Chemistry of Earth's Earliest Atmospheres

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Conclusions I.

- Lunar rocks give oxidation state of early Earth at time of lunar formation – more reduced than present Bulk Silicate Earth (BSE) by several log units
- Early Earth was more reduced – consistent with large amount of reduced material needed to make the Earth and the identical oxygen isotopic composition of highly reduced enstatite meteorites
- Outgassed volatiles include and/or dominated by CH_4, NH_3, H_2 and give an early atmosphere that is favorable for organic compound formation via Miller-Urey reactions

Conclusions II.

- Earth oxidized during Late Heavy Bombardment (~ 4.2 – 3.8 Gyr ago) when more oxidized material like ordinary or carbonaceous chondrites delivered to Earth
- Reducing early Earth concept explains low fO_2 of lunar rocks and reducing atmosphere on early Earth that is favorable for Miller-Urey reactions (ultimately) leading to origin of life

Outline of this Talk

- Secondary origin of Earth’s atmosphere
- Sources for its Volatiles
- Outgassing of chondritic material
- Outgassing of present BSE
- Origin of Moon and Origin of Life
- Chemistry of its early gaseous atmosphere
- Brief discussion of the earlier silicate vapor and steam atmospheres

Secondary origin of 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
- ^{3}He & other solar noble gases from mantle not primordial, due to solar wind implanted gases

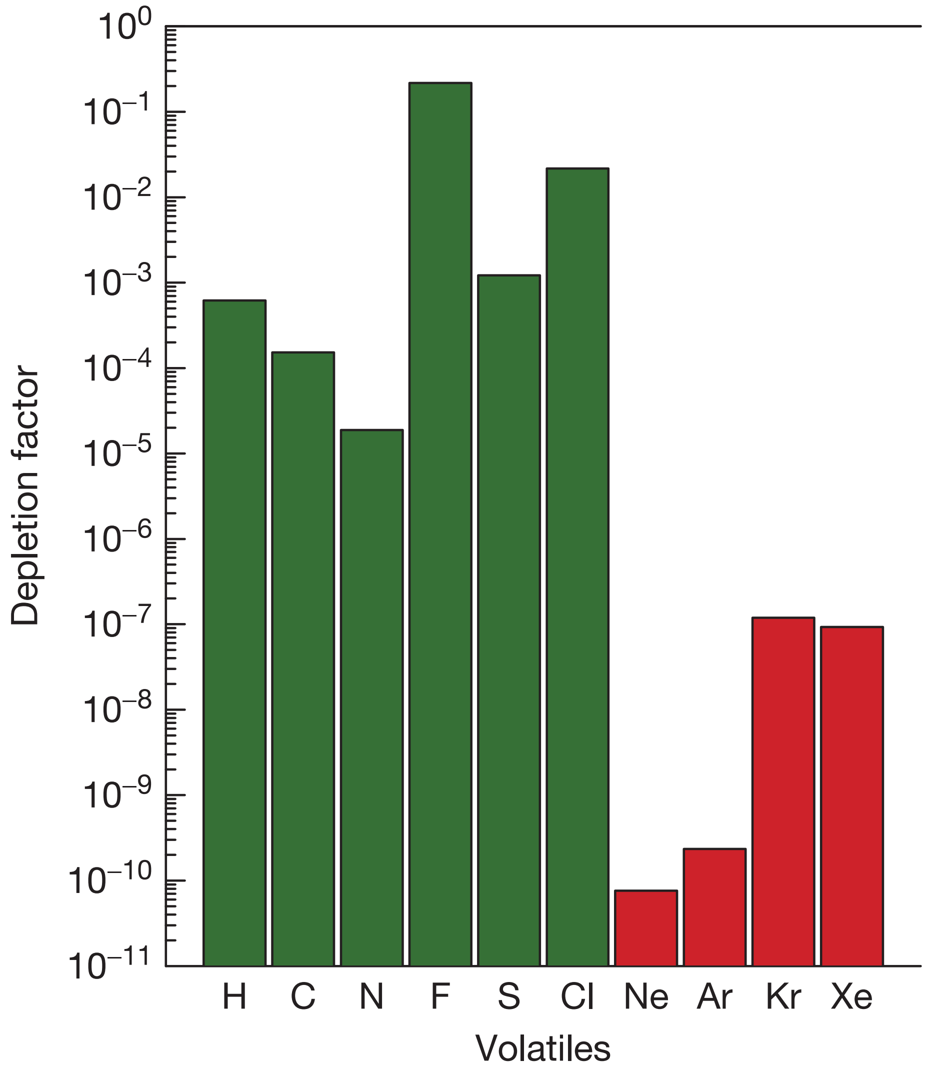


Figure 1 Depletion factors for inert gases and chemically reactive volatiles on Earth relative to their abundances in the solar nebula. See **Table 1** and the text for details.

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		

Table 1 Volatile inventories and depletion factors on the Earth

Volatile	*Solar abundance*[a]	*μg g^{-1} in BSE*[b]	*Inventory (kg)*	*Depletion factor*	*Notes*[c]
H (water)	1.27×10^{7}	1072	4.32×10^{21}	6.2×10^{-4}	Solar $A_{water} = A_O - A_{Mg} - 2A_{Si}$, adjusted for O in rock BSE water calculated from 120 μg g^{-1} H in BSE
C	7.19×10^{6}	100	4.03×10^{20}	1.5×10^{-4}	C in BSE is 46–250 μg g^{-1}, see Table 6.9 of LF98
N	2.12×10^{6}	2	8.06×10^{18}	1.9×10^{-5}	Atmosphere ~50% of total N in BSE
F	804	25	1.01×10^{20}	0.22	F in BSE is 19–28 μg g^{-1}, see Table 6.9 of LF98
Ne	3.29×10^{6}	1.6×10^{-5}	6.50×10^{13}	7.6×10^{-11}	Taking atmospheric Ne as the total inventory
S	4.21×10^{5}	124	5.00×10^{20}	1.2×10^{-3}	S in BSE is 13–1000 μg g^{-1}, see Table 6.9 of LF98
Cl	5170	30	1.21×10^{20}	2.2×10^{-2}	Cl in BSE is 8–44 μg g^{-1}, see Table 6.9 of LF98
$^{36+38}$Ar	9.27×10^{4}	6.0×10^{-6}	2.40×10^{13}	2.3×10^{-10}	Taking atmospheric Ar as total inventory of $^{36+38}$Ar
Kr	55.8	4.2×10^{-6}	1.69×10^{13}	1.2×10^{-7}	Taking atmospheric Kr as the total inventory
Xe	5.46	5.0×10^{-7}	2.03×10^{12}	9.3×10^{-8}	Taking atmospheric Xe as the total inventory

[a] Solar abundance per 10^{6} Si atoms, Table 1.2 of Lodders and Fegley (2011).

[b] Concentrations in the bulk silicate Earth (BSE) for H, C, N, F, and Cl are from Palme and O'Neill (**Chapter 3.1**). Sulfur is from Table 4.4 of Lodders and Fegley (2011).

[c] The range of published estimates for H, C, N, F, S, and Cl are in Table 6.9 of Lodders and Fegley (1998). The solar abundance of water is calculated from the oxygen abundance adjusted for the amount of oxygen in rock ($MgO + SiO_2$). Other values that are used in the calculations are the Si concentration in the BSE (21.22%), the mean molecular weight of Earth's atmosphere (28.97 g mol^{-1}), total atmospheric mass (5.137×10^{18} kg), mass of the BSE (4.03×10^{24} kg), and the concentrations of Ne, Ar, Kr, and Xe in dry air (18.18 ppmv, 9340 ppmv, 1.14 ppmv, and 87 ppbv). The Ar abundance in air is corrected for ^{40}Ar, which is 99.6% of terrestrial Ar. Calculations compare terrestrial and solar abundances of ^{36}Ar and ^{38}Ar.

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

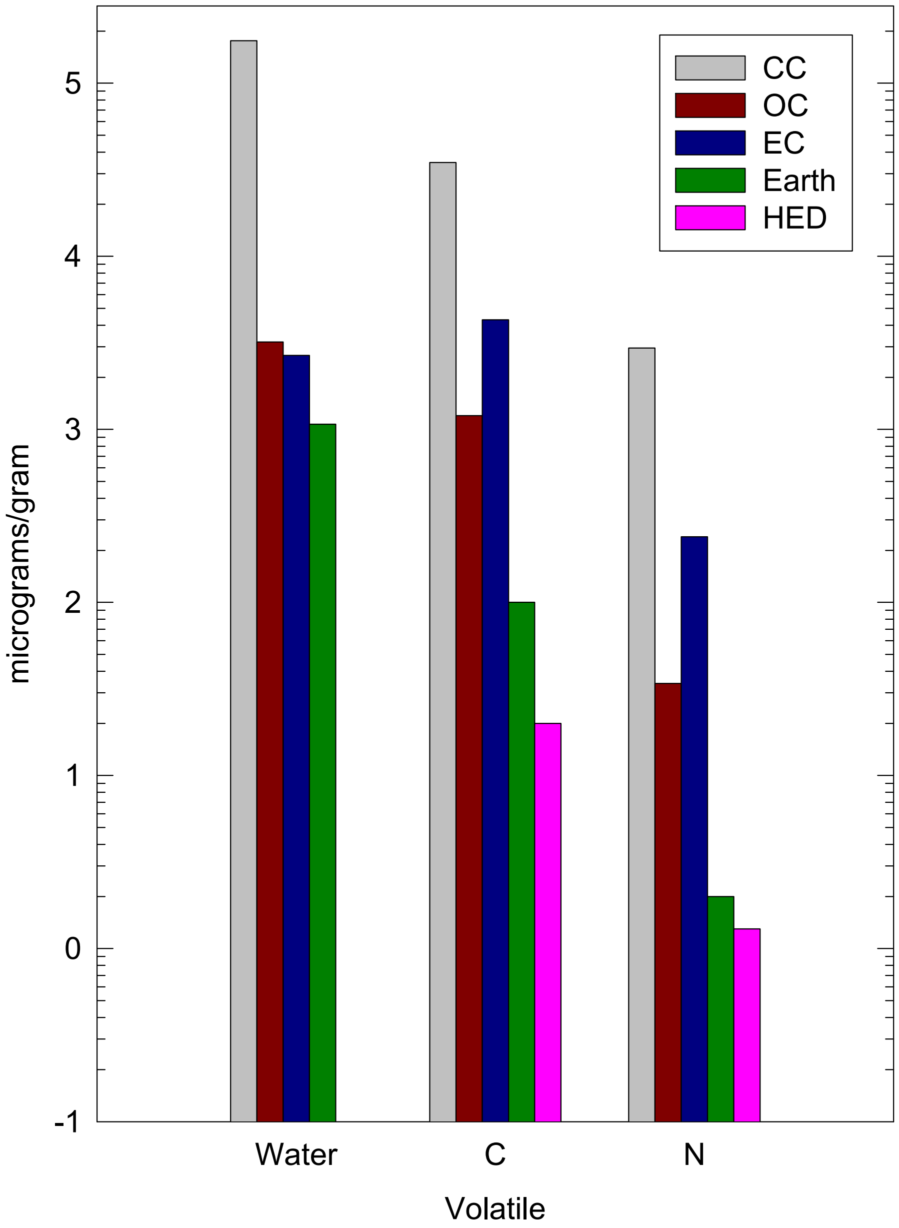

CC
OC
EC
Earth
HED
micrograms/gram
5
4
3
2
1
0
-1
Water
C
N
Volatile

Table 2 Some volatile-bearing phases in chondrites and potential outgassed volatiles

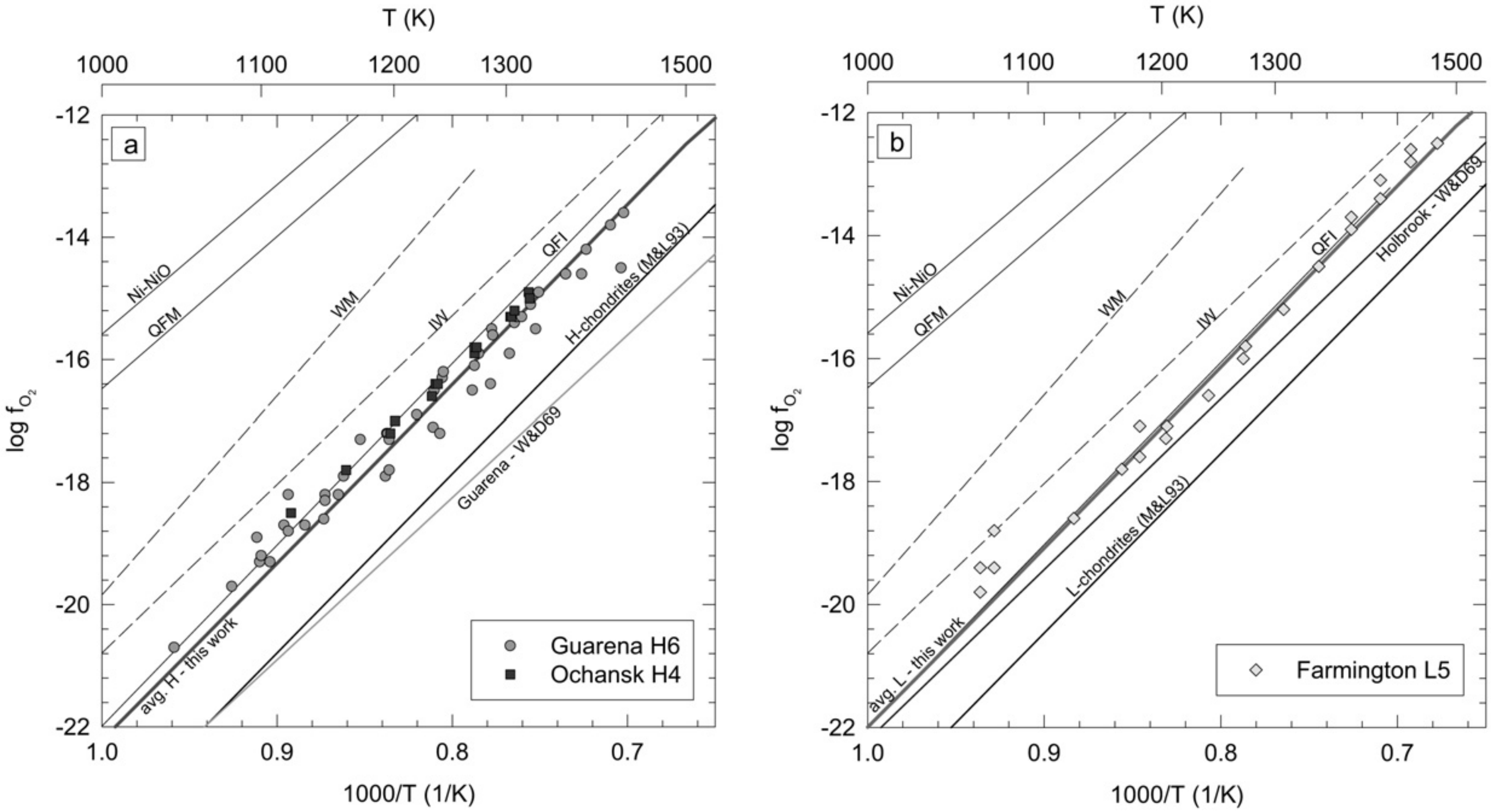
Name	*Ideal chemical formula*	*Chondrite*[a]	*Potential volatiles*[b]
Apatite	$Ca_5(PO_4)_3(F, Cl, Br, OH)$	Many	HF, HCl, Cl_2, HBr, Br_2, H_2O, H_2, O_2
Calcite	$CaCO_3$	C	CO, CO_2
Cohenite	$(Fe, Ni)_3C$	Many	CH_4, CO, CO_2
Dolomite	$CaMg(CO_3)_2$	C	CO, CO_2
Graphite	C	C	CH_4, CO, CO_2
Gypsum	$CaSO_4 \cdot 2H_2O$	C, OC	SO_2, H_2S, OCS, S_x
Halite	NaCl	C, OC	HCl, Cl_2
Insoluble organic matter	$C_{100}H_{72}N_3O_{22}S_{4.5}$	C, UOC	CH_4, CO, CO_2, H_2O, H_2, N_2, NH_3, S_x, H_2S, OCS, SO_2
Nierite	Si_3N_4	E	N_2, NH_3
Osbornite	TiN	E, CH	N_2, NH_3
Sinoite	Si_2N_2O	E	N_2, NH_3
Serpentine	$(Mg, Fe)_3Si_2O_5(OH)_4$	C	H_2O, H_2, O_2
Sodalite	$Na_4Al_3Si_3O_{12}Cl$	C	HCl, Cl_2
Talc	$(Mg, Fe)_3Si_4O_{10}(OH)_2$	C	H_2O, H_2, O_2
Troilite	FeS	Many	S_x, H_2S, OCS, SO_2

[a] The abbreviations denote the following types of chondrites: C, carbonaceous chondrites; CH, CH chondrites; E, enstatite (EH, EL) chondrites; OC, ordinary (H, L, LL) chondrites; UOC, unequilibrated ordinary chondrites, or many for phases found in many types of chondrites.

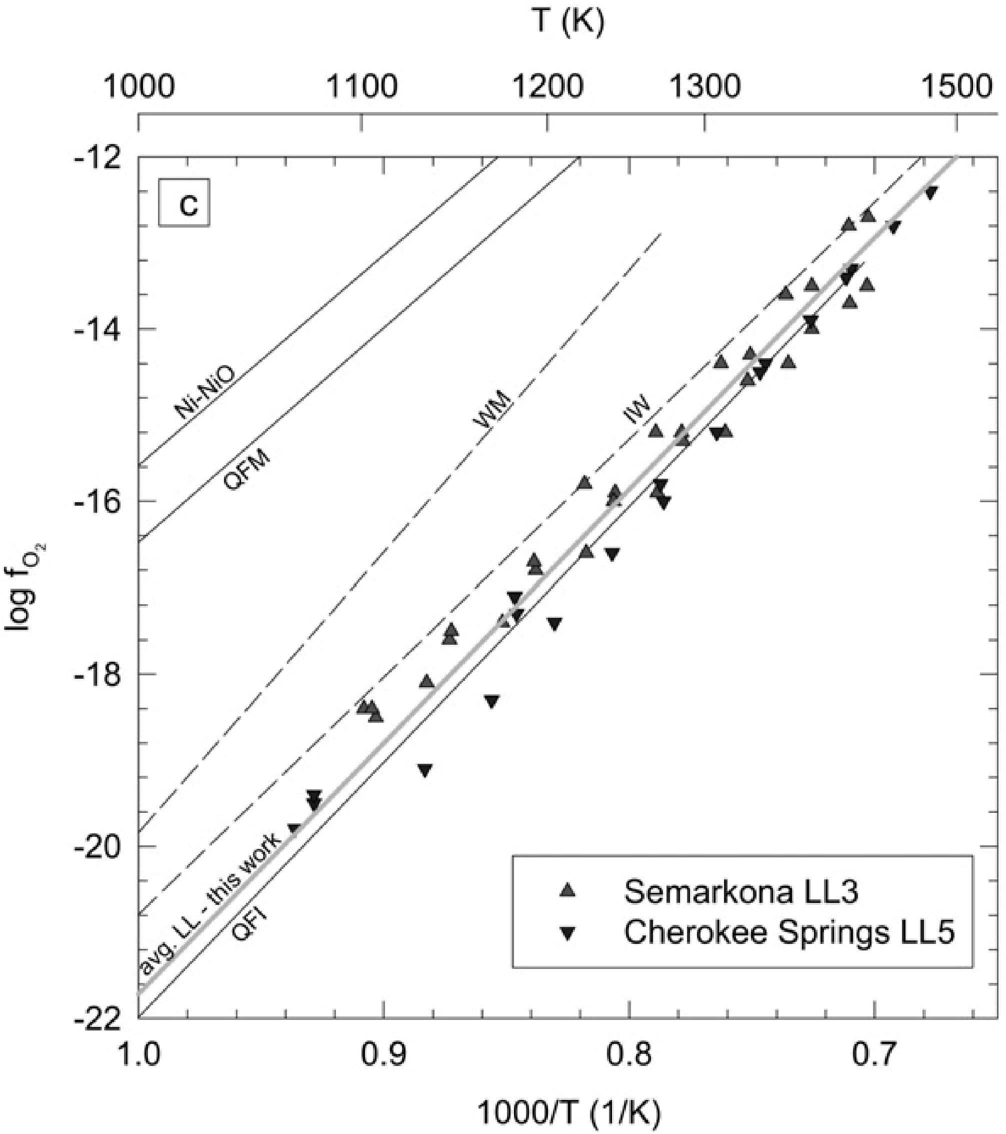
[b] The nature of the potential outgassed volatiles depends on several factors including the temperature, pressure, and oxygen fugacity during outgassing. Elemental fluorine does not form because it is too reactive. Hydrogen and oxygen are generated via equilibria of water vapor with Fe-bearing phases such as metal, magnetite, and FeO-bearing silicates.

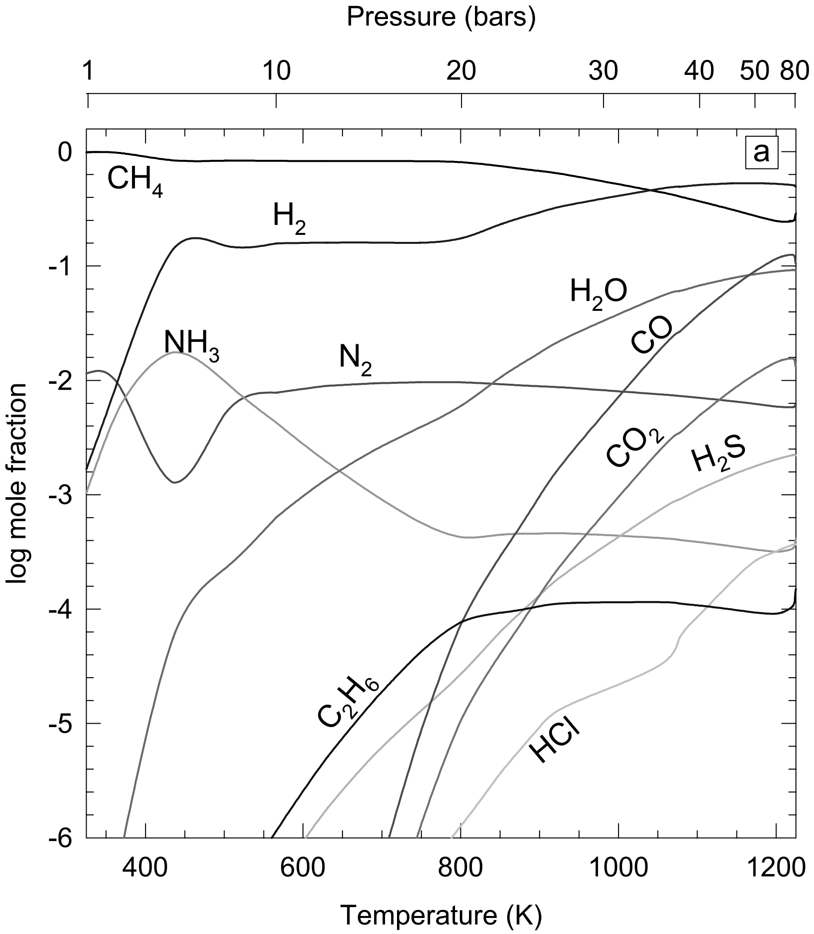
Outgassing of chondritic material

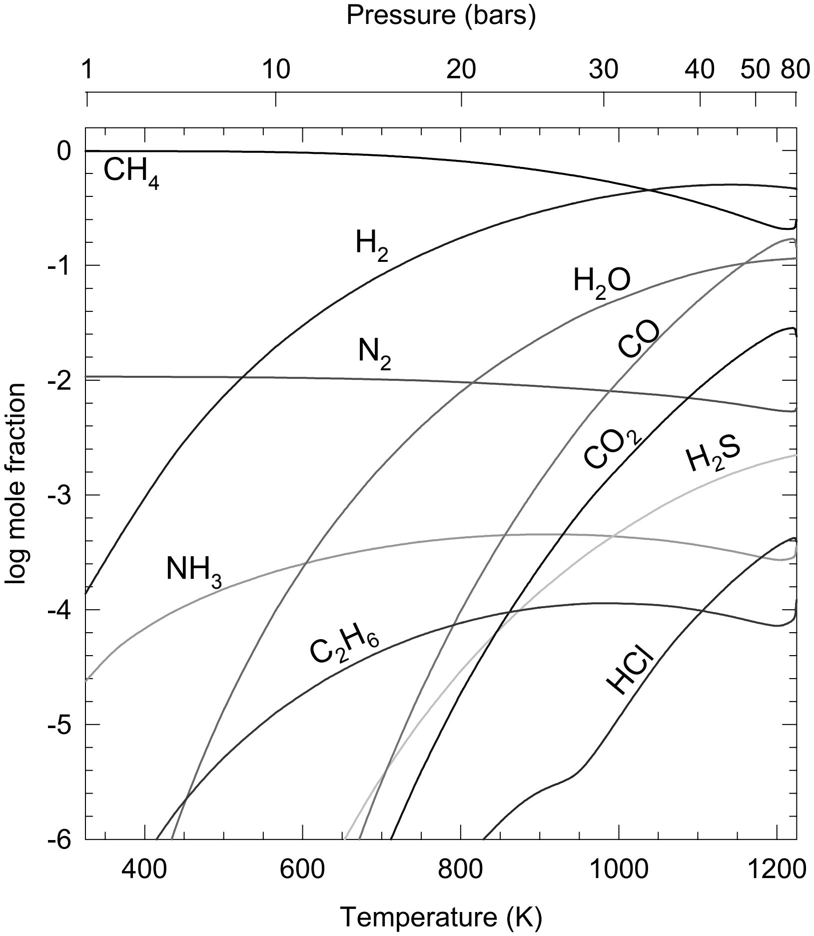
- Look at a few examples of gaseous atmospheres produced by heating up and outgassing chondritic material (computer calculations)
- Show agreement of calculated and measured oxygen fugacity (fO_2) values for meteorites where measurements are available - ordinary chondrites (H, L, LL)



a
T (K)
1000
1100
1200
1300
1500
log f$_{O_2}$
-12
-14
-16
-18
-20
-22
1000/T (1/K)
1.0
0.9
0.8
0.7
Ni-NiO
QFM
WM
IW
QFI
H-chondrites (M&L93)
Guarena - W&D69
avg. H - this work
Guarena H6
Ochansk H4
b
Ni-NiO
QFM
WM
IW
QFI
Holbrook - W&D69
L-chondrites (M&L93)
avg. L - this work
Farmington L5


T (K)
1000
1100
1200
1300
1500
-12
-14
-16
-18
-20
-22
log f_{O_2}
c
Ni-NiO
QFM
WM
IW
avg. LL - this work
QFI
▲ Semarkona LL3
▼ Cherokee Springs LL5
1.0
0.9
0.8
0.7
1000/T (1/K)


Pressure (bars)
1
10
20
30
40
50
80
a
0
-1
-2
-3
-4
-5
-6
log mole fraction
CH_4
H_2
NH_3
N_2
H_2O
CO
CO_2
H_2S
C_2H_6
HCl
400
600
800
1000
1200
Temperature (K)


Pressure (bars)
1
10
20
30
40
50
80
0
-1
-2
-3
-4
-5
-6
log mole fraction
CH_4
H_2
H_2O
N_2
CO
CO_2
H_2S
NH_3
C_2H_6
HCl
400
600
800
1000
1200
Temperature (K)

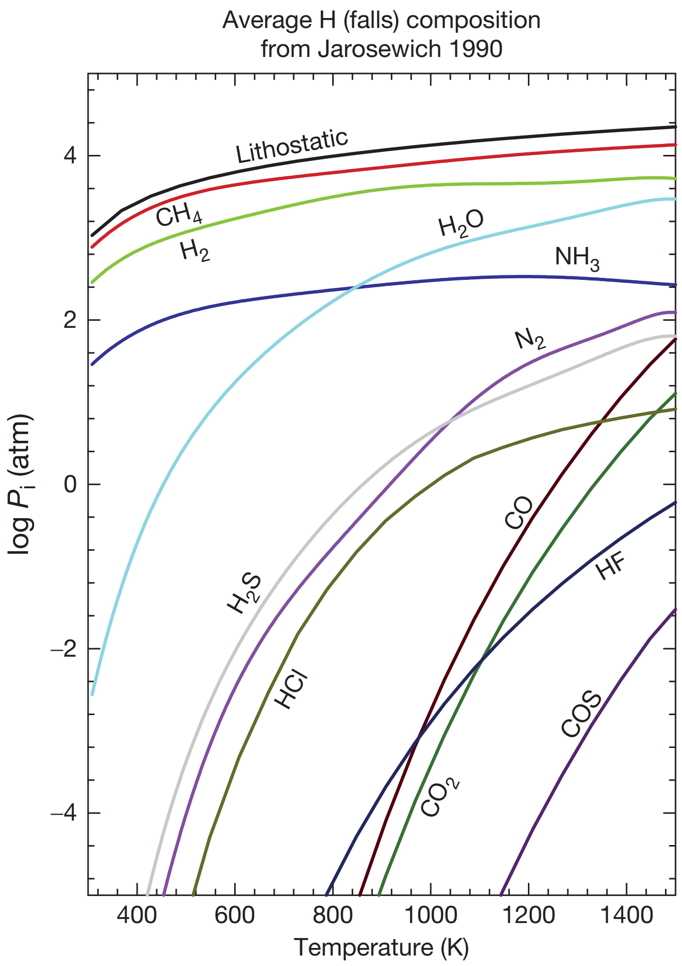


Figure 7 Chemical equilibrium abundances of gases produced by heating average H chondritic material along a terrestrial geotherm.

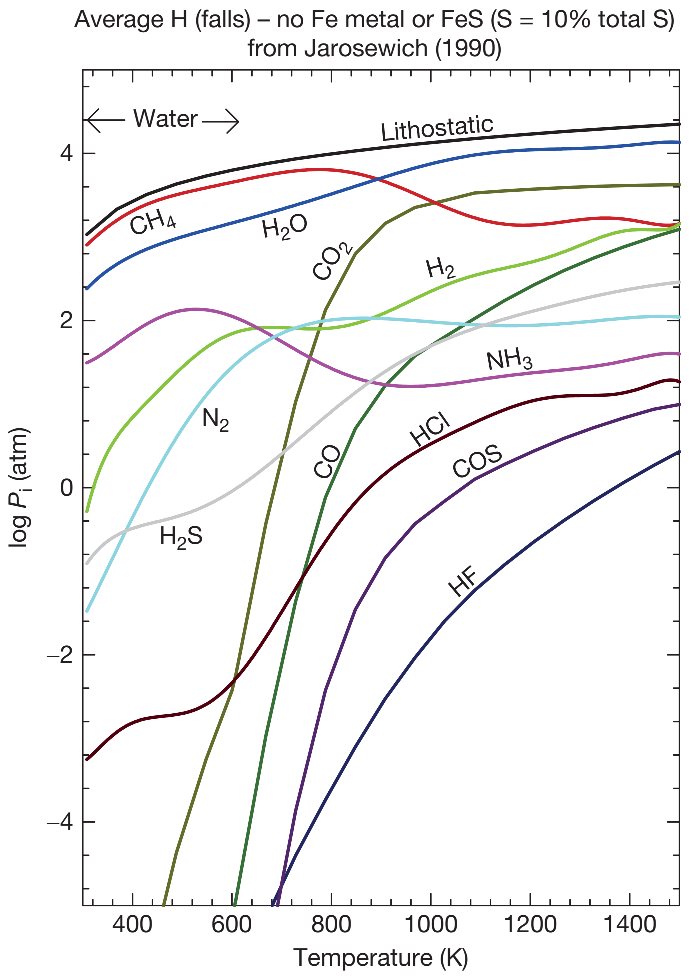


Figure 8 Same as in **Figure 7**, but after removal of all Fe metal and FeS before doing the computations.

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

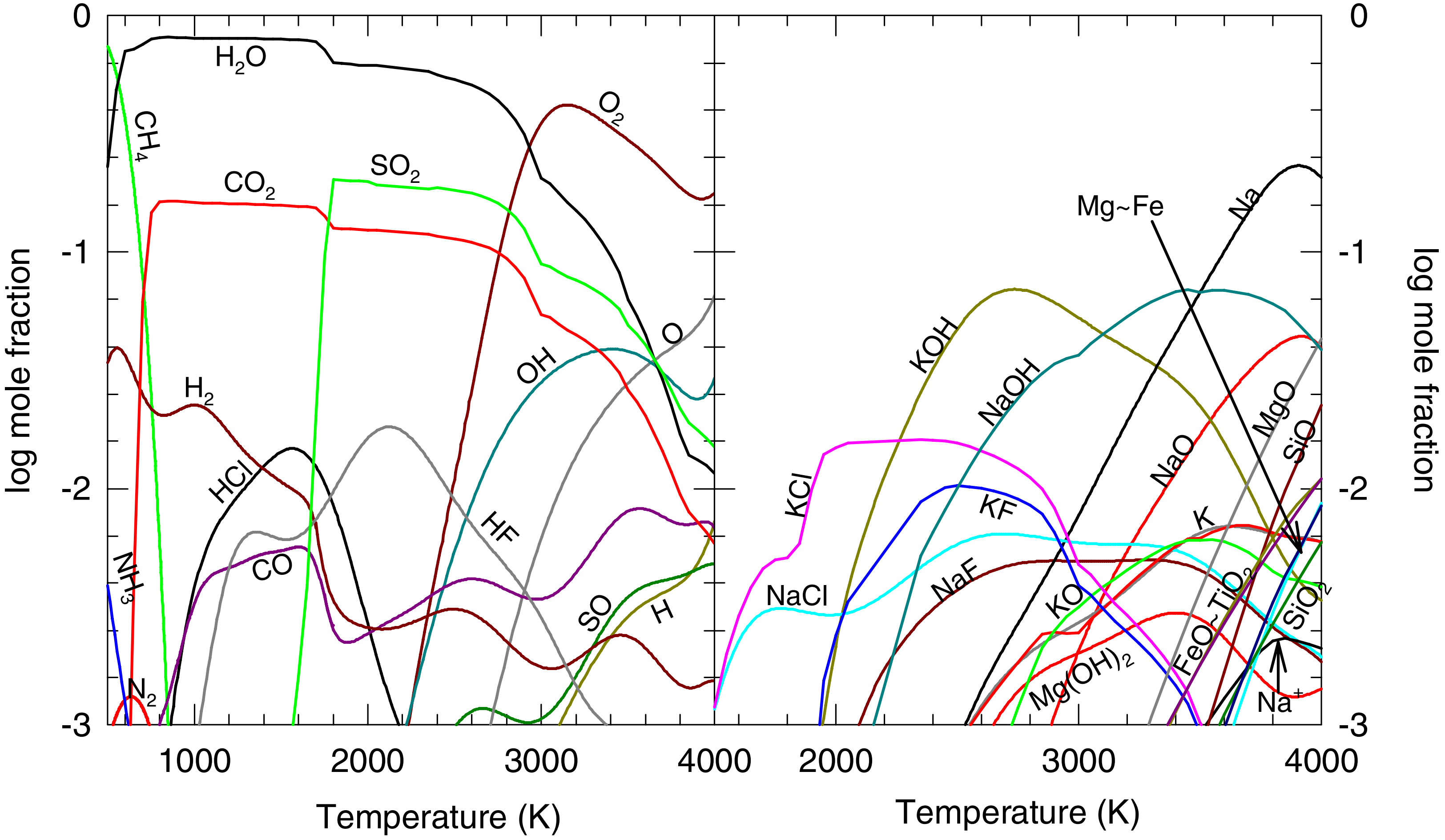
[a] 'Other' includes gases of the rock-forming elements Cl, F, K, Na, P, and S.

Outgassing of Chondritic Material

- Ordinary & enstatite chondritic material produces CH_4-bearing & CH_4-rich atmospheres
- CI and CM carbonaceous chondritic material produces CO_2-bearing & CO_2-rich atmospheres

Outgassing of the BSE

- CO_2-bearing & CO_2-rich atmospheres produced by outgassing of the bulk silicate Earth
- One example on the next slide
- The transition from reducing to oxidizing took place early in Earth history, prior to 3.9 Gyr ago based on Cr and V abundances in ancient rocks (Delano 2001)


log mole fraction
0
-1
-2
-3
H₂O
CH₄
CO₂
SO₂
O₂
H₂
HCl
CO
HF
OH
O
SO
H
NH₃
N₂
1000
2000
3000
4000
Temperature (K)
Mg~Fe
Na
KOH
NaOH
KCl
KF
NaCl
NaF
KO
NaO
K
MgO
SiO
FeO~TiO₂
SiO₂
Mg(OH)₂
Na⁺
2000
3000
4000
Temperature (K)
0
-1
-2
-3
log mole fraction

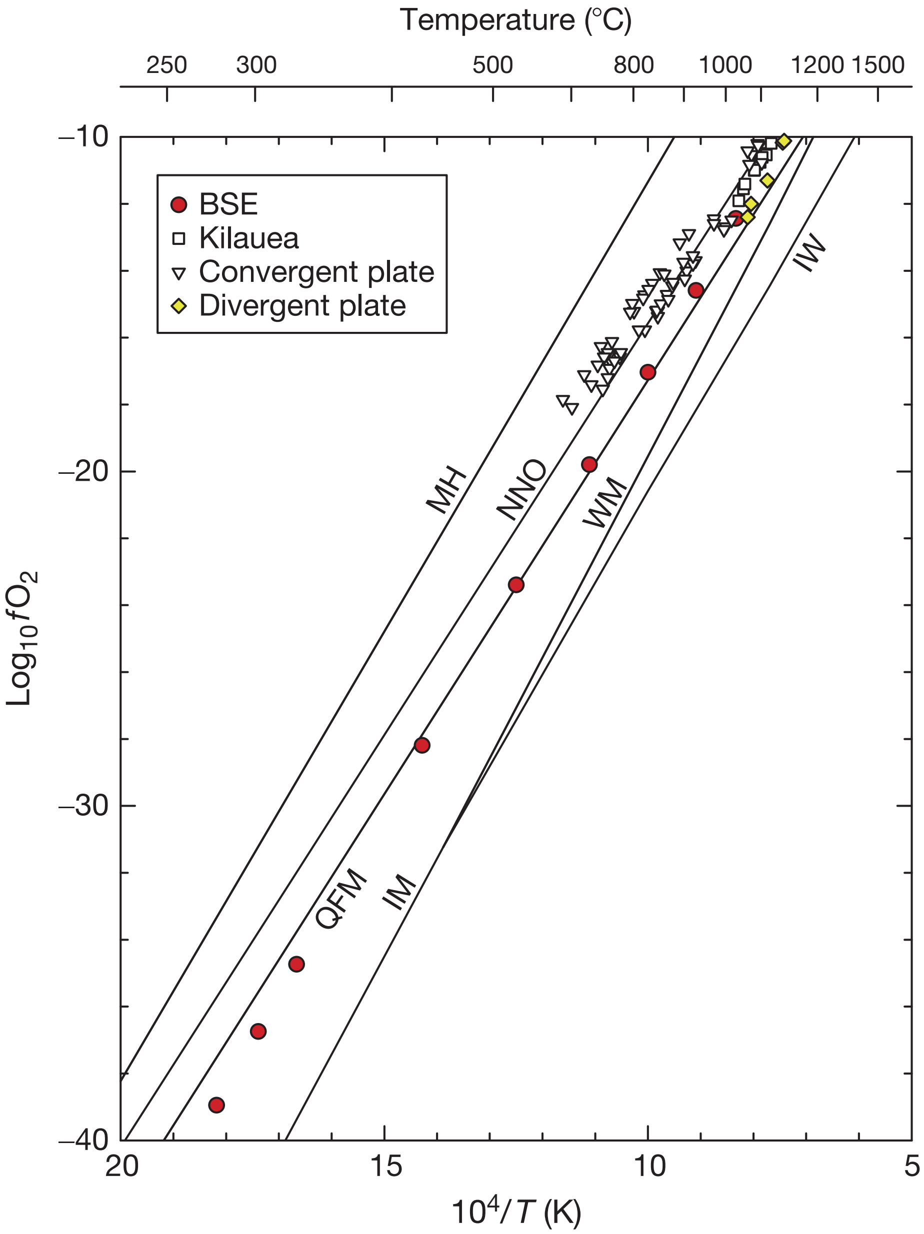


Figure 6 Temperature-dependent oxygen fugacities for modern day volcanic gases and the heated bulk silicate Earth (Schaefer et al., 2012)

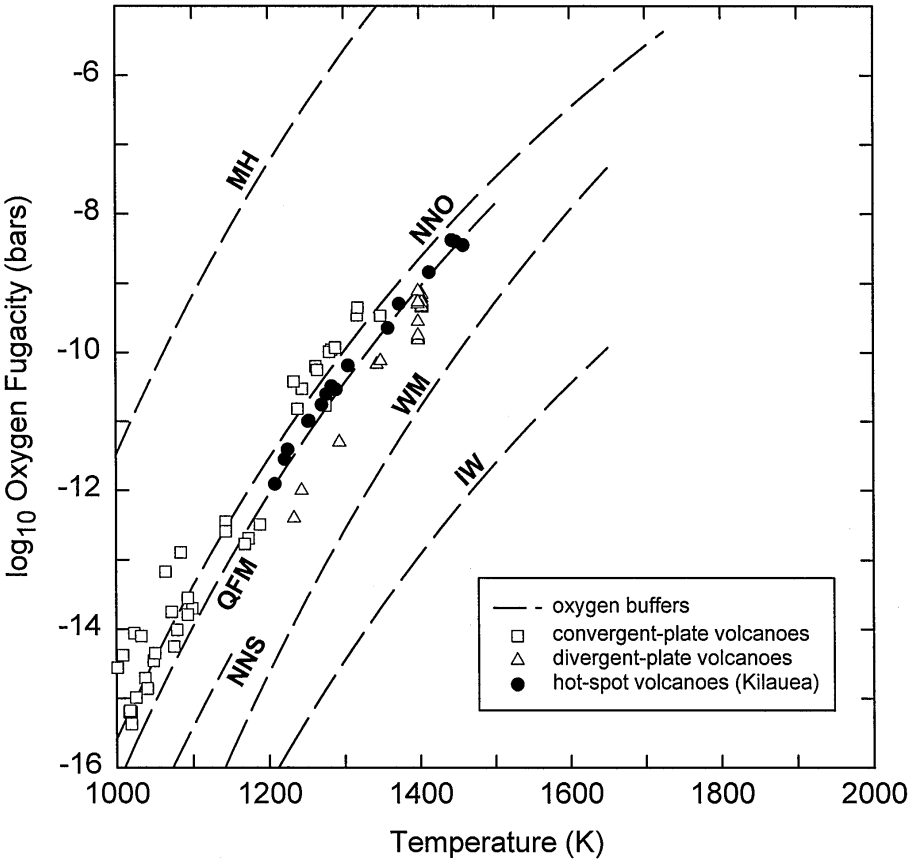


FIG. 10. The oxygen fugacities of terrestrial volcanic gases are plotted as a function of vent temperature. Mineral buffer f_{O_2} curves are shown for comparison. The calculated f_{O_2} values and vent temperatures for the volcanic gases are from Symonds *et al*. (1994).

Origin of the Moon and Origin of Life

from Bulk Silicate Earth

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

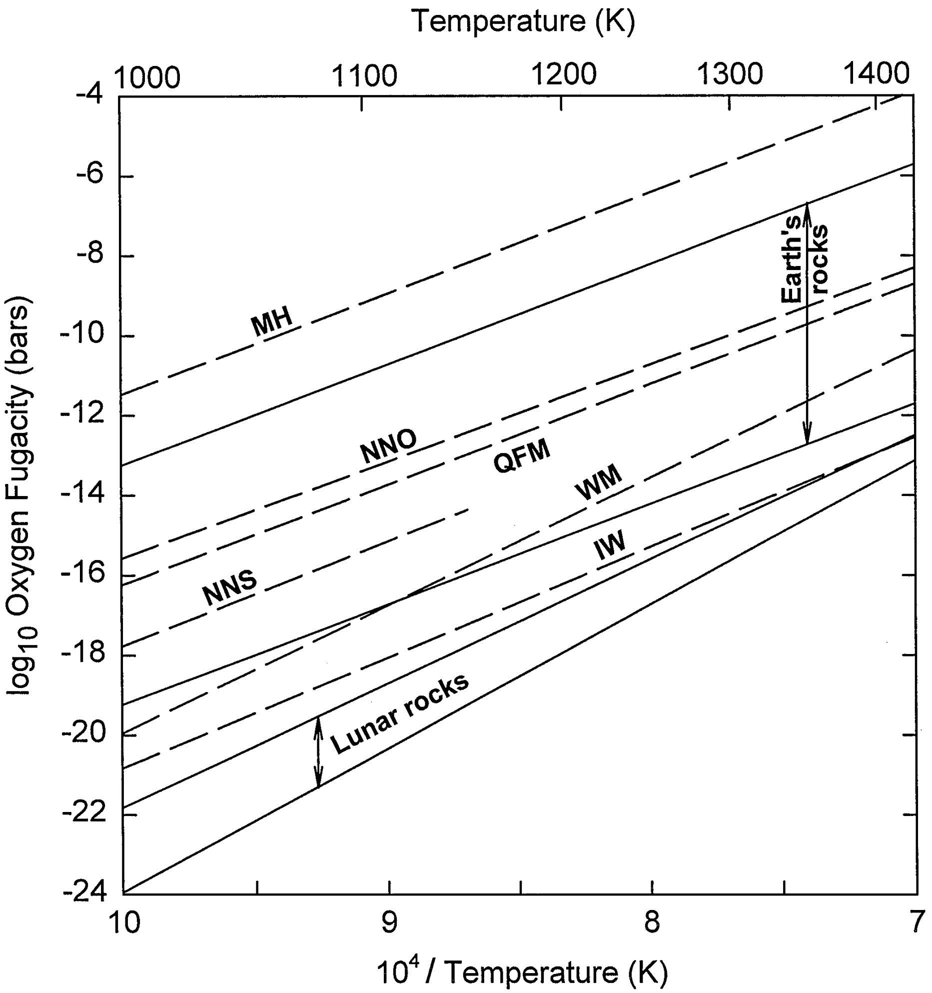
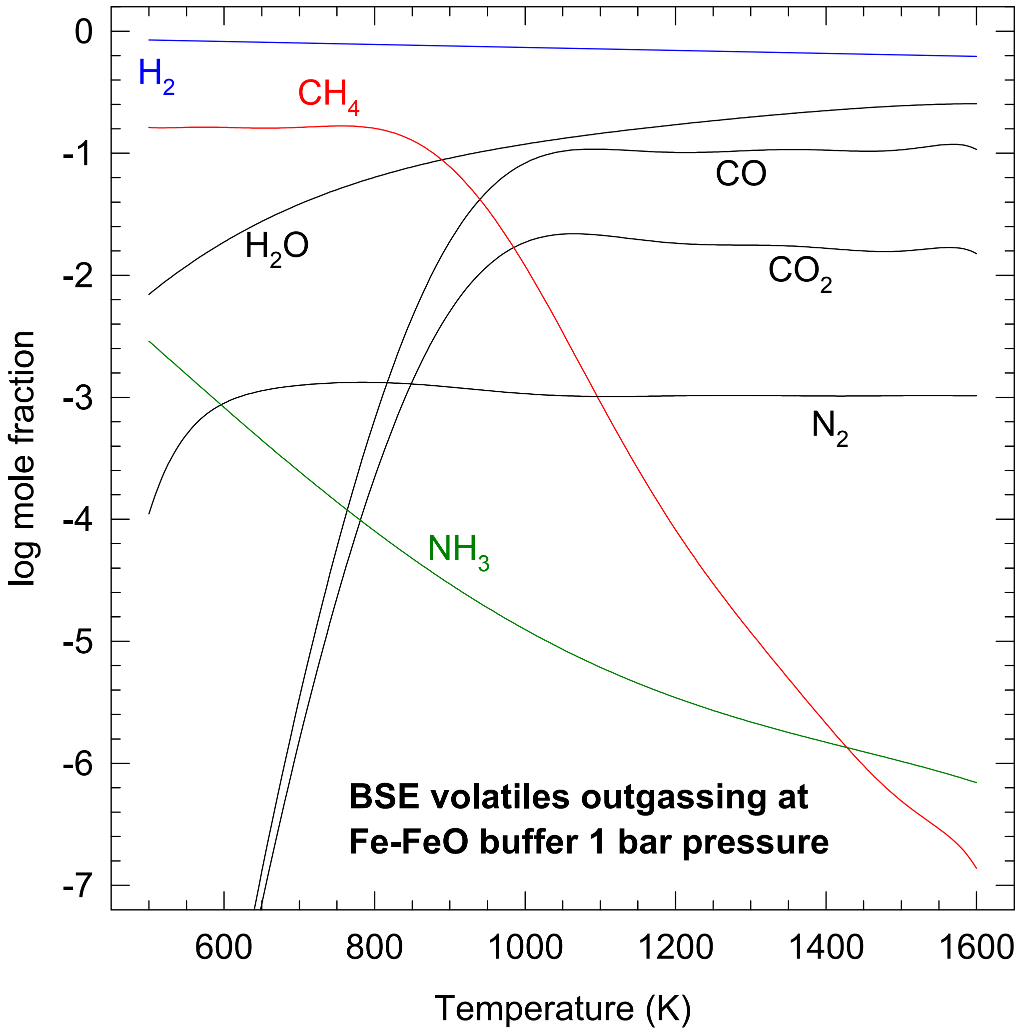
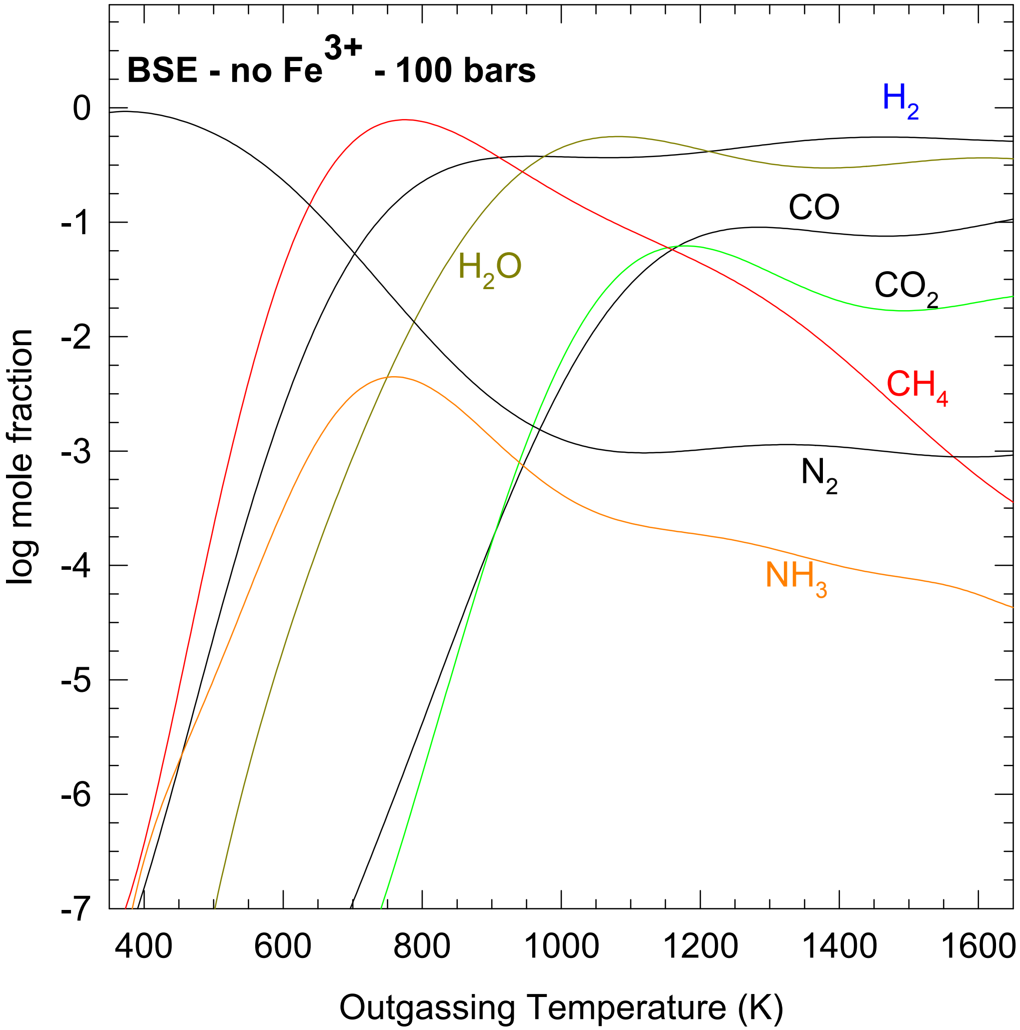


FIG. 11. Typical oxygen fugacity ranges for terrestrial (Carmichael 1991, Ballhaus 1993) and lunar igneous rocks (Papike *et al*. 1991).

Implications for Atmospheric Chemistry

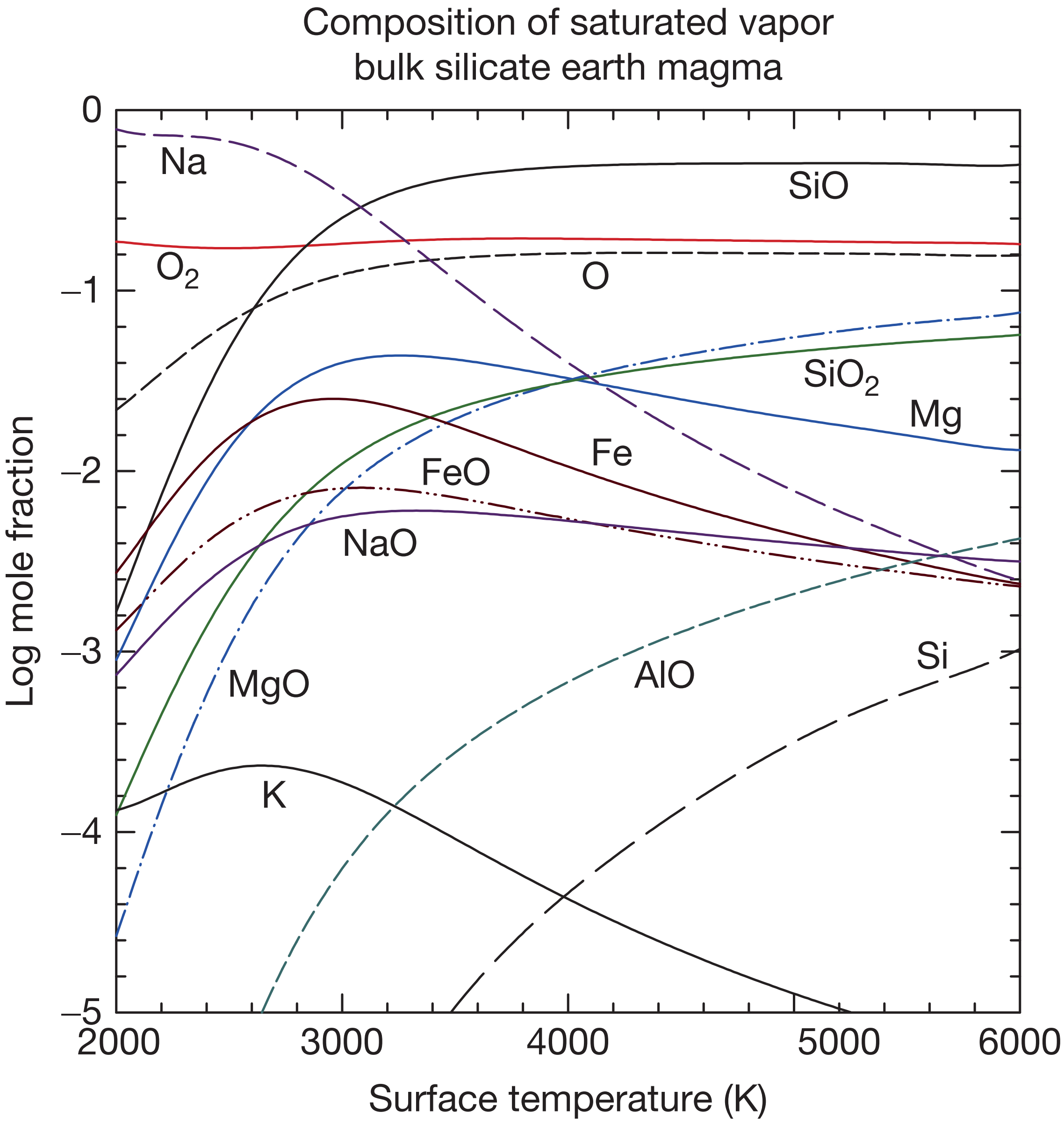
- Lower fO_2 leads to volcanic outgassing of reduced gases such as H_2, $CH_{4,}$ and NH_3
- (1) Calculations at fixed fO_2 of Fe-FeO buffer with BSE abundances for volatiles – show this example next
- (2)Calculations using Fe^{3+}-free BSE: MgO, SiO_2, FeO, CaO, Al_2O_3, Na_2O, K_2O, TiO_2, Cr_2O_3, MnO, NiO, etc. but without the few % Fe^{3+} in upper mantle – produces graphite at low T


0
-1
-2
-3
-4
-5
-6
-7
log mole fraction
600
800
1000
1200
1400
1600
Temperature (K)
H_2
CH_4
H_2O
CO
CO_2
N_2
NH_3
BSE volatiles outgassing at
Fe-FeO buffer 1 bar pressure


BSE - no Fe^{3+} - 100 bars
H_2
CO
H_2O
CO_2
CH_4
N_2
NH_3
0
-1
-2
-3
-4
-5
-6
-7
log mole fraction
400
600
800
1000
1200
1400
1600
Outgassing Temperature (K)

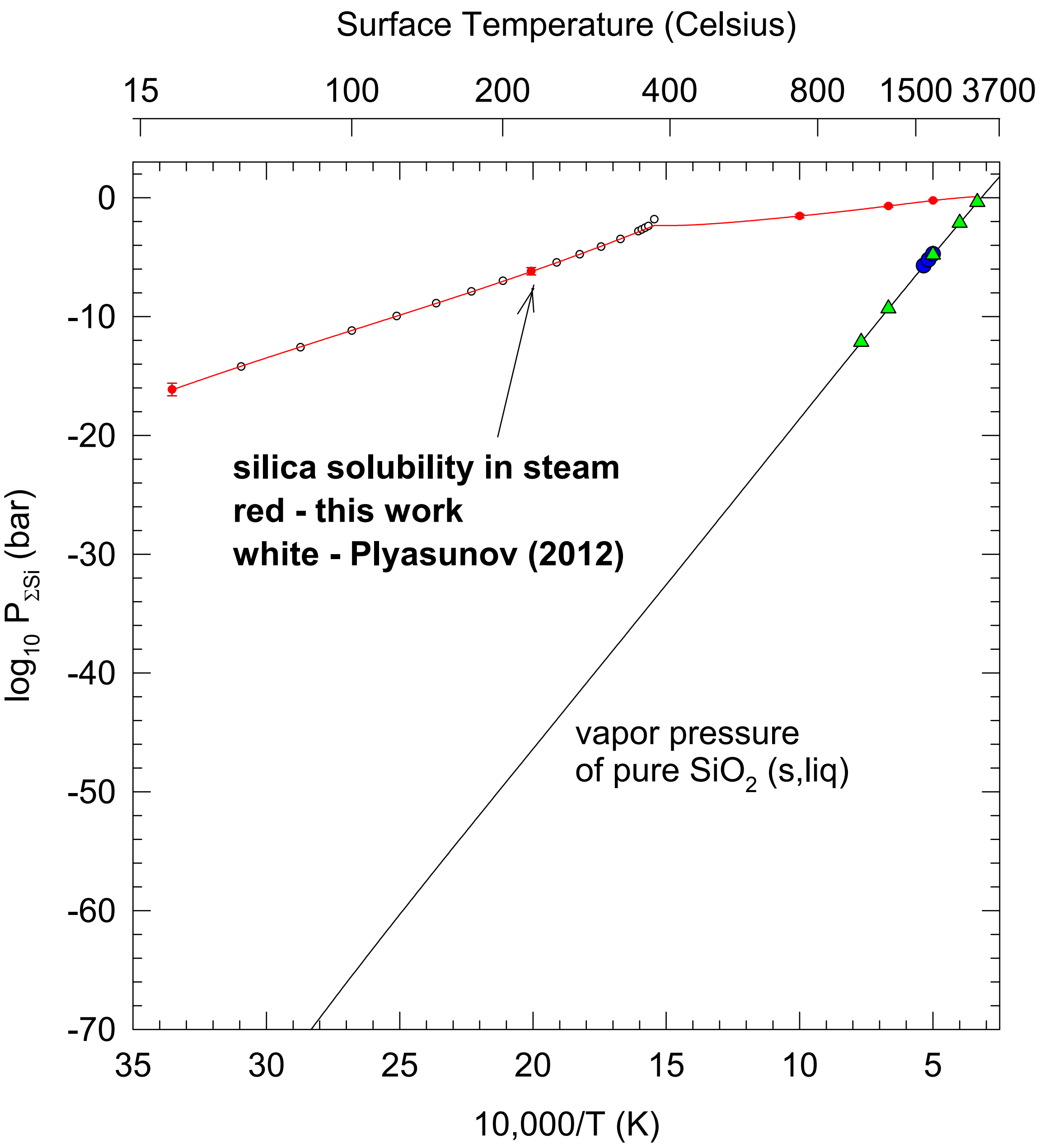
Silicate vapor atmosphere

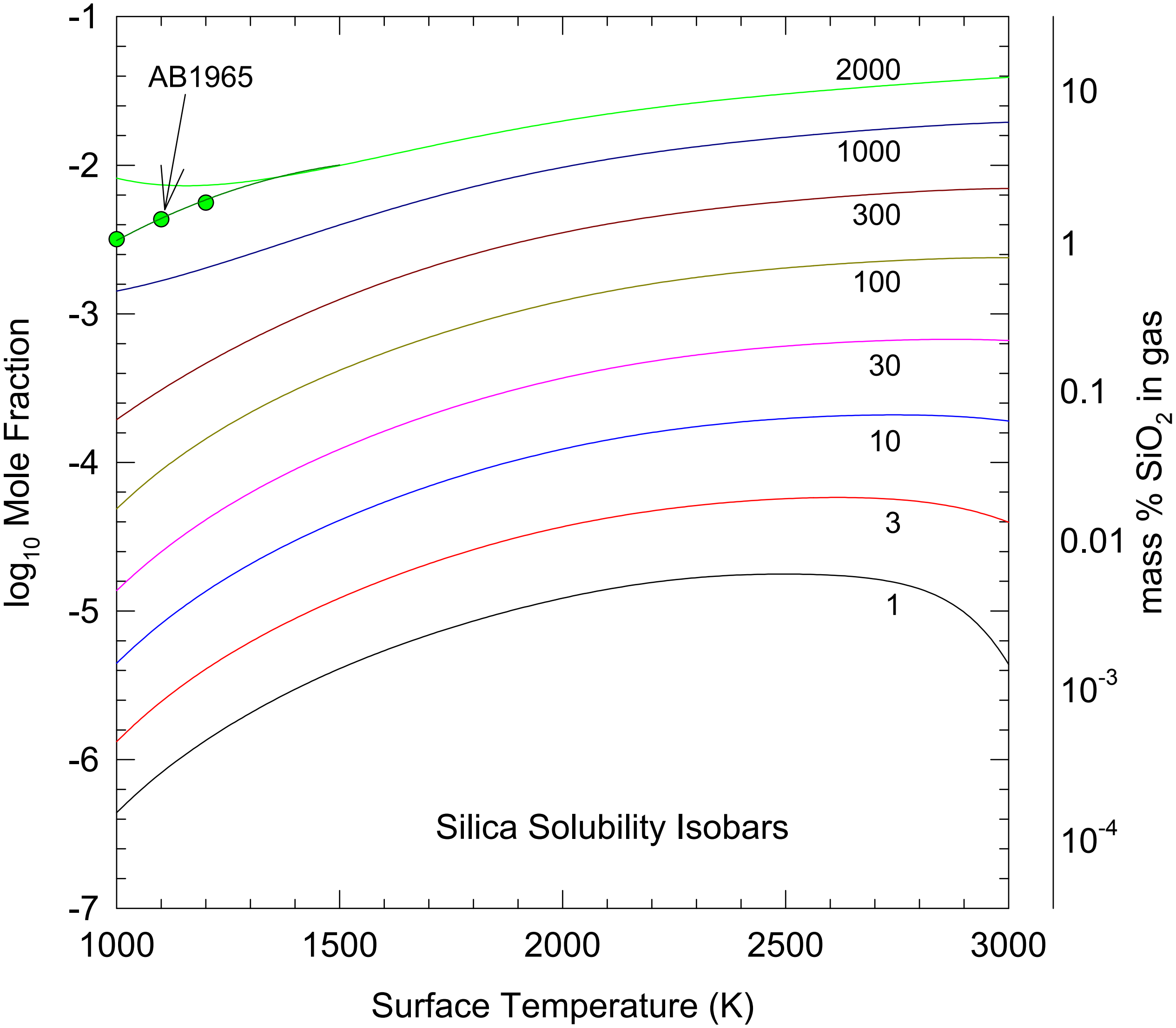
- High temperatures during Earth's accretion can lead to silicate vapor atmosphere
- Dry molten silicate vapor atmosphere (BSE composition) in next slide
- Applied to hot rocky exoplanets such as CoRoT-7b, Kepler-10b


Composition of saturated vapor
bulk silicate earth magma
Log mole fraction
Surface temperature (K)
0
−1
−2
−3
−4
−5
2000
3000
4000
5000
6000
Na
SiO
O2
O
SiO2
Mg
Fe
FeO
NaO
MgO
AlO
Si
K

Steam Atmosphere

- Impact-induced outgassing of H_2O and other volatiles (e.g., Arrhenius et al 1974, Lange & Ahrens 1982, Abe & Matsui 1985, 1987)
- Interesting aspect is solubility of SiO_2 and other rock-forming oxides in steam
- Two examples on next slides


Surface Temperature (Celsius)
15
100
200
400
800
1500
3700
0
-10
-20
-30
-40
-50
-60
-70
log10 PΣSi (bar)
35
30
25
20
15
10
5
10,000/T (K)
silica solubility in steam
red - this work
white - Plyasunov (2012)
vapor pressure
of pure SiO2 (s,liq)



-1
-2
-3
-4
-5
-6
-7
log$_{10}$ Mole Fraction
AB1965
2000
1000
300
100
30
10
3
1
Silica Solubility Isobars
1000
1500
2000
2500
3000
Surface Temperature (K)
10
1
0.1
0.01
10^{-3}
10^{-4}
mass % SiO$_2$ in gas

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