A Venus-like atmosphere on the early Earth from magma ocean outgassing

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**Planetary atmospheres**

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What did Earth’s first atmosphere look like?
Warm, little ponds

*ON THE EARLY CHEMICAL HISTORY OF THE EARTH AND THE ORIGIN OF LIFE*

**By Harold C. Urey**

Institute for Nuclear Studies, University of Chicago

Communicated January 26, 1952

**Miller-Urey experiment (1952)**

Reducing atmosphere \((\text{CH}_4-\text{NH}_3)\) on early Earth

Spark discharge in presence of \(\text{H}_2\text{O}\)

Produced ~23 amino-acids, some necessary for life

Did such an atmosphere exist?
A primary atmosphere?

Noble gases are depleted by orders of magnitude relative to major volatiles.
Secondary atmosphere

Earth has a secondary (i.e., post-nebular) atmosphere
Formed by magma ocean outgassing

Uncertainty as to the redox state of the early atmosphere

At equilibrium
\[ f_{O_2} \text{ of mantle} = f_{O_2} \text{ of atmosphere} \]
Magma ocean – atmosphere link

\[ Fe^{2+}O \text{ (silicate)} + \frac{1}{4} O_2 \text{ (atmosphere)} = Fe^{3+}O_{1.5} \text{ (silicate)} \]

At equilibrium between the magma ocean and the atmosphere,

\[
K = \frac{X(Fe^{3+}O_{1.5}) \gamma(Fe^{3+}O_{1.5})}{X(Fe^{2+}O) \gamma(Fe^{2+}O) f(O_2)^{0.25}}
\]

\[ K = \exp \left( \frac{-\Delta G(r)}{RT} \right) \]

\text{Activity coefficients}

Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio of magma ocean at its surface at a given fO\textsubscript{2} depends on:

1) Composition
2) Temperature

Well known for basalts; unknown for peridotites
Experimental approach

Natural processes
- Adiabatic
- Constant amount of O

Experiments
- Isothermal
- Constant $f_{O_2}$

Fe dominant redox-sensitive species in planetary compositions

**Approach:** Use $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio as a proxy for oxygen content
Experimental Set-up

Molten silicate Earth in a controlled atmosphere

Aerodynamic laser levitation furnace, IPG, Paris

- Synthetic peridotite composition (~KLB-1) ≈ Earth’s mantle

<table>
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<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
<th>FeO$^{(T)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
<td>46.53</td>
<td>4.37</td>
<td>38.05</td>
<td>2.06</td>
<td>8.44</td>
</tr>
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</table>

- Melted by aerodynamic levitation with 125 W CO$_2$ laser at $1900\pm50$ °C for ~ 30 s

- log$f_{O_2}$ varied by changing gas mixture (O$_2$, Ar-CO$_2$-H$_2$) between $\Delta$IW-1.5 and $\Delta$IW+6.5

- Quenched to glass by cutting power to laser
Fe$^{3+}$/Fe$^{2+}$ in peridotite glasses

*X-Ray Absorption Near-Edge Structure*

- Fe K-edge at beamline 13 IDE, APS, Chicago
- Position of **pre-edge centroid** and **0.8 edge energy** correlate with Fe$^{3+}$/Fe$^{2+}$
- Calibrated by Fe$^{3+}$/Fe$^{2+}$ in synthetic MORB glasses determined by Mössbauer spectroscopy
- Uncertainty $\sim \pm 0.015$ relative on Fe$^{3+}/\Sigma$Fe
Oxidation state of Fe in peridotite

\[ Fe^{2+}O \text{(silicate)} + \frac{1}{4}O_2 = Fe^{3+}O_{1.5} \text{(silicate)} \]

- Slope reflects the reaction stoichiometry (0.25 = ideal)
- Equilibrium constant of reaction is given by the intercept
- Reaction should tend towards ideality at high temperatures

Use of calibration requires estimation of Bulk Silicate Earth Fe\(^{3+}/\text{Fe}^{2+}\)
Fe$^{3+}$/Fe$^{2+}$ in peridotites

*Canil et al., 1994; Canil and O’Neill, 1996*

- Fe$^{3+}$/Fe$^{2+}$ correlated inversely with MgO (also other indices of melt depletion)
- Due to greater incompatibility of Fe$^{3+}$ compared to Fe$^{2+}$ during partial melting
- At the MgO content of the primitive mantle (36.77 wt. %), Fe$^{3+}$/∑Fe = 0.037 ± 0.005
Oxidation state of Fe in peridotite

\[ Fe^{2+}O \text{ (silicate)} + \frac{1}{4} O_2 = Fe^{3+}O_{1.5} \text{ (silicate)} \]

- Presume present-day bulk silicate Earth (BSE) = magma ocean
- \( \text{Fe}^{3+}/\Sigma\text{Fe} \) of 0.037 (Canil et al. 1994) yields an \( f_O^2 \) depending on calibration for molten peridotite at liquidus temperature
- Fixes \( \text{CO}_2/\text{CO} \) and \( \text{H}_2\text{O}/\text{H}_2 \) ratios in atmosphere

Used to calculate composition of earliest atmosphere
Composition of early Earth atmosphere

To solve for speciation in an H-C-N-O atmosphere requires **3 constraints**

1) $f_{O_2}$
   Given by $Fe^{3+}/Fe^{2+}$ in peridotite liquid

2) H/C

3) H/N
   Computed by
   
   i) *Bulk Silicate Earth abundances* (Hirschmann 2018)
   
   ii) *Solubility laws in peridotite* (e.g. Moore et al. 1998)
Composition of early Earth atmosphere

Atmospheric speciation calculated during closed-system cooling

**Major volatile species at these conditions**

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<th>Atmosphere</th>
<th>High T</th>
<th>Low T</th>
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<td>CH₄, N₂</td>
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BSE molar \( \text{H/C} \sim 5 \)
But likely lower as H solubility >> C solubility in magma ocean

We find composition of terrestrial atmosphere was ~Venus today
## Planetary Atmospheres

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Atmospheric Loss

\[ \lambda_{esc} = \frac{mv_{esc}^2}{2k_B T} \]

“Escape parameter”

Loss is most efficient for:

1. Lighter masses (H)
2. Smaller bodies (low \( v_{esc} \))
3. Hotter atmospheres (high \( T_{exobase} \))

\[ T_{exobase} = C \frac{F_{XUV}}{g} + T_{min} \]

Lammer et al. (2003)
Hydrogen Isotope Fractionation

Jeans Escape ($\lambda \gg 1$)

$$
\frac{\left( \frac{dt}{dm_H} \right)}{\left( \frac{dt}{dm_D} \right)} = \sqrt{\frac{m_D}{m_H}}
$$

Use D/H ratio to constrain hydrogen loss fraction

Earth retains liquid H$_2$O on its surface over geological timescales
Why H$_2$O counts - the Urey Reaction

$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$

Reaction catalysed by the dissolution of CO$_2$ in water (Urey, 1952)

Global crustal recycling process on Earth helped C burial

Effective mechanism for drawing down atmospheric CO$_2$ levels

May occur over 100 Myr

Sleep et al. 2001
Development of life?

CO₂-N₂ atmospheres inefficient in synthesising amino-acids (glycine only; Schlesinger and Miller 1983)

AAs produced in presence of pH-buffered H₂O at ~7 with CaCO₃ (Cleaves et al. 2008)

Yields are halved compared with reducing atmospheres

Warm, little ponds?
Conclusions

• Calibrated dependence of Fe\(^{2+}/Fe^{3+}\) on \(f_O_2\) in peridotite liquids relevant to planetary magma oceans

• Earth had a neutral, Venus-like atmosphere produced by magma ocean outgassing

• Earth is bracketed heliocentrically by planets with CO\(_2\)-N\(_2\) (97:3) atmospheres

• Large mass and distance from Sun minimised H-loss on Earth compared to Venus and Mars

• Atmosphere underwent significant CO\(_2\) draw-down post magma-ocean on Earth