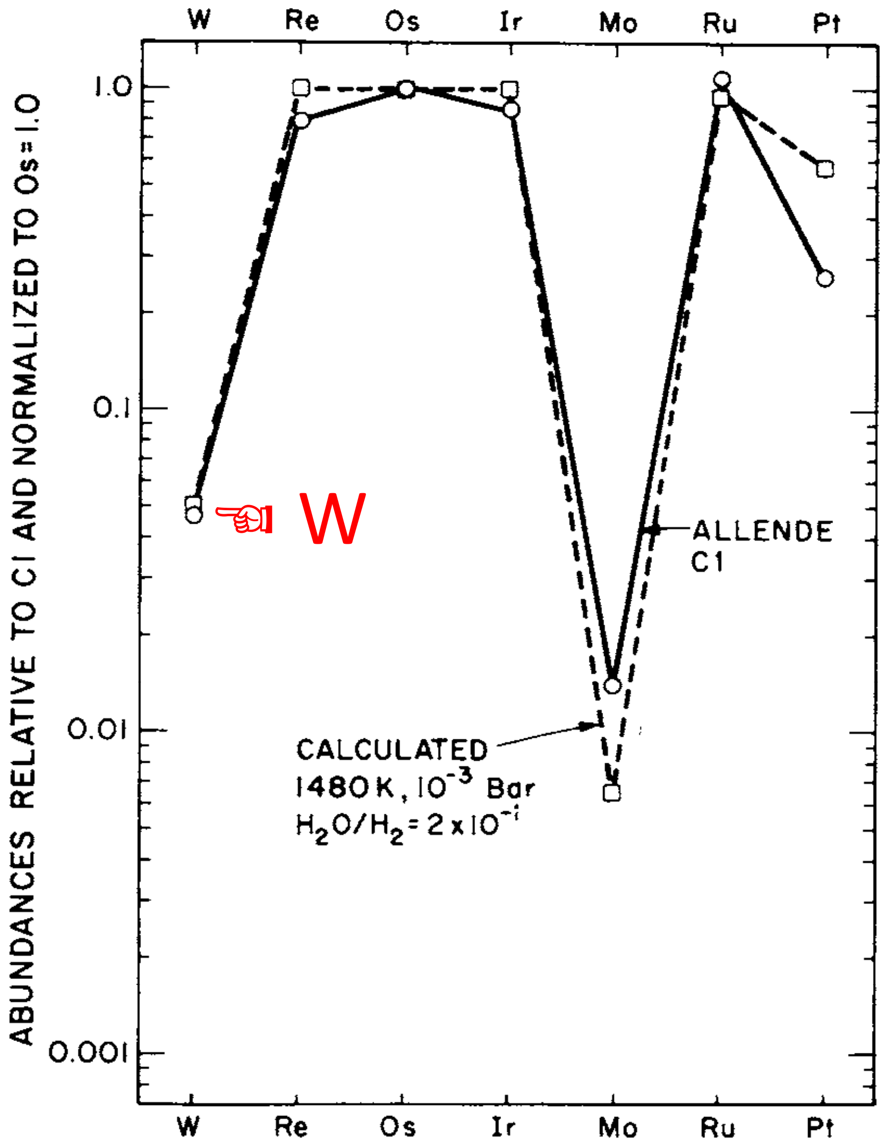
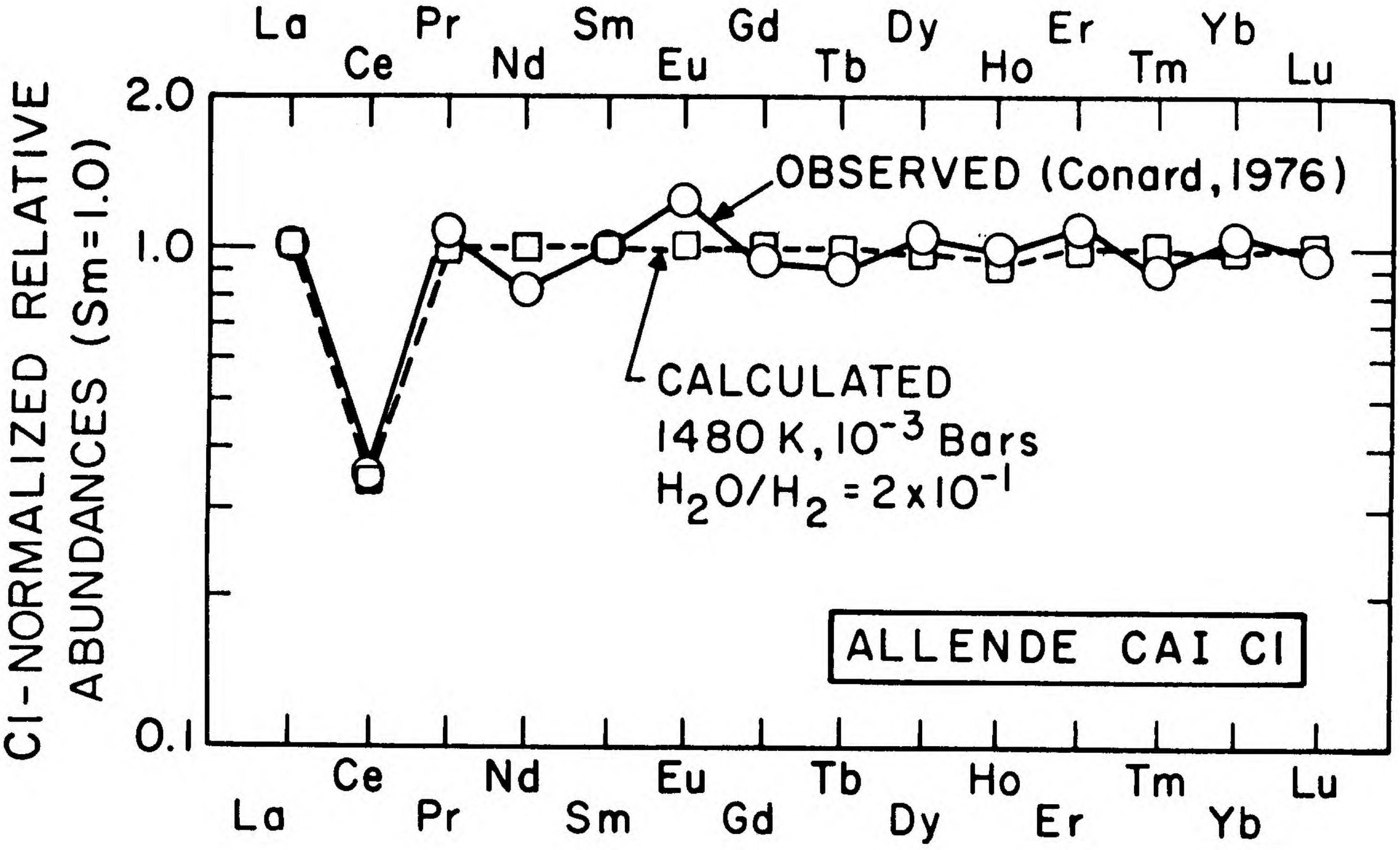


Fig. 7.7.4. Observed and calculated refractory-metal abundances in Allende FUN inclusion C1. The observed composition is from EDS/SEM analyses of metal grains by D. A. Wark.

From: Fegley & Palme 1985 EPSL 72, 311-326



From: Fegley 1986 Lunar Planet Sci 18, pp. 220-221.

Lu/Hf Fractionation

- Hf – more refractory than Lu at high fO_2
- HfO/Hf ~ 772,000 vs LuO/Lu ~ 23,000
- At 3300 K and 10 bars BSE vapor
- 2 LuO (gas) + ½ O_2 (gas) → Lu_2O_3 (melt)
- HfO (gas) + ½ O_2 (gas) → HfO_2 (melt)
- Higher fO_2 drives condensation reactions
- Much larger MO/M for Hf makes it more refractory than Lu

Rb/Sr Fractionation

- Higher fO_2 makes Rb *slightly* more refractory
- Rb/RbO ~ 2.7 vs Sr/SrO ~ 0.07 – gas phase
- At 3300 K, 10 bars BSE vapor
- $2\ Rb\ (gas) + \frac{1}{2}\ O_2\ (gas) \rightarrow Rb_2O\ (melt)$
- But this reaction also occurs
- $2\ RbO \leftarrow Rb_2O\ (melt) + \frac{1}{2}\ O_2\ (gas)$
- In contrast, no effect of fO_2 on
- SrO (gas) = SrO (melt)
- BSE-normalized Rb/Sr ~ 10^{-3}, 3300 K 10 bars

K/U Fractionation

- Opposite effects of higher fO_2 on K and U
- K/KO ~ 5 vs U/UO_3 ~ 2×10^{-12} – gas phase
- At 3300 K, 10 bars BSE vapor
- $2\ K\ (gas) + \frac{1}{2}\ O_2\ (gas) \rightarrow K_2O\ (melt)$
- Higher fO_2 makes K more refractory
- $UO_3\ (gas) \leftarrow UO_2\ (melt) + \frac{1}{2}\ O_2\ (gas)$
- Higher fO_2 makes Uranium more volatile
- BSE-normalized K/U ~ 0.004, 3300 K 10 bars

Key Points

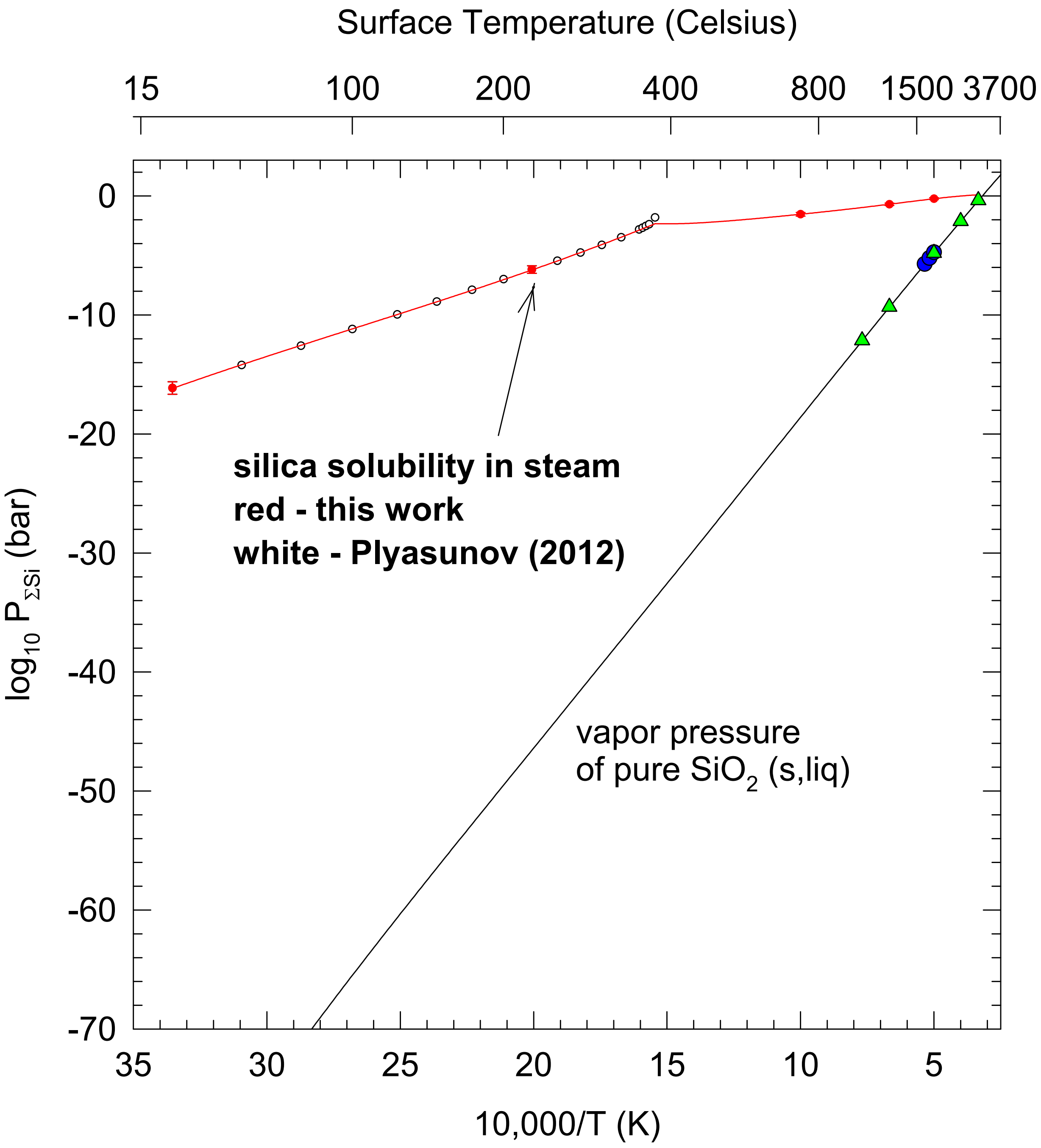
- High O_2 partial P in hot silicate vapor
- Giant Impact models predict hot silicate melt – vapor system
- The high $P(O_2)$ and high T fractionate trace elements: Ce, Hf/W, K/U, Th/U
- These effects are not seen, either
- (a) No high T vapor lost as isotopes show OR
- (b) Melt – vapor separated between some T_{max} and T_{min} constrained by equilibrium results

(2) Steam Atmosphere Chemistry on the early Earth.

A few examples about this

- Silica and many other oxides dissolve in steam
- Greatly different solubility for different oxides
- If steam atmosphere is lost the steam soluble element inventory is changed
- This is potentially important for bulk composition, density, heat balance, interior structure, volatile element inventory
- Spectroscopically active gases in steam atmosphere
- Details are in Fegley et al 2016 ApJ 824:103

From: Fegley et al 2016 ApJ 824:103



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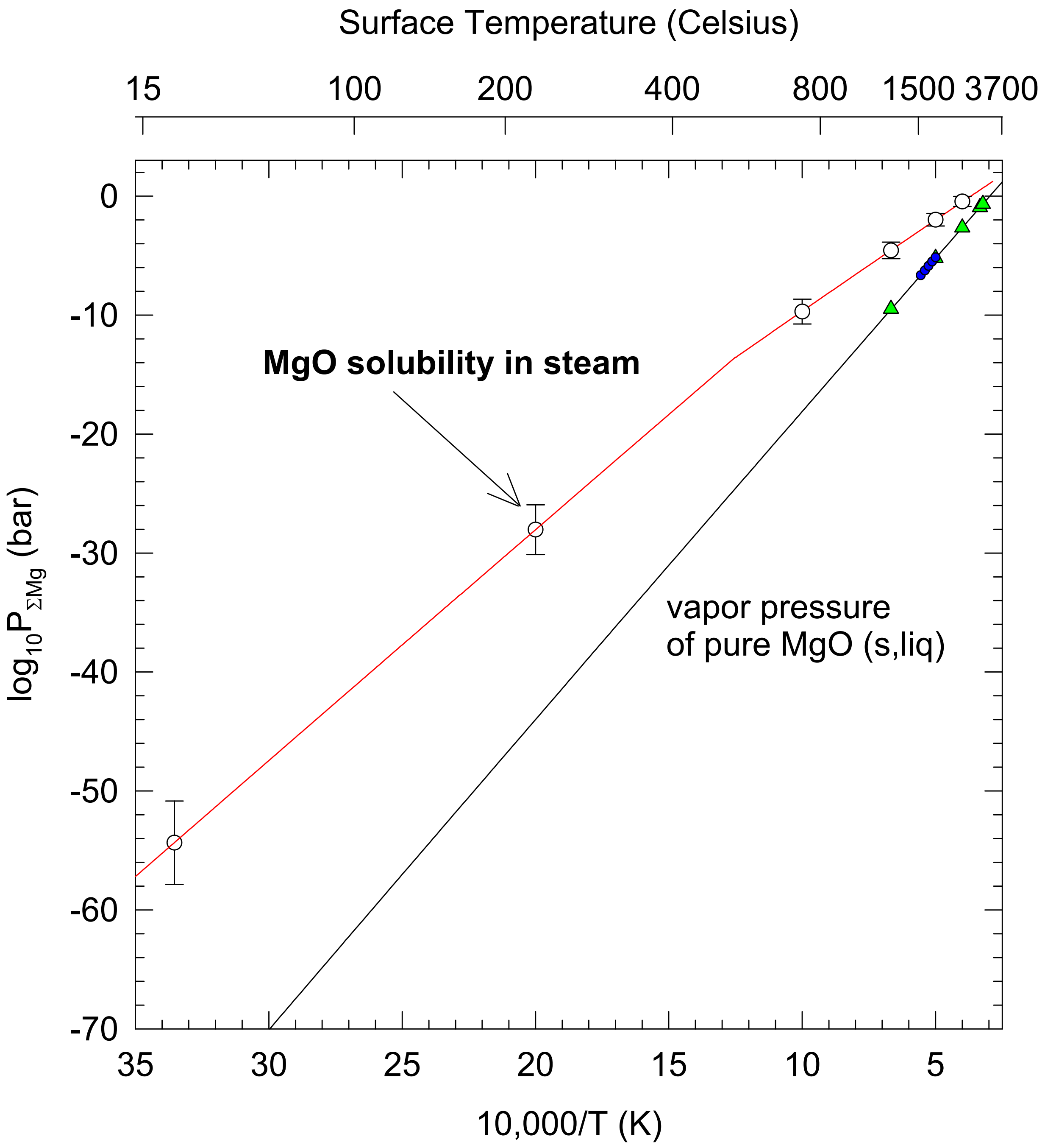

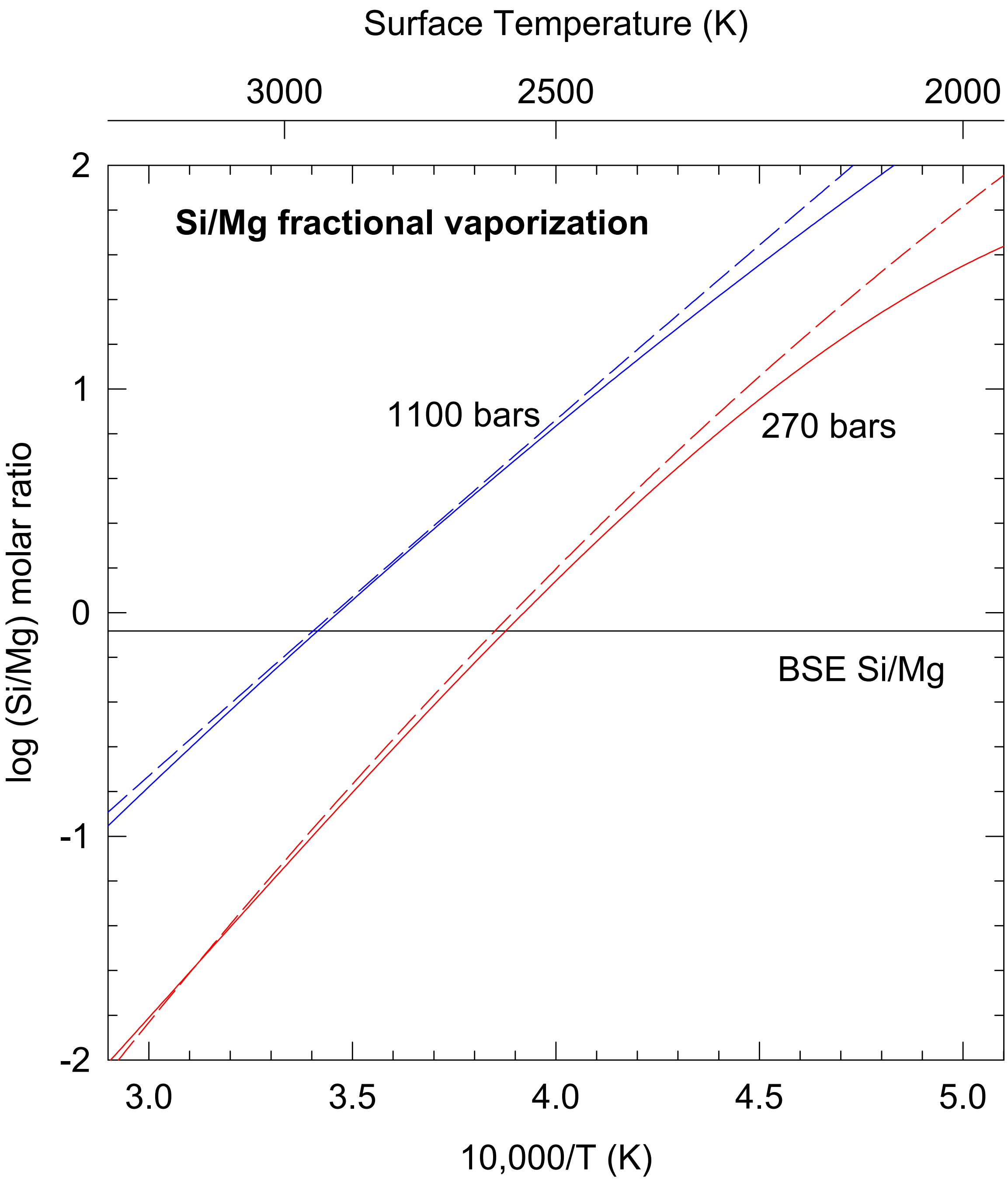

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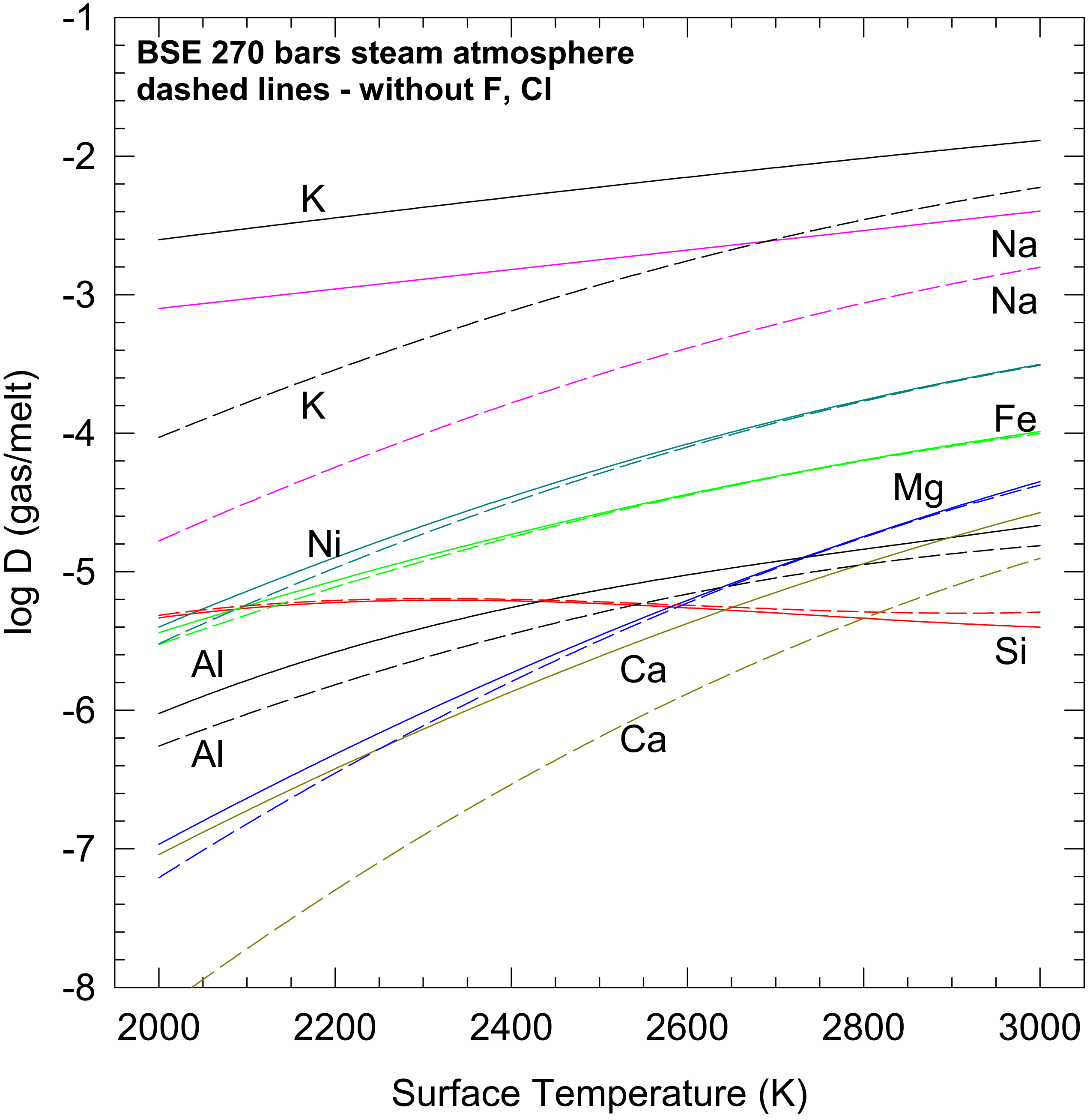
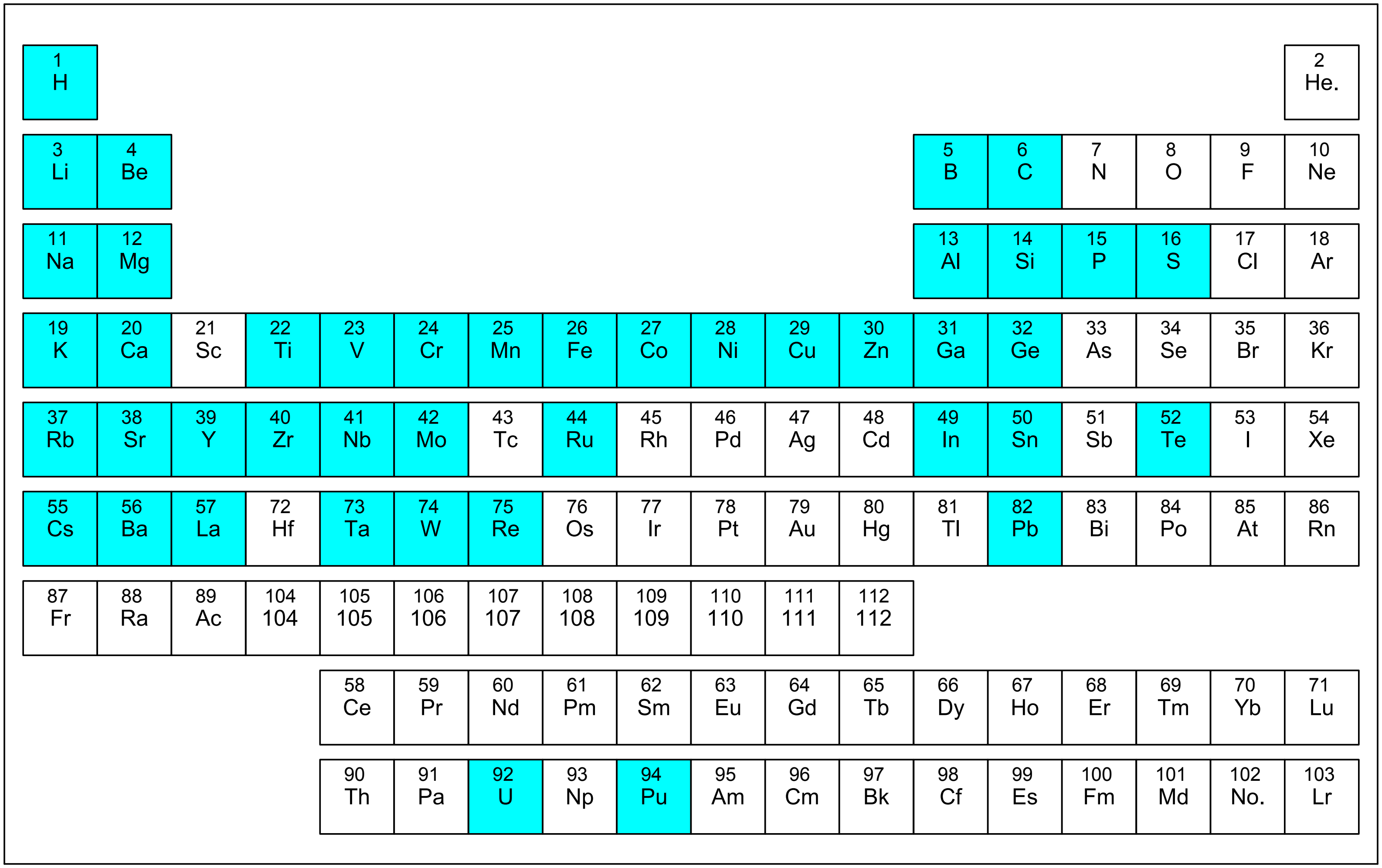
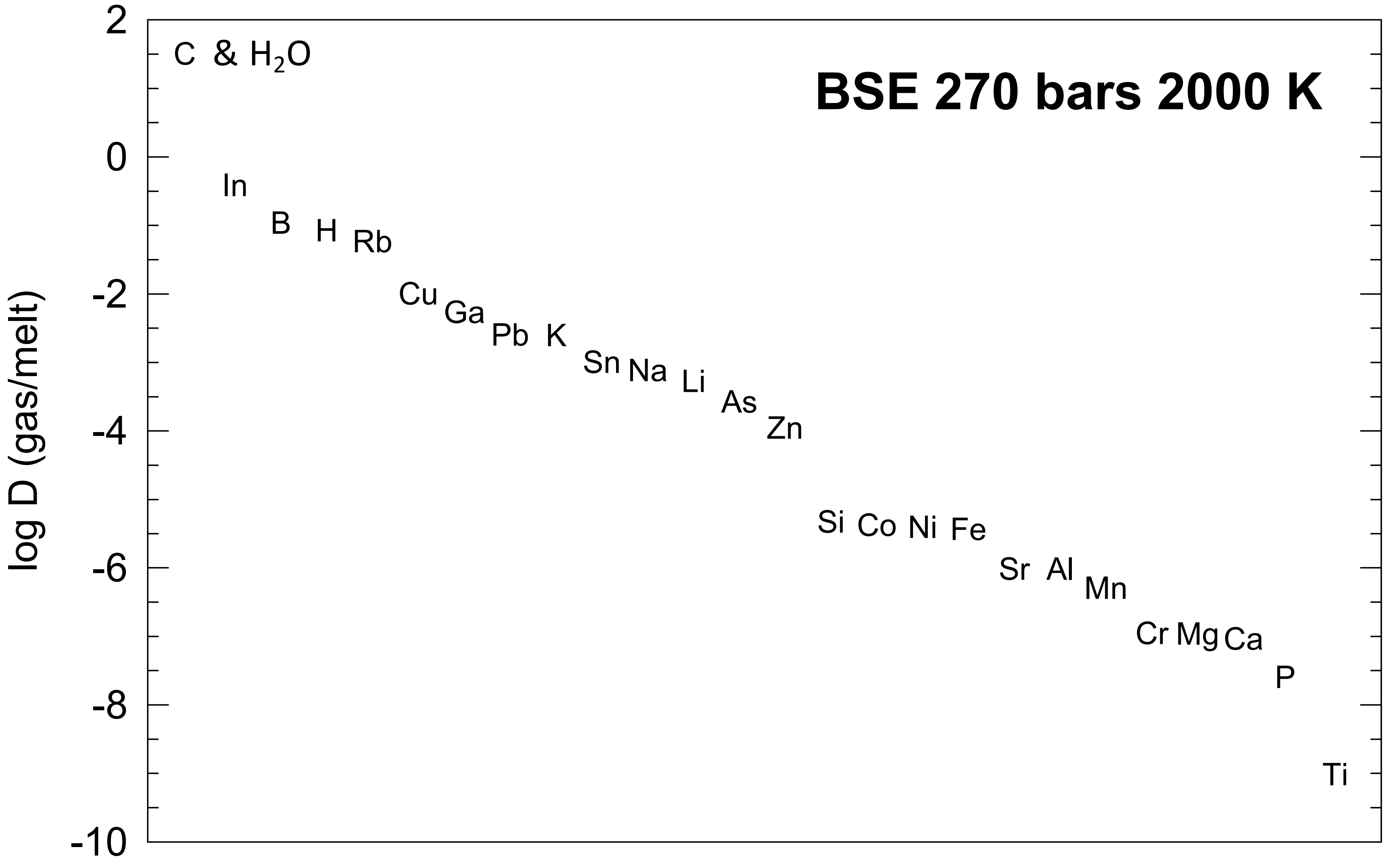


Steam Soluble Elements
(from references cited in Fegley et al 2016 ApJ)



1 H																	2 He.
3 Li	**4 Be**											**5 B**	**6 C**	7 N	8 O	9 F	10 Ne
11 Na	**12 Mg**											**13 Al**	**14 Si**	**15 P**	**16 S**	17 Cl	18 Ar
19 K	**20 Ca**	21 Sc	**22 Ti**	**23 V**	**24 Cr**	**25 Mn**	**26 Fe**	**27 Co**	**28 Ni**	**29 Cu**	**30 Zn**	**31 Ga**	**32 Ge**	33 As	34 Se	35 Br	36 Kr
37 Rb	**38 Sr**	**39 Y**	**40 Zr**	**41 Nb**	**42 Mo**	43 Tc	**44 Ru**	45 Rh	46 Pd	47 Ag	48 Cd	**49 In**	**50 Sn**	51 Sb	**52 Te**	53 I	54 Xe
55 Cs	**56 Ba**	**57 La**	72 Hf	**73 Ta**	**74 W**	**75 Re**	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	**82 Pb**	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 104	105 105	106 106	107 107	108 108	109 109	110 110	111 111	112 112						
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	**92 U**	93 Np	**94 Pu**	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No.	103 Lr

From: Fegley et al 2019 Chemie der Erde (Geochemistry)



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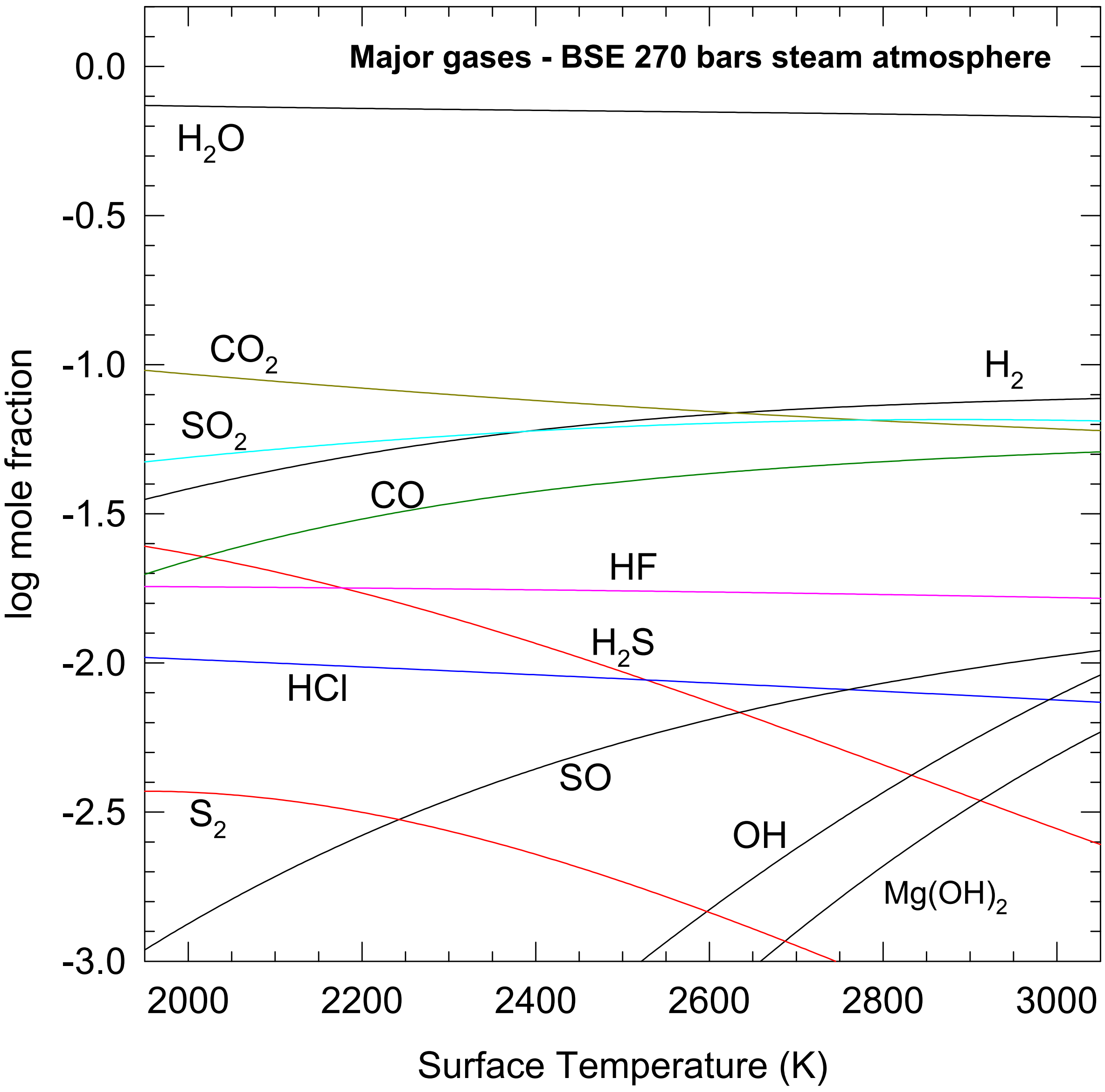

Key Points

- Steam atmosphere – magma ocean phase:
- Silicon and several other major rock-forming elements dissolve in steam
- Very different solubility for different elements
- If steam atmosphere is lost the steam soluble element inventory is changed
- Many potentially observable gases – applies to hot rocky exoplanets