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

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Planetary atmospheres

	Venus	Earth	Mars
CO_2/N_2 Initial atmosphere	?	**????**	?
CO_2/N_2 Present atmosphere	43.3	7.8×10^{-4}	55
Total bars	92	1.013	0.0061

What did Earth's first atmosphere look like?

Warm, little ponds

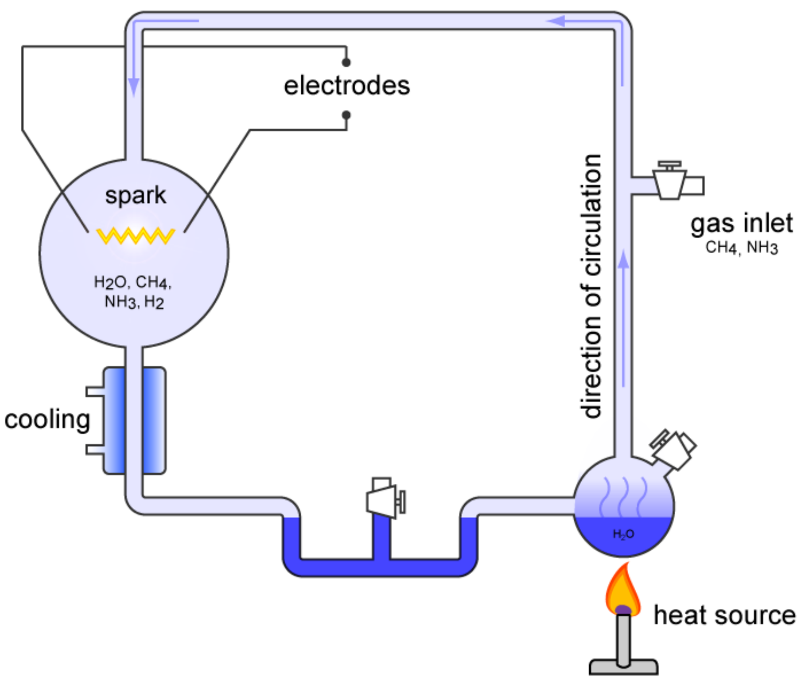
ON THE EARLY CHEMICAL HISTORY OF THE EARTH AND THE ORIGIN OF LIFE

BY HAROLD C. UREY

INSTITUTE FOR NUCLEAR STUDIES, UNIVERSITY OF CHICAGO

Communicated January 26, 1952

Miller-Urey experiment (1952)



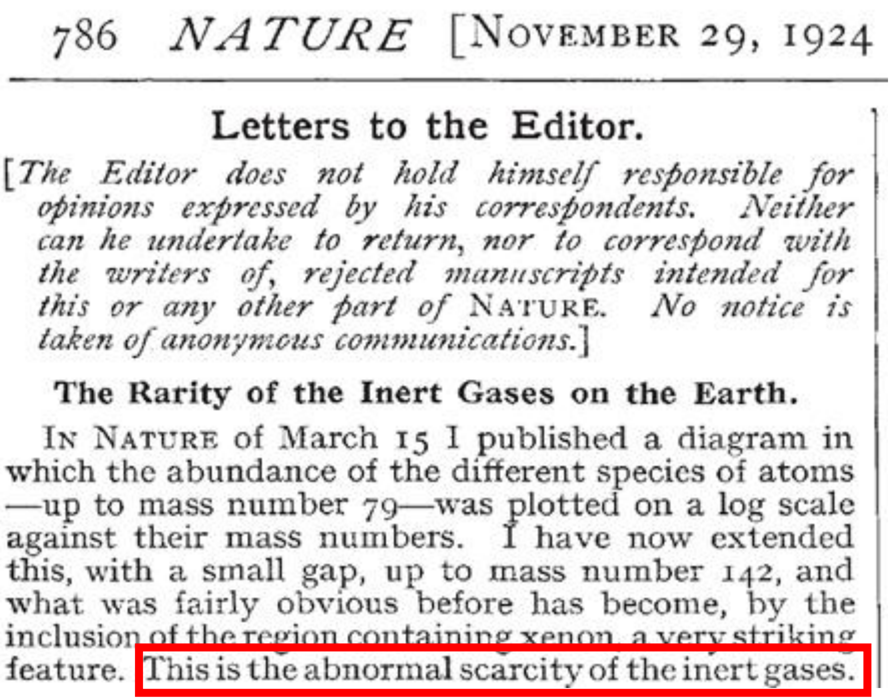
Reducing atmosphere (CH_4-NH_3) on early Earth

Spark discharge in presence of H_2O

Produced ~23 amino-acids, some necessary for life

Did such an atmosphere exist?

A primary atmosphere?


786 *NATURE* [NOVEMBER 29, 1924

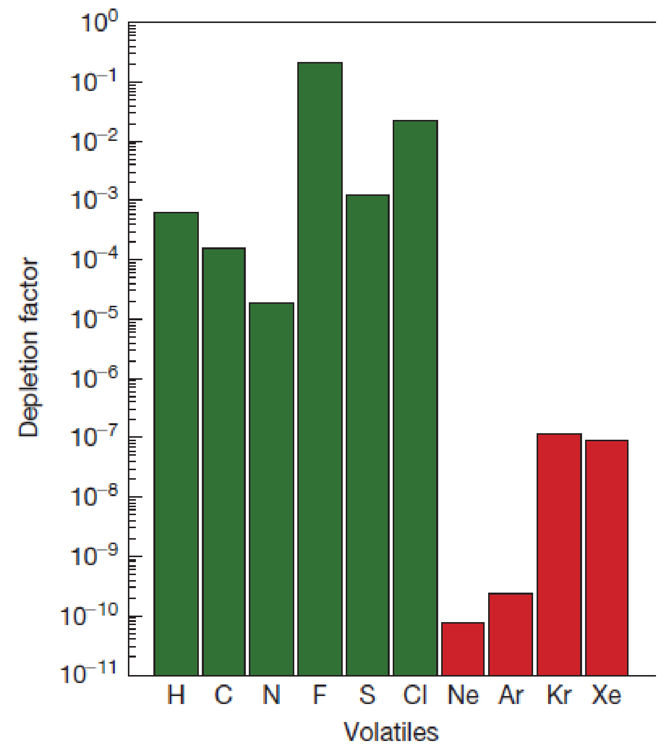
Letters to the Editor.

[*The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, nor to correspond with the writers of, rejected manuscripts intended for this or any other part of* NATURE. *No notice is taken of anonymous communications.*]

The Rarity of the Inert Gases on the Earth.

IN NATURE of March 15 I published a diagram in which the abundance of the different species of atoms —up to mass number 79—was plotted on a log scale against their mass numbers. I have now extended this, with a small gap, up to mass number 142, and what was fairly obvious before has become, by the inclusion of the region containing xenon, a very striking feature. This is the abnormal scarcity of the inert gases.

Aston (1924)

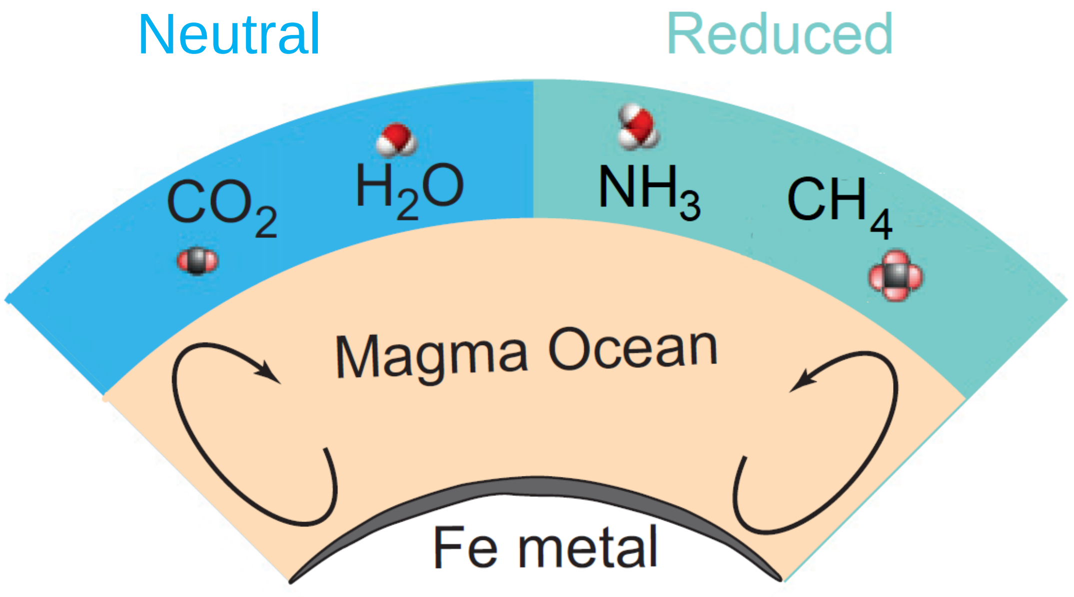


Fegley and Schaefer (2014)

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
fO_2 of mantle = *f*O_2 of atmosphere

Magma ocean – atmosphere link

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

At equilibrium between the **magma ocean** and the **atmosphere**,

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

$$K = \exp\left(\frac{-\Delta G_{(r)}}{RT}\right)$$

Activity coefficients

Fe^{3+}/Fe^{2+} ratio of magma ocean **at its surface** at a **given *f*O$_2$** depends on:

1) Composition
2) Temperature

Well known for basalts; **unknown for peridotites**

Experimental approach

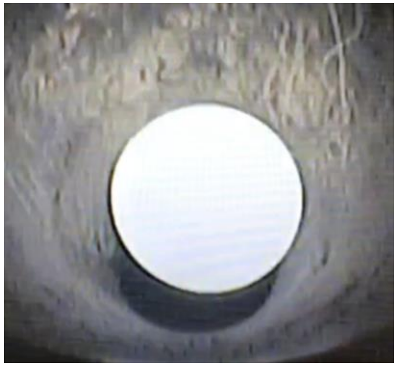
Natural processes

Adiabatic
Constant amount of O

Experiments

Isothermal
Constant fO_2

↔



Fe dominant redox-sensitive species in planetary compositions

Approach: **Use Fe^{3+}/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

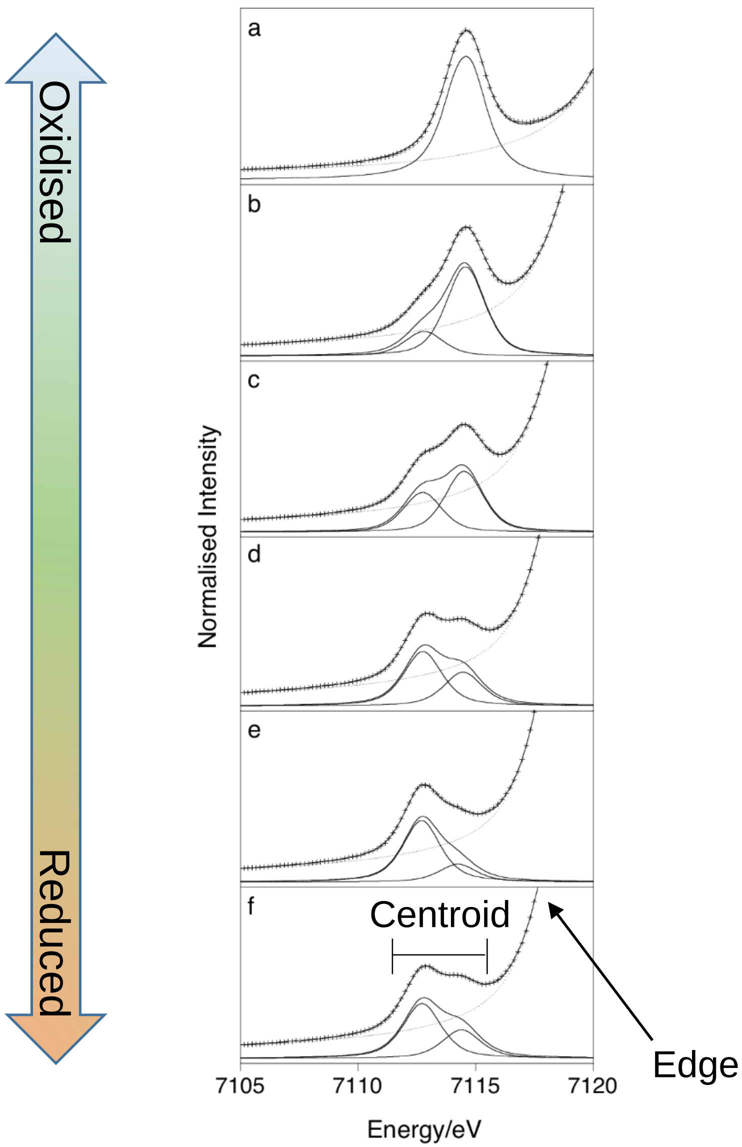
SiO_2	Al_2O_3	MgO	CaO	$FeO^{(T)}$
46.53	4.37	38.05	2.06	8.44

- Melted by aerodynamic levitation with 125 W CO_2 laser at **1900±50 °C** for **~ 30 s**

- logfO_2 varied by changing gas mixture (O_2, Ar-CO_2-H_2) between **ΔIW-1.5** and **ΔIW+6.5**

- Quenched to glass by cutting power to laser

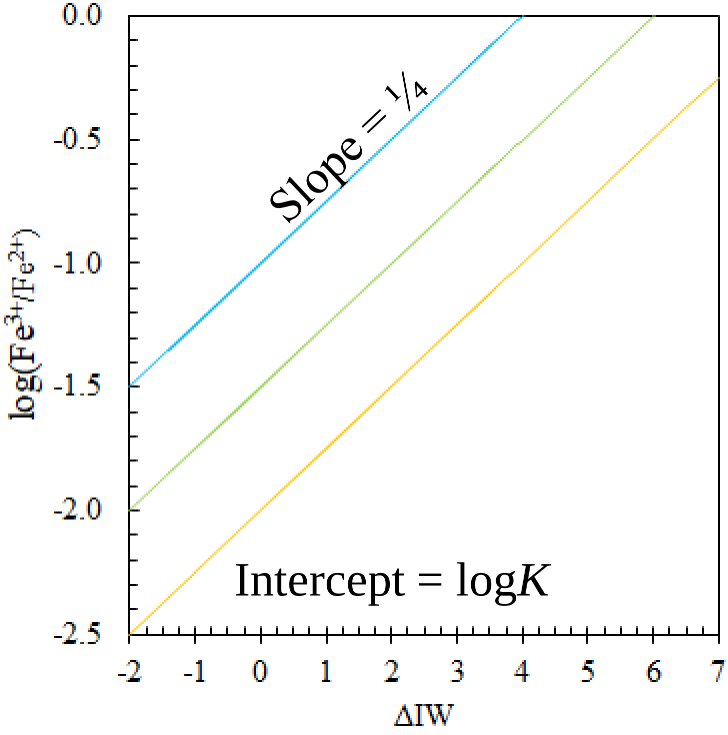
Fe^{3+}/Fe^{2+} in peridotite glasses



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 ~±0.015 relative on $Fe^{3+}/\sum Fe$

Oxidation state of Fe in peridotite



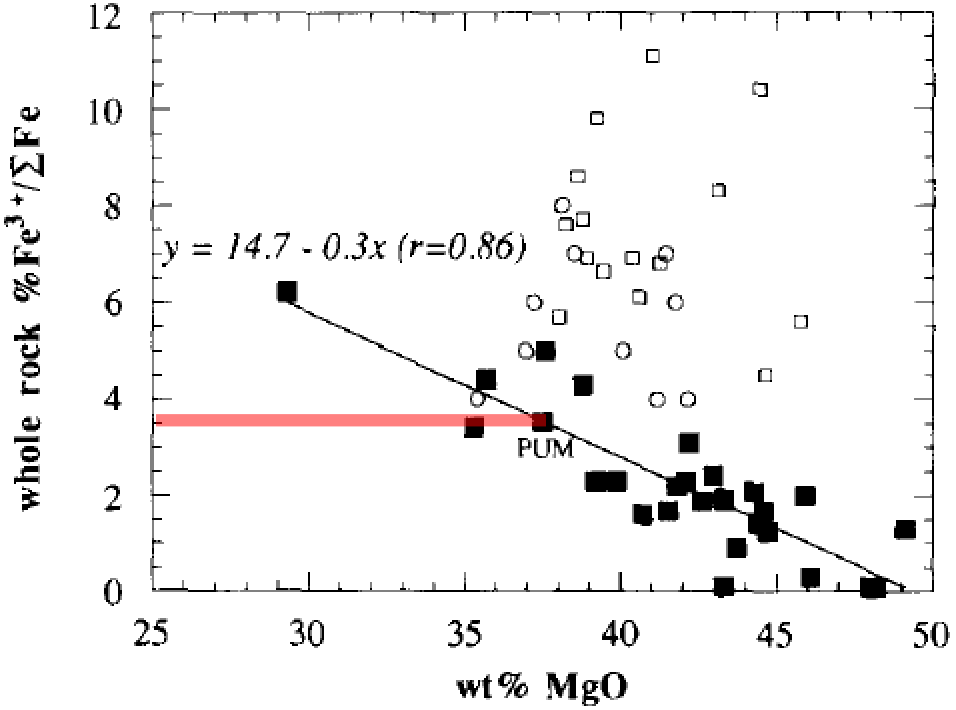
$$Fe^{2+}O\ (silicate) + \frac{1}{4}O_2 = Fe^{3+}O_{1.5}\ (silicate)$$

- 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+}/Fe^{2+}

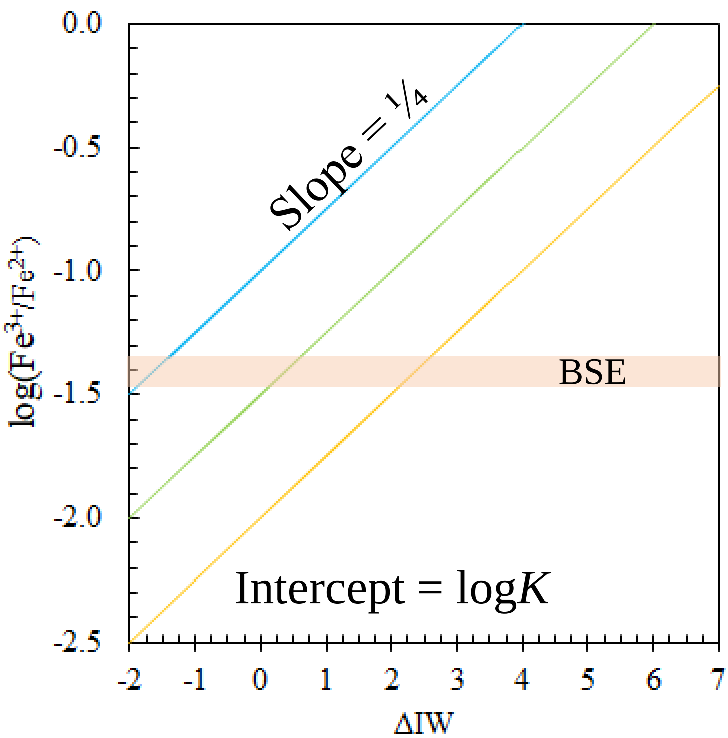
Fe^{3+}/Fe^{2+} in peridotites

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. %), $Fe^{3+}/\sum Fe = 0.037 \pm 0.005$

Oxidation state of Fe in peridotite



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

- Presume present-day bulk silicate Earth (BSE) = magma ocean
- $Fe^{3+}/\sum Fe$ of 0.037 (Canil et al. 1994) yields an fO_2 **depending on calibration for** molten peridotite at liquidus temperature
- Fixes CO_2/CO and H_2O/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) fO_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

Atmosphere	High T	Low T
<IW (H/C = 5)	**H_2**, **CO**, H_2O	**CH_4**, N_2
>IW (H/C = 5)	**H_2O**, **CO**, H_2, CO_2	**CO_2**, N_2
H/C < 5 (~IW)	**CO**, CO_2	**CO_2**, N_2
H/C > 5 (~IW)	H_2O, H_2	**CH_4**, N_2, (NH_3)

BSE molar **H/C ~ 5**

But likely lower as H solubility >> C solubility in magma ocean

We find composition of terrestrial atmosphere was ~Venus today

Planetary atmospheres

	Venus	Earth	Mars
CO_2/N_2 Initial atmosphere	?	**~35**	?
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Atmospheric Loss

Mass of gas species

Velocity required for escape

$$\lambda_{esc} = \frac{m v_{esc}^2}{2k_B T}$$

Mean thermal velocity of gas

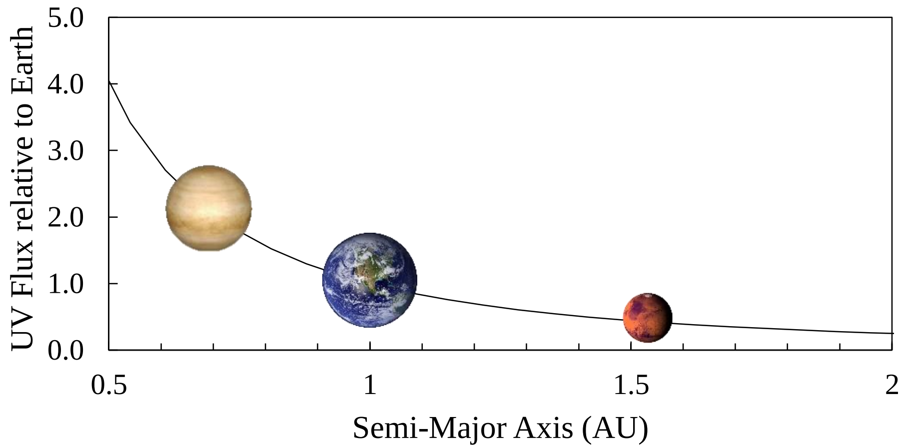
"Escape parameter"

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)

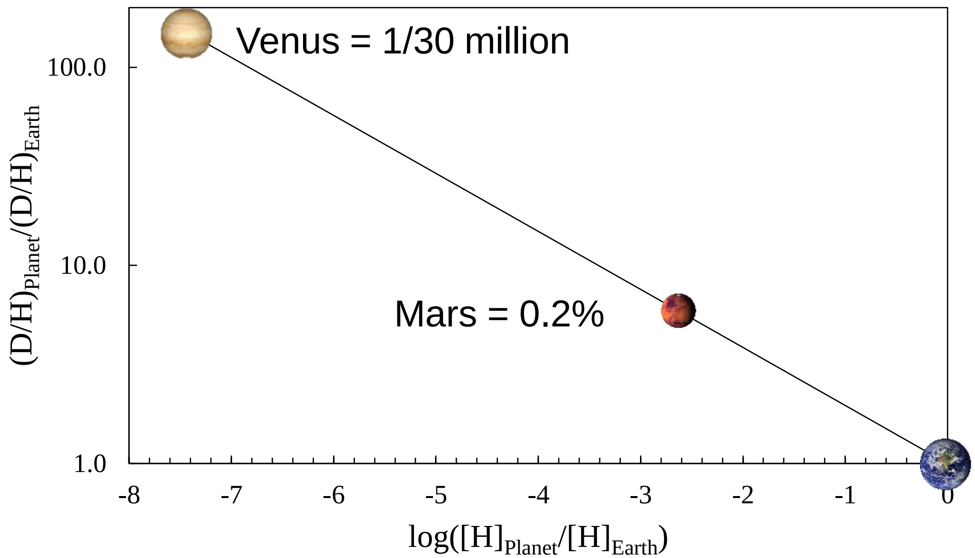


Hydrogen Isotope Fractionation

Jeans Escape (λ >> 1)

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

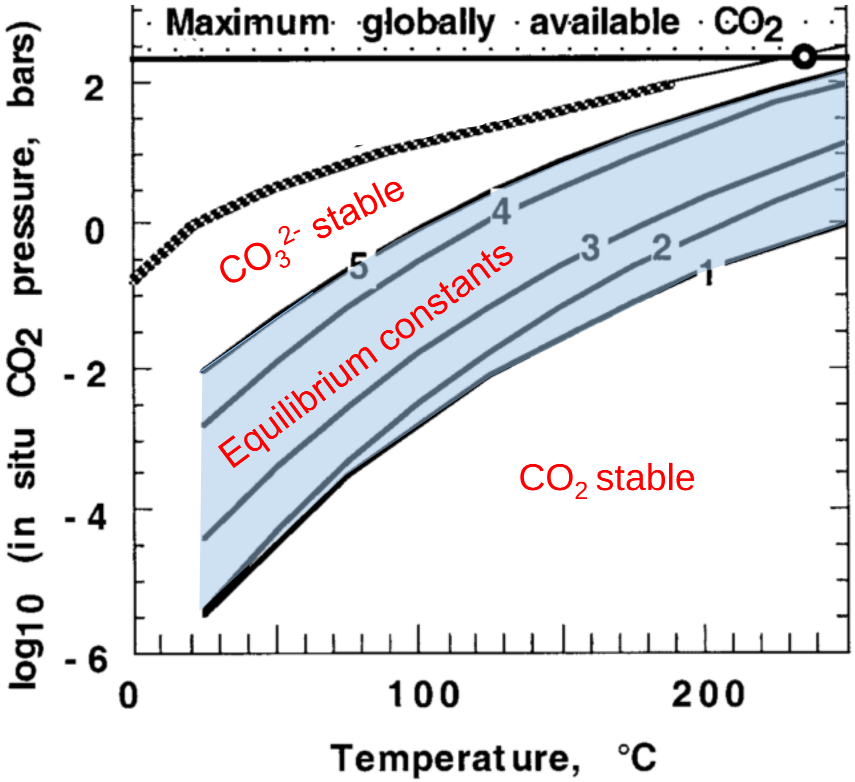
Use D/H ratio to constrain hydrogen loss fraction



Earth retains liquid H_2O on its surface over geological timescales

Why H_2O counts - the Urey Reaction

$$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$$



Sleep et al. 2001

Reaction catalysed by the dissolution of CO_2 in water (Urey, 1952)

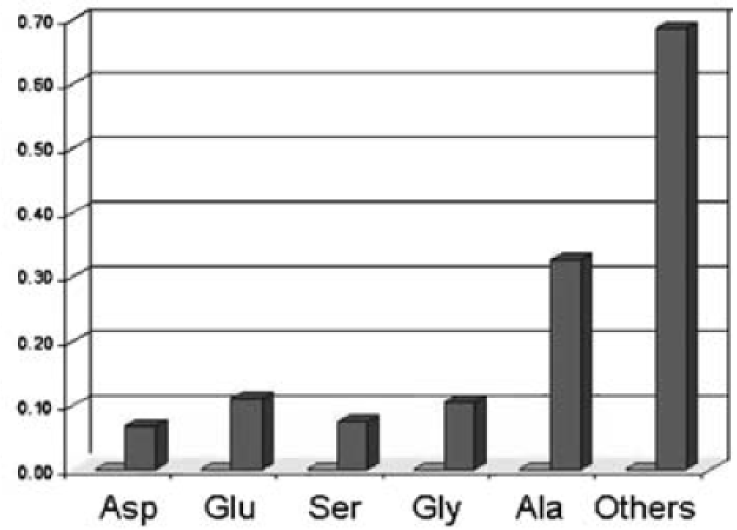
Global crustal recycling process on Earth helped C burial

Effective mechanism for drawing down atmospheric CO_2 levels

May occur over 100 Myr

Development of life?

CO_2-N_2 atmospheres inefficient in synthesising amino-acids (glycine only; Schlesinger and Miller 1983)



Cleaves et al. 2008

AAs produced in presence of pH-buffered H_2O at ~7 with $CaCO_3$ (Cleaves et al. 2008)

Yields are halved compared with reducing atmospheres

Warm, little ponds?

Conclusions

- Calibrated dependence of Fe^{2+}/Fe^{3+} on fO_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