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Building planetary atmospheres from magma oceans

Paolo A. Sossi

with Dan J. Bower, Antony D. Burnham, Pete Tollan, James Badro, Kaustubh Hakim, Antonio Lanzirotti, Matt Newville, Patrick Sanan, Hugh St.C. O'Neill

Planetary Atmospheres

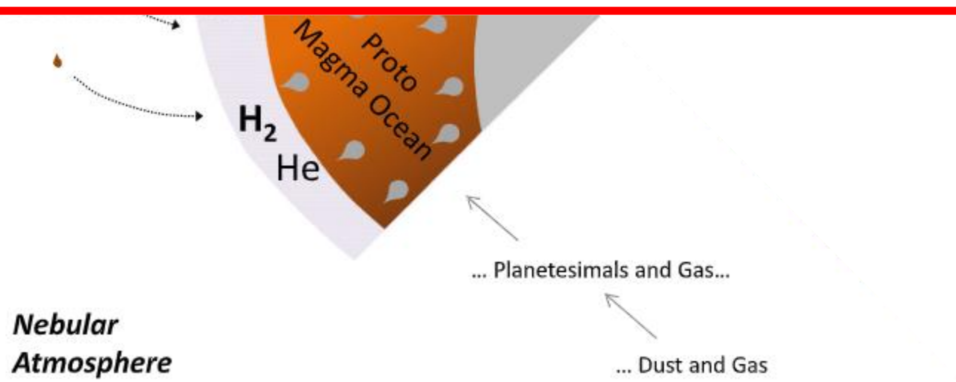
	Venus	Earth	Mars
CO_2/N_2 Initial atmosphere	?	?	?
CO_2/N_2 Present atmosphere	43.3	7.8×10^{-4}	55
Total bars	92	1.013	0.0061

Classification

2°

Gaillard and Scaillet (2014)

1°



3°

Why do they matter?

Warm little ponds

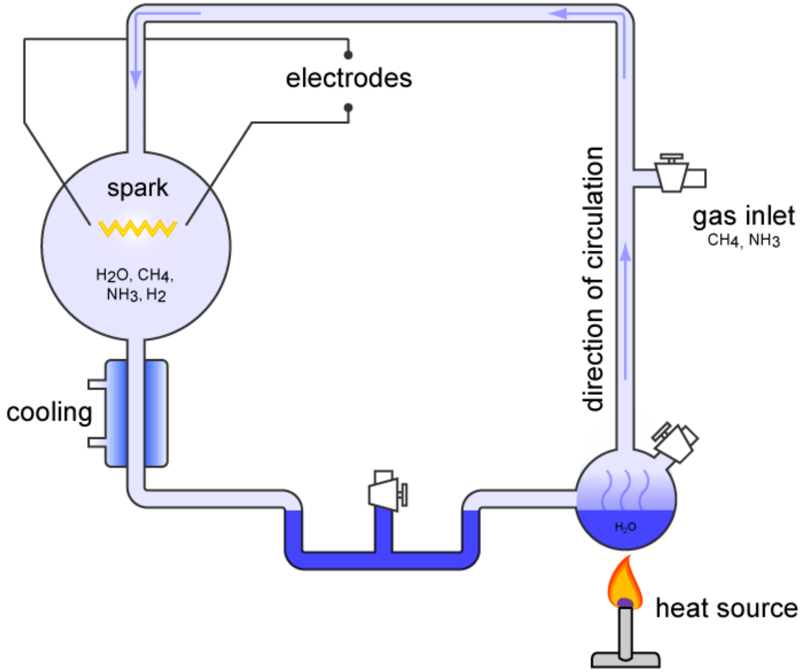
ON THE EARLY CHEMICAL HISTORY OF THE EARTH AND THE ORIGIN OF LIFE

BY HAROLD C. UREY

INSTITUTE FOR NUCLEAR STUDIES, UNIVERSITY OF CHICAGO

Communicated January 26, 1952

Miller-Urey experiment (1952)



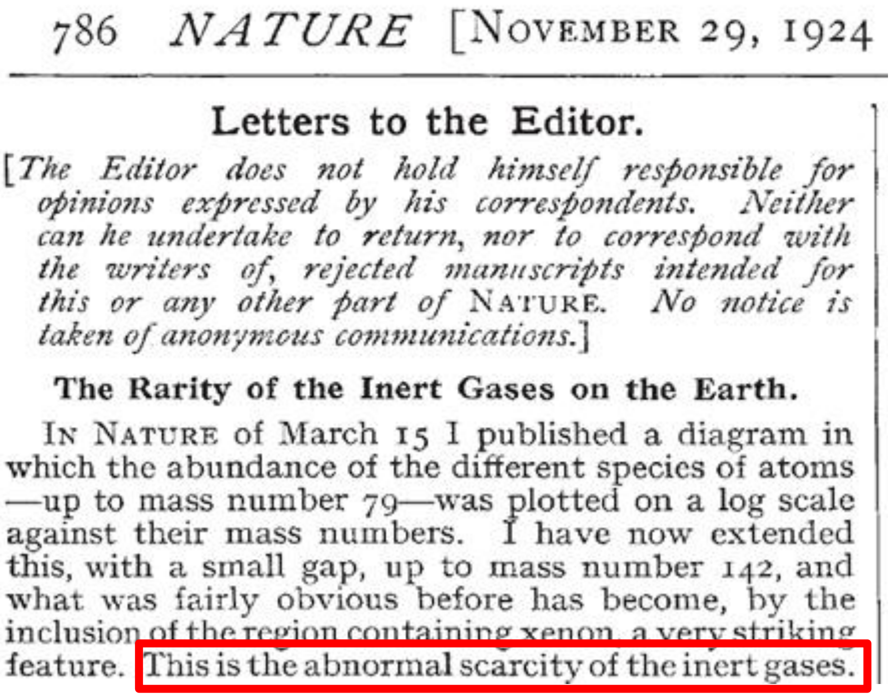
Reducing atmosphere (CH_4-NH_3)

Spark discharge in presence of H_2O

Produced ~23 amino-acids, some necessary for life

Did such atmospheres exist?

Evolution of Earth's atmopshere



786 NATURE [November 29, 1924

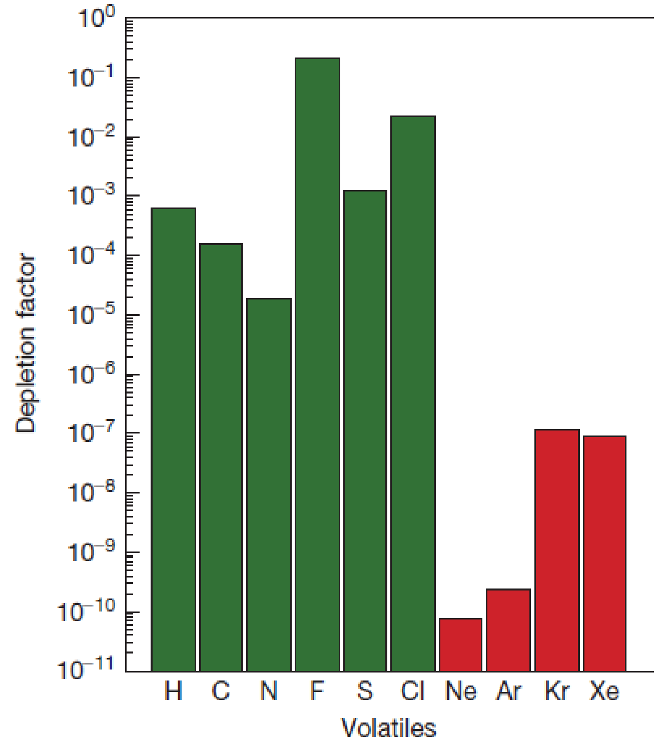
Letters to the Editor.

[*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)



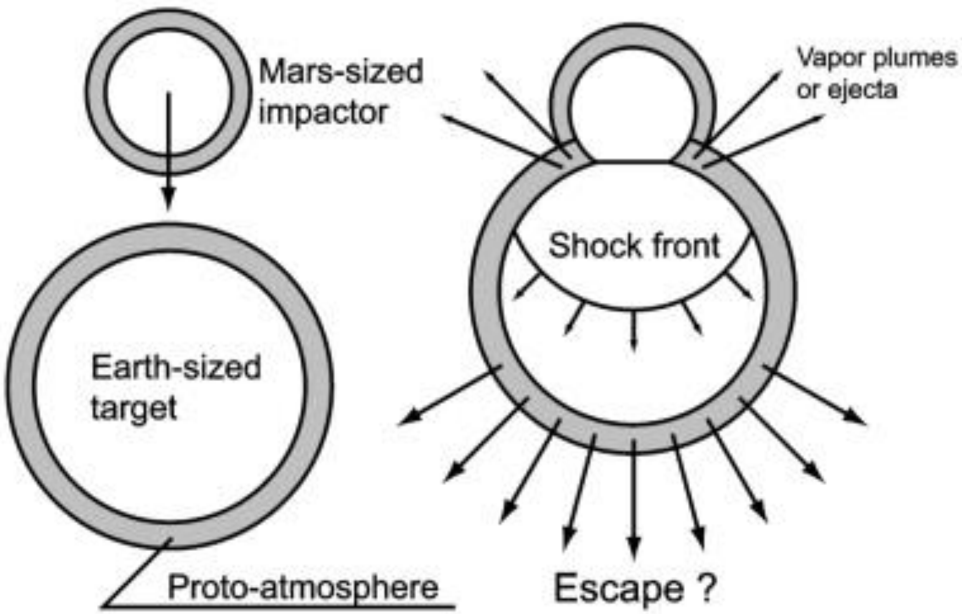
Fegley and Schaefer (2014)

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

Earth has a *secondary* (i.e., post-nebular) atmosphere

Moon-forming impact

Genda and Abe (2003)

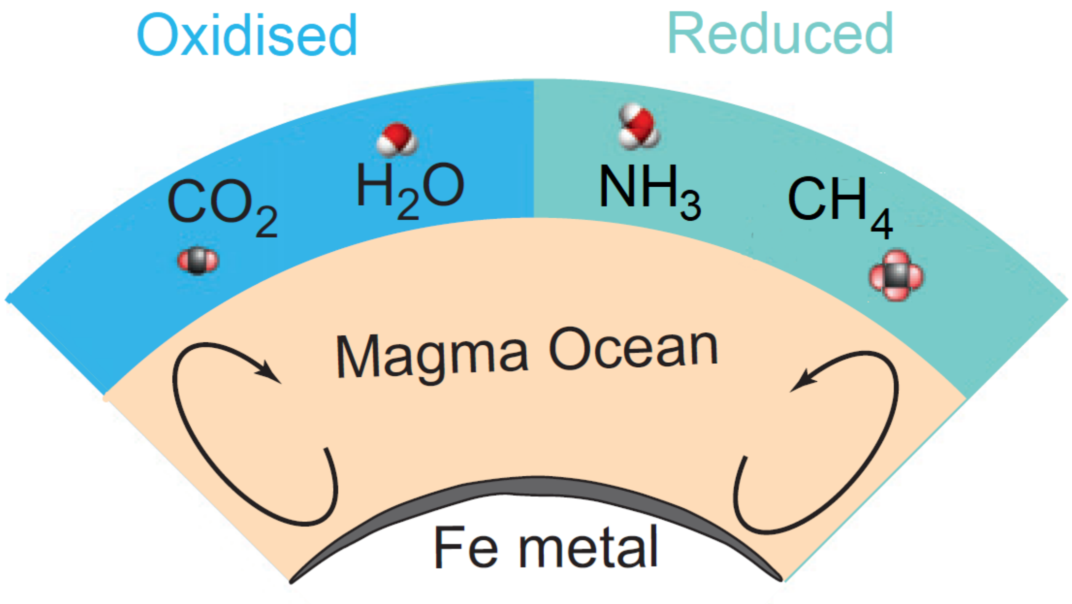


Provides enough energy to melt entire mantle

>97% of Xe (and other noble gases) lost before ~ 100 Myr (Porcelli et al. 2001)
40 – 50 Myr considering further Xe loss in Archean (Pujol et al. 2011)

A Secondary Atmosphere

Magma Ocean stage (post Moon-forming impact)



Uncertainty as to the redox state of the early atmosphere

At equilibrium
fO_2 of mantle = fO_2 of atmosphere

Oxidation state of Earth's atmosphere

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

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

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

Equilibrium constant (known)

Activities (measured)

Oxygen fugacity (controlled/calculated)

Fe^{3+}/Fe^{2+} ratio of a magma at a **given fO_2** depends on:

1) Composition
2) Temperature

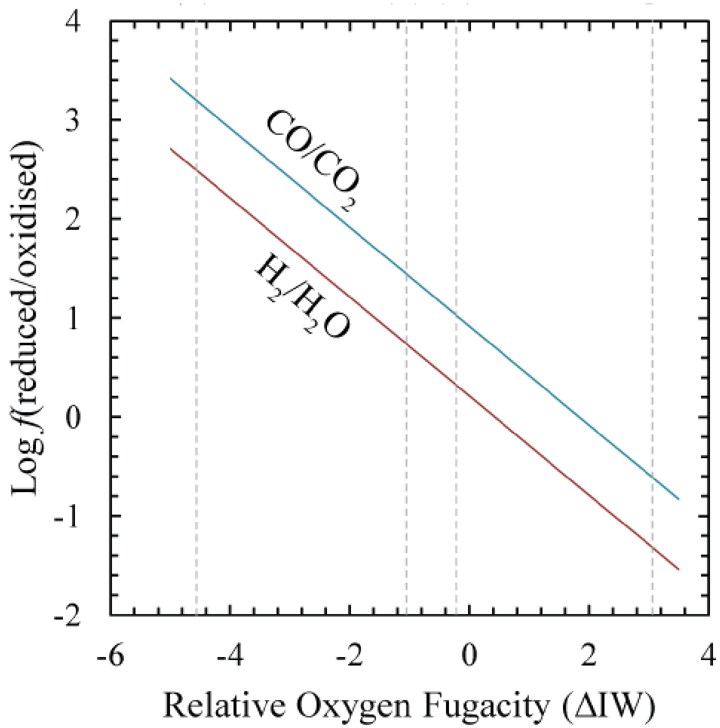
Well known for basalts; **unknown for peridotites (Earth-like)**

Magma ocean-atmosphere link

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

Existing models relate Fe^{3+}/Fe^{2+} to fO_2 for basaltic melts

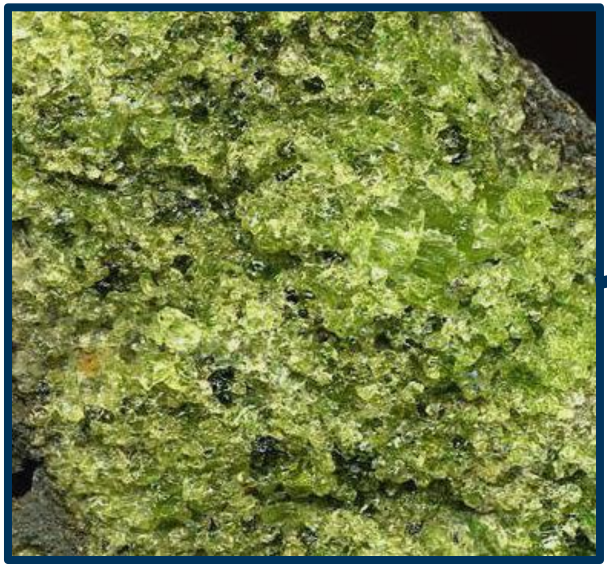
Do models work for a **magma ocean peridotite** with $Fe^{3+}/Fe^{2+} = 0.037$ at 2173 K?

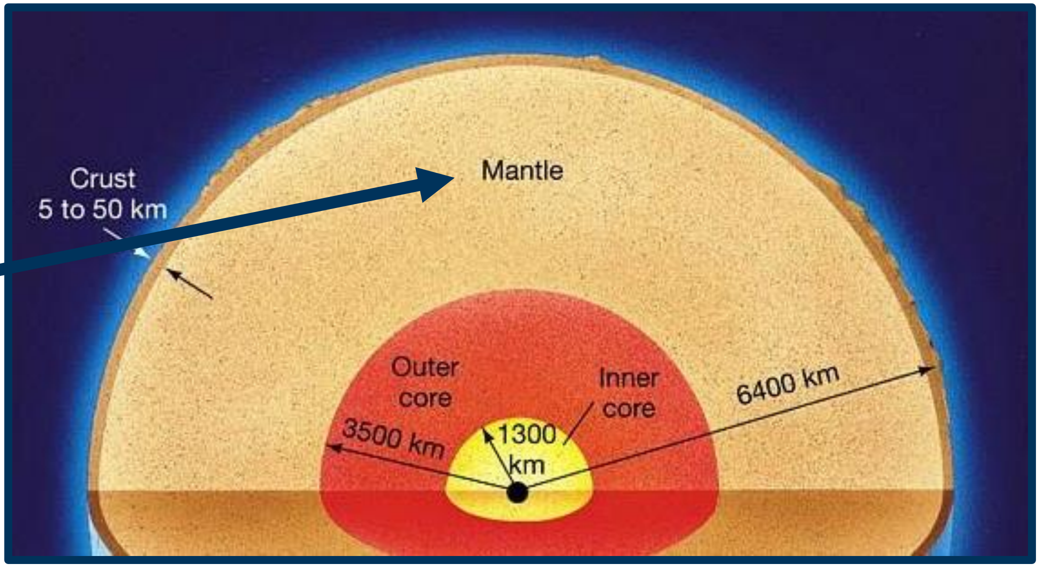


Aim: Calibration of the reaction for a realistic peridotite liquid composition

Why peridotite?

Most common rock on (in) the Earth

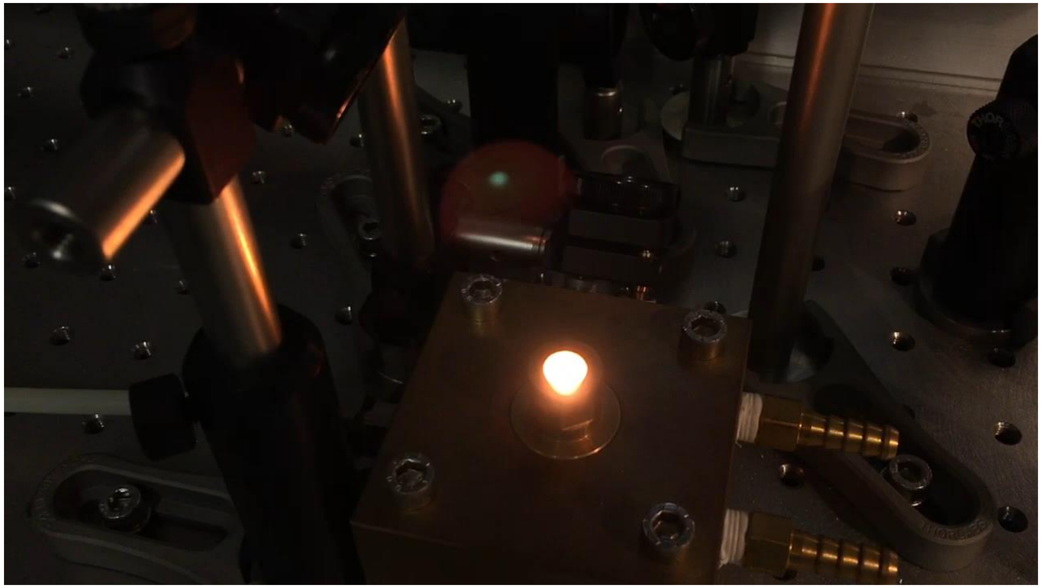




- 60 % olivine, 30 % orthopyroxene, 15 % clinopyroxene, <5 % other
- Very **high** melting temperature (> 1700 °C at 1 bar)
- Hard to quench into a glass

Experimental Set-up

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**

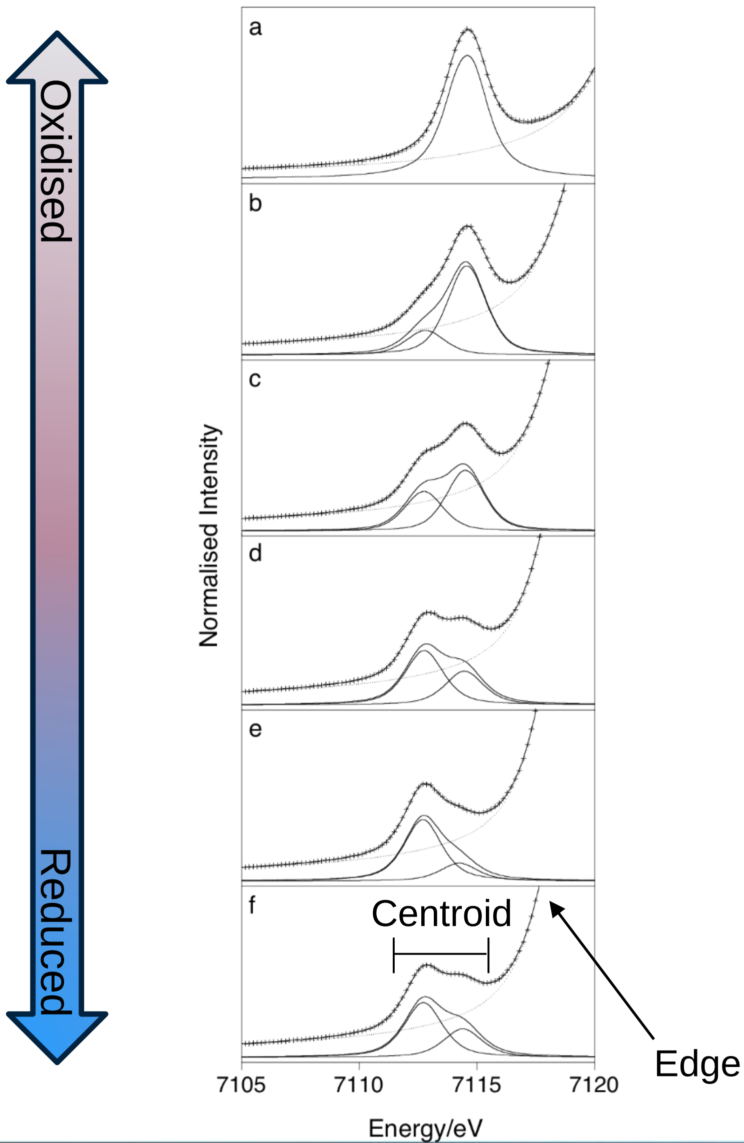
- Gas fugacities varied by changing gas mixture (O_2, Ar-CO_2-H_2)

reduced *fO_2* *oxidised*

ΔIW-1.5 **ΔIW+5**

- Determine $Fe^{3+}/Fe^{(T)}$ in glasses

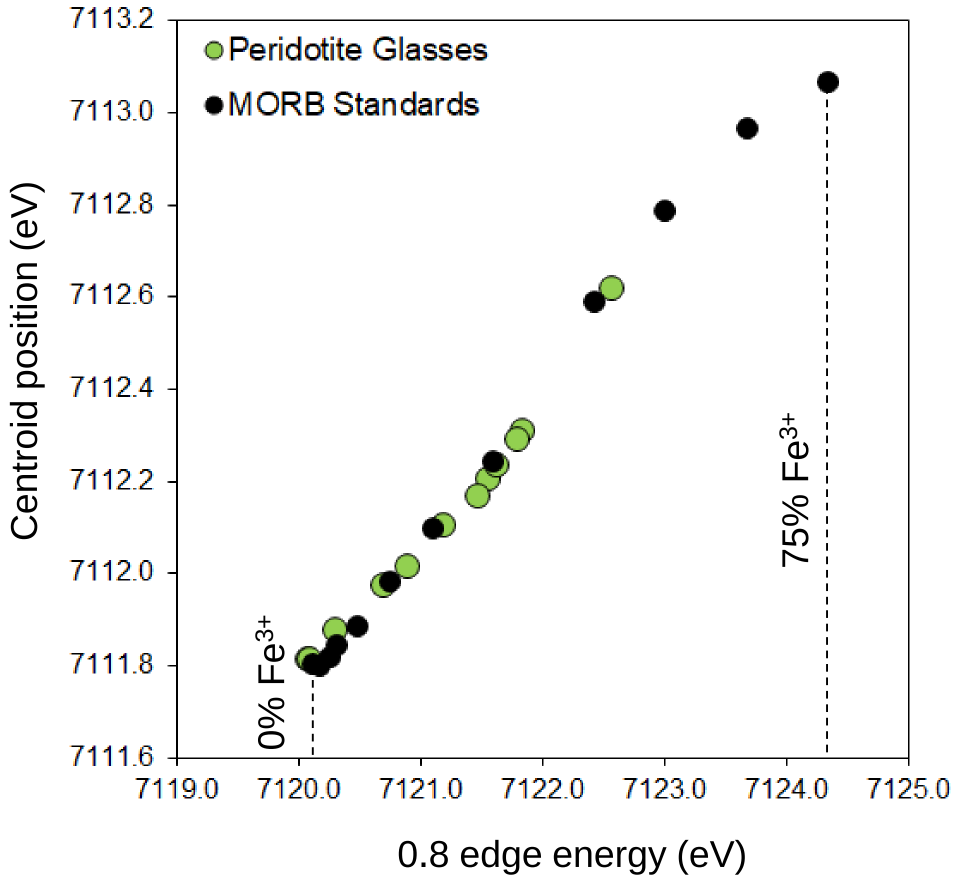
XANES



X-Ray Absorption Near-Edge Structure

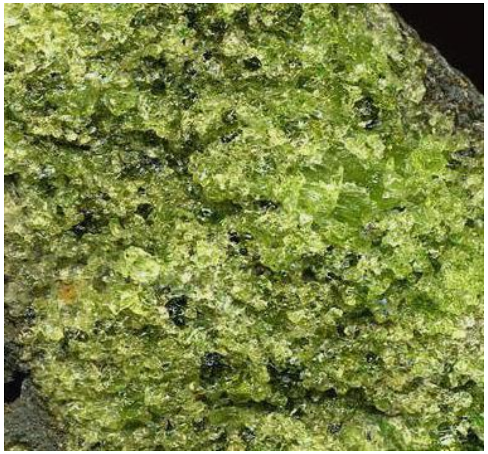
- Fe K-edge at beamline 13 IDE, APS, Chicago
- 10 µm focused beam
- Pre-edge peaks were fit by a Gaussian and a Lorentzian peak
- Position of **pre-edge centroid** and **0.8 edge energy** used to determine $Fe^{3+}/\sum Fe$

XANES



- Calibrated by $Fe^{3+}/\sum Fe$ measured in MORB glasses using Mössbauer
- Peridotite glasses have **same** dependence as MORB glasses
- Uncertainty ~±0.015 relative on $Fe^{3+}/\sum Fe$

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

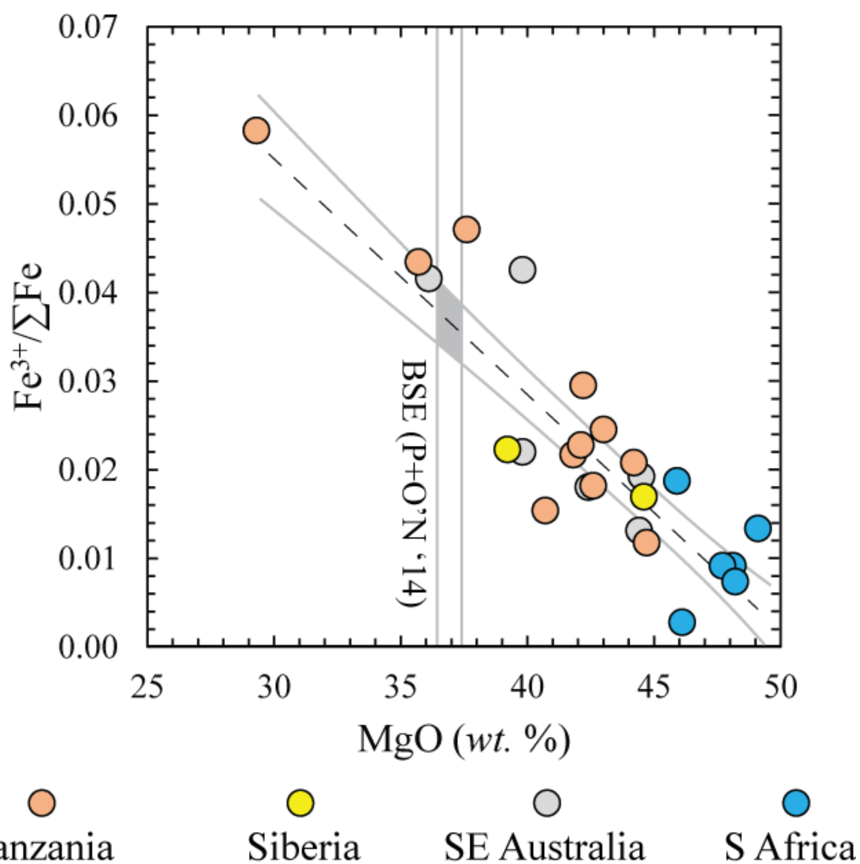


Phase	Mode (%)	$Fe^{3+}/\sum Fe$	FeO (wt. %)
Olivine	55	<0.01	10
Orthopyroxene	25	0.04-0.06	6-7
Clinopyroxene	18	0.12-0.22	2.3-3.5
Spinel	2	0.15-0.25	~7-12

- Measurement of Fe^{3+}/Fe^{2+} in individual mantle minerals by Mössbauer spectroscopy (Canil et al., 1994; Canil and O'Neill, 1996)
- Whole rock Fe^{3+}/Fe^{2+} reconstructed by mass balance
- Global array of peridotites (orogenic, continental xenolith, cratonic)

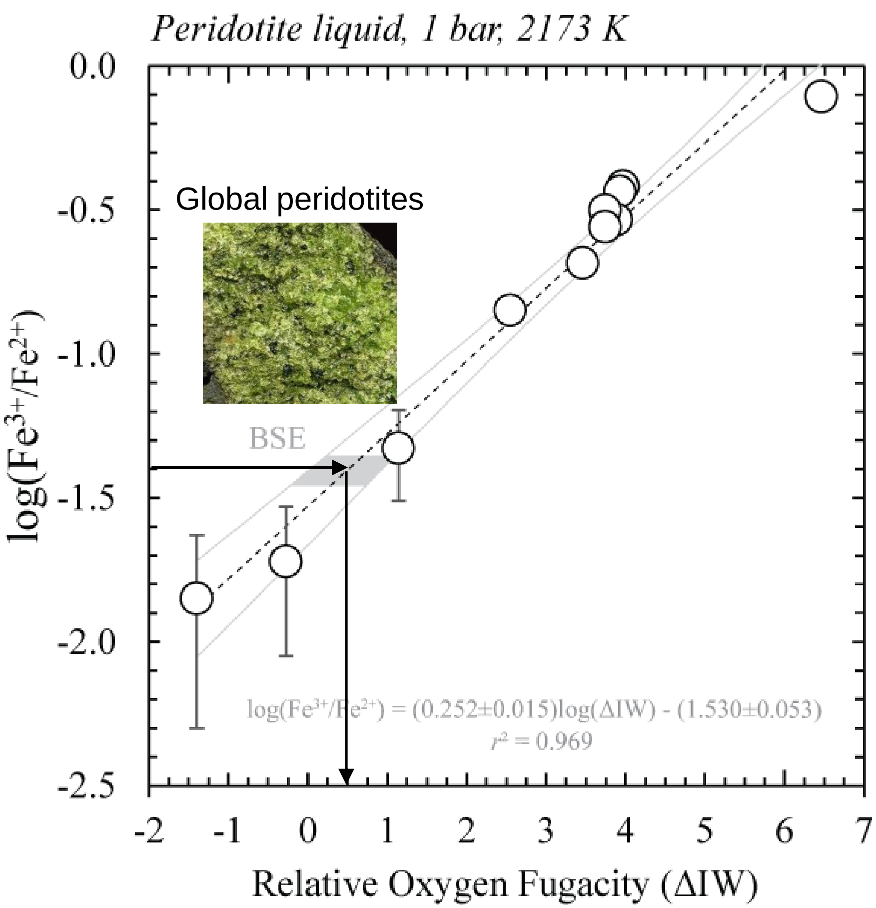
Fe^{3+}/Fe^{2+} in peridotites

Canil et al., 1994; Canil and O'Neill, 1996



- Fe^{3+}/Fe^{2+} correlated inversely with MgO (& other indices of melt depletion)
- Fe^{3+} is more incompatible than Fe^{2+} during partial melting
  - At MgO content of the primitive mantle (36.77 wt. %), $Fe^{3+}/\sum Fe = 0.037 \pm 0.005$

Oxygen fugacity of the magma ocean



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

- Presume present-day bulk silicate Earth (BSE) = magma ocean
  - $Fe^{3+}/\sum Fe$ of **0.037±0.005** in peridotite → $fO_2 = \Delta IW+0.5\pm0.7$ for molten peridotite
- Fixes **CO_2/CO** and **H_2O/H_2** ratios in atmosphere

Composition of the early Earth's atmosphere

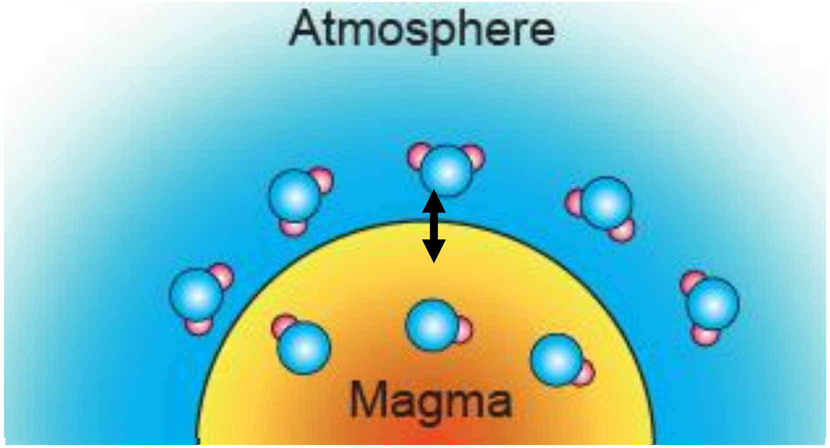
To solve for speciation in an H-C-N-O atmosphere requires
3 constraints

1) fO_2 = ΔIW+0.5
Given by Fe^{3+}/Fe^{2+}

2) H/C
3) H/N
Computed by
   i) Bulk Silicate Earth abundances
   ii) Solubility laws in peridotite

Steam atmospheres?

Early Earth is assumed to have a **steam (H_2O-rich)** atmosphere



Solubility Law

Mole fraction dissolved in melt ← $\boxed{X} = \boxed{\alpha}\boxed{P}^{\boxed{\beta}}$ → Stoichiometric coefficient

Partial pressure in atmosphere

Solubility constant

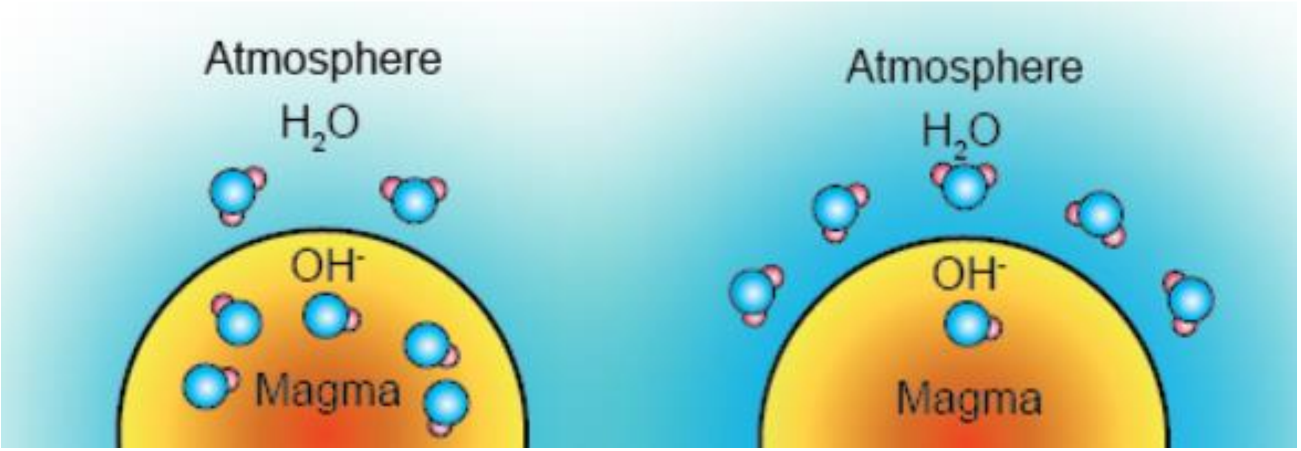
No studies on realistic silicate mantle **compositions** and **temperatures** relevant to magma oceans

Determination of solubility

Aim: Quantify H solubility in **peridotite melt**

α = high
Small Atmosphere

α = low
Large Atmosphere



Mole fraction dissolved

Measured by FTIR of quenched glasses

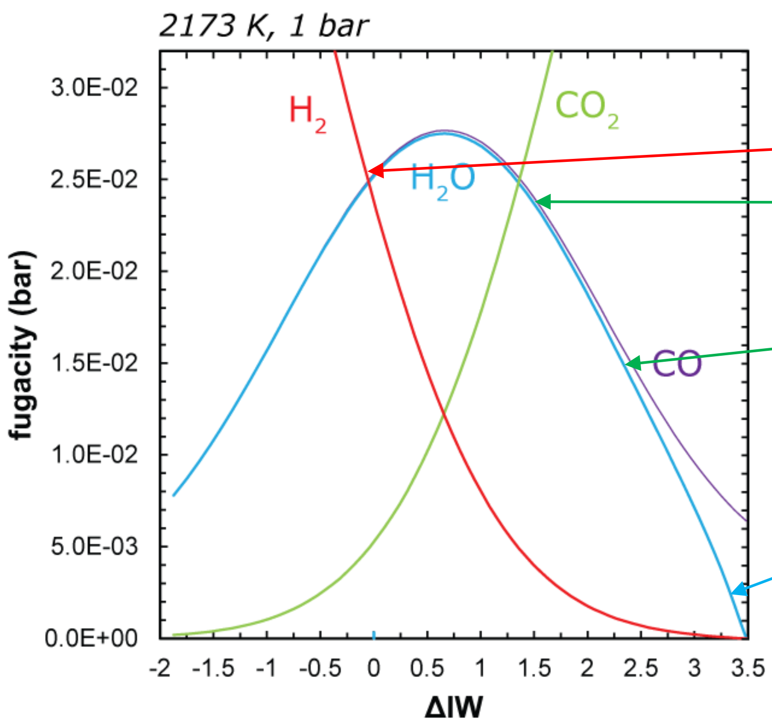
$$X = \alpha P^{\beta}$$

Partial pressure in atmosphere

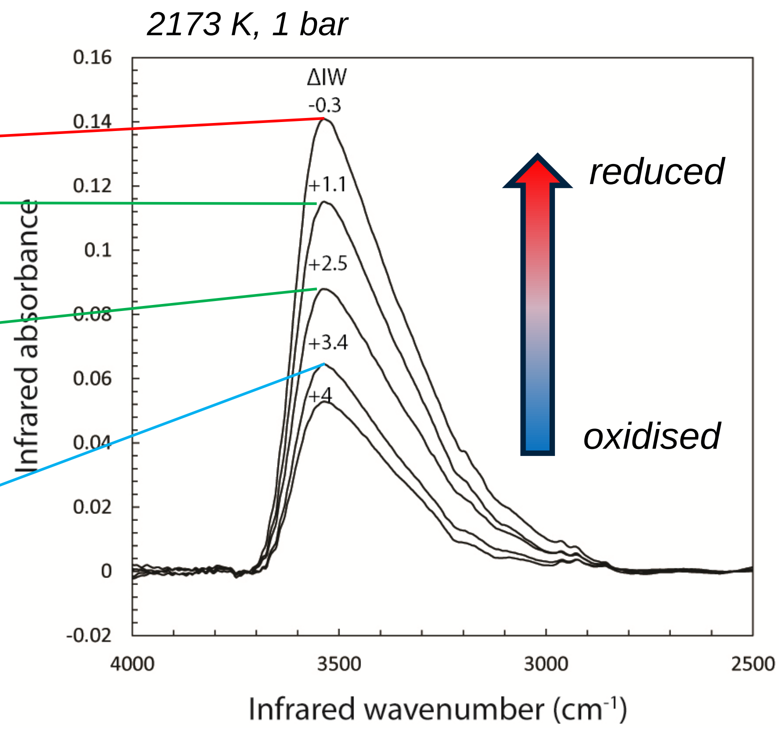
Calculated using thermodynamic data for gases

Solubility of water in peridotite melt

Partial pressure (*P*)



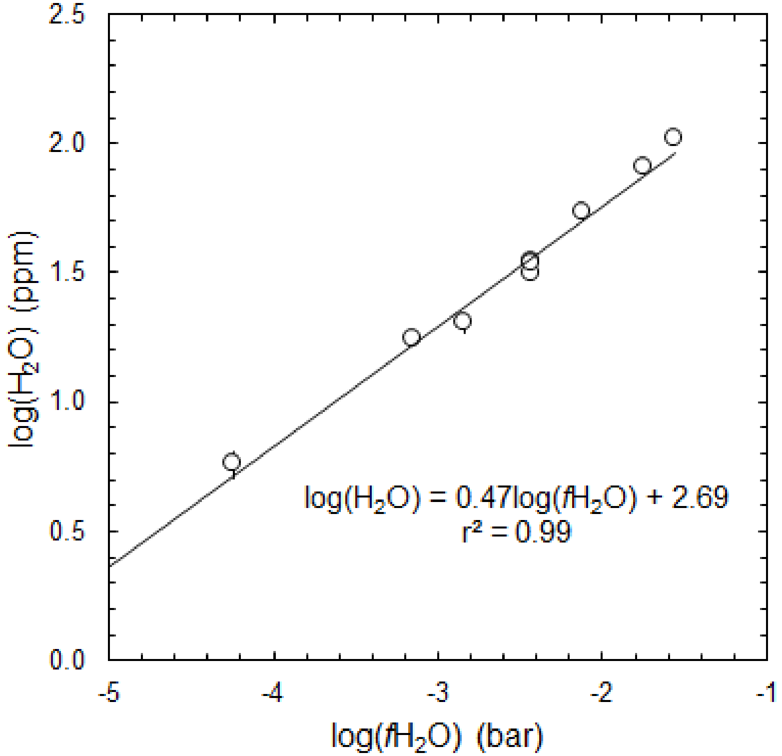
Quantity in melt (*X*)



At constant T and P, can define the value of α and β

Solubility of water in peridotite melt

2173 K, 1 bar



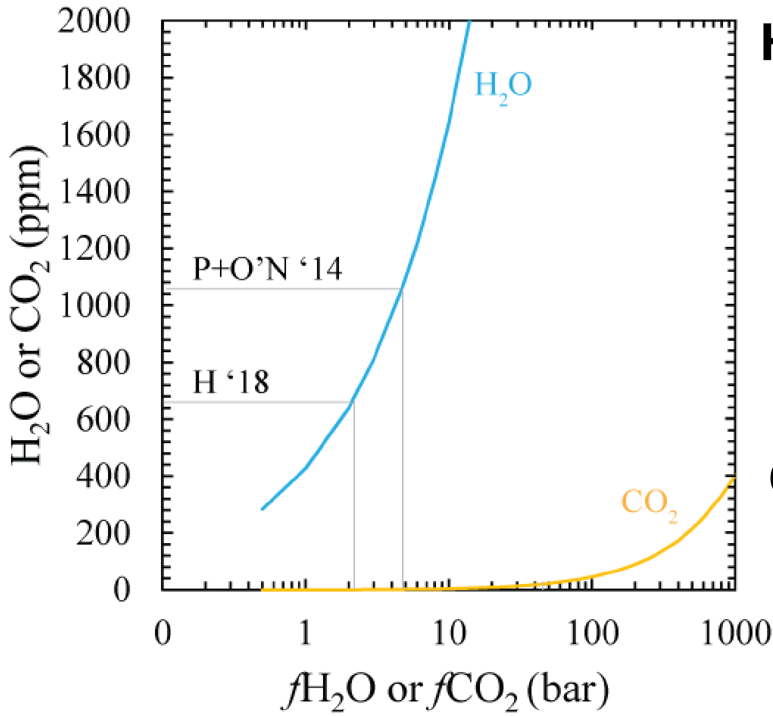
$$X = \alpha P^{\beta}$$

α = 524±16 ppm/bar$^{0.5}$

β = 0.47±0.02

General law for the solubility of H_2O in mantle-like compositions

Solubility of major volatiles in silicate melt



H_2O (This work)

CO_2 (Dixon et al. 1995)

Solubility of H_2O ~ 100 × greater than that of CO_2*

Mass Balance

Mass fraction in atmosphere

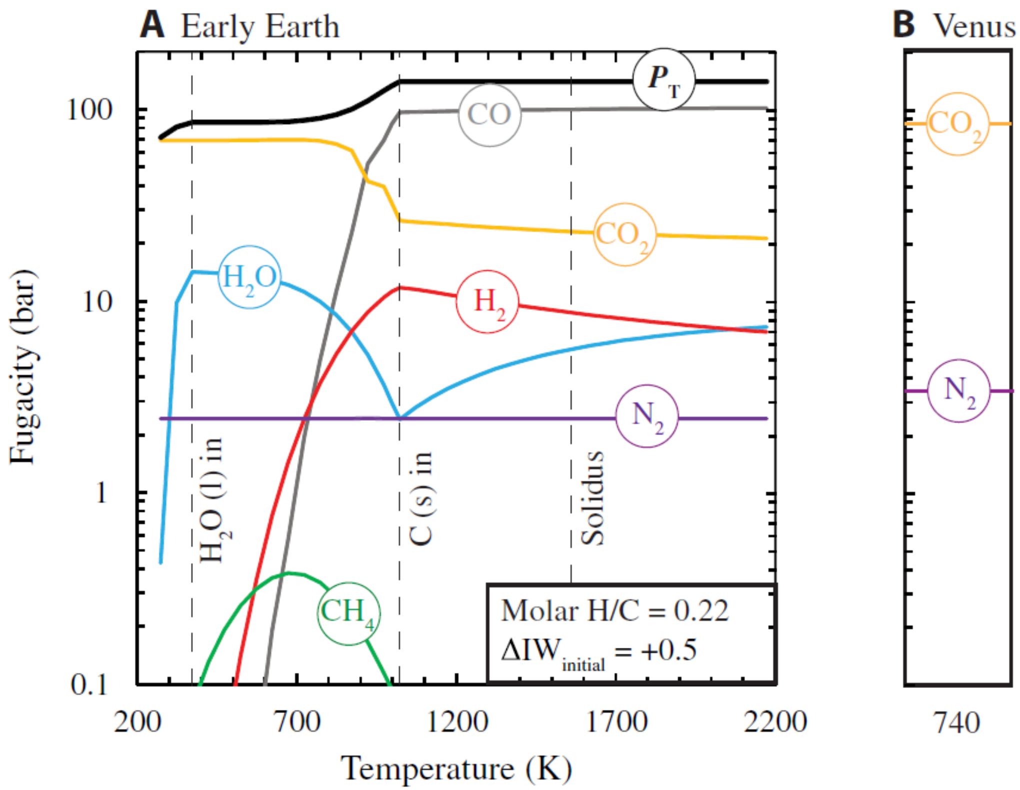
Mass fraction in mantle

$$M_{planet} X_v = \boxed{p_v \frac{4\pi r^2}{g}} + \boxed{M_{melt} X_v}$$

* Solubilities of CO and H_2 are negligible

Cooling of early Earth's atmosphere

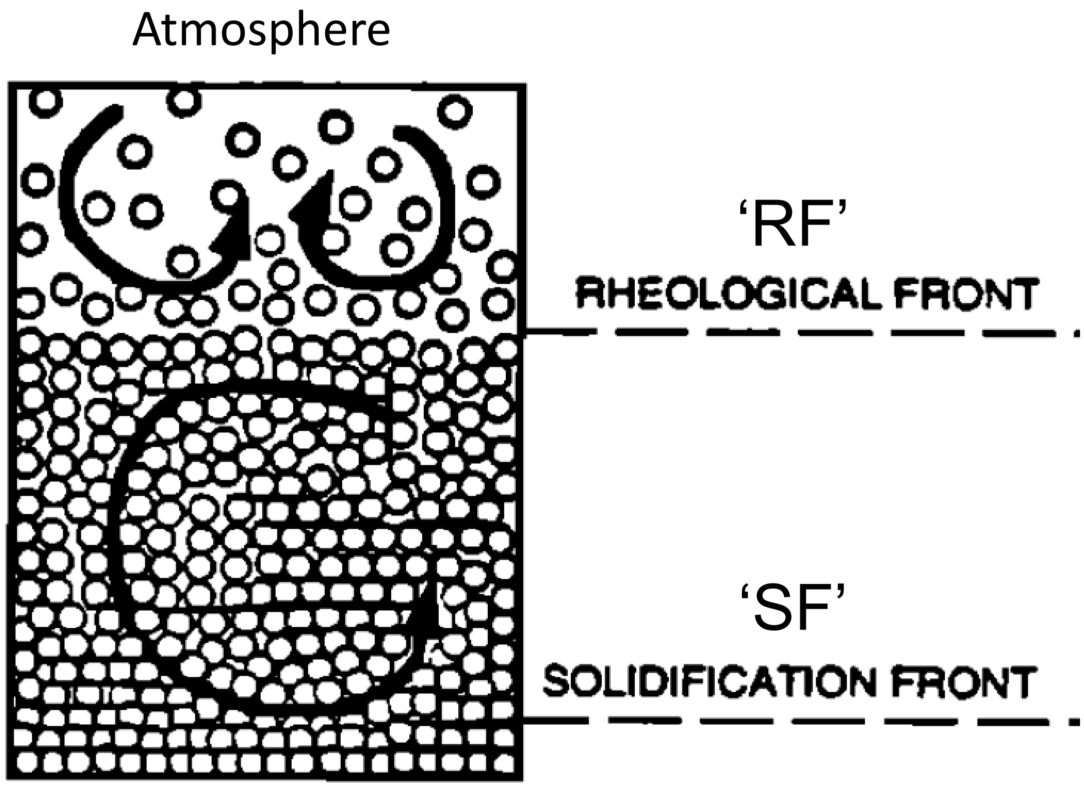
Atmospheric speciation calculated during closed-system cooling



~ 70 bar CO_2, ~ 2 bar N_2; **CO_2/N_2 ~ 35**

Composition of terrestrial atmosphere resembled that of Venus

Equilibrium and fractional crystallisation



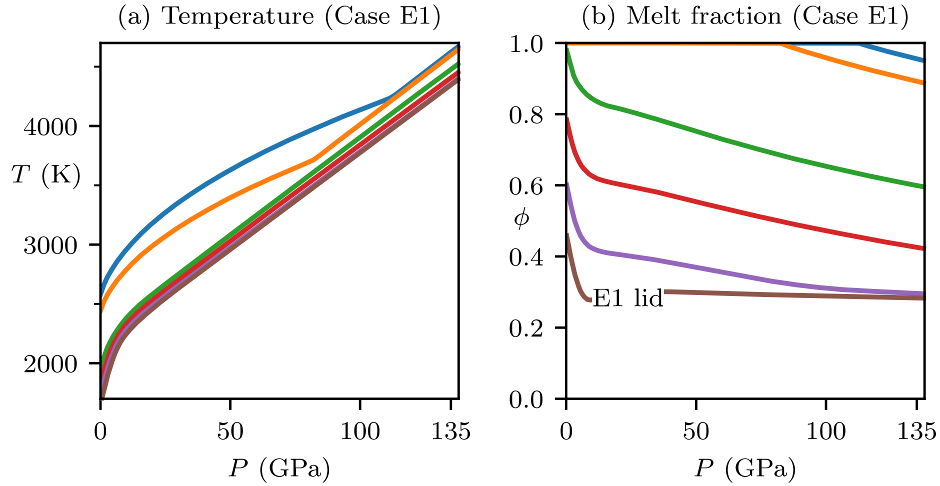
Velocity of RF >> Velocity of SF
→ **Equilibrium** crystallisation
System freezes at $\varphi = 0.3$

Velocity of RF ~ Velocity of SF
→ **Fractional** crystallisation
System can outgas below $\varphi = 0.3$

Solomatov and Stevenson (1993)

Equilibrium and fractional crystallisation

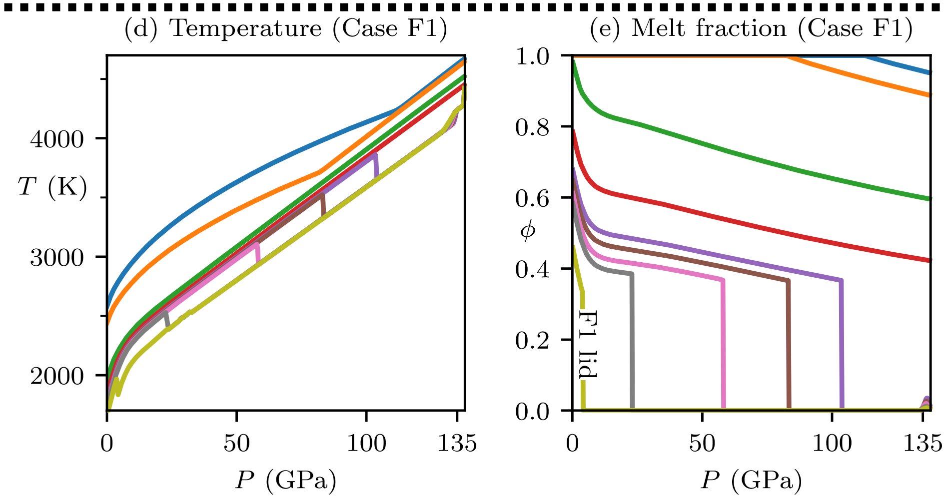
Equilibrium



Velocity of RF >> Velocity of SF

→ **Equilibrium** crystallisation

Fractional

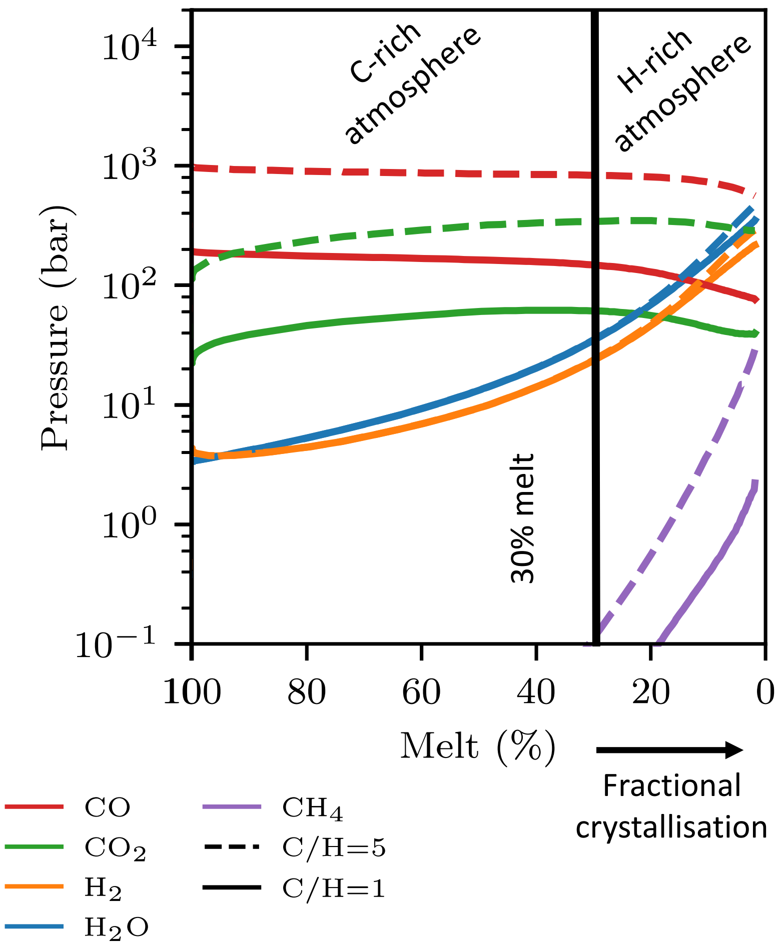


Velocity of RF ~ Velocity of SF

→ **Fractional** crystallisation

Gas speciation with crystallisation

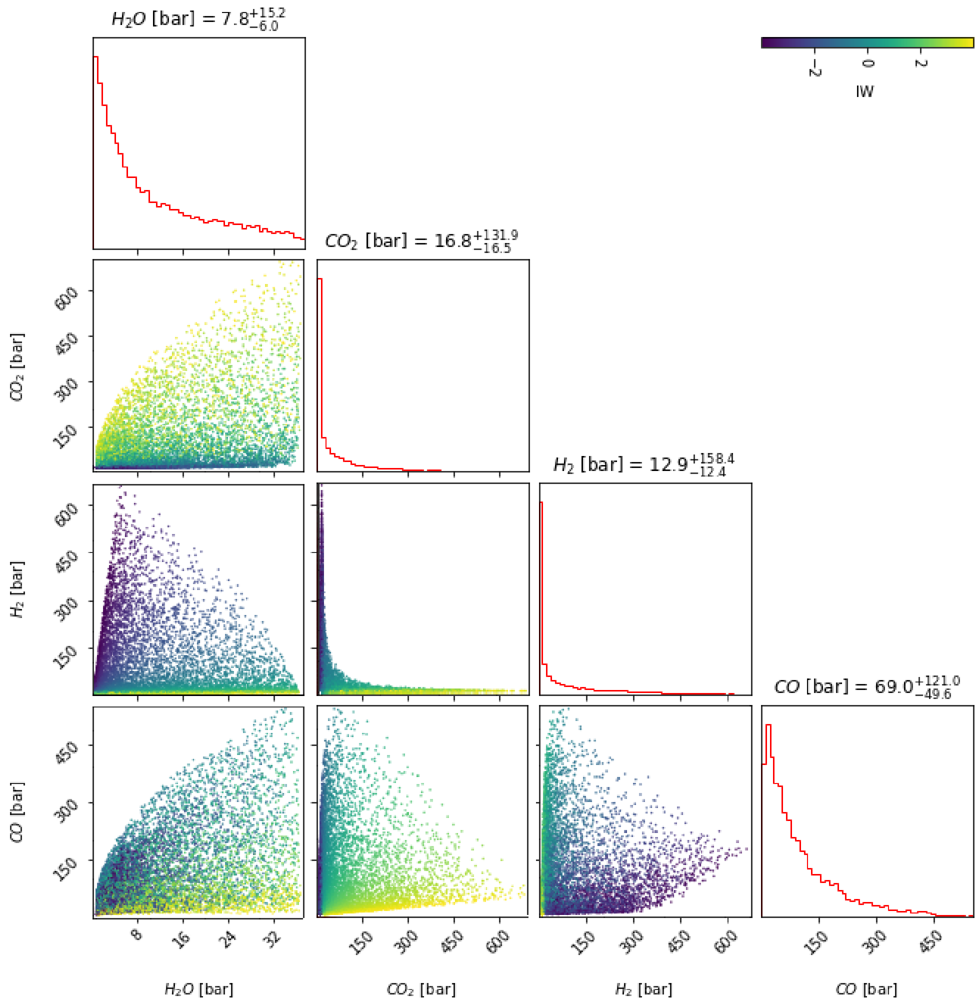
$fO_2 = \Delta IW+0.5$



- ~95% H is dissolved at F = 30%
- Only outgassed if fractional crystallisation proceeds
- **Minimum estimate because** neglects:
  - Trapped melt
  - Storage in minerals
  - Mantle overturn

Magma ocean-generated atmospheres under neutral or oxidising conditions are C-rich

Prevalence of steam atmospheres



Monte-Carlo simulations of Earth-like planets at 2173 K

$$\{H/C \in \mathbb{R} \mid 1 < H/C < 10\}$$

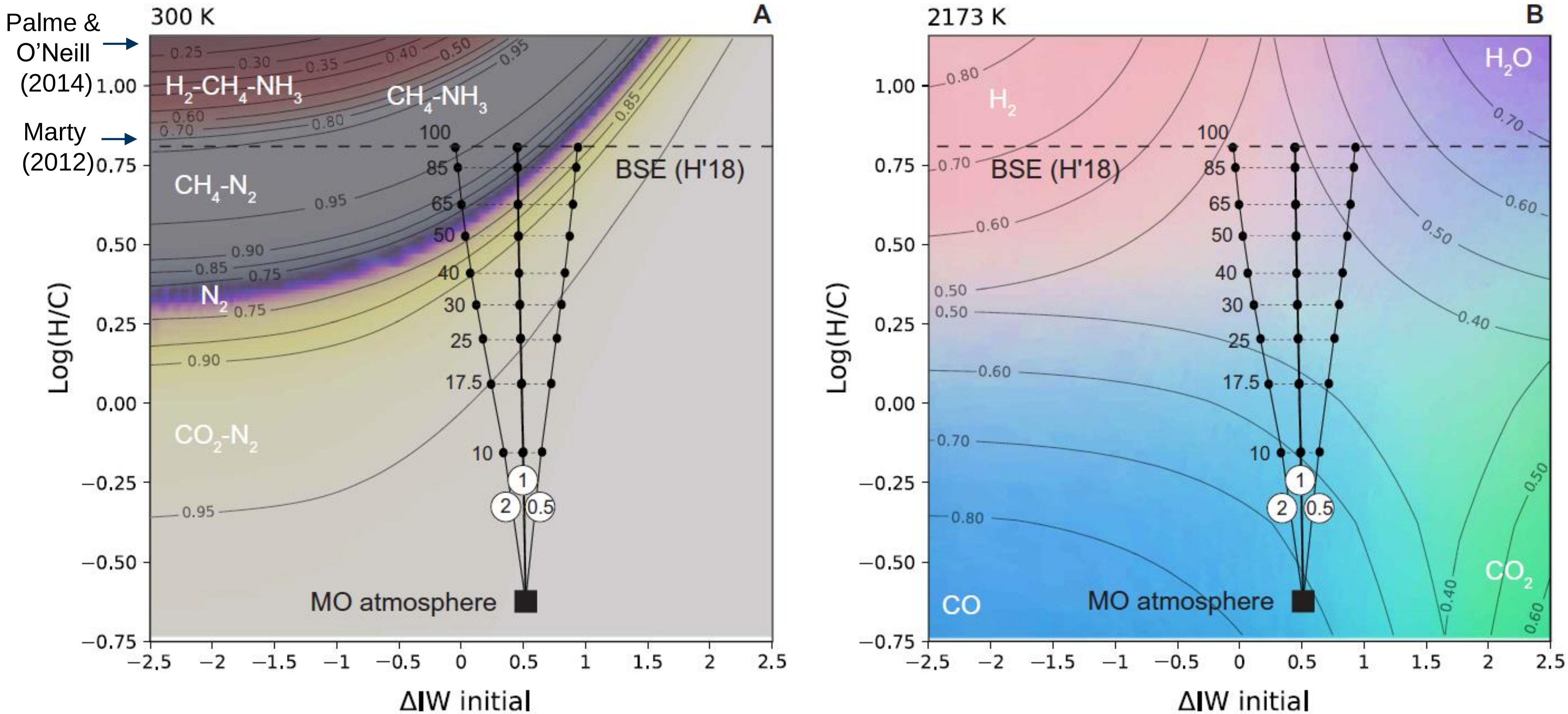
$$\{N_{Ocean} \in \mathbb{R} \mid 1 < N_{Ocean} < 10\}$$

$$\{\Delta IW \in \mathbb{R} \mid -4 < \Delta IW < 4\}$$

- Steam atmospheres ($XH_2O > 0.5$) do not form
- Reduced atmospheres are **large**
- CO_2-H_2 atmospheres are **excluded**

Continual H_2O degassing

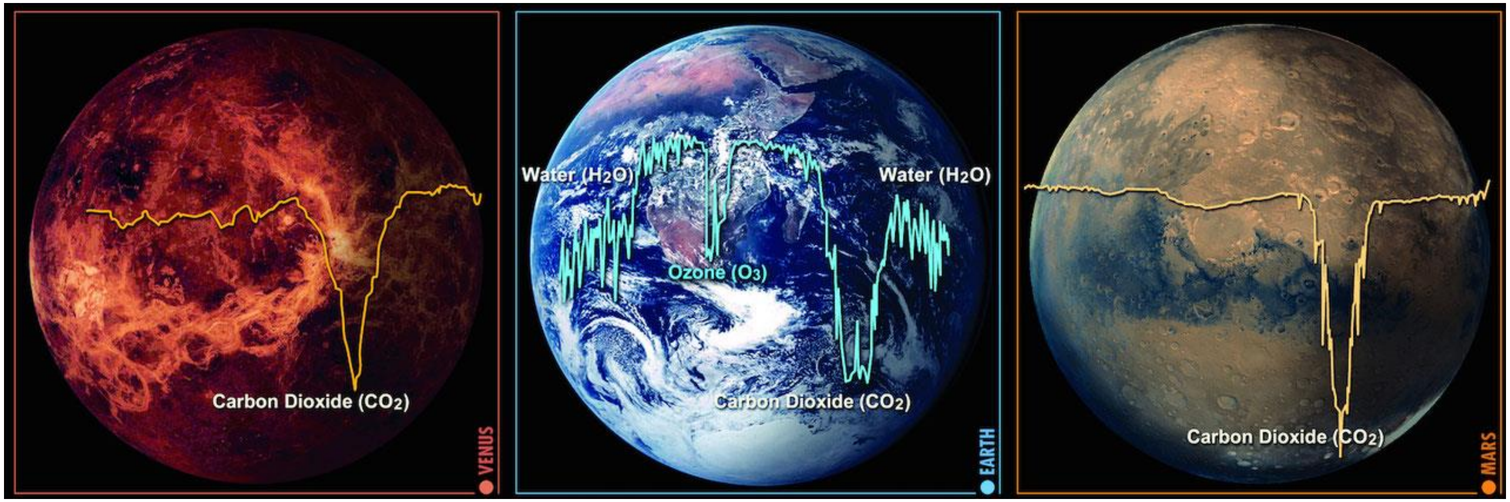
How atmosphere composition changes with H_2O outgassing



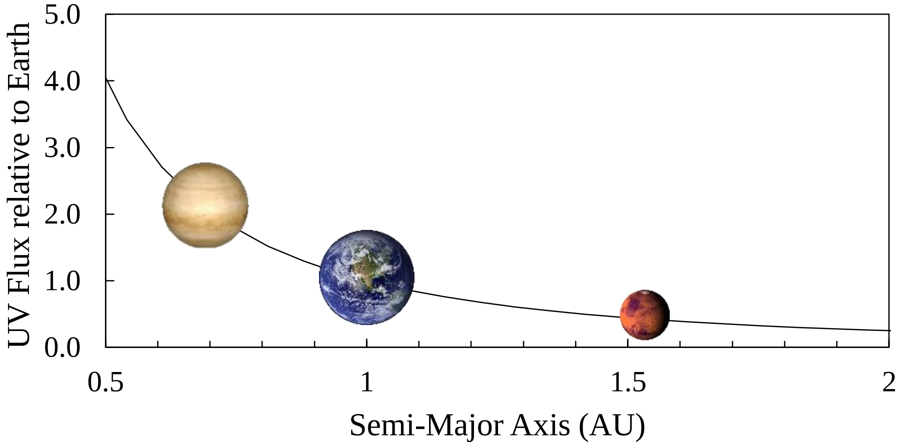
Planetary atmospheres

	Venus	Earth	Mars
CO_2/N_2 Initial atmosphere	?	~**40**	?
CO_2/N_2 Present atmosphere	43.3	7.8×10^{-4}	55
Total bars	92	1.013	0.0061

Comparative planetology



Earth is bracketed heliocentrically by planets with CO_2:N_2 atmospheres in ratio ~97:3



Physical controls

Earth receives ½ as much solar irradiance as Venus
But twice as much as Mars

Earth is similar in size to Venus but much larger than Mars

Atmospheric escape

Mass of gas species

Velocity required for escape

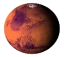
$$\lambda_{esc} = \frac{\boxed{m}\boxed{v_{esc}{}^{2}}}{\boxed{2k_B T}}$$

Mean thermal velocity of gas

"Escape parameter"

Loss is most efficient for:

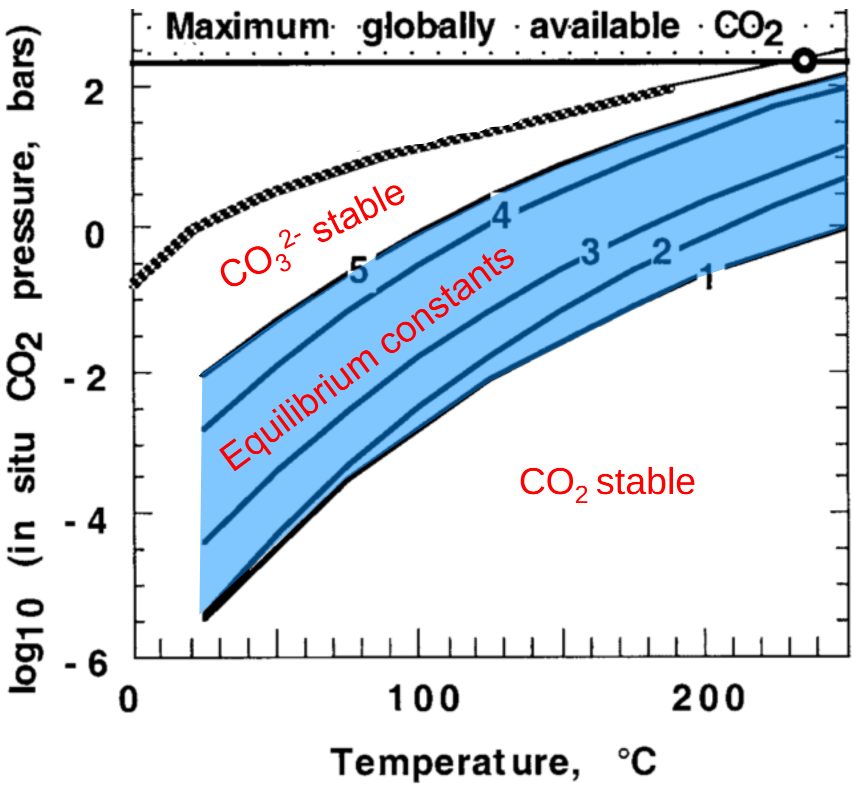
1. Lighter masses (*e.g.*, H, He)
2. Smaller bodies (low v_{esc})
3. Hotter atmospheres (high $T_{exobase}$)

	D/H (vs. Earth)
	~150
	1
	~6

Earth retains H_2O(l) 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)

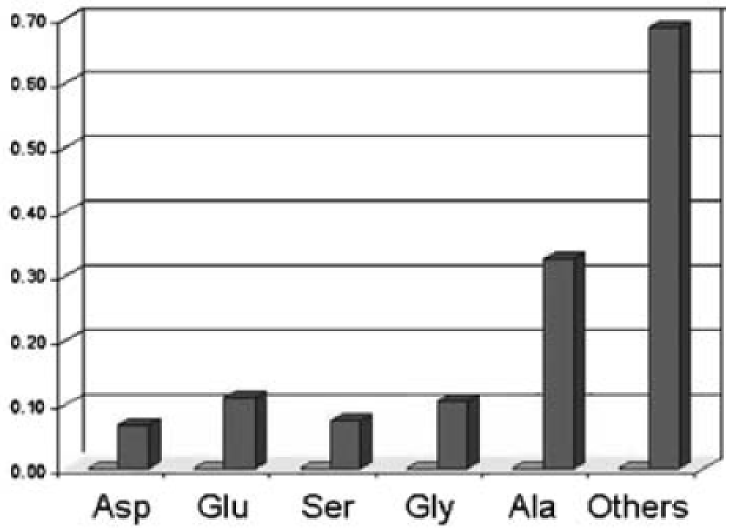
Global crustal recycling process on Earth helped C burial

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+} and H_2O solubility on fO_2 in peridotite liquids
- For oxidising conditions, water is highly soluble and is stored in interiors, leaving behind a CO_2-rich atmosphere
- Steam atmospheres are **rare** unless significant outgassing occurs
- Earth magma ocean fO_2 = IW+0.5±0.5 → neutral, Venus-like atmosphere, CO_2-N_2 (97:3)
- 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

In-situ gas determination

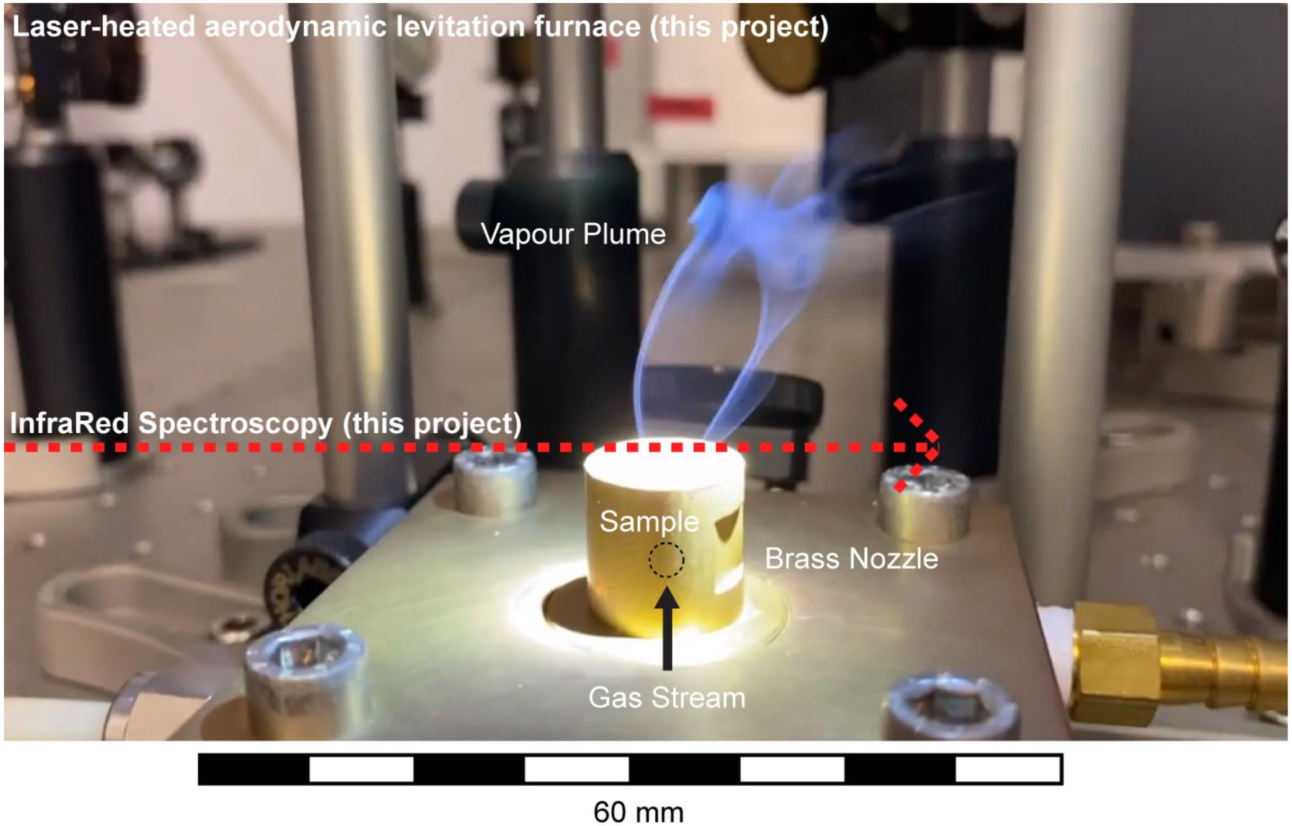


Image courtesy J. Badro (IPGP)

- **Direct** analysis of the gas phase by Fourier-Transform Infra-Red
- Controlled **atmosphere**, **temperature**, and total **pressure**
- **Container-less** CO_2 laser-heating of samples > 2000 °C
- Controlled sample geometry and gas flow regime

Hydrogen loss rates

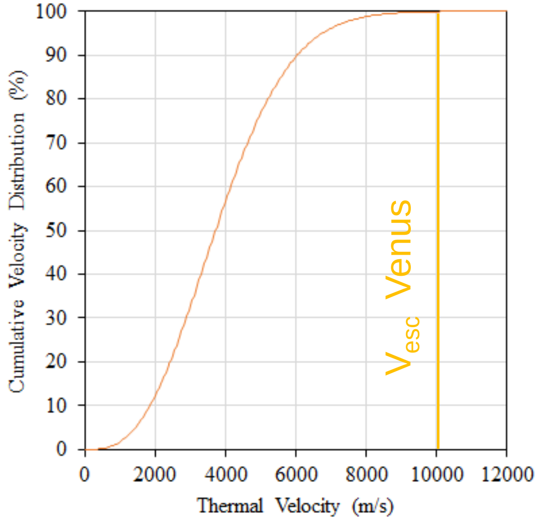
Jeans Escape (λ >> 1)

$$\left(\frac{dm}{dt}\right)_J = n\left(\frac{2k_BT}{\pi m}\right)^{\frac{1}{2}}(1+\lambda_{esc})e^{-\lambda_{esc}}$$

$T_{exobase} = 1400\ \mathrm{K}$

Kasting et al. (1988)

$\boldsymbol{\lambda = 9.2}$

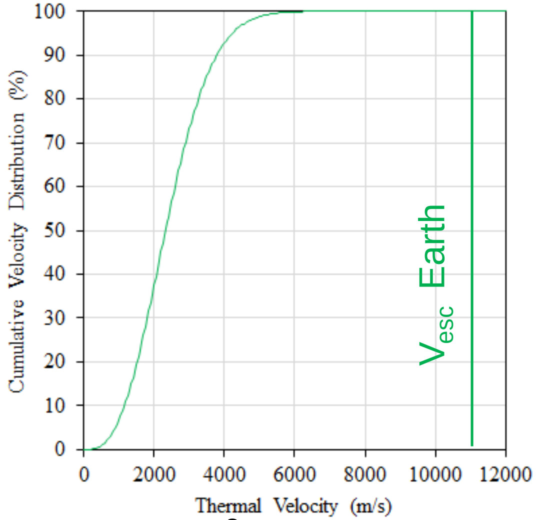


0.16 bar H/Myr

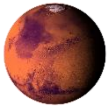
$T_{exobase} = 550\ \mathrm{K}$

Wordsworth & Pierrehumbert (2013)

$\boldsymbol{\lambda = 27}$



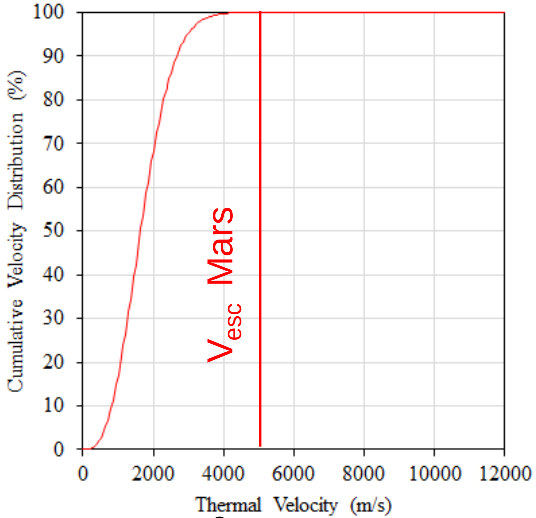
10^{-8} bar H/Myr



$T_{exobase} = 273\ \mathrm{K}$

Zhang et al. (1993)

$\boldsymbol{\lambda = 11}$



10^{-2} bar H/Myr