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

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Solar</th>
<th>Bulk Silicate Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne/N$_2$</td>
<td>3.1</td>
<td>2.3 × 10$^{-5}$</td>
</tr>
<tr>
<td>$^{36+38}$Ar/S*</td>
<td>0.25</td>
<td>5 × 10$^{-8}$</td>
</tr>
<tr>
<td>$^{36+38}$Ar/Cl*</td>
<td>0.055</td>
<td>2 × 10$^{-7}$</td>
</tr>
</tbody>
</table>

*mass ratio
The nature of the potential outgassed volatiles depends on several factors including the temperature, pressure, and oxygen fugacity during outgassing. Elemental fluorine does not react 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.

### Table 1: Volatile inventories and depletion factors on the Earth

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

$^a$ 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, 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 $\times 10^{18}$ kg), mass of the BSE (4.03 $\times 10^{24}$ 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
Figure 4.24

Volatile Water C N micrograms/gram

- CC
- OC
- EC
- Earth
- HED

Volatiles

HED

3

CC

2

OC

1

EC

0

Earth

N

Water

CC

OC

EC

Earth

HED

micrograms/gram

-1
Table 2  Some volatile-bearing phases in chondrites and potential outgassed volatiles

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal chemical formula</th>
<th>Chondrite&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Potential volatiles&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>Ca₅(PO₄)₃(F, Cl, Br, OH)</td>
<td>Many</td>
<td>HF, HCl, Cl₂, HBr, Br₂, H₂O, H₂, O₂</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>C</td>
<td>CO, CO₂</td>
</tr>
<tr>
<td>Cohenite</td>
<td>(Fe, Ni)₃C</td>
<td>Many</td>
<td>CH₄, CO, CO₂</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>C</td>
<td>CO, CO₂</td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>C</td>
<td>CH₄, CO, CO₂</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>C, OC</td>
<td>SO₂, H₂S, OCS, S₈</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
<td>C, OC</td>
<td>HCl, Cl₂</td>
</tr>
<tr>
<td>Insoluble organic matter</td>
<td>C₁₀₀H₂₀N₂O₂₂S₄.₅</td>
<td>C, UOC</td>
<td>CH₄, CO, CO₂, H₂O, H₂, N₂, NH₃, Sₓ, H₂S, OCS, SO₂</td>
</tr>
<tr>
<td>Nierite</td>
<td>Si₃N₄</td>
<td>E</td>
<td>N₂, NH₃</td>
</tr>
<tr>
<td>Osbornite</td>
<td>TiN</td>
<td>E, CH</td>
<td>N₂, NH₃</td>
</tr>
<tr>
<td>Sinoite</td>
<td>Si₃N₂O</td>
<td>E</td>
<td>N₂, NH₃</td>
</tr>
<tr>
<td>Serpentine</td>
<td>(Mg, Fe)₃Si₂O₅(OH)₄</td>
<td>C</td>
<td>H₂O, H₂, O₂</td>
</tr>
<tr>
<td>Sodalite</td>
<td>Na₄Al₆Si₄O₁₂Cl</td>
<td>C</td>
<td>HCl, Cl₂</td>
</tr>
<tr>
<td>Talc</td>
<td>(Mg, Fe)₂Si₄O₁₀(OH)₂</td>
<td>C</td>
<td>H₂O, H₂, O₂</td>
</tr>
<tr>
<td>Troilite</td>
<td>FeS</td>
<td>Many</td>
<td>Sₓ, H₂S, OCS, SO₂</td>
</tr>
</tbody>
</table>

<sup>a</sup>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.

<sup>b</sup>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)
Outgassing of ordinary chondritic material

Fig. 8. (a) The chemical equilibrium oxygen fugacity of average H-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Guareña (H6) and Ochansk (H4) chondrites measured by Brett and Sato (1984). Also shown are the intrinsic oxygen fugacities of the Guareña (H6) chondrite measured by Walter and Doan (1969) and the calculated oxygen fugacities for average H4–H6 chondrites from McSween and Labotka (1993).

(b) The chemical equilibrium oxygen fugacity of average L-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Farmington (L5) chondrite measured by Brett and Sato (1984). Also shown are the intrinsic oxygen fugacities of the Holbrook (L6) chondrite measured by Walter and Doan (1969) and the calculated oxygen fugacities for average L4–L6 chondrites from McSween and Labotka (1993).

(c) The chemical equilibrium oxygen fugacity of average LL-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Semarkona (LL3) and Cherokee Springs (LL5) chondrites measured by Brett and Sato (1984). (IW = iron–wüstite, QFI = quartz–fayalite–iron, QFM = quartz–fayalite–magnetite, WM = wüstite–magnetite).

Labotka (1993) calculated oxygen fugacities for average H4–H6 and L4–L6 chondrites from the compositions of coexisting olivine, orthopyroxene, and metal using the fayalite–ferrosilite–iron (FFI) oxygen fugacity buffer

\[
2\text{Fe}_2\text{SiO}_4 \text{ (fayalite)} = 2\text{FeSiO}_3 \text{ (ferrosilite)} + 2\text{Fe} \text{ (metal)} + \text{O}_2 \text{ (g)}.
\]

(The lines shown on the graphs are extrapolations of their data to higher temperatures.) Calculated oxygen fugacities from McSween and Labotka (1993) are lower than the measured values of Brett and Sato (1984) and our calculated fO$_2$ values. Their results for H chondrites agree at lower temperatures with the oxygen fugacities for one H chondrite measured by Walter and Doan (1969).
Outgassing of ordinary chondritic material

Fig. 8. (a) The chemical equilibrium oxygen fugacity of average H-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Guareña (H6) and Ochansk (H4) chondrites measured by Brett and Sato (1984). Also shown are intrinsic oxygen fugacities of the Guareña (H6) chondrite measured by Walter and Doan (1969) and the calculated oxygen fugacities for average H4–H6 chondrites from McSween and Labotka (1993). (b) The chemical equilibrium oxygen fugacity of average L-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Farmington (L5) chondrite measured by Brett and Sato (1984). Also shown are the intrinsic oxygen fugacities of the Holbrook (L6) chondrite measured by Walter and Doan (1969) and the calculated oxygen fugacities for average L4–L6 chondrites from McSween and Labotka (1993). (c) The chemical equilibrium oxygen fugacity of average LL-chondritic material as a function of temperature compared to different solid-state oxygen fugacity buffers. The points are intrinsic oxygen fugacities of the Semarkona (LL3) and Cherokee Springs (LL5) chondrites measured by Brett and Sato (1984). (IWO = iron–wüstite, QFI = quartz–fayalite–iron, QFM = quartz–fayalite–magnetite, WM = wüstite–magnetite). The lines shown on the graphs are extrapolations of their data to higher temperatures. Calculated oxygen fugacities from McSween and Labotka (1993) are lower than the measured values of Brett and Sato (1984) and our calculated fO2 values. Their results for H chondrites agree at lower temperatures with the oxygen fugacities for one H chondrite measured by Walter and Doan (1969).
the NH$_3$/N$_2$ ratio reaches unity at a lower temperature than the CH$_4$/CO$_2$ ratio. Frost and McCammon (2008) and Frost et al. (2008) note that during core formation, the BSE was in equilibrium with Fe–Ni-rich alloy and would have had an oxidation state 4.5 log units below QFM at a given temperature, that is, at the iron–wustite buffer. The more reduced mantle would move the CH$_4$–CO$_2$ crossover to higher temperatures at a given total pressure.

A significantly more reduced Earth would outgas a reduced atmosphere. At the suggestion of his advisor J. S. Lewis, Bukvic (1979) did chemical equilibrium calculations for gas–solid equilibria in the upper layers of an Earth-like planet that he modeled as H chondritic material or a mixture of 90% H and 10% CI chondritic material. He found outgassed atmospheres composed of CH$_4$ + H$_2$ in all cases.

Schaefer and Fegley (2005, 2007) computed outgassing of average H chondritic material along the same thermal profile used by Bukvic (1979) and found a reduced atmosphere dominated by CH$_4$ and H$_2$ (see Figure 7). Similar results were obtained by Saxena and Fei (1988) who modeled outgassing of a carbonaceous chondritic planet. Schaefer and Fegley (2005) also studied outgassing from H chondritic material depleted in Fe metal and FeS (see Figure 8). A comparison of Figures 7 and 8 shows that a highly reduced atmosphere is produced in both cases, even after Fe metal and FeS have been removed, for example, by core formation on the 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 (S = 10% total S) before doing the computations.
and CM carbonaceous chondritic material produced H₂O pressure and temperature. They found that degassing of CI enstatite, and ordinary chondritic material as a function of volatiles released during impact degassing of carbonaceous, for this ratio that is above that for carbonaceous chondrites but after collapse of the steam atmosphere may have been more reducing. If this were the case, the ‘traditional’ volatiles left and thus the resulting ‘steam’ atmosphere may have been more reducing than the present day Earth, chondrite-like material. The proto-Earth (and also the impact and enstatite chondritic-like material, for example, up to 70% enstatite chondrite-like material and up to 21% H₂O)

Chemists believe that the HSE elements were added to Earth early in accretion (Figure 1 of Zahnle et al., 2010) after the Moon-forming impact. However, recent measurements of the Highly Siderophile Elements (HSE, which are Os, Ir, Pt, Ru, Rh, Pd, Re, and Au) in the terrestrial mantle are larger than would be expected from equilibrium partitioning.

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

<table>
<thead>
<tr>
<th>Gas (vol. %)</th>
<th>CI</th>
<th>CM</th>
<th>CV</th>
<th>H</th>
<th>L</th>
<th>LL</th>
<th>EH</th>
<th>EL</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>4.36</td>
<td>2.72</td>
<td>0.24</td>
<td>48.49</td>
<td>42.99</td>
<td>42.97</td>
<td>43.83</td>
<td>14.87</td>
</tr>
<tr>
<td>H₂O</td>
<td>69.47</td>
<td>73.38</td>
<td>17.72</td>
<td>18.61</td>
<td>17.43</td>
<td>23.59</td>
<td>16.82</td>
<td>5.71</td>
</tr>
<tr>
<td>CH₄</td>
<td>2 × 10⁻⁷</td>
<td>2 × 10⁻⁸</td>
<td>8 × 10⁻¹¹</td>
<td>0.74</td>
<td>0.66</td>
<td>0.39</td>
<td>0.71</td>
<td>0.17</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.39</td>
<td>18.66</td>
<td>70.54</td>
<td>3.98</td>
<td>5.08</td>
<td>5.51</td>
<td>4.66</td>
<td>9.91</td>
</tr>
<tr>
<td>CO</td>
<td>3.15</td>
<td>1.79</td>
<td>2.45</td>
<td>26.87</td>
<td>32.51</td>
<td>26.06</td>
<td>31.47</td>
<td>67.00</td>
</tr>
<tr>
<td>N₂</td>
<td>0.82</td>
<td>0.57</td>
<td>0.01</td>
<td>0.37</td>
<td>0.33</td>
<td>0.29</td>
<td>1.31</td>
<td>1.85</td>
</tr>
<tr>
<td>NH₃</td>
<td>5 × 10⁻⁶</td>
<td>2 × 10⁻⁶</td>
<td>8 × 10⁻⁹</td>
<td>0.01</td>
<td>0.01</td>
<td>9 × 10⁻⁵</td>
<td>0.02</td>
<td>5 × 10⁻⁵</td>
</tr>
<tr>
<td>H₂S</td>
<td>2.47</td>
<td>2.32</td>
<td>0.56</td>
<td>0.59</td>
<td>0.61</td>
<td>0.74</td>
<td>0.53</td>
<td>0.18</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.08</td>
<td>0.35</td>
<td>7.41</td>
<td>1 × 10⁻⁸</td>
<td>1 × 10⁻⁸</td>
<td>3 × 10⁻⁸</td>
<td>1 × 10⁻⁵</td>
<td>1 × 10⁻⁸</td>
</tr>
<tr>
<td>Otherᵃ</td>
<td>0.25</td>
<td>0.17</td>
<td>1.02</td>
<td>0.33</td>
<td>0.35</td>
<td>0.41</td>
<td>0.64</td>
<td>0.29</td>
</tr>
</tbody>
</table>

ᵃOther 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)
of orders of magnitude smaller than the solar composition value are O-rich and C-poor and have C other elements remaining fixed at their nominal abundances. Described later. Each element was varied individually, with all abundances were done using a smaller range of abundances as ranges to illustrate trends. The calculations for variable oxygen and H abundances are so different from our adopted nominal. As discussed below, there is no evidence that the actual C for C and H, for both the continental crust and the BSE.

Calculations were done from 0.1 to 10 we did a series of calculations at 100 bars for both the continental crust and the BSE.
Modern day volcanic gases, $CH_4$, have a fugacity of $10^{10}$ times lower than the oxygen fugacity corresponding to the steam content and total pressure of primordial volcanic gases. This involves the implicit assumption that the major volatile species are the same as today, which is supported by analyses for convergent plate, divergent plate, and hot spot volcanoes (Symonds et al., 1994). Figure 6 shows 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

- 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
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$_2$O$_3$, Na$_2$O, K$_2$O, TiO$_2$, Cr$_2$O$_3$, MnO, NiO, etc. but without the few % Fe$^{3+}$ in upper mantle – produces graphite at low T
BSE volatiles outgassing at Fe-FeO buffer 1 bar pressure

Temperature (K)

log mole fraction

-7  -6  -5  -4  -3  -2  -1  0

H₂  CH₄  H₂O  CO  CO₂  N₂  NH₃
BSE - no Fe$^{3+}$ - 100 bars

Outgassing Temperature (K)

Mole fraction

H$_2$, H$_2$O, CO, CO$_2$, CH$_4$, N$_2$, NH$_3$
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
Figure 4 shows the composition of saturated vapor in equilibrium with bulk silicate Earth magma. The partial pressures of various species are plotted against surface temperature (K). The species include Na, SiO, O, Mg, Fe, MgO, NaO, O₂, FeO, Si, AlO, K, and MgO. The graph illustrates how the abundances of these species change with temperature, highlighting the dominant gases such as SiO and O, and showing the relative volatility of different elements such as Na, Mg, and Fe.
Steam Atmosphere

• Impact-induced outgassing of H$_2$O 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
Silica solubility in steam

- Red: this work
- White: Plyasunov (2012)

Surface Temperature (Celsius)

$log_{10} P_{\Sigma Si} (\text{bar})$

Vapor pressure of pure SiO$_2$ (s,liq)
Silica Solubility Isobars

![Graph of Silica Solubility Isobars](image.png)

- **Surface Temperature (K)**: 1000, 1500, 2000, 2500, 3000

- **log$_{10}$ Mole Fraction**
  - -7
  - -6
  - -5
  - -4
  - -3
  - -2
  - -1

- **mass % SiO$_2$ in gas**
  - 10
  - 30
  - 100
  - 300
  - 1000
  - 2000
  - AB1965

- **Silica Solubility Isobars**
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