

Chemistry during Formation of the Earth and Moon

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Outline

- Describe our work on modeling chemistry during the accretion of rocky planets in our solar system and extrasolar planetary systems.
- Review two interesting topics:
 - (1) Chemical constraints on formation of the Moon
 - (2) Atmosphere formation and evolution on the early Earth.

Acknowledgments

- **Laura Schaefer (now ASU, Tempe)**
- >(18 papers at Wash U in 7 years before grad school)
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- Kevin Zahnle, NASA Ames

(1) Chemical constraints on formation of the Moon

Summary

- Unique trace element abundances produced by vaporization / condensation at high fO_2
- **Very Promising, can explain:**
- No Ce depletion in bulk silicate Moon
- Lunar Lu/Hf, Hf/W, Nd/Sm, Th/U \approx 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 - 2

- **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) Atmosphere
formation and
evolution on the
early Earth.

Summary -1

- Reducing gases produced by outgassing for most kinds of chondritic matter, e.g., CV, H, L, LL, EH, EL chondritic material
- Many Earth accretion models predict large amounts (70 – 85%) of EH-like material Dauphas, Lodders, Ringwood, Rubie, Wänke
- Late veneer plausibly also reducing – H, L, LL, EH, EL, e.g., see Palme & O'Neill 2014
- Outgassing of Fe³⁺-free BSE also gives reducing atmospheres
- Reducing atmosphere on Early Earth?

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

<i>Gas (vol. %)</i>	<i>CI</i>	<i>CM</i>	<i>CV</i>	<i>H</i>	<i>L</i>	<i>LL</i>	<i>EH</i>	<i>EL</i>
H ₂	4.36	2.72	0.24	48.49	42.99	42.97	43.83	14.87
H ₂ O	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 ₂ S	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

^aOther' includes gases of the rock-forming elements Cl, F, K, Na, P, and S.

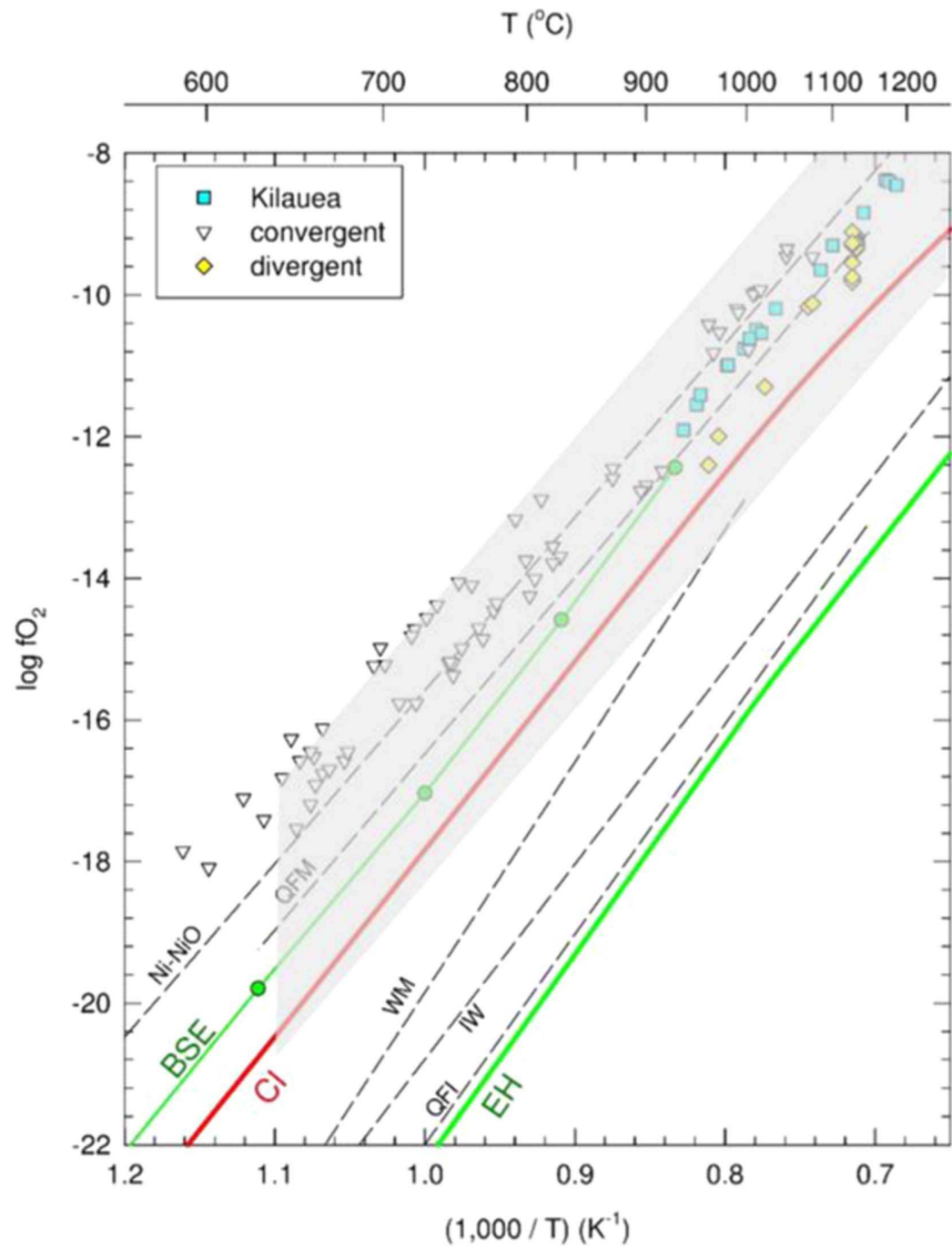
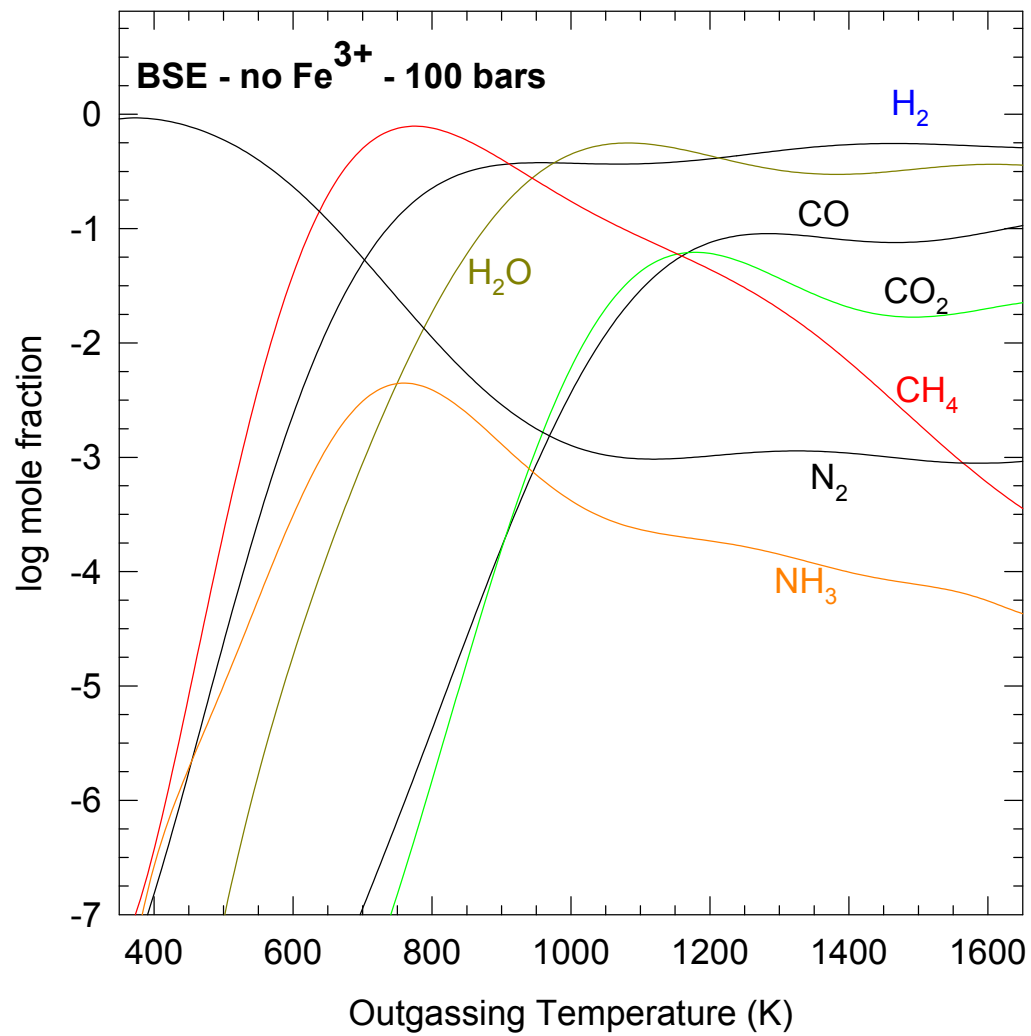
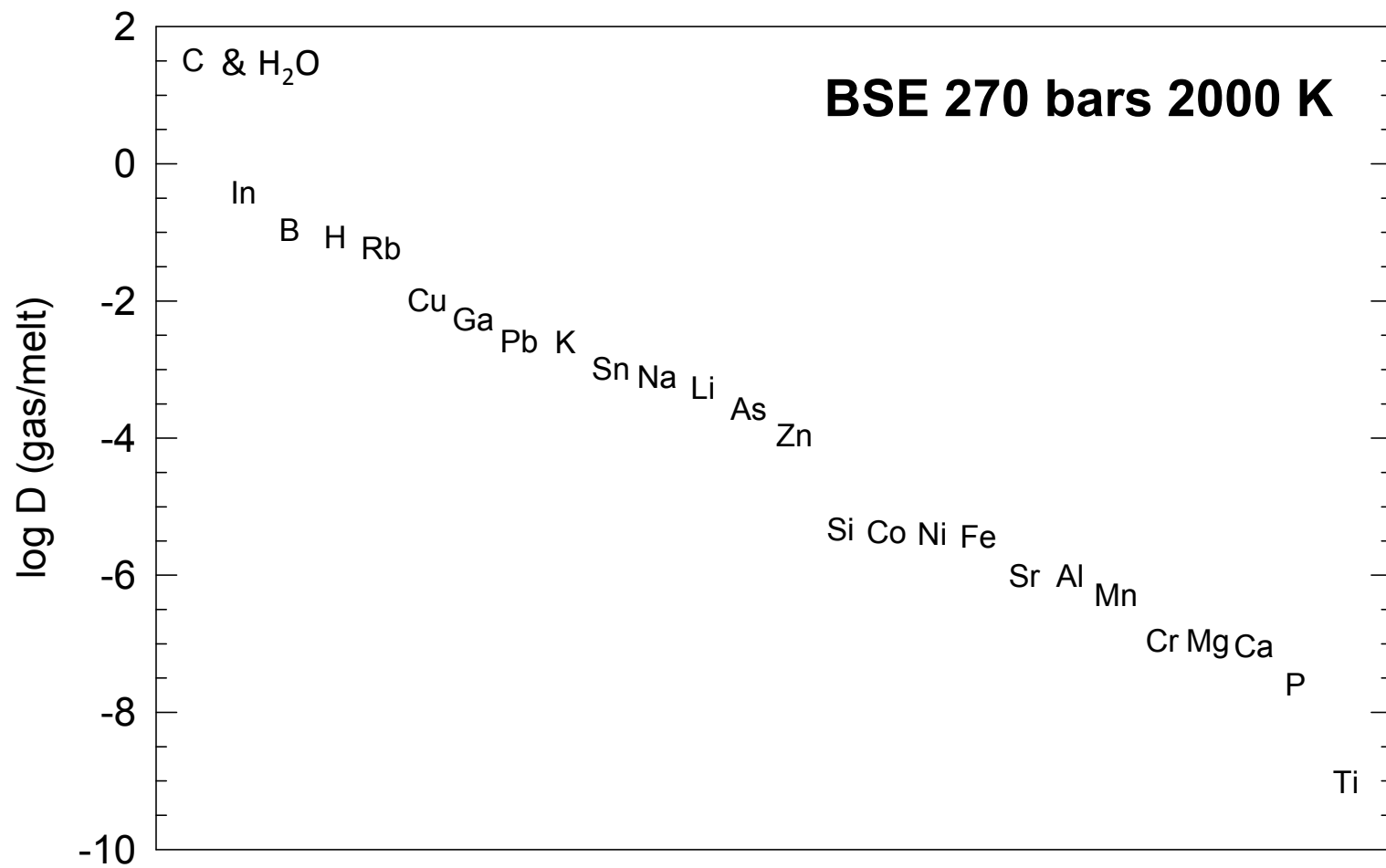


Figure 9. Oxygen fugacity of the Bulk Silicate Earth (BSE) compared to



Summary -2

- Steam atmosphere – magma ocean phase:
- Silicon and several other major rock-forming elements dissolve in steam
- Greatly different solubility for different elements (see next slide)
- If steam atmosphere is lost the steam soluble element inventory is changed



(1) Chemical constraints on formation of the Moon

Introduction & Background

- Potassium and zinc isotopic anomalies indicate lunar material formed at high temperatures from ejecta after a giant impact on the early Earth
- 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 not say BSM = BSE, this is a model composition

Introduction & Background - 2

- High temperature vaporization/condensation at high fO_2 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

Oxygen fugacity of silicate vapor

- Look at two examples:
- Knudsen effusion mass spectrometry (KEMS) of pure silica (Kazenas et al 1985)
- Calculated f_{O_2} of BSE vapor along liquid – vapor saturation curve (Visscher & Fegley 2013 *Astrophys J* 767, L12)

 Shown on next two slides

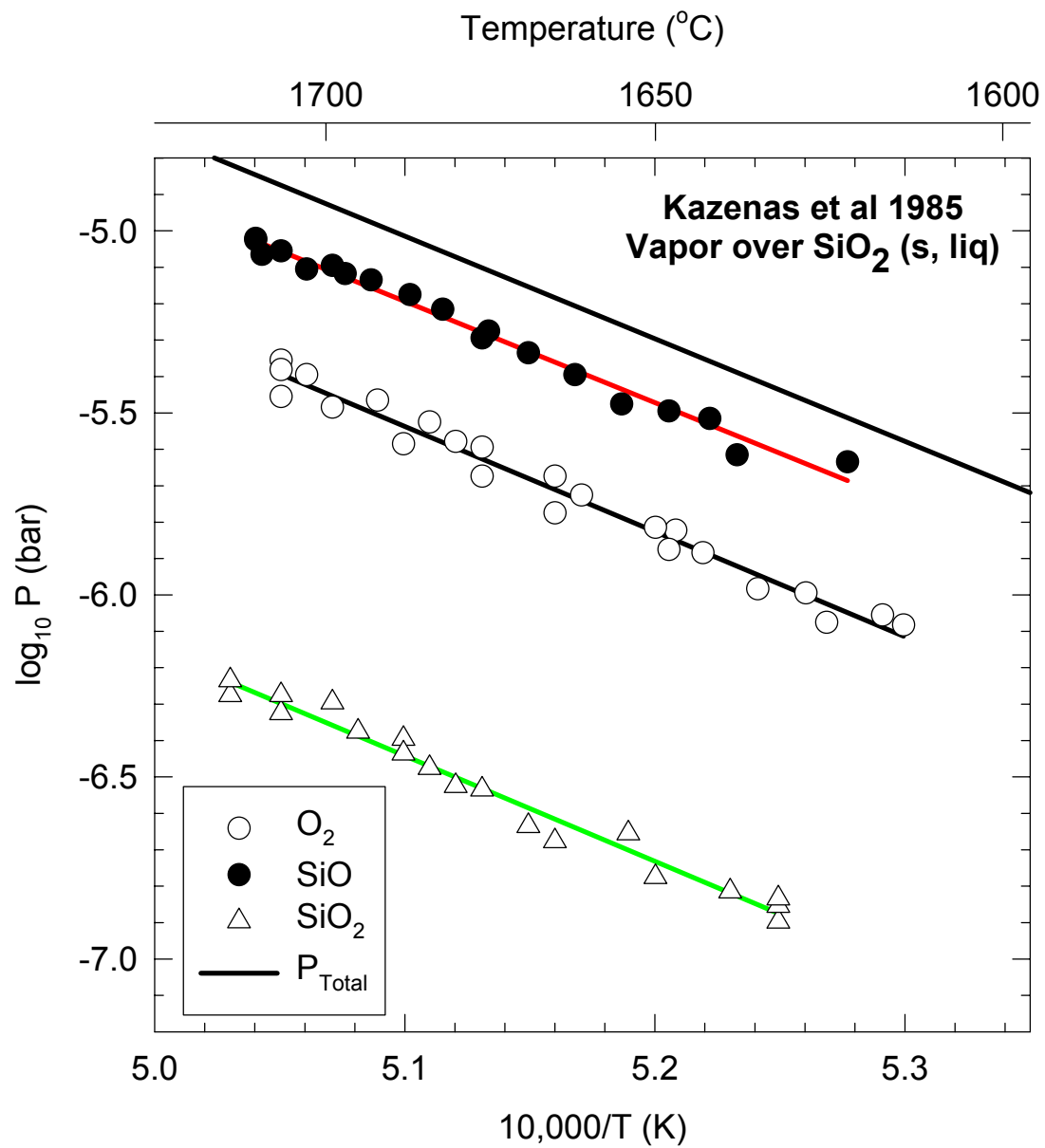
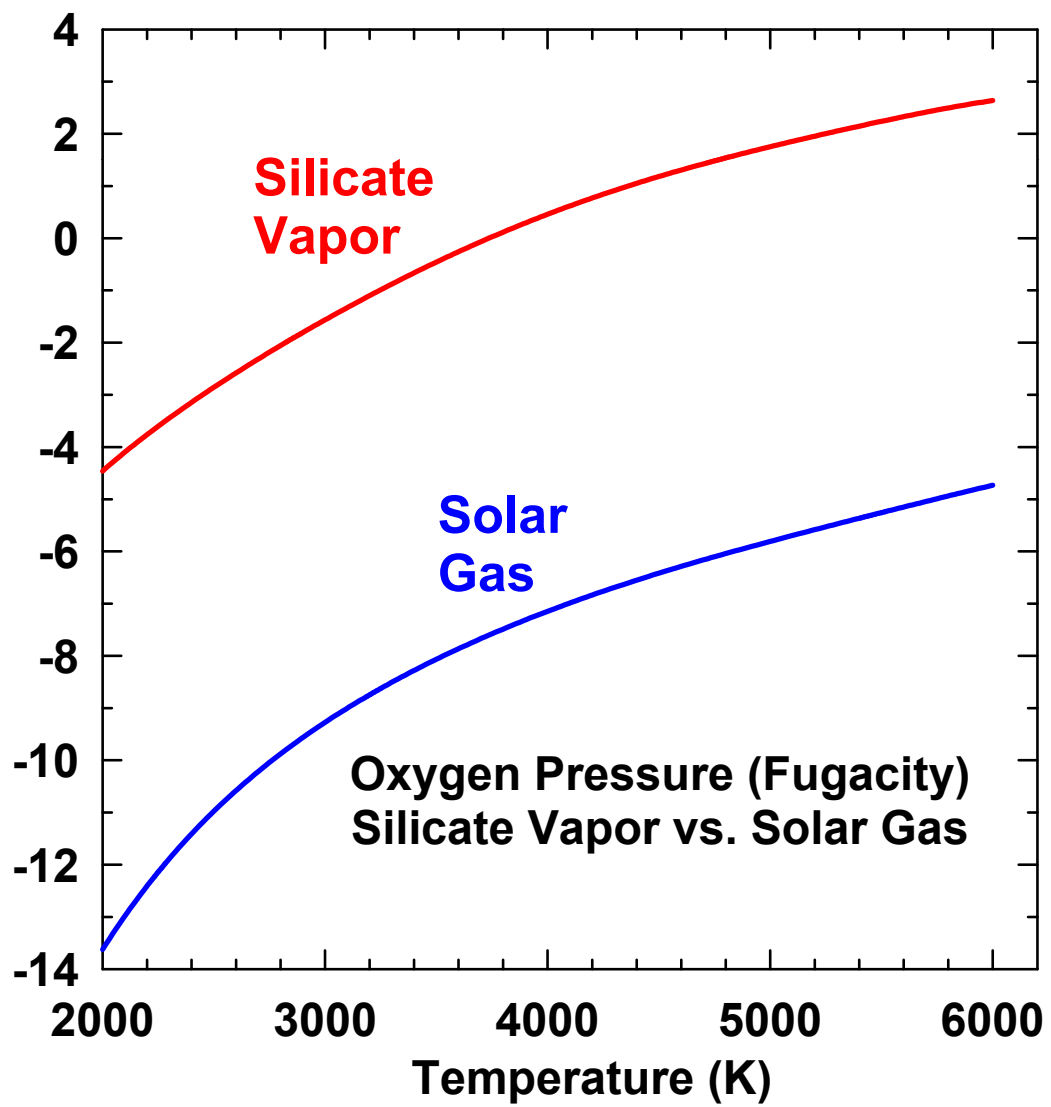


Figure 7-9, Fegley & Osborne, *Practical Chemical Thermodynamics for Geoscientists*

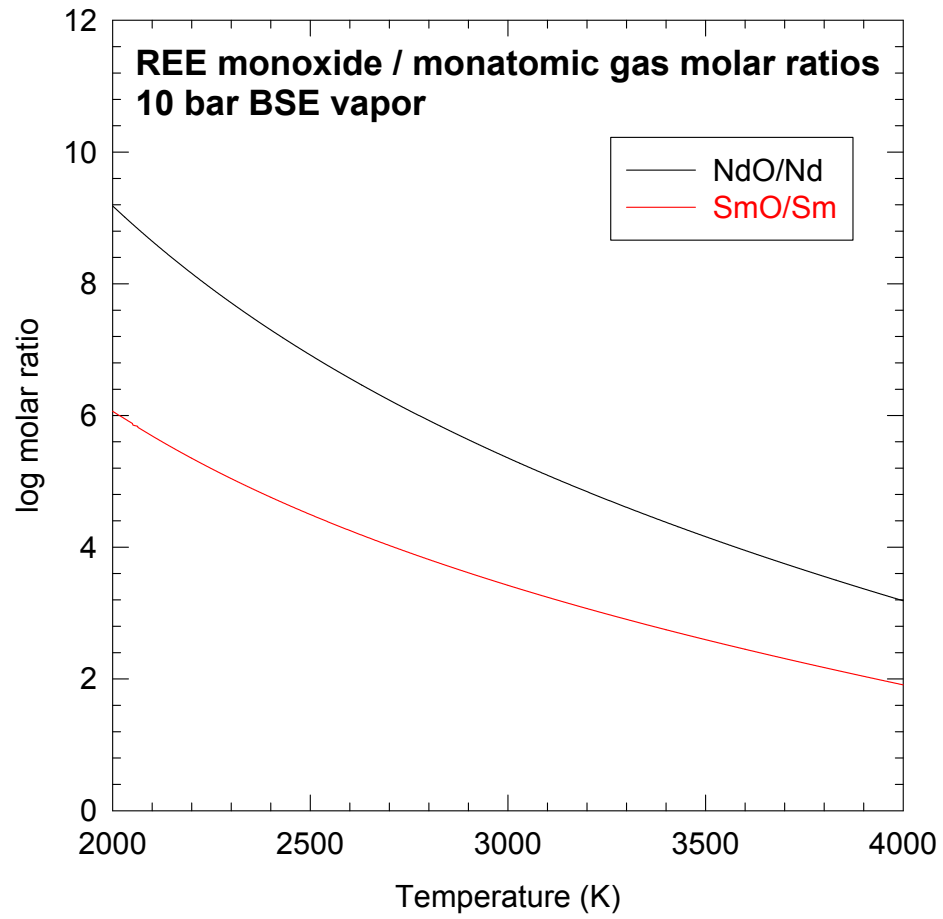


Chemistry at high fO_2 in silicate vapor

- 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
- $2 \text{ RO (gas)} + \frac{1}{2} \text{ O}_2 \text{ (gas)} \rightarrow \text{R}_2\text{O}_3 \text{ (melt)}$
- $2 \text{ R (gas)} + \frac{3}{2} \text{ O}_2 \text{ (gas)} \rightarrow \text{R}_2\text{O}_3 \text{ (melt)}$
- **High fO_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 $f\text{O}_2$ CeO_2 is major gas
- Condensation reaction is
- $2 \text{CeO}_2 (\text{gas}) \leftarrow \text{Ce}_2\text{O}_3 (\text{melt}) + \frac{1}{2} \text{O}_2 (\text{gas})$
- Higher $f\text{O}_2$ makes Ce more volatile
- (Boynton 1978 LPS IX, 120-122)

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

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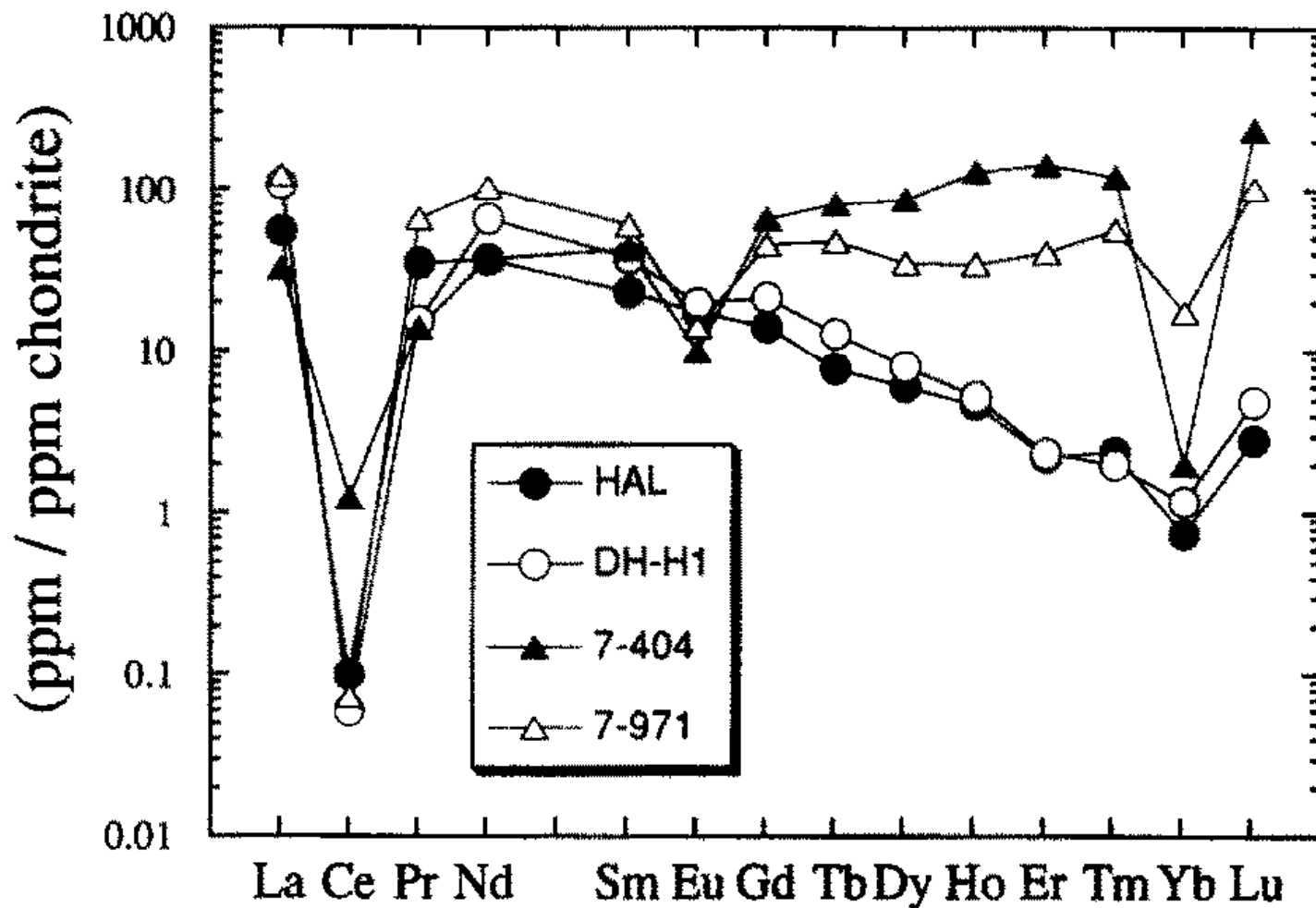
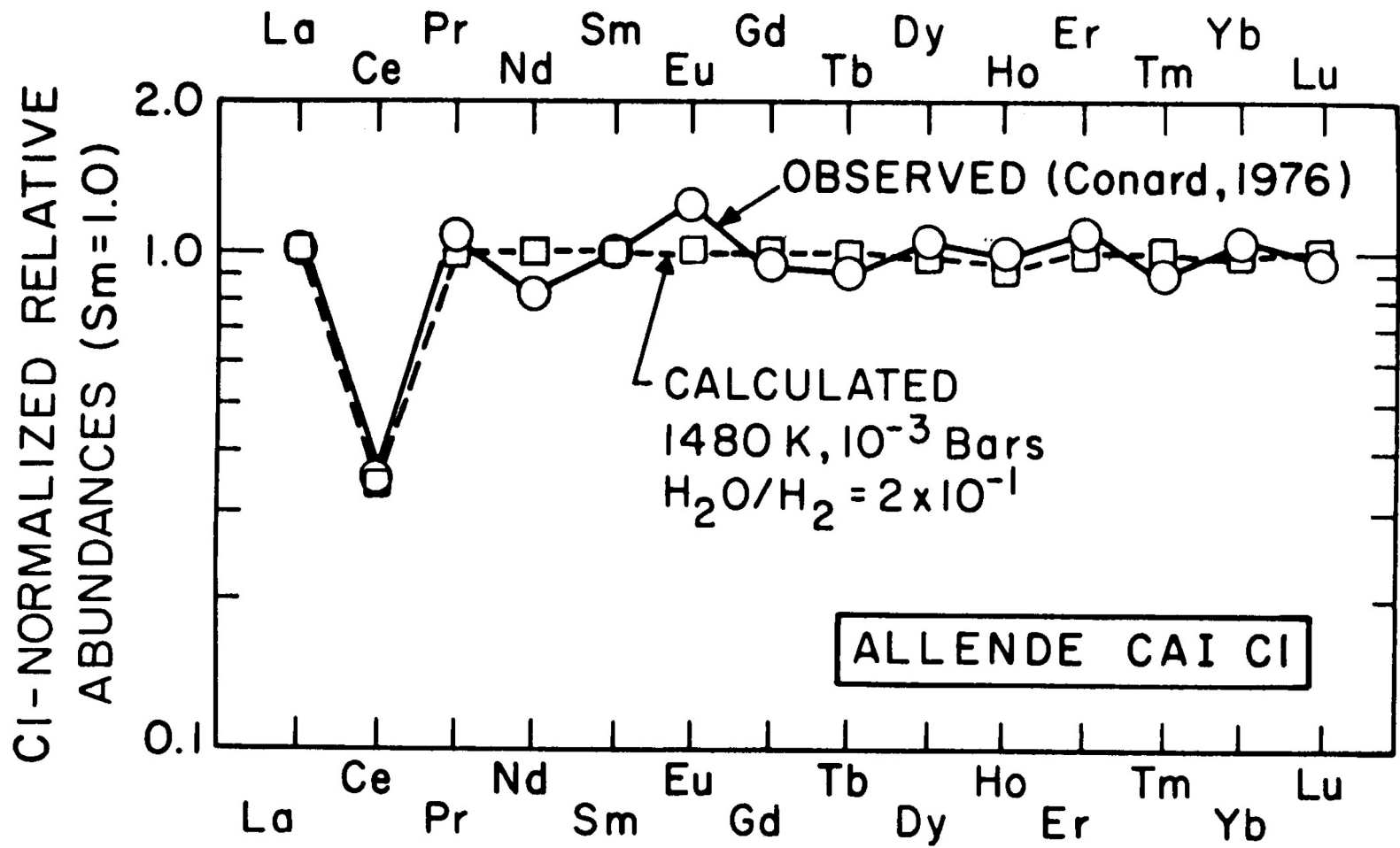


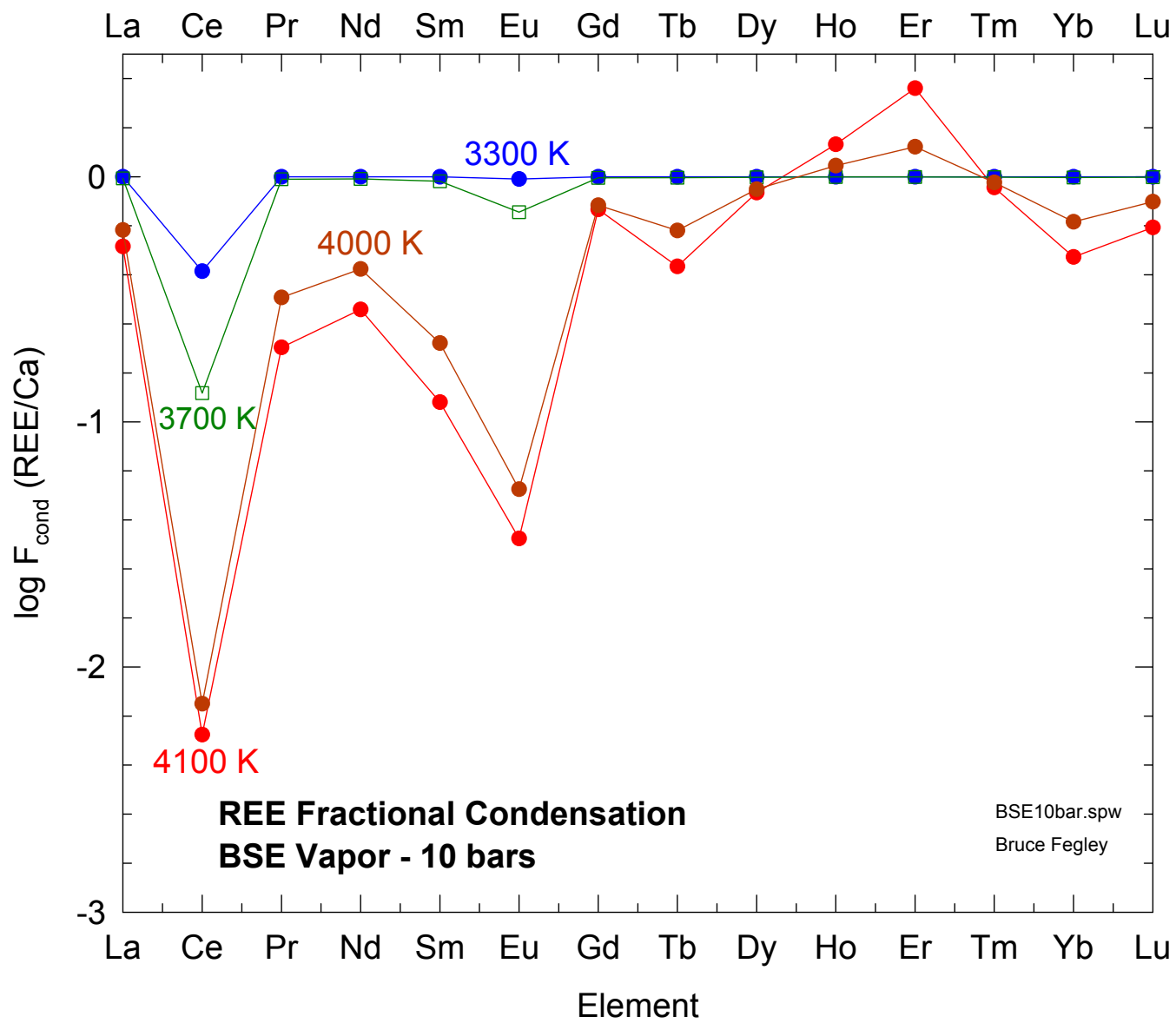
FIG. 8. Trace-element abundances in four HAL-type inclusions show distinctive Ce depletions. Ytterbium is also depleted in all four inclusions, while Pr and Eu are depleted in DH-H1, 7-404, and 7-971. REEs in HAL and DH-H1 are fractionated according to ionic radius, with depleted HREEs indicating melt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



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

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



$f\text{O}_2$ and Th/U Fractionation

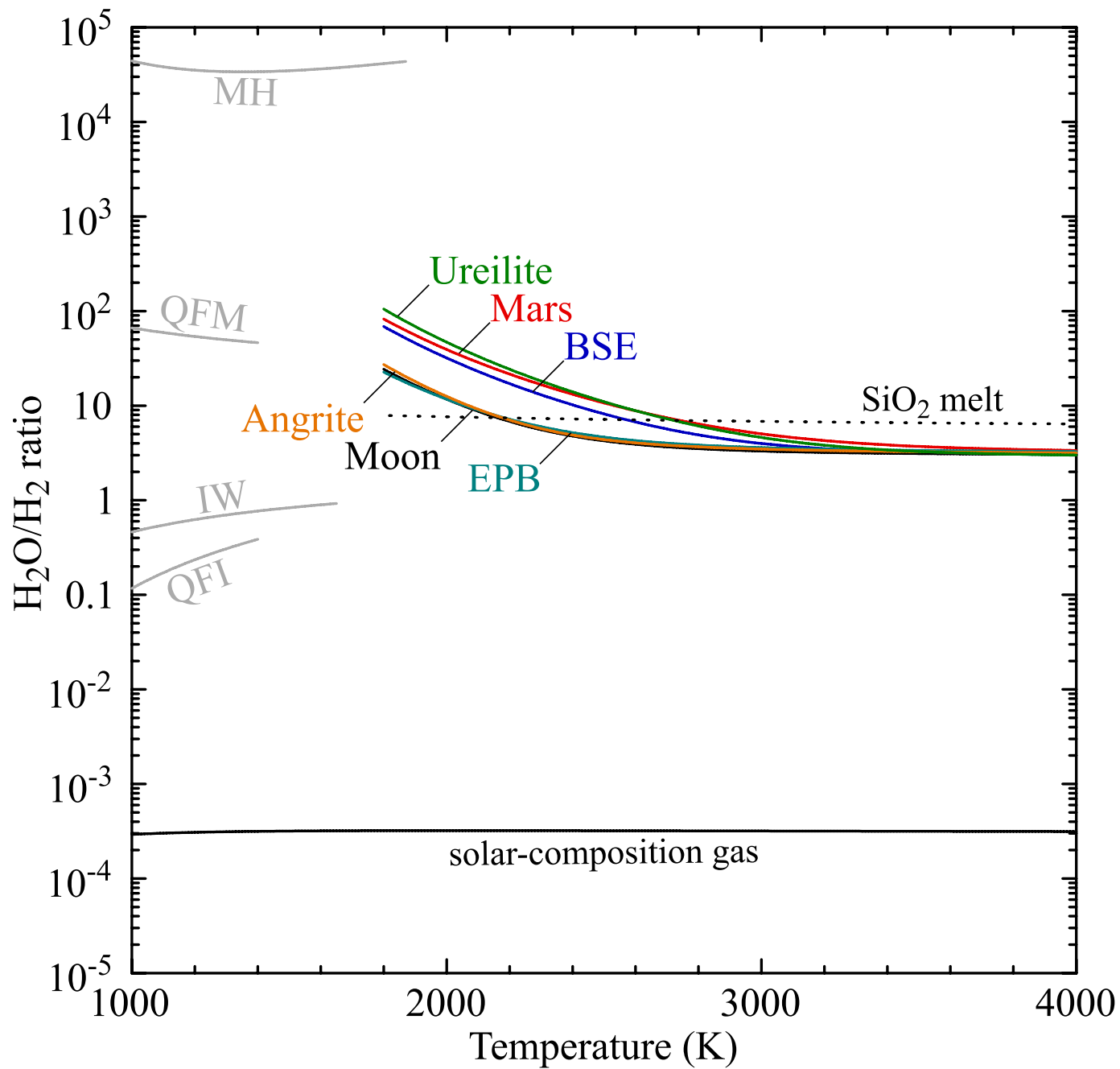
- UO_3 (gas) \leftarrow UO_2 (melt) + $\frac{1}{2}$ O_2 (gas)
- **Higher $f\text{O}_2$ makes Uranium more volatile**
- ThO (gas) + $\frac{1}{2}$ O_2 (gas) \rightarrow ThO_2 (melt)
- **Higher $f\text{O}_2$ makes Thorium more refractory**
- BSE-normalized atomic Th/U \sim 2.4 at 3300 K, 10 bars BSE vapor (should be unity if unfractionated from BSE model composition)

$f\text{O}_2$ and W/Hf Fractionation

- **Higher $f\text{O}_2$ makes W more volatile**
Fegley & Palme 1985 EPSL 72, 311-326
- WO_3 (gas) \leftarrow W (metal) + $3/2$ O_2 (gas)
- **Higher $f\text{O}_2$ makes Hf more refractory**
Fegley et al 2012 Bull Am Astron Soc 44, #301.01
- HfO (gas) + $1/2$ 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 $\ll 1$ 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



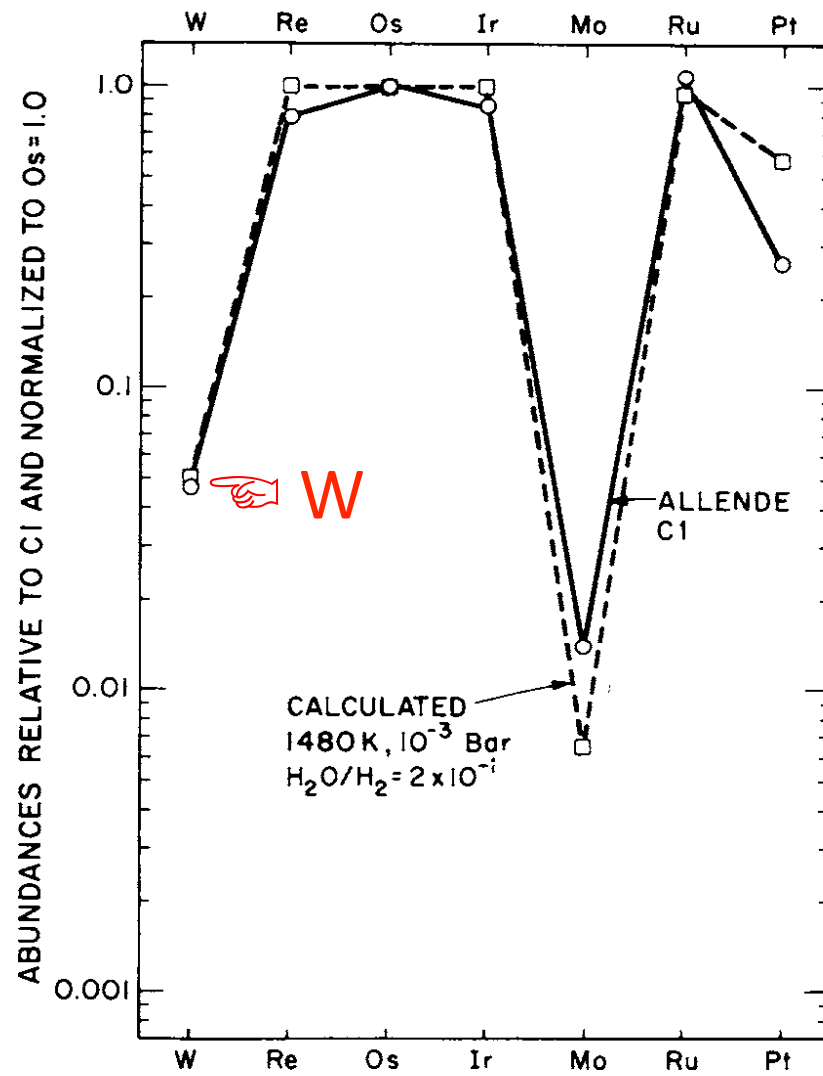
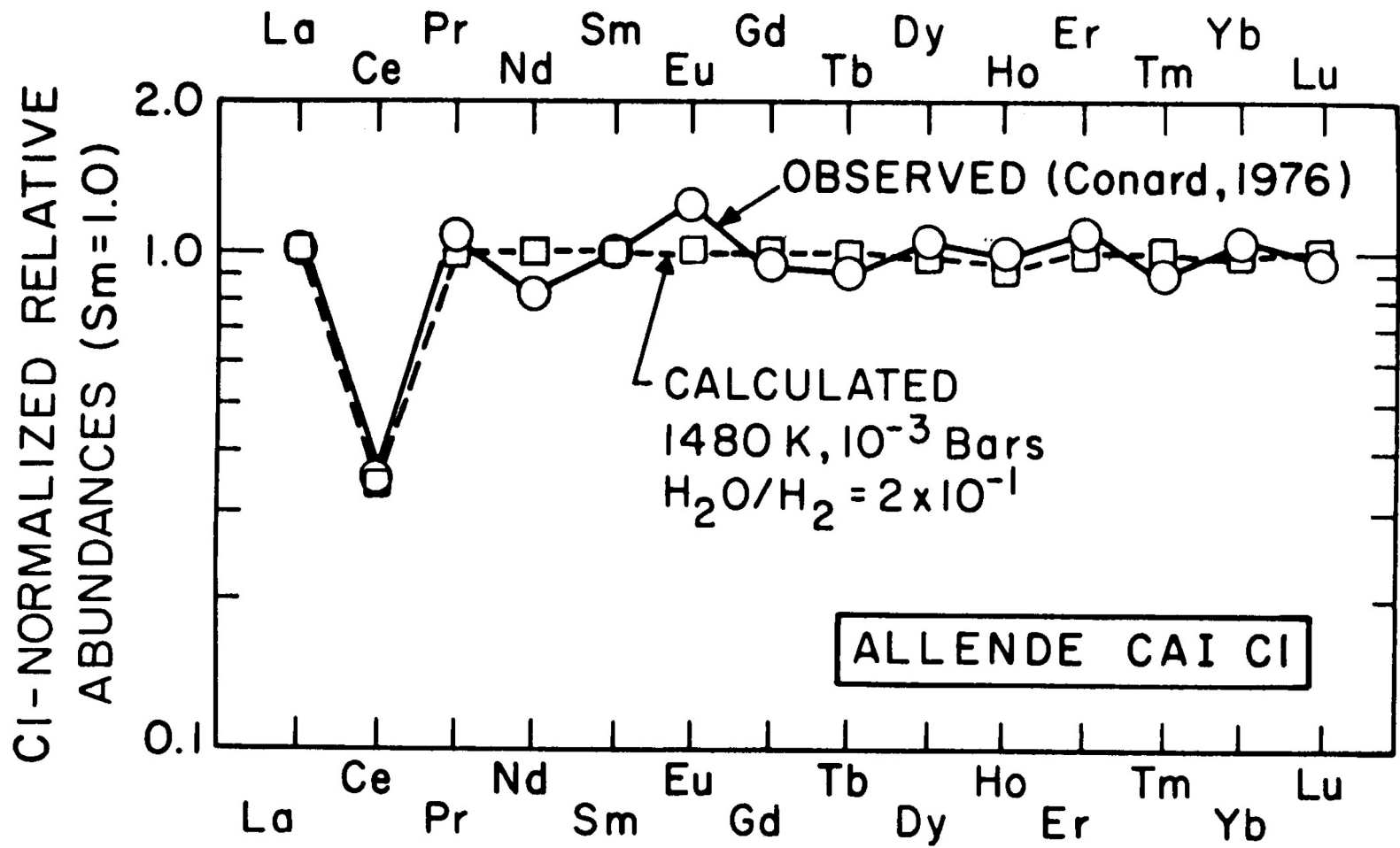


Fig. 7.7.4. Observed and calculated refractory-metal abundances in Allende FUN inclusion C1. The observed composition is from EDS/SEM analyses of metal grains by D. A. Wark.



Lu/Hf Fractionation

- Hf – more refractory than Lu at high fO_2
- $HfO/Hf \sim 772,000$ vs $LuO/Lu \sim 23,000$
- At 3300 K and 10 bars BSE vapor
- $2 LuO (gas) + \frac{1}{2} O_2 (gas) \rightarrow Lu_2O_3 (melt)$
- $HfO (gas) + \frac{1}{2} O_2 (gas) \rightarrow HfO_2 (melt)$
- Higher fO_2 drives condensation reactions
- Much larger MO/M for Hf makes it more refractory than Lu

Rb/Sr Fractionation

- Higher f_{O_2} makes Rb *slightly* more refractory
- Rb/RbO ~ 2.7 vs Sr/SrO ~ 0.07 – gas phase
- At 3300 K, 10 bars BSE vapor
- $2 \text{ Rb (gas)} + \frac{1}{2} \text{ O}_2 \text{ (gas)} \rightarrow \text{Rb}_2\text{O (melt)}$
- But this reaction also occurs
- $2 \text{ RbO} \leftarrow \text{Rb}_2\text{O (melt)} + \frac{1}{2} \text{ O}_2 \text{ (gas)}$
- In contrast, no effect of f_{O_2} on
- SrO (gas) = SrO (melt)
- BSE-normalized Rb/Sr $\sim 10^{-3}$, 3300 K 10 bars

K/U Fractionation

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

Summary

- Unique trace element abundances produced by vaporization / condensation at high fO_2
- **Very Promising, can explain:**
- No Ce depletion in bulk silicate Moon
- Lunar Lu/Hf, Hf/W, Nd/Sm, Th/U \approx 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

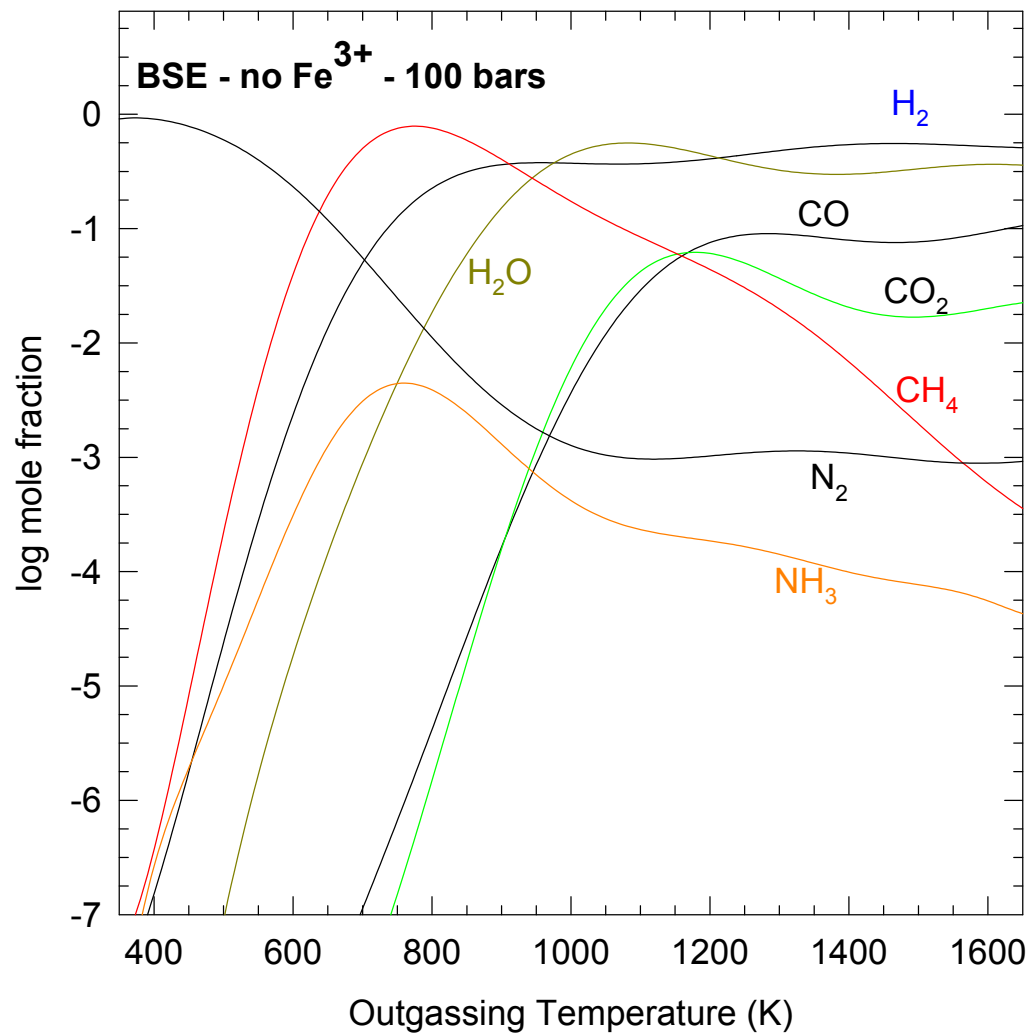
Summary - 2

- **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) Atmosphere
formation and
evolution on the
early Earth.

Summary -1

- Reducing gases produced by outgassing for most kinds of chondritic matter, e.g., CV, H, L, LL, EH, EL chondritic material
- Many Earth accretion models predict large amounts (70 – 85%) of EH-like material Dauphas, Lodders, Ringwood, Rubie, Wänke
- Late veneer plausibly also reducing – H, L, LL, EH, EL, e.g., see Palme & O'Neill 2014
- Outgassing of Fe³⁺-free BSE also gives reducing atmospheres
- Reducing atmosphere on Early Earth?



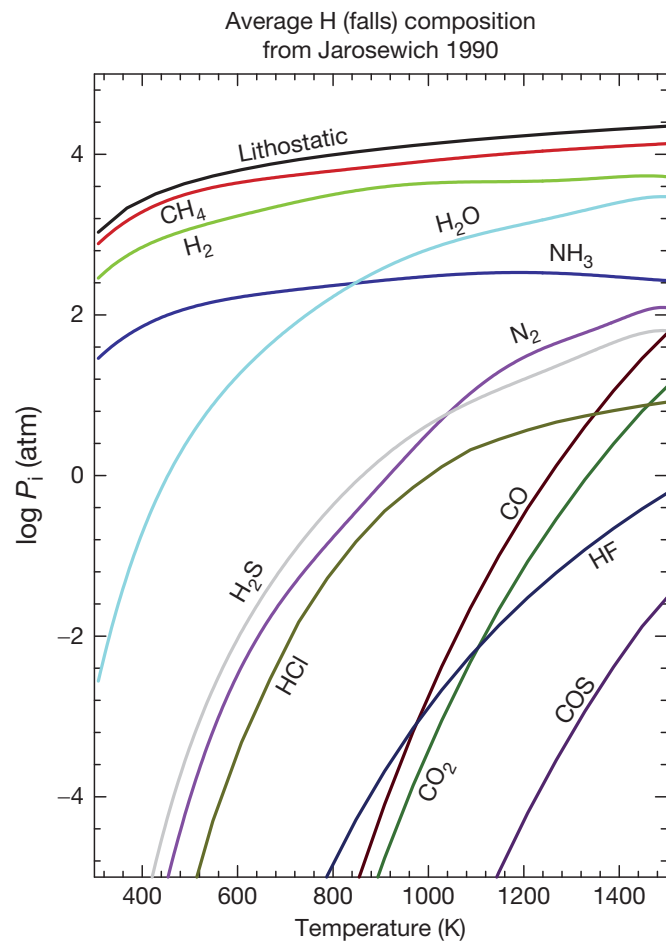


Figure 7 Chemical equilibrium abundances of gases produced by heating average H chondritic material along a terrestrial geotherm.

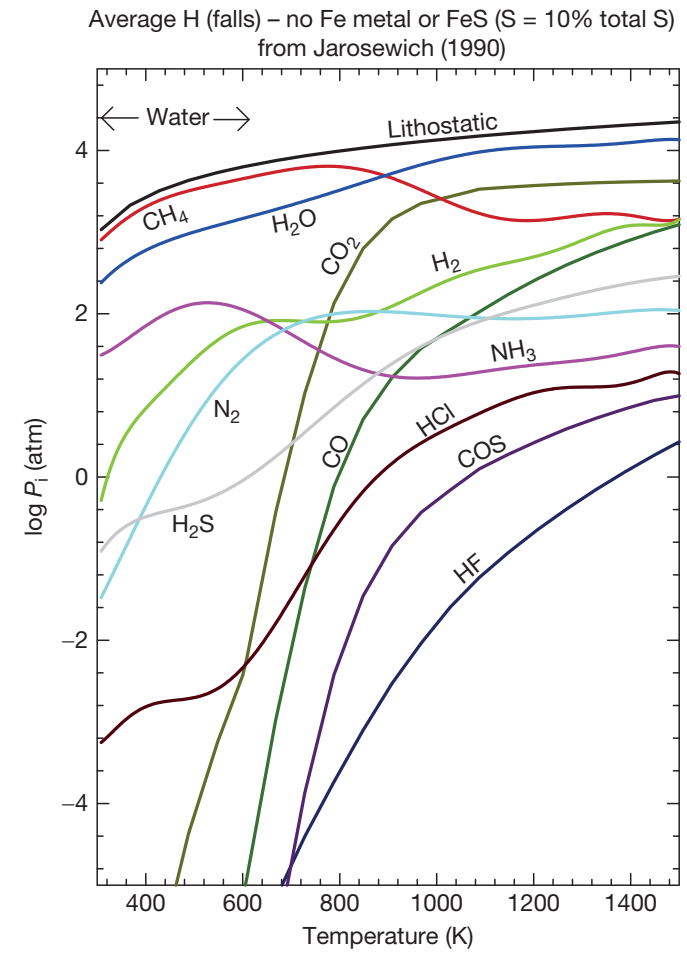
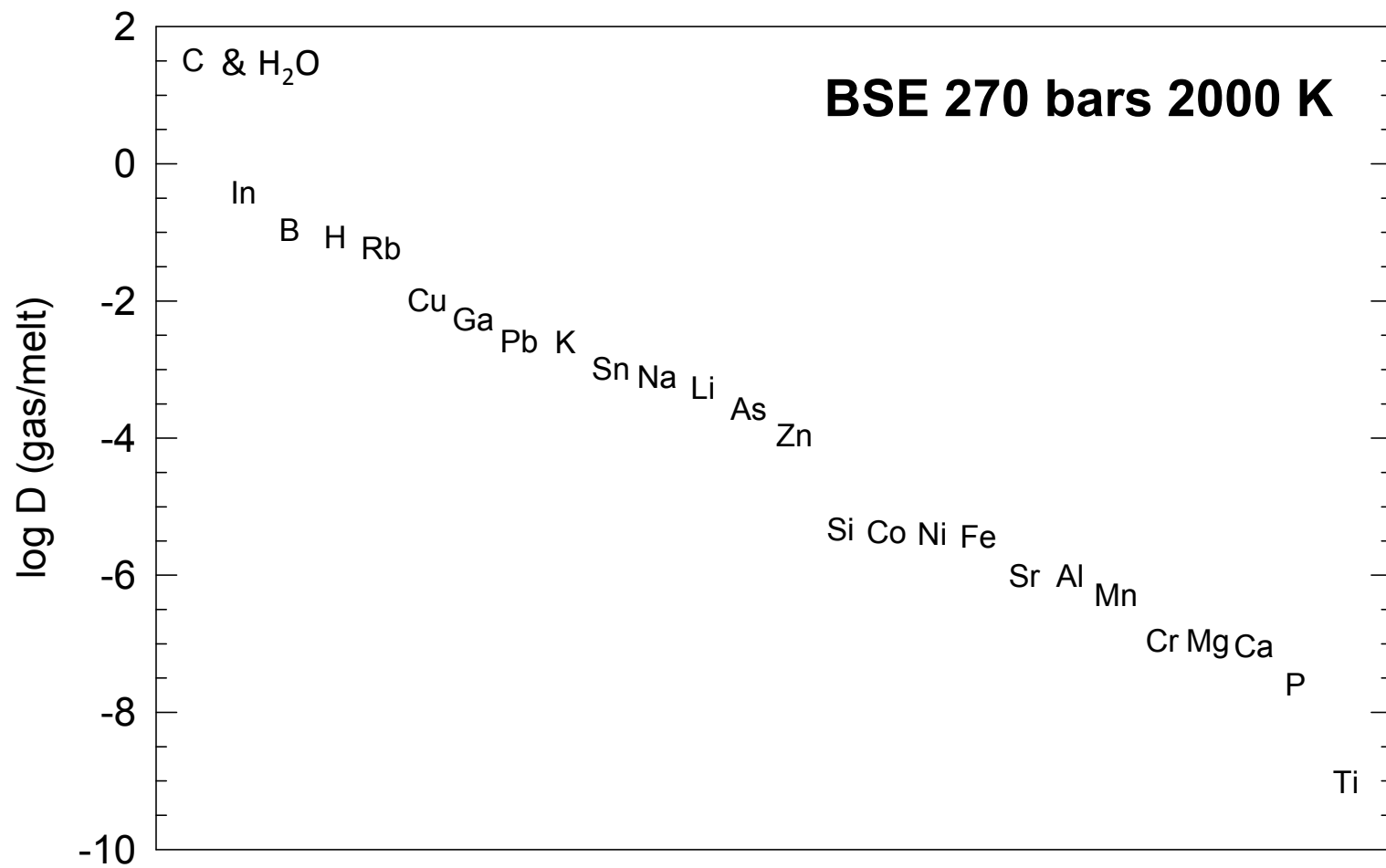


Figure 8 Same as in **Figure 7**, but after removal of all Fe metal and FeS before doing the computations.

Summary -2

- Steam atmosphere – magma ocean phase:
- Silicon and several other major rock-forming elements dissolve in steam
- Greatly different solubility for different elements (see next slide)
- If steam atmosphere is lost the steam soluble element inventory is changed



6.3 Chemistry of Earth's Earliest Atmosphere

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6.3.1 Introduction and Overview

In this chapter, we describe the chemistry of Earth's early atmosphere during and shortly after its formation where there is little, if any, geological record. Nevertheless, current thinking about the silicate vapor, steam, and gaseous stages of atmospheric evolution on the early Earth is potentially testable by spectroscopic observations of transiting rocky exoplanets. This assertion is supported by the rapid growth of extrasolar planetary astronomy, from the discovery of one extrasolar

ago (Harrison et al., 2005; Wilde et al., 2001). The metavolcanic and metasedimentary rocks from the Nuvvuagittuq (Porpoise Cove) greenstone belt near Hudson Bay in northern Quebec have a ^{146}Sm - ^{142}Nd isochron age of ~ 4280 Ma (O'Neil et al., 2009), which probably indicates that these rocks were derived from material extracted from Earth's mantle at that time (Arndt and Nisbet, 2012; O'Neil et al., 2009; Sleep, 2010). The oldest dated rock is the Acasta Gneiss in the Northwest Territories of Canada with an age of 4031 Ma (Bowring and Williams, 1999).

Secondary origin of Earth's atmosphere

- Not captured from the solar nebula (proto-planetary accretion disk)
- Formed by outgassing of solid & molten Earth material during & after accretion
- Supported by large noble gas depletions in observable parts (atm, oceans, crust, upper mantle) – Aston, H. Suess, H. Brown
- ^3He & other solar noble gases from mantle not primordial, due to solar wind implanted gases

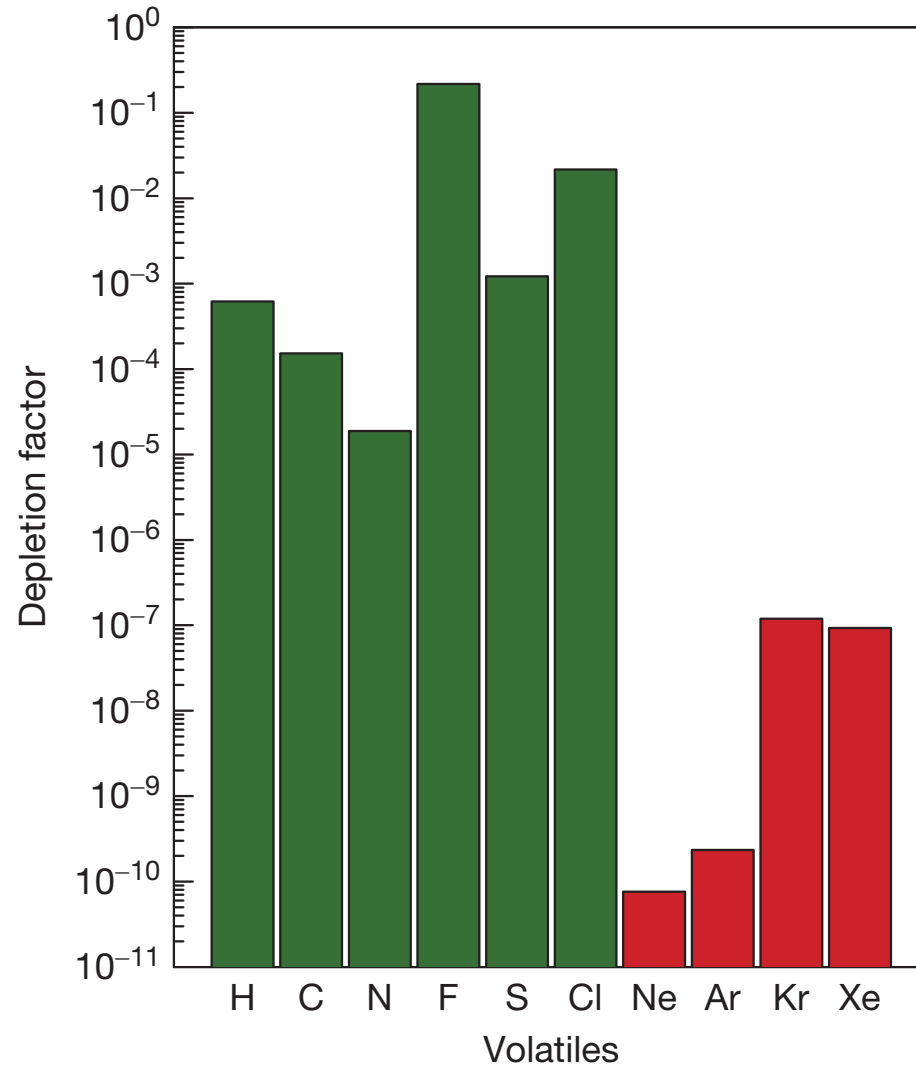


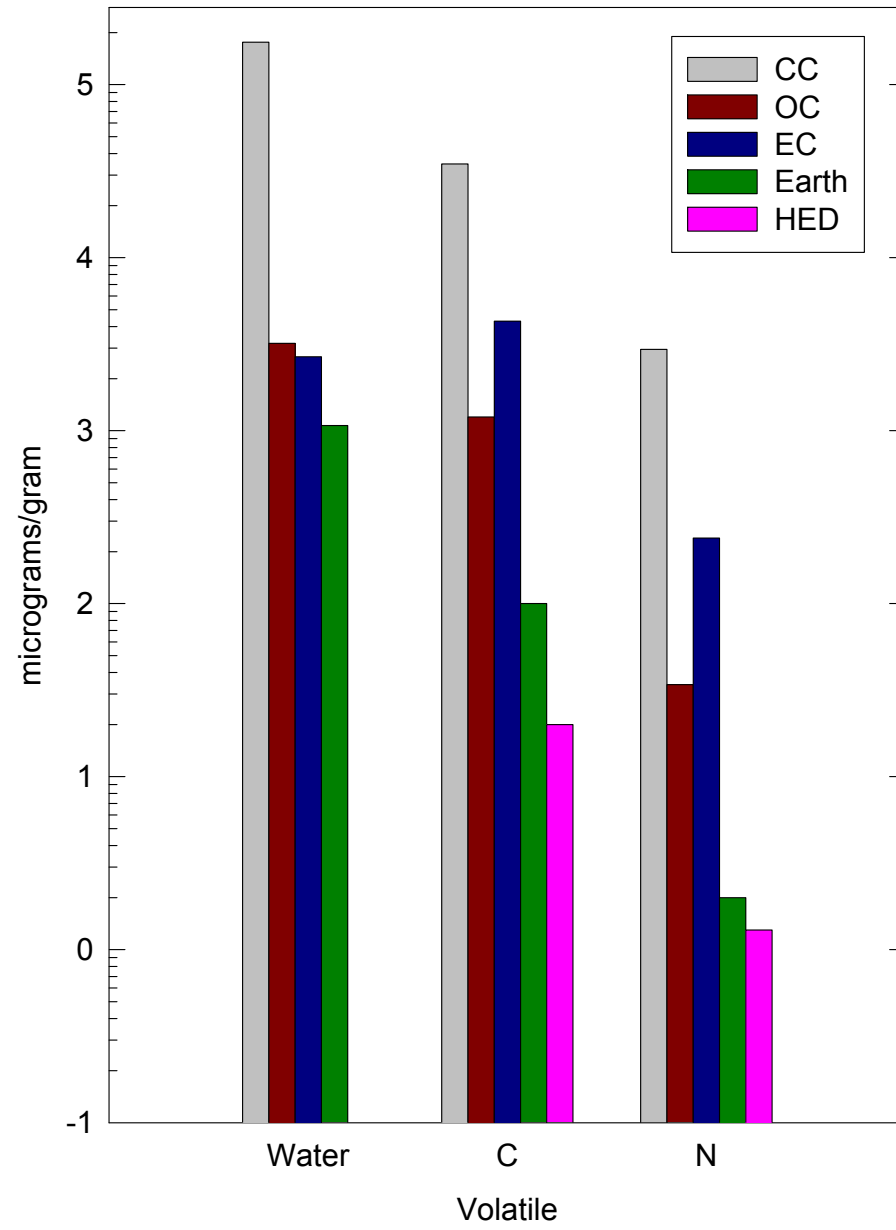
Figure 1 Depletion factors for inert gases and chemically reactive volatiles on Earth relative to their abundances in the solar nebula. See **Table 1** and the text for details.

Examples of Noble Gas Depletions

Ratio	Solar	Bulk Silicate Earth
Ne/N ₂	3.1	2.3×10^{-5}
³⁶⁺³⁸ Ar/S*	0.25	5×10^{-8}
³⁶⁺³⁸ Ar/Cl*	0.055	2×10^{-7}
*mass ratio		

Sources of Volatiles

- Earth accreted mixture of reduced & oxidized material from range of radial distance in solar nebula (e.g., models of Anders, J.S. Lewis, Lodders, Ringwood, Rubie, Wänke)
- Large % of Fe metal in the Earth requires large amounts of reduced material, e.g., 60-70% EH-chondritic like material
- Chondritic material good source of volatiles, achondritic material poor in volatiles



Outgassing Models

- What is being heated?
- ☞ (What was accreted to form the Earth)
- What is the volatile content of this stuff?
- How was it heated?
- ☞ (e.g., Open or closed system)
- How hot was it heated and to what pressure?
- Was equilibrium reached or not?
- Start with some simple models

Outgassing of chondritic material

- Look at a few examples of gaseous atmospheres produced by heating up and outgassing chondritic material (computer calculations)
- Show agreement of calculated and measured oxygen fugacity (fO_2) values for meteorites where measurements are available - ordinary chondrites (H, L, LL)

Outgassing of ordinary chondritic material and some of its implications for the chemistry of asteroids, planets, and satellites

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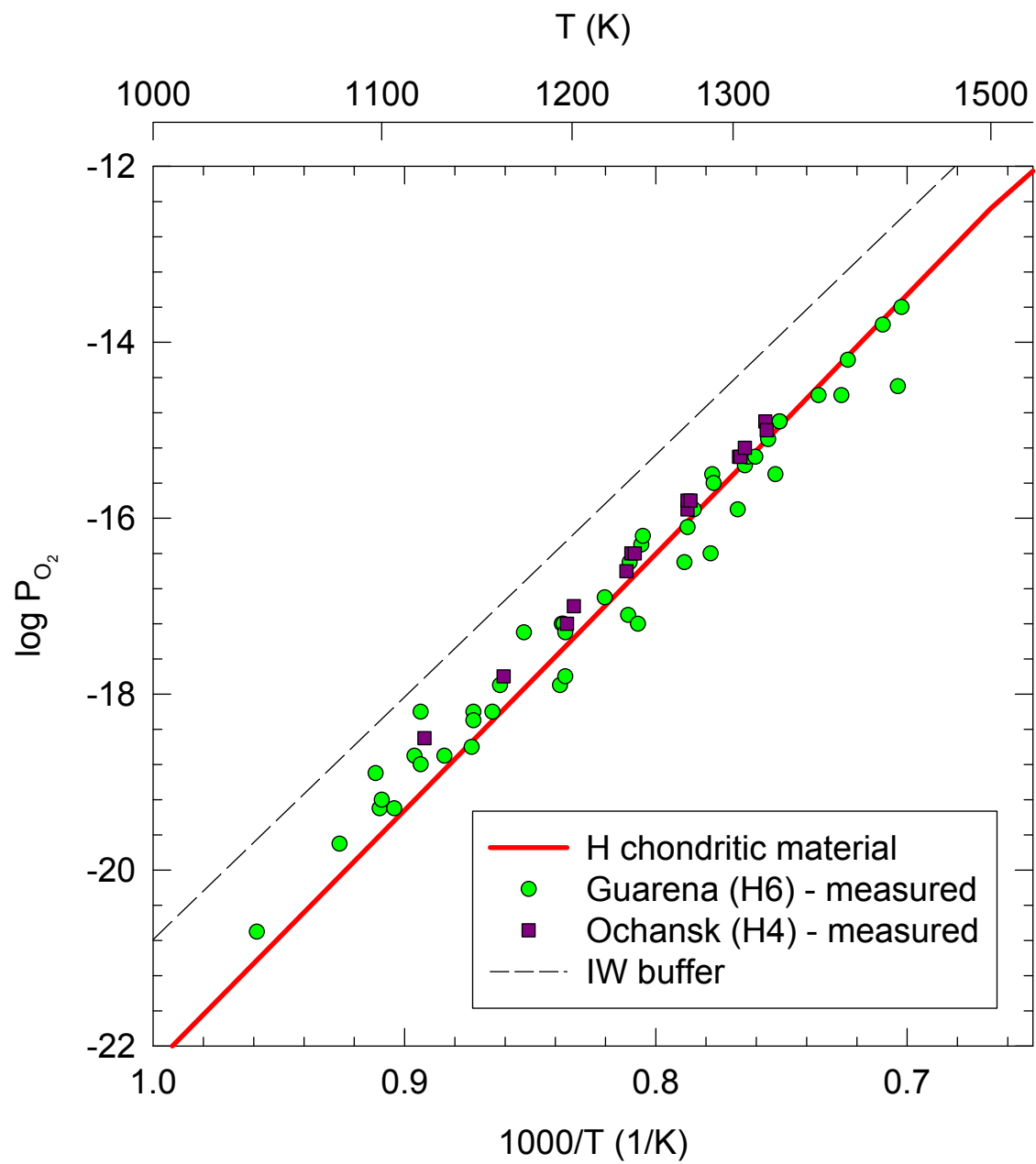
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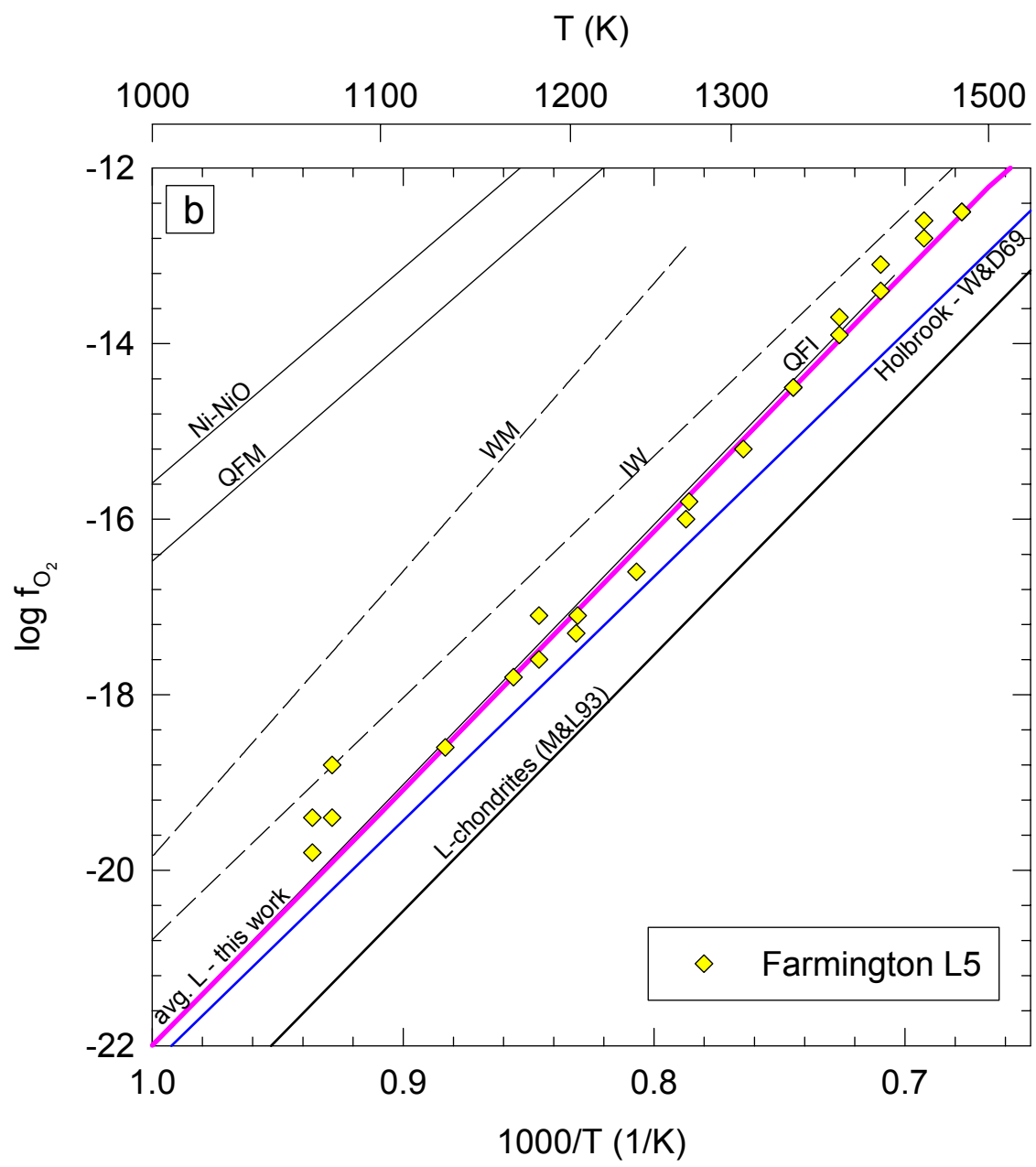
Abstract

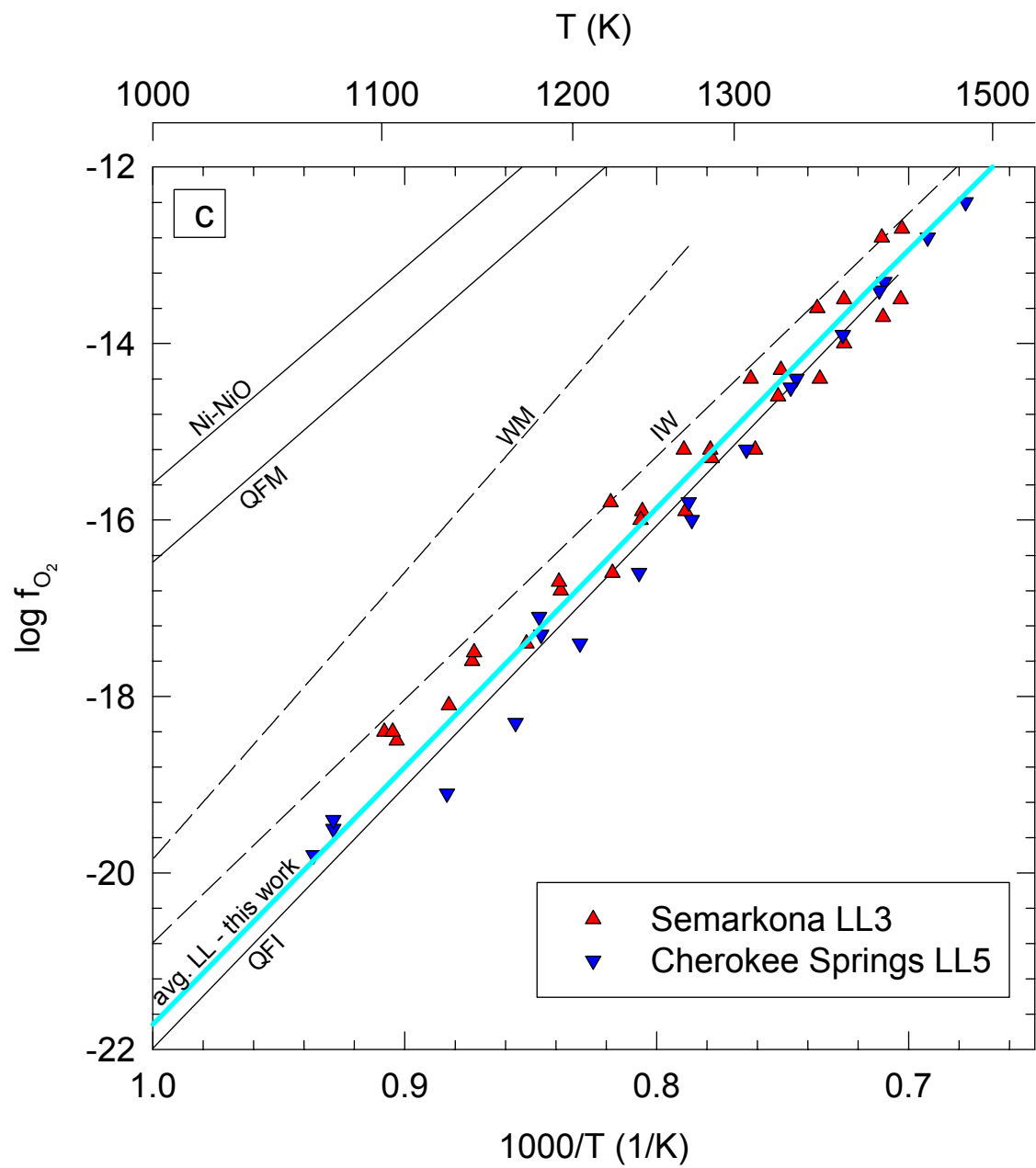
We used chemical equilibrium calculations to model thermal outgassing of ordinary chondritic material as a function of temperature, pressure, and bulk composition and use our results to discuss outgassing on asteroids and the early Earth. The calculations include ~1000 solids and gases of the elements Al, C, Ca, Cl, Co, Cr, F, Fe, H, K, Mg, Mn, N, Na, Ni, O, P, S, Si, and Ti. The major outgassed volatiles from ordinary chondritic material are CH₄, H₂, H₂O, N₂, and NH₃ (the latter at conditions where hydrous minerals form). Contrary to widely held assumptions, CO is never the major C-bearing gas during ordinary chondrite metamorphism. The calculated oxygen fugacity (partial pressure) of ordinary chondritic material is close to that of the quartz–fayalite–iron (QFI) buffer. Our results are insensitive to variable total pressure, variable volatile element abundances, and kinetic inhibition of C and N dissolution in Fe metal. Our results predict that Earth's early atmosphere contained CH₄, H₂, H₂O, N₂, and NH₃; similar to that used in Miller—Urey synthesis of organic compounds.

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Keywords: Atmospheres, evolution; Atmospheres, chemistry; Asteroids; Meteorites; Terrestrial planets; Satellites, atmospheres







Chemistry of atmospheres formed during accretion of the Earth and other terrestrial planets

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ABSTRACT

We used chemical equilibrium and chemical kinetic calculations to model chemistry of the volatiles released by heating different types of carbonaceous, ordinary and enstatite chondritic material as a function of temperature and pressure. Our results predict the composition of atmospheres formed by outgassing during accretion of the Earth and other terrestrial planets. Outgassing of *CI* and *CM* carbonaceous chondritic material produces H₂O-rich (steam) atmospheres in agreement with the results of impact experiments. However, outgassing of other types of chondritic material produces atmospheres dominated by other gases. Outgassing of ordinary (*H*, *L*, *LL*) and high iron enstatite (*EH*) chondritic material yields H₂-rich atmospheres with CO and H₂O being the second and third most abundant gases. Outgassing of low iron enstatite (*EL*) chondritic material gives a CO-rich atmosphere with H₂, CO₂, and H₂O being the next most abundant gases. Outgassing of *CV* carbonaceous chondritic material gives a CO₂-rich atmosphere with H₂O being the second most abundant gas. Our results predict that the atmospheres formed during accretion of the Earth and Mars were probably H₂-rich unless the accreted material was dominantly *CI* and *CM* carbonaceous chondritic material. We also predict significant amounts of S, P, Cl, F, Na, and K in accretionary atmospheres at high temperatures (1500–2500 K). Finally, our results may be useful for interpreting spectroscopic observations of accreting extrasolar terrestrial planets.

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

<i>Gas (vol. %)</i>	<i>CI</i>	<i>CM</i>	<i>CV</i>	<i>H</i>	<i>L</i>	<i>LL</i>	<i>EH</i>	<i>EL</i>
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H ₂ O	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 ₂ S	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.

Chemical Kinetics 1.

- H_2 , CO , CO_2 , H_2O are the four major gases in the 1500 K, 100 bar models
- Water gas reaction important for these
- $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$
- Compute chemical lifetime t_{chem} defined as
- $t_{\text{chem}} = [i]/d[i]/dt$ where $[i]$ = number density for plausible elementary reactions
- Elementary reactions are the reactions that actually take place in the reaction mechanism
- First, consider CO conversion to CO_2
- This can occur via the reaction

Chemical Kinetics 2.

- (1) $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$
- $\text{Log } k_1 = 3.94 \times 10^{-4}T - 12.95 \text{ cm}^3\text{s}^{-1}$
- $t_{\text{chem}}(\text{CO}) = (k_1[\text{OH}])^{-1}$
- [OH] from the chemical equilibrium calculations
- $t_{\text{chem}} \sim 0.03 - 0.4 \text{ seconds}$

Chemical Kinetics - 3

- Same procedure for another plausible elementary reaction
- (2) $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$
- $k_2 = 6.82 \times 10^{-12} (T/298)^{1.6} \exp(-9720/T) \text{ cm}^3\text{s}^{-1}$
- $t_{\text{chem}}(\text{H}_2\text{O}) = (k_2[\text{H}])^{-1}$
- $[\text{H}]$ from the chemical equilibrium calculations
- $t_{\text{chem}} \sim 0.01 - 0.17$ seconds

Chemical Kinetics - 4

- Temperature Dependence for $\text{CO} \rightarrow \text{CO}_2$

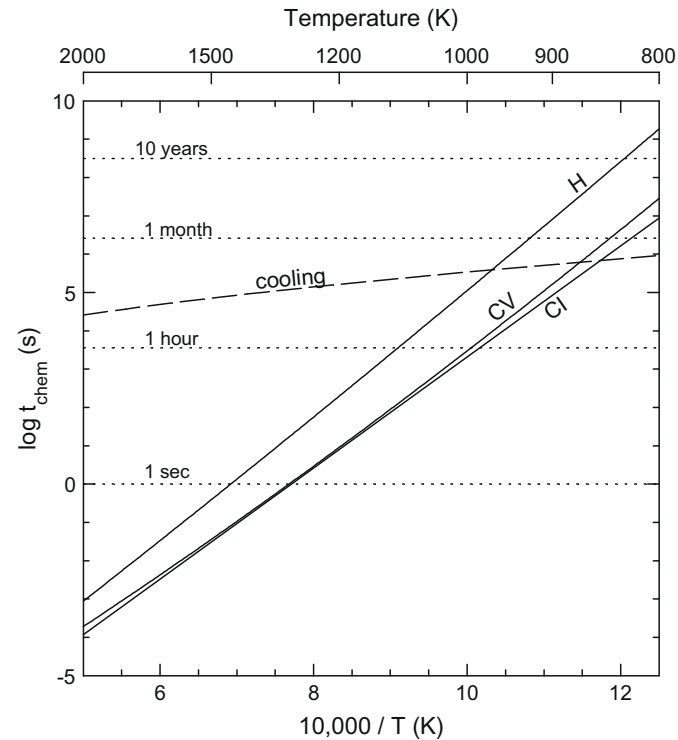


Fig. 7. The chemical lifetime for CO conversion to CO_2 in impact generated atmospheres from H, CV, and CI chondritic material. The curves for EH and EL or CM chondritic material are very similar to the curves for H or CI chondritic material, respectively.



Redox States of Initial Atmospheres Outgassed on Rocky Planets and Planetesimals

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Abstract

The Earth and other rocky planets and planetesimals in the solar system formed through the mixing of materials from various radial locations in the solar nebula. This primordial material likely had a range of oxidation states as well as bulk compositions and volatile abundances. We investigate the oxygen fugacity produced by the outgassing of mixtures of solid meteoritic material, which approximate the primitive nebular materials. We find that the gas composition and oxygen fugacity of binary and ternary mixtures of meteoritic materials vary depending on the proportion of reduced versus oxidized material, and also find that mixtures using differentiated materials do not show the same oxygen fugacity trends as those using similarly reduced but undifferentiated materials. We also find that simply mixing the gases produced by individual meteoritic materials together does not correctly reproduce the gas composition or oxygen fugacity of the binary and ternary mixtures. We provide tabulated fits for the oxygen fugacities of all of the individual materials and binary mixtures that we investigate. These values may be useful in planetary formation models, models of volatile transport on planetesimals or meteorite parent bodies, or models of trace element partitioning during metal-silicate fractionation.

Key words: meteorites, meteors, meteoroids – planets and satellites: atmospheres – planets and satellites: terrestrial planets

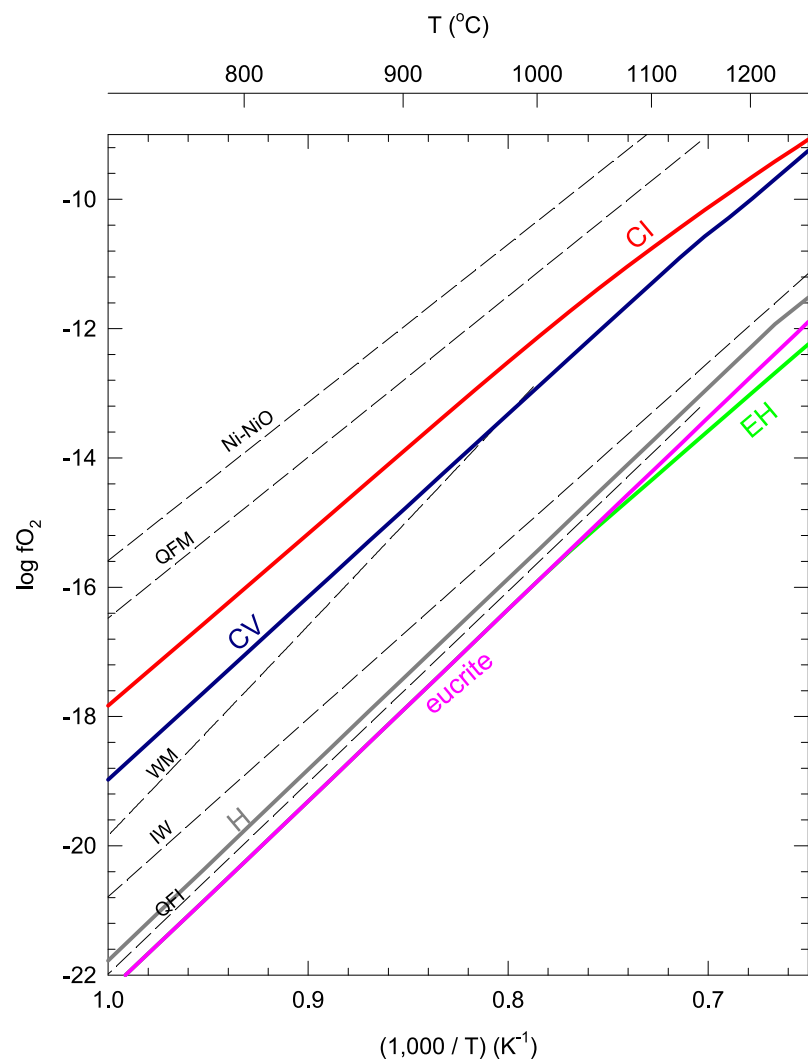


Figure 2. Oxygen fugacity of individual meteoritic components as a function of temperature compared with standard buffers. QFM = quartz–fayalite–magnetite, WM = wüstite–magnetite, IW = iron–wüstite, QFI = quartz–fayalite–iron. Meteoritic material compositions are given in Table 1 and the regressions for f_{O_2} of the meteoritic materials are given in Table 2.

6.3 Chemistry of Earth's Earliest Atmosphere

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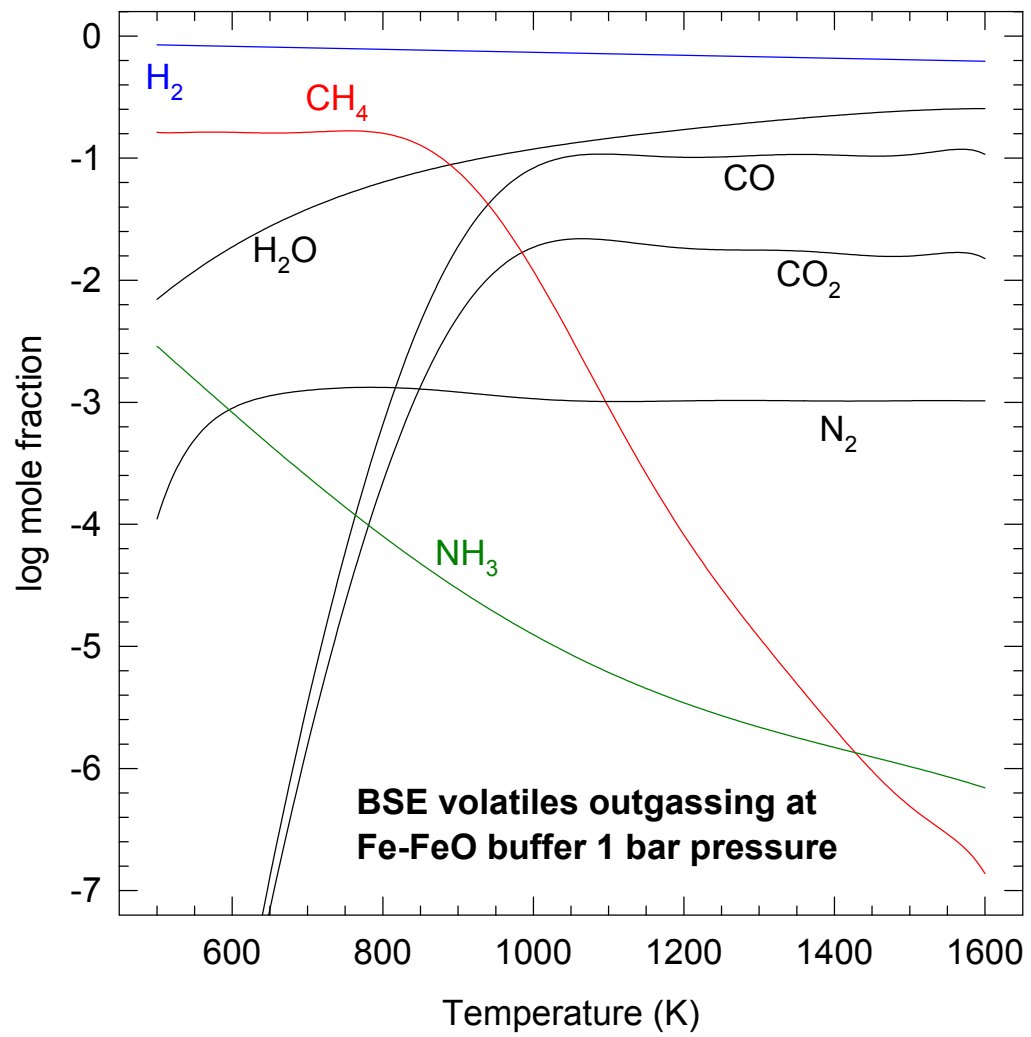
6.3.1 Introduction and Overview

In this chapter, we describe the chemistry of Earth's early atmosphere during and shortly after its formation where there is little, if any, geological record. Nevertheless, current thinking about the silicate vapor, steam, and gaseous stages of atmospheric evolution on the early Earth is potentially testable by spectroscopic observations of transiting rocky exoplanets. This assertion is supported by the rapid growth of extrasolar planetary astronomy, from the discovery of one extrasolar

ago (Harrison et al., 2005; Wilde et al., 2001). The metavolcanic and metasedimentary rocks from the Nuvvuagittuq (Porpoise Cove) greenstone belt near Hudson Bay in northern Quebec have a ^{146}Sm - ^{142}Nd isochron age of ~ 4280 Ma (O'Neil et al., 2009), which probably indicates that these rocks were derived from material extracted from Earth's mantle at that time (Arndt and Nisbet, 2012; O'Neil et al., 2009; Sleep, 2010). The oldest dated rock is the Acasta Gneiss in the Northwest Territories of Canada with an age of 4031 Ma (Bowring and Williams, 1999).

Implications for Atmospheric Chemistry

- Lower fO_2 leads to volcanic outgassing of reduced gases such as H_2 , CH_4 , and NH_3
- (1) Calculations at fixed fO_2 of Fe-FeO buffer with BSE abundances for volatiles – show this example next
- (2) Calculations using Fe^{3+} -free BSE: MgO, SiO_2 , FeO, CaO, Al_2O_3 , Na_2O , K_2O , TiO_2 , Cr_2O_3 , MnO, NiO, etc. but without the few % Fe^{3+} in upper mantle – produces graphite at low T

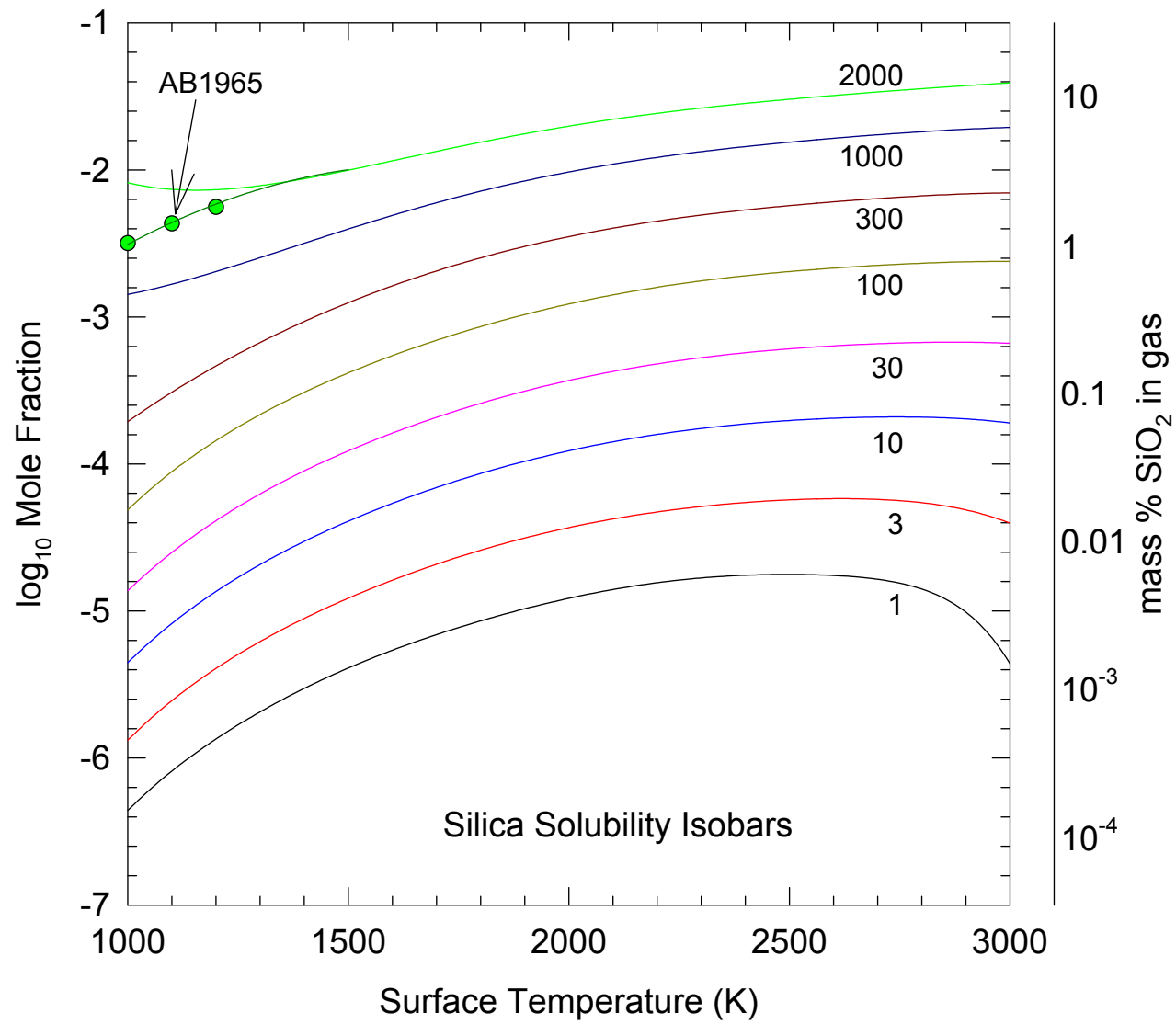


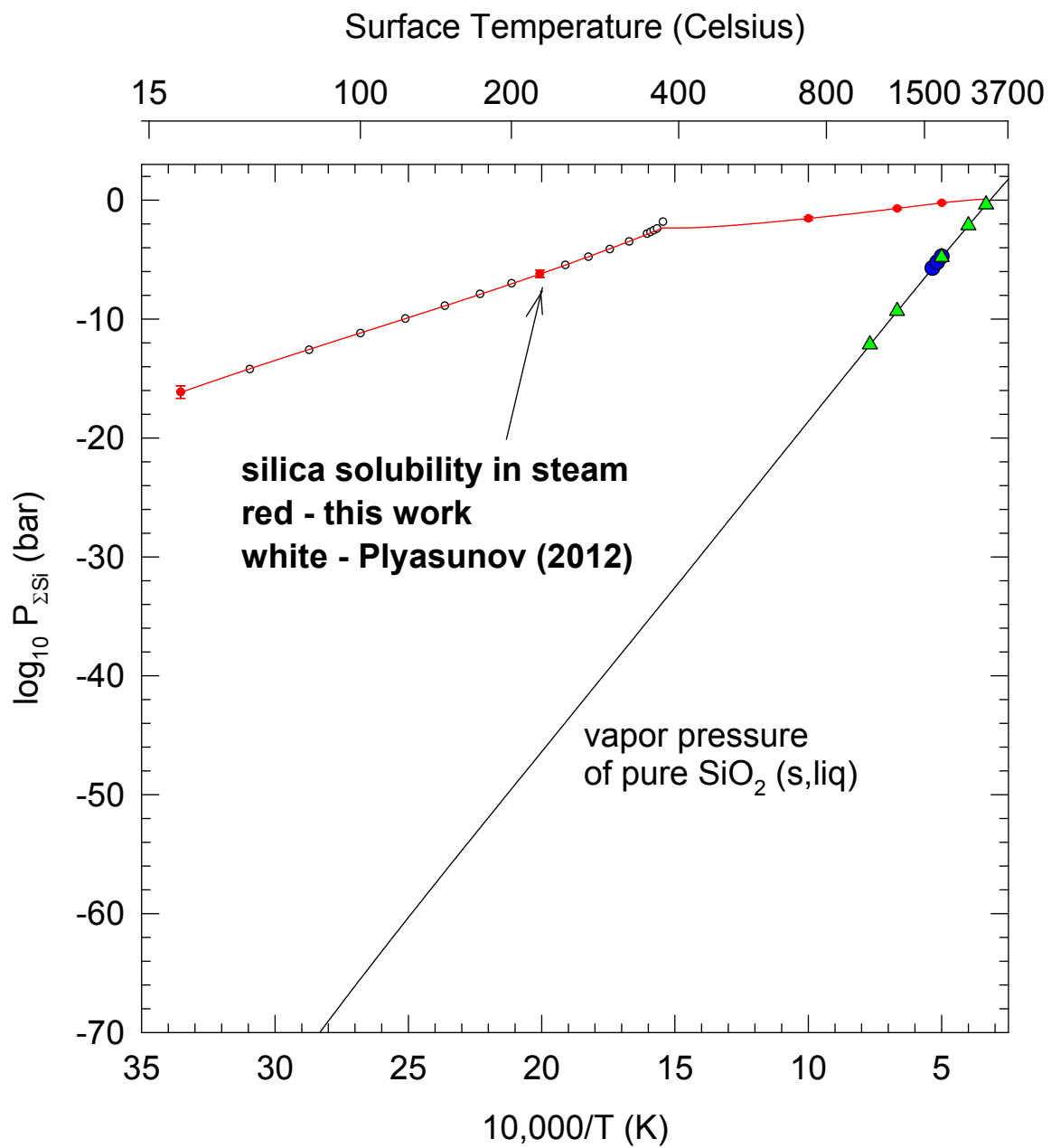
Outgassing of Chondritic Material

- Ordinary & enstatite chondritic material produces CH₄-bearing & CH₄-rich atmospheres
- CI and CM carbonaceous chondritic material produces CO₂-bearing & CO₂-rich atmospheres

Steam Atmosphere

- Impact-induced outgassing of H₂O and other volatiles (e.g., Arrhenius et al 1974, Lange & Ahrens 1982, Abe & Matsui 1985, 1987)
- Interesting aspect is solubility of SiO₂ and other rock-forming oxides in steam
- Two examples on next slides

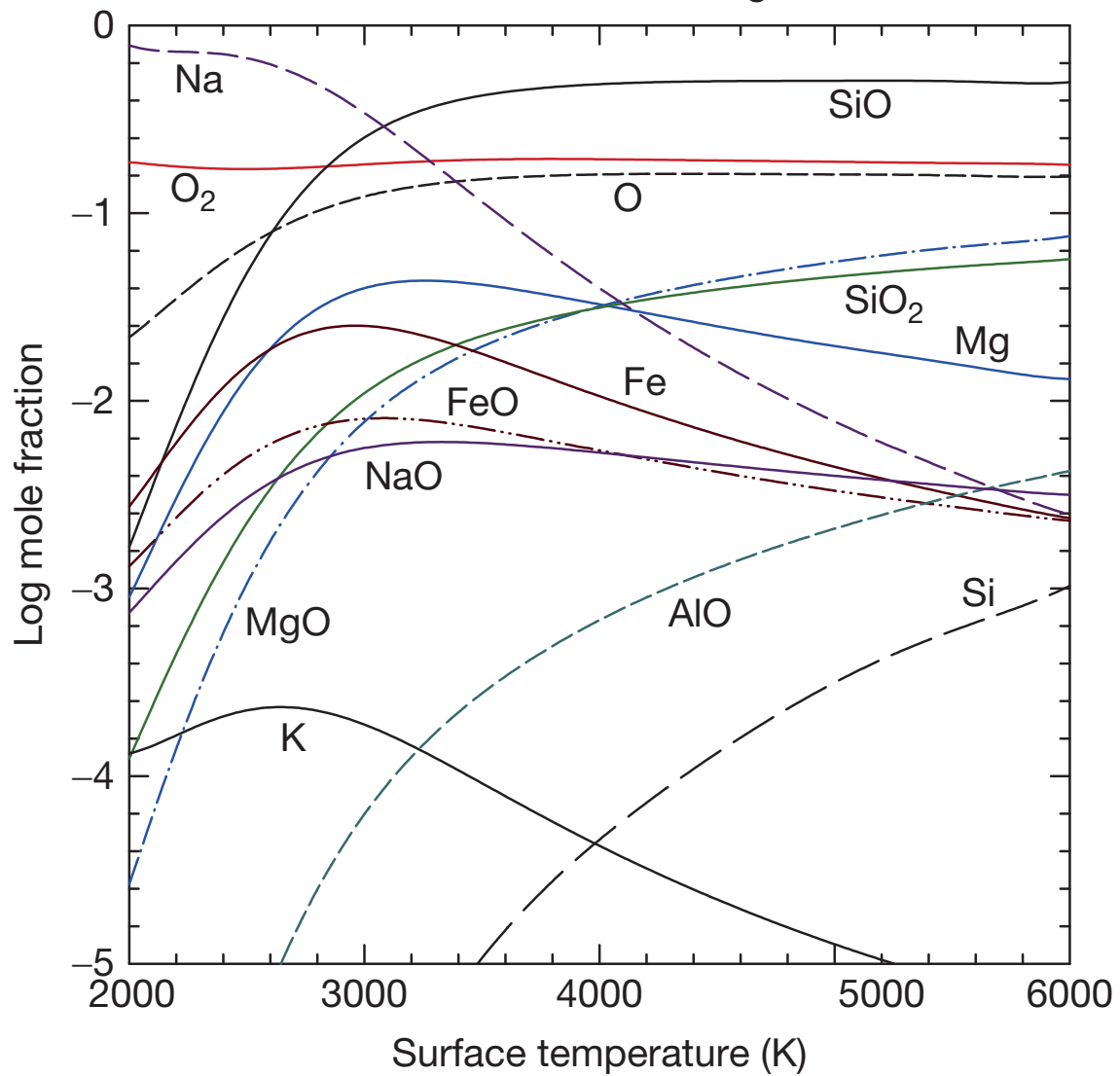




Silicate vapor atmosphere

- High temperatures during Earth's accretion can lead to silicate vapor atmosphere
- Dry molten silicate vapor atmosphere (BSE composition) in next slide
- Applied to hot rocky exoplanets such as CoRoT-7b, Kepler-10b

Composition of saturated vapor
bulk silicate earth magma



Comparison to other results

- Canup et al 2015 Nat GeoSci 8, 918-921
- Higher Temperatures than our results
- Wang & Jacobsen 2016 Nature 538, 487-490
- Preliminary results suggest we are consistent

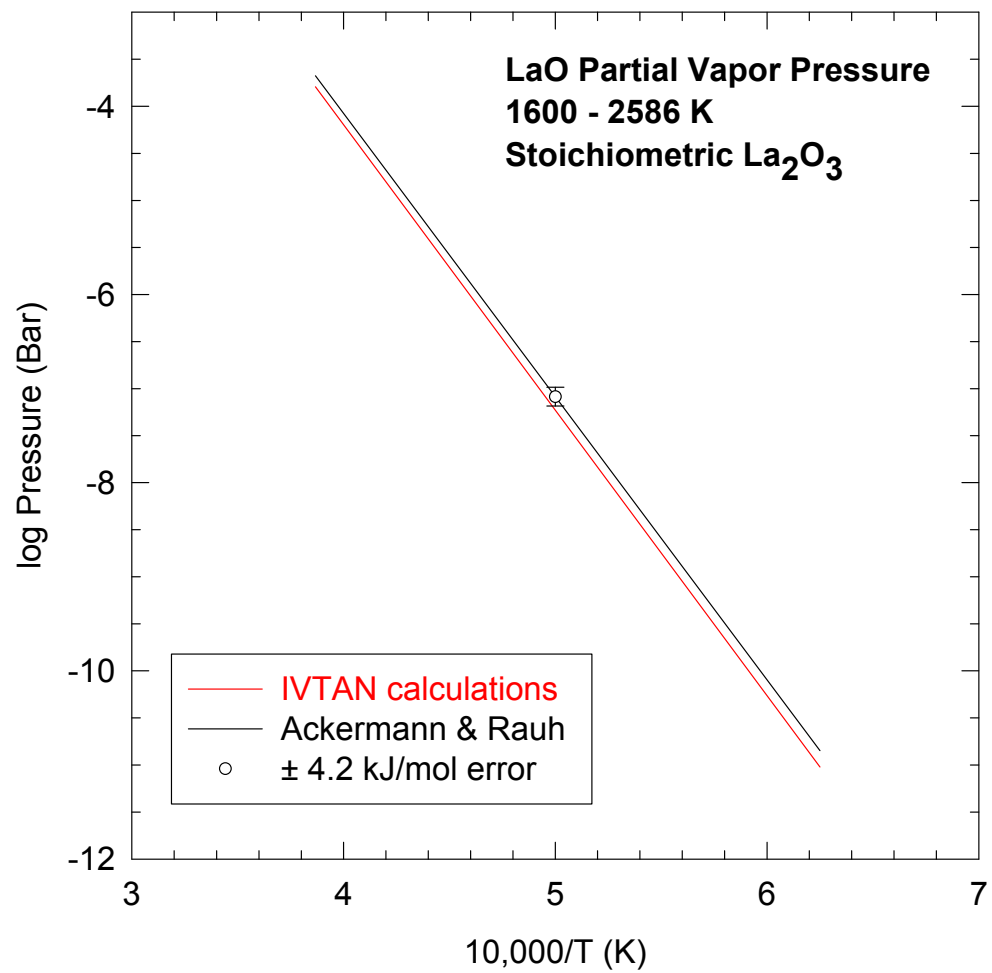
BSE & BSM Element Ratios

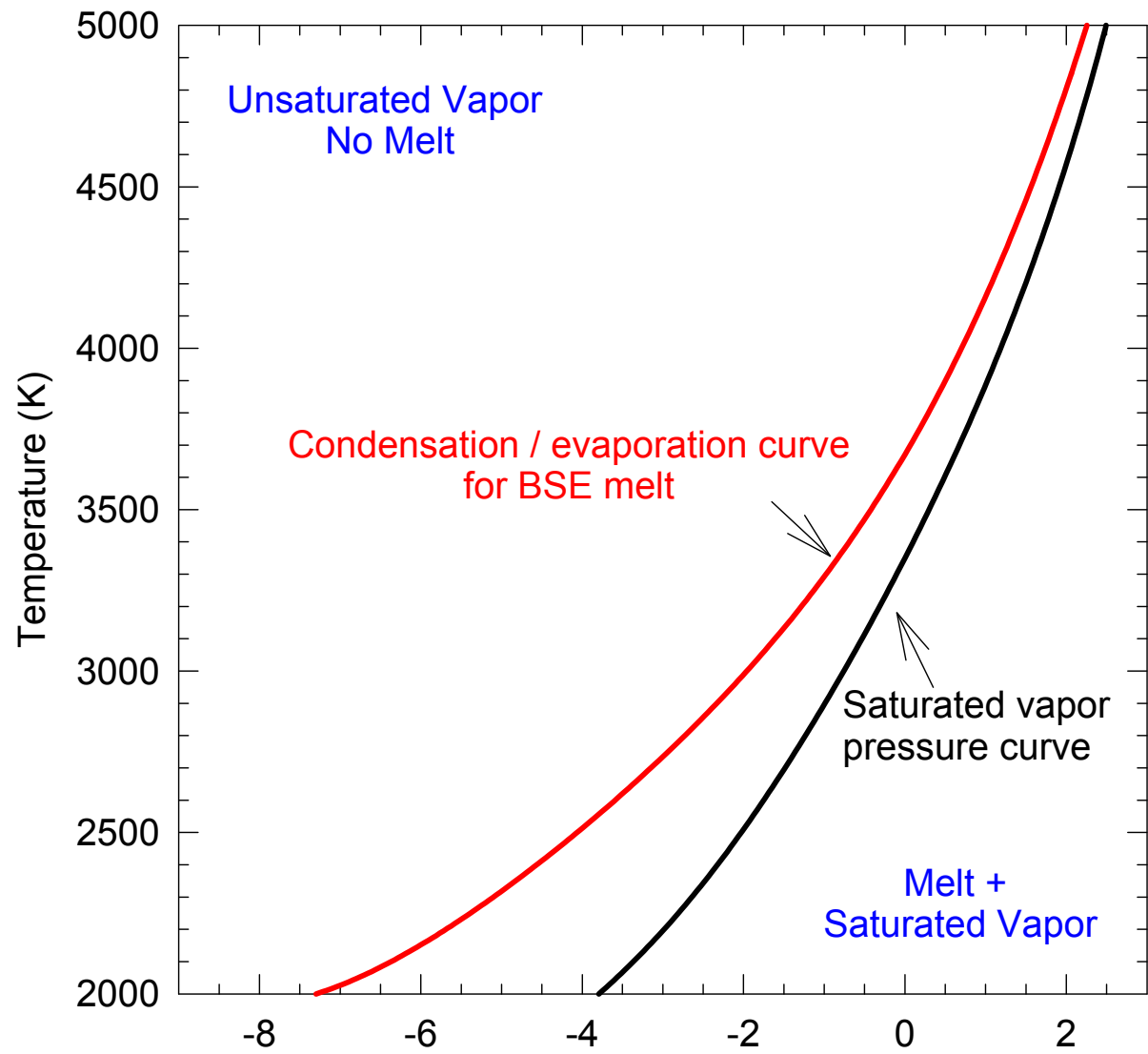
Ratio	Bulk Silicate Earth*	Bulk Silicate Moon*
K/U	32,100	2,050
Rb/Sr	0.0275	0.007
Hf/W	25.1	21.4
Th/U	3.71	3.50

*BSE - Palme & O'Neill 2014; BSM – Warren 2005, O'Neill 2001

Relative size of ΔG° Contributions

- ΔG° for condensation $>$ ΔG° from activity coefficient
- Use La_2O_3 as an example
- $2 \text{LaO (gas)} + \frac{1}{2} \text{O}_2 \text{(gas)} = \text{La}_2\text{O}_3 \text{(melt)}$
- ΔG° (2600 K) – 1,330 kJ/mol
- ΔG° from activity coefficient $\gamma = -RT \ln \gamma$
- FACTSAGE γ values (2600 K) for other M_2O_3 in BSE melt are $\sim 10^{-6}$ to 10^{-1}
- $RT \ln \gamma$ terms are 300 – 50 kJ/mol
- Measured γ values for R_2O_3 in solid solutions with ZrO_2 in 2600 – 2800 K range are $\sim 10^{-2}$



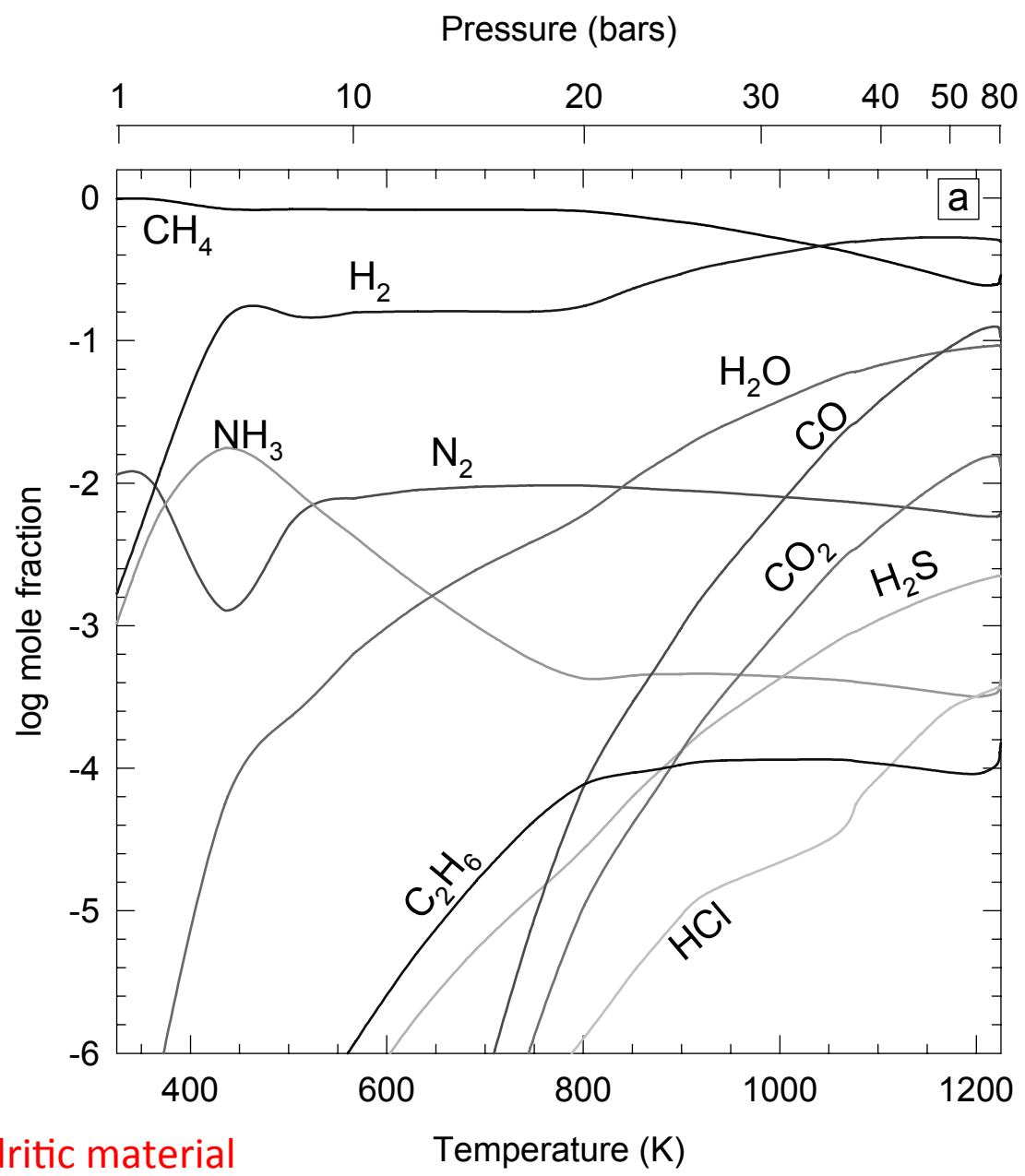


Exoplanet Observations

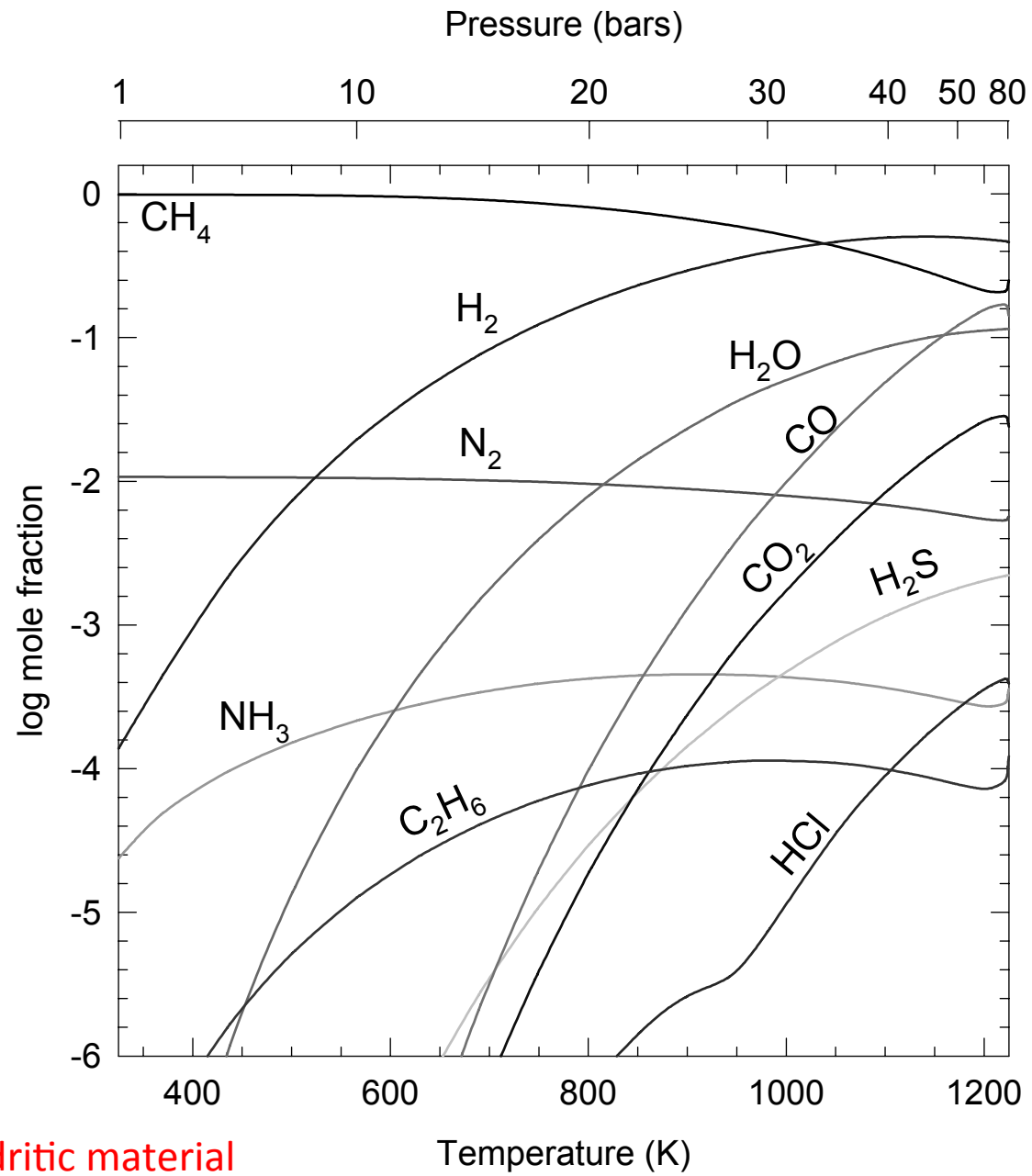
- Impossible to go back in time on Earth
- Eventually possible to observe atmospheres of rocky exoplanets that are in different evolutionary stages comparable to those postulated for the early Earth
- ExoPlanetary Time Machine to the Early Earth
- “Thus, ideas about Earth’s early atmosphere, which cannot be constrained by biological or geological evidence, may be indirectly constrained in the near future by astronomical observations.” Fegley & Schaefer 2014 TOG

Important Results

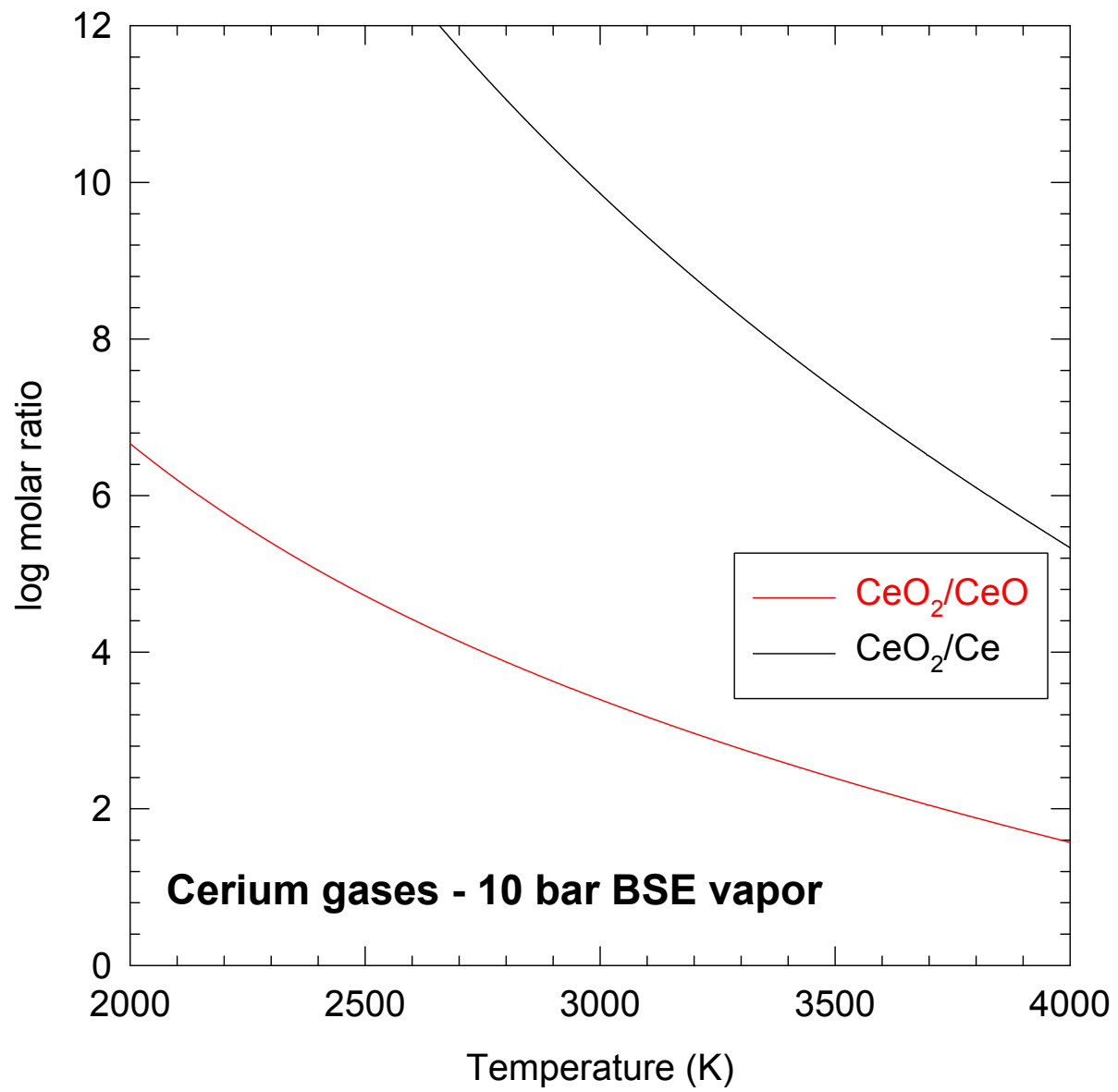
- Reducing atmospheres from most kinds of chondritic material, e.g., CV, H, L, LL, EH, EL



Average H-chondritic material



Average L-chondritic material



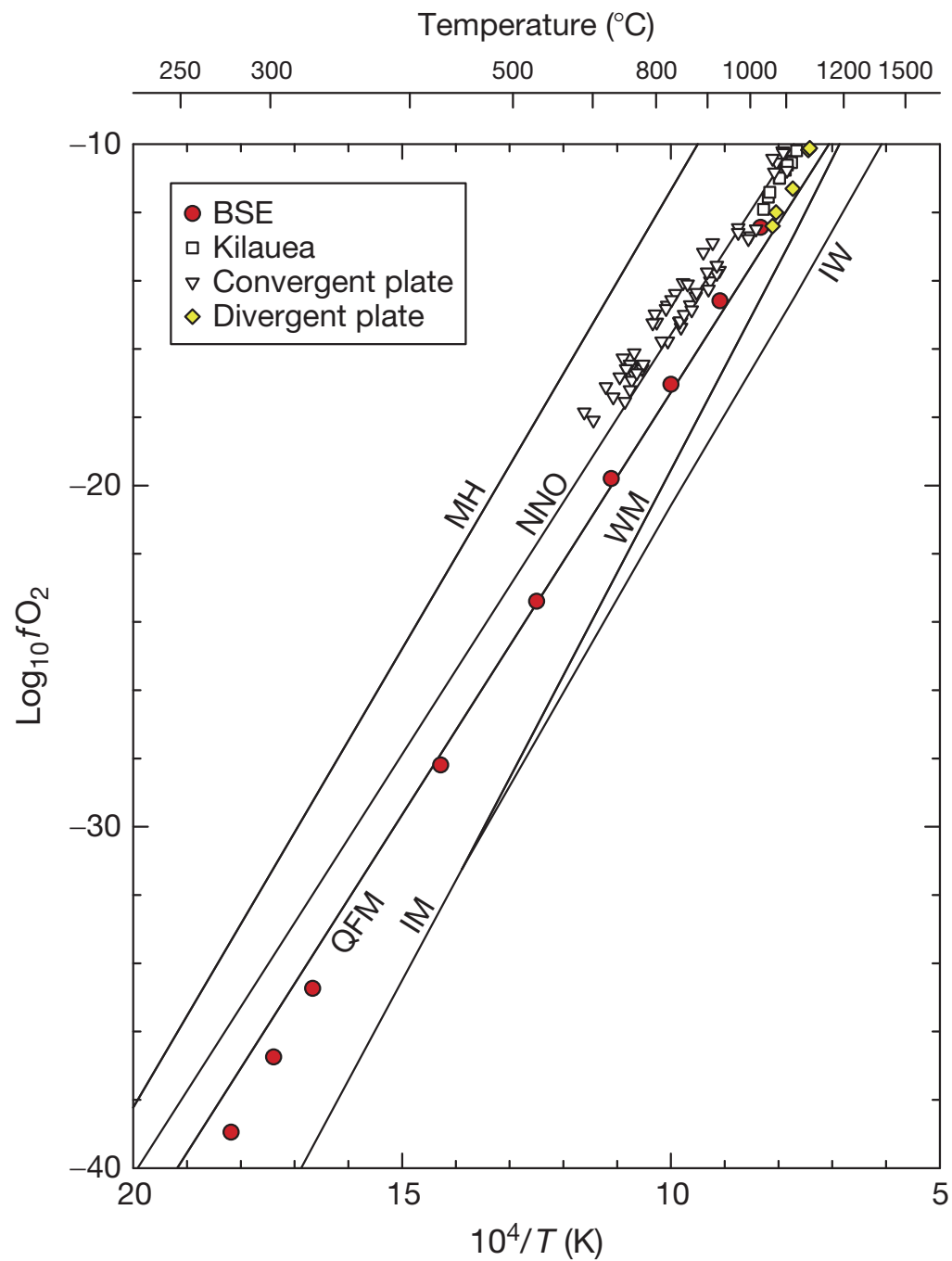


Figure 6 Temperature-dependent oxygen fugacities for modern day

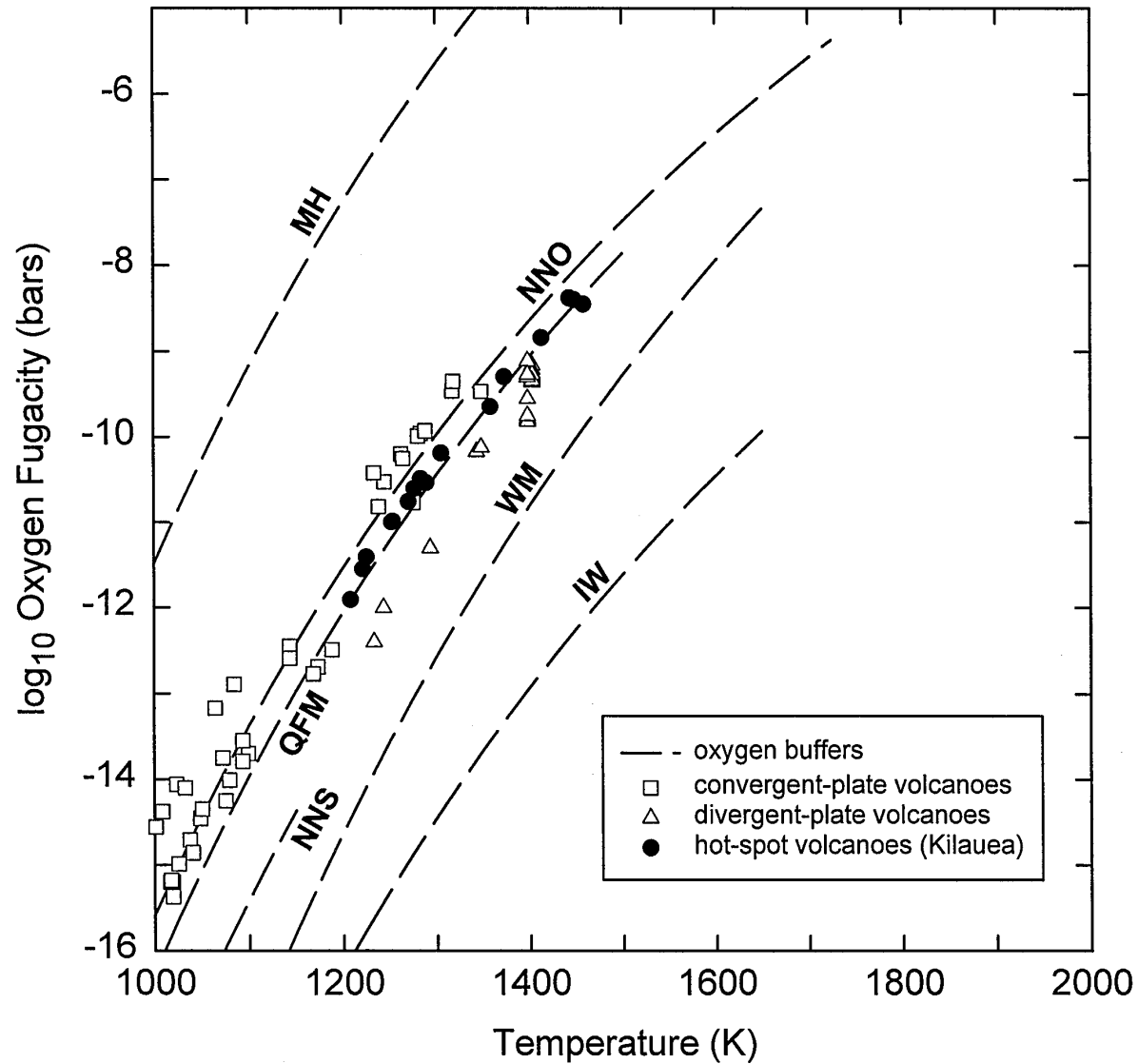


FIG. 10. The oxygen fugacities of terrestrial volcanic gases are plotted as a function of vent temperature. Mineral buffer f_{O_2} curves are shown for comparison. The calculated f_{O_2} values and vent temperatures for the volcanic gases are from Symonds *et al.* (1994).

Origin of the Moon and Origin of Life

- Accept Ringwood's arguments that Moon formed from Bulk Silicate Earth
- Lunar oxidation state = that of BSE at time of Moon-forming impact
- Significantly more reduced than BSE (~ IW versus ~ QFM)
- BSE became more oxidized at some later time
- Explicitly postulate this was AFTER the abiotic origin of life via Miller-Urey type reactions in a reduced atmosphere

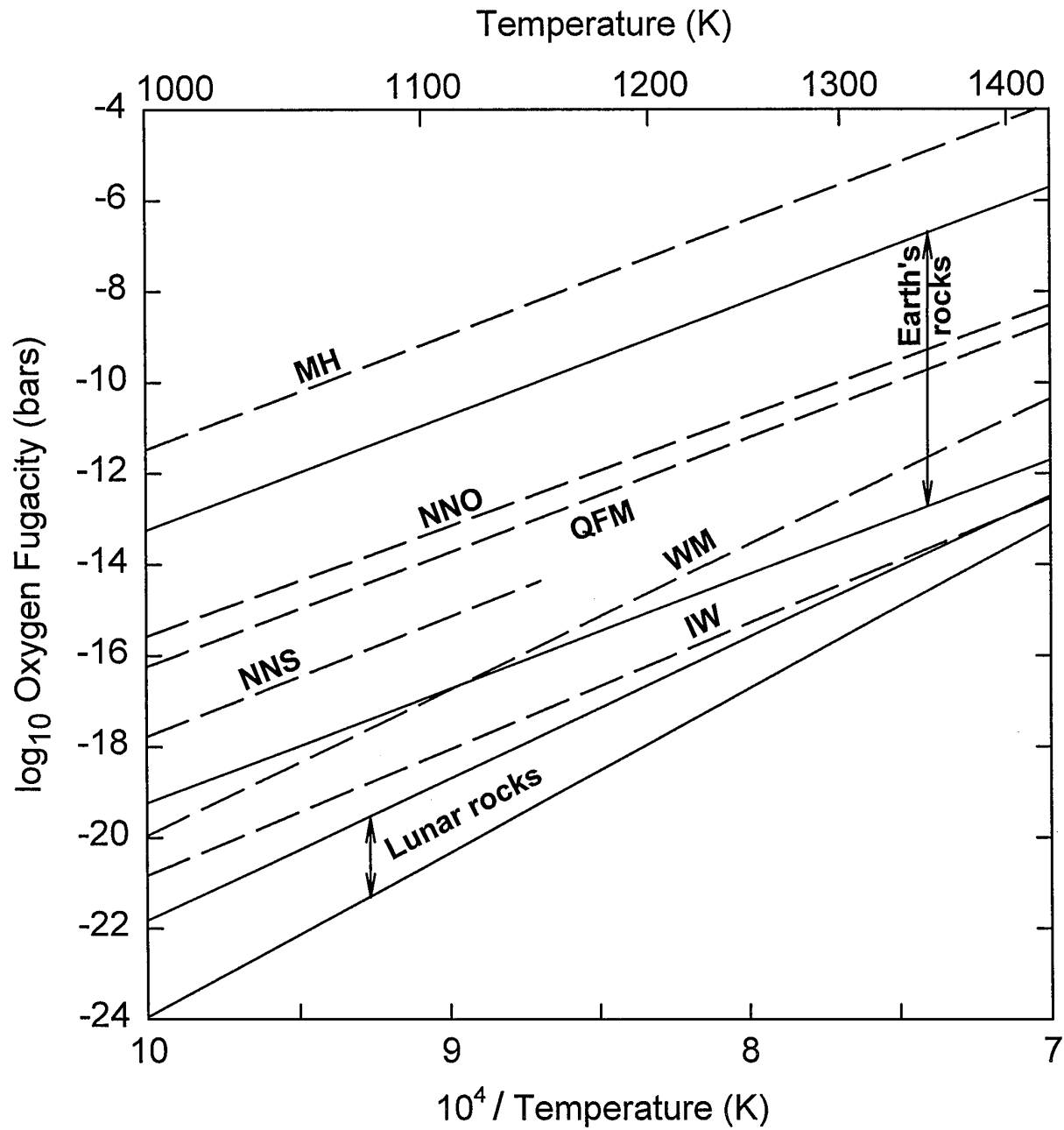


FIG. 11. Typical oxygen fugacity ranges for terrestrial (Carmichael 1991, Ballhaus 1993) and lunar igneous rocks (Papike *et al.* 1991).

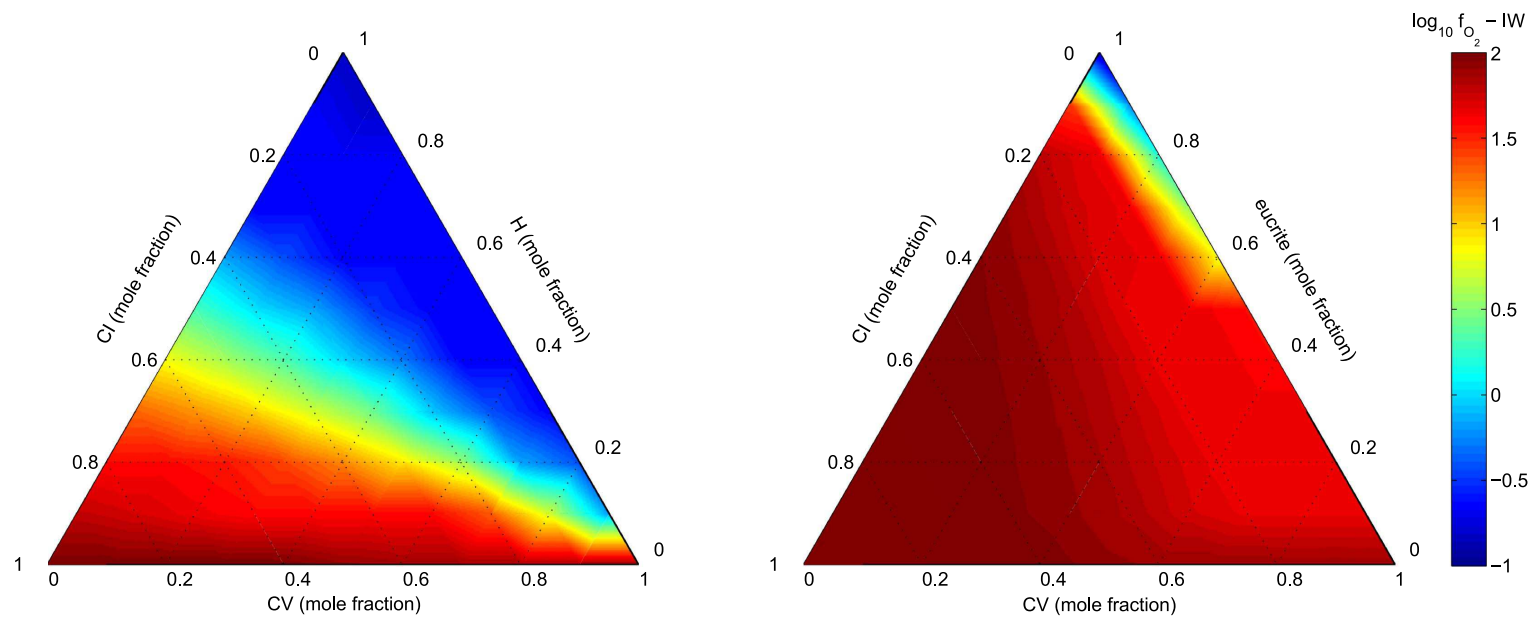


Figure 6. Oxygen fugacity of a CI-CV-H (left) and CI-CV-eucrite (right) ternary at 1 bar and 1500 K. Oxygen fugacities are given relative to the iron-wüstite (IW) buffer.