Supplementary Materials for

Redox state of Earth’s magma ocean and its Venus-like early atmosphere

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1. Temperature profiles and summary of laser levitation experiments

Summary of experimental conditions

Table S1. Conditions (temperature, run time, gas mixtures) of synthesis of peridotite glasses by aerodynamic laser levitation.

| Sample     | Temperature (°C) | Run time (s) | Ar (%) | CO$_2$ (%) | H$_2$ (%) | log/O$_2$ | Gas Mixture     |
|------------|------------------|--------------|--------|------------|-----------|-----------|----------------|
| Per-fO$_2$ (1) | 1900±21         | 30           |        |            |           | 0.00      | O$_2$          |
| Per-fO$_2$ (2) | 1893±40         | 40           | 92     | 8          |           | -2.49     | CO$_2$         |
| Per-fO$_2$ (3) | 1861±29         | 32           | 92     | 7.92       | 0.08      | -2.53     | 99CO$_2$:1H$_2$ |
| Per-fO$_2$ (6) | 1878±23         | 25           | 92     | 7.84       | 0.16      | -2.58     | 98CO$_2$:2H$_2$ |
| Per-TS1     | 1851±13         | 10           | 92     | 7.6        | 0.4       | -2.72     | 95CO$_2$:5H$_2$ |
| Per-fO$_2$ (7) | 1866±13         | 27           | 92     | 7.6        | 0.4       | -2.72     | 95CO$_2$:5H$_2$ |
| Per-TS2     | 1875±41         | 120          | 92     | 7.6        | 0.4       | -2.72     | 95CO$_2$:5H$_2$ |
| Per-fO$_2$ (8) | 1924±13         | 31           | 92     | 7.2        | 0.8       | -3.00     | 90CO$_2$:10H$_2$ |
| Per-fO$_2$ (9) | 1902±15         | 30           | 92     | 6          | 2         | -3.92     | 75CO$_2$:25H$_2$ |
| Per-fO$_2$ (10)| 1900±21         | 30           | 92     | 4          | 4         | -5.32     | 50CO$_2$:50H$_2$ |
| Per-fO$_2$ (11)| 1896±16         | 28           | 92     | 2          | 6         | -6.74     | 25CO$_2$:75H$_2$ |
| Per-fO$_2$ (12)| 1839±17         | 33           | 92     | 0.8        | 7.2       | -7.86     | 10CO$_2$:90H$_2$ |
Recorded temperature-time traces of experiments

a) Per-fO2 (2)

b) Per-fO2 (3)

c) Per-fO2 (6)
Fig. S1. a) to k) Temperature-time profiles of experimental glasses. Temperature of the melt bead during aerodynamic laser levitation experiments recorded *in-situ* by optical pyrometry. Sample name is given on the graph.

The temperature fluctuations observed at the commencement of the heating procedure (particularly in samples Per-f02 (2), (3), (12) and TS2) pertain to the instability of the sphere in the gas flow stream. The glass beads may randomly oscillate in the stream prior to entering a stable, aerodynamically levitated state, at which point the temperature control is precise to within ±15 °C (Table S1). The run time was calculated over the plateau for which heating was isothermal. The temperature uncertainty quoted in the main text (±50 °C) represents the temperature variability among the samples synthesised, rather than the inherent run precision. Longer sample runs tend to be more unstable (TS2) because of the drift in energy fluence of the CO2 laser.
### 2. Compositions of experimental glasses

Table S2: Electron microprobe analyses of experimental peridotite glasses, with elemental abundances expressed as wt. % oxide.

| Sample   | SiO$_2$  | Al$_2$O$_3$ | FeO(T)  | MgO     | CaO     | Na$_2$O | K$_2$O | SO$_2$ | Total  |
|----------|----------|-------------|---------|---------|---------|---------|--------|--------|--------|
| Per-$f$/O$_2$ (1) | 47.04±0.21 | 4.34±0.06   | 8.38±0.17 | 37.61±0.10 | 2.02±0.02 | 0.01    | 0.00   | 0.00   | 99.39  |
| Per-$f$/O$_2$ (2)  | 46.69±0.11 | 4.39±0.03   | 8.53±0.08 | 37.81±0.15 | 2.07±0.02 | 0.01    | 0.00   | 0.01   | 99.49  |
| Per-$f$/O$_2$ (3)  | 46.61±0.22 | 4.38±0.05   | 8.63±0.09 | 37.79±0.12 | 2.07±0.02 | 0.01    | 0.00   | 0.00   | 99.49  |
| Per-$f$/O$_2$ (6)  | 46.72±0.25 | 4.31±0.05   | 8.58±0.09 | 37.68±0.13 | 2.07±0.04 | 0.00    | 0.00   | 0.01   | 99.36  |
| Per-$f$/O$_2$ (7)  | 46.75±0.22 | 4.36±0.04   | 8.71±0.25 | 37.66±0.10 | 2.07±0.01 | 0.00    | 0.00   | 0.00   | 99.54  |
| Per-$f$/O$_2$ (8)  | 46.06±0.14 | 4.39±0.04   | 8.66±0.07 | 38.13±0.13 | 2.08±0.02 | 0.00    | 0.00   | 0.00   | 99.32  |
| Per-$f$/O$_2$ (9)  | 46.11±0.26 | 4.37±0.05   | 8.21±0.17 | 38.79±0.06 | 1.96±0.01 | 0.00    | 0.00   | 0.00   | 99.43  |
| Per-$f$/O$_2$ (10) | 46.71±0.15 | 4.43±0.04   | 8.47±0.15 | 37.80±0.30 | 2.11±0.03 | 0.00    | 0.00   | 0.01   | 99.51  |
| Per-$f$/O$_2$ (11) | 46.22±0.28 | 4.42±0.04   | 7.89±0.13 | 38.91±0.18 | 2.12±0.02 | 0.00    | 0.00   | 0.00   | 99.55  |
| Per-$f$/O$_2$ (12) | 46.53±0.12 | 4.45±0.08   | 7.80±0.08 | 38.52±0.16 | 2.15±0.02 | 0.00    | 0.00   | 0.00   | 99.44  |
| Per-TS1        | 46.45±0.16 | 4.32±0.05   | 8.87±0.13 | 37.62±0.10 | 2.04±0.02 | 0.01    | 0.00   | 0.01   | 99.30  |
| Per-TS2        | 46.50±0.11 | 4.36±0.05   | 8.56±0.09 | 38.01±0.18 | 2.08±0.02 | 0.00    | 0.00   | 0.01   | 99.51  |
3. **Treatment and quantification of XANES spectra**

*Normalised XANES spectra of peridotite glasses*

![Fe K-edge XANES pre-edge feature of oxidised glasses](image)

**Fig. S2. Fe K-edge XANES pre-edge feature of oxidised glasses.** Normalised (to 1) absorption spectra of Fe K-edge XANES depicting the pre-edge feature in the four most oxidised peridotite glasses (as labelled on the figure), scans offset vertically for clarity.
Fig. S3. Fe K-edge XANES pre-edge feature of intermediate glasses. Normalised (to 1) absorption spectra of Fe K-edge XANES depicting the pre-edge feature in the three ‘time-series’ experiments (as labelled on the figure), scans offset vertically for clarity.
Fig. S4. Fe K-edge XANES pre-edge feature of reduced glasses. Normalised (to 1) absorption spectra of Fe K-edge XANES depicting the pre-edge feature in the five most reduced peridotite glasses (as labelled on the figure), scans offset vertically for clarity.
Calculation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from XANES spectra of peridotite glasses

In order to calculate the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the peridotite glasses, two features of the XANES spectra, the 0.8 edge energy (hereafter, ‘Edge’) and the centroid energy of the pre-edge feature (1s$\rightarrow$3d electron transition; hereafter ‘Centroid’) are compared with those measured in synthetic Mid-Ocean Ridge Basalt (MORB) glasses, whose $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio is calibrated by independent means, namely, Mössbauer spectroscopy (31).

The XANES spectra of both the peridotite glasses and the MORB glasses were collected during the same analytical session at beamline 13IDE, Advanced Photon Source, Argonne National Laboratories (IL, USA). As such, the Edge and Centroid energies of the MORB glasses differ from the values given in ref. (31), their Table 2, due to a systematic offset in the energy calibration of 1.2±0.1 eV between beamline I18, Diamond Light Source, Oxford, UK and beamline 13IDE. As such, in this study, the energy calibration is internally consistent between MORB glass standards and peridotite glass samples. As the glasses are the same samples analysed in ref. (31), both $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $fO_2$ of the MORB standard glasses are known (their Table 2).

To calculate the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the peridotite glasses, a global fit to the recorded Edge and Centroid energy values as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the MORB glasses was performed. In this model, we derive expressions relating the Edge and Centroid energies to the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values determined by the Mössbauer-based model global fit of ref. (31) (their Table 2). In order to do so with the least misfit, one must consider:

1) The appropriate peak shape (Gaussian, Lorentzian, or a combination) to fit the $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ contributions to the pre-edge Centroid energy

2) A functional form relating the Edge energy and Centroid energy to $\text{Fe}^{3+}/\Sigma\text{Fe}$

We therefore test several models, including fits using 2 Gaussian peaks, 2 Lorentzian peaks, and 1 Lorentzian and 1 Gaussian to the Centroid energy; and $n$-order polynomials ($n = 3, 4$) to quantify the relationship between $n$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$, by minimising the misfit to the objective function:

$$\chi^2 = \sum \frac{(\text{Edge}_{\text{meas}} - \text{Edge}_{\text{calc}})^2}{\sigma(\text{Edge})} + \sum \frac{(\text{Centroid}_{\text{meas}} - \text{Centroid}_{\text{calc}})^2}{\sigma(\text{Centroid})}$$  \hspace{1cm} (S1)

Where ‘Edge’ and ‘Centroid’ are in eV and $\sigma$ is their associated standard deviation, in eV. For the synthetic tests, we make the transformation ‘Centroid’ = Centroid$_{\text{meas}} - 7111$ eV and ‘Edge’ = Edge$_{\text{meas}} - 7120$ eV, in order to make the minimisation more tractable. The results of these tests are presented in Table S3, below.
Table S3. Results of synthetic tests with XANES spectra of the MORB glasses of ref. (31) used to determine the goodness of fit of polynomial functions relating (A) Fe$^{3+}$/ΣFe to 0.8 Edge Energy (B) Fe$^{3+}$/ΣFe to Centroid Energy and (C) Fe$^{3+}$/ΣFe (Centroid energy) to Fe$^{3+}$/ΣFe (0.8 Edge Energy).

| MORB glasses (31) | A) Fe$^{3+}$/ΣFe vs. 0.8 Edge Energy | B) Fe$^{3+}$/ΣFe vs. Centroid Energy | C) Fe$^{3+}$/ΣFe (Centroid Energy) vs. Fe$^{3+}$/ΣFe (0.8 Edge Energy) |
|------------------|-------------------------------------|---------------------------------------|----------------------------------------------------------|
|                  | a0 -0.016 b0 -0.78 -0.61 -0.76      | c0 -2.24 -1.18 -1.61                  |                                                          |
|                  | a1 0.150 b1 1.34 1.44 1.48           | c1 2.74 2.14 1.99                     |                                                          |
|                  | a2 -0.008 b2 -0.64 -0.88 -0.83       | c2 0.19 0.22 0.39                     |                                                          |
|                  | a3 0.17 b3 0.25 0.23                 | c3                                     |                                                          |

Data Misfit (3-term) Misfit (4-term) Misfit (3-term)

| Fe$^{3+}$/ΣFe | σ | 2 Gau | 2 Lor | 1 Gau & 1 Lor | 2 Gau | 2 Lor | 1 Gau & 1 Lor |
|--------------|---|-------|-------|---------------|-------|-------|---------------|
| 0.775        | 0.010 | -1.75 |       |               | 0.18  | 0.24  | 0.15          |
| 0.662        | 0.001 | 1.39  | -0.03 | -0.70         | -0.94 | -0.06 | -0.09         |
| 0.524        | 0.001 | 1.43  | -2.65 | -1.17         | -1.06 | -0.21 | -0.15         |
| 0.404        | 0.002 | 0.33  | -0.73 | -0.34         | -0.22 | -0.10 | -0.09         |
| 0.251        | 0.007 | 0.65  | 3.89  | 2.54          | 2.53  | 0.21  | 0.20          |
| 0.162        | 0.006 | 0.65  | 0.46  | 0.04          | -0.46 | 0.09  | 0.15          |
| 0.098        | 0.005 | 0.81  | -0.83 | -1.86         | -1.72 | 0.05  | 0.07          |
| 0.059        | 0.004 | -0.16 | 1.11  | 1.05          | 0.64  | 0.03  | 0.05          |
| 0.034        | 0.003 | 0.04  | -0.52 | -0.79         | 0.14  | -0.04 | -0.04         |
| 0.019        | 0.002 | -2.95 | -0.52 | 0.70          | 0.31  | -0.02 | -0.02         |
| 0.011        | 0.001 | -0.44 | 6.29  | 4.38          | 3.93  | -0.03 | -0.07         |
| 0.006        | 0.001 | 1.89  | -6.41 | -4.63         | -4.13 | -0.12 | -0.13         |

Global misfit ($\chi^2$)

|                  | 3 term | 4 term |
|------------------|--------|--------|
|                 | 20.68  | 8.00   |
|                 | 118.5  | 107.4  |
|                 | 104.5  | 55.8   |
|                 | 68.4   | 46.0   |
|                 | 0.16   | 0.03   |
|                 | 0.23   | 0.02   |
|                 | 0.14   | 0.02   |

* Misfit relative to the MORB glass data is shown for the different peak forms for the 4-term polynomial (Centroid Energy) and a 3-term polynomial (0.8 Edge Energy), with global misfit shown for both 3- and 4-term polynomials. Bold text represents the calibration chosen.

In finding a function to fit the dependence of Edge energy on Fe$^{3+}$/ΣFe (synthetic test A), the misfit improves only marginally from the 3- to 4-term polynomial, and is already low in both cases (<21). This relates to a mean offset of calculated Fe$^{3+}$/ΣFe compared to measured values of ±0.005. When compared to the Fe$^{3+}$/ΣFe determined by Mössbauer spectroscopy, the 1 Gaussian and 1 Lorentzian peak fits to the Centroid Energy yield lower (i.e., better) misfit to the observed Fe$^{3+}$/ΣFe for both the 3-term and 4-term fits (synthetic test B). The global $\chi^2$ of 46.0 in the 4 term fit reflects an absolute uncertainty in Fe$^{3+}$/ΣFe of ±0.006. Moreover, the 1 Gaussian + Lorentzian peak fit produced Fe$^{3+}$/ΣFe values that were in closest agreement with the 3-term polynomial fit to the 0.8 Edge energy (synthetic test C), and were therefore adopted throughout. The misfit between the observed and calculated Centroid energy improves markedly when passing from a 3-term to a 4-term polynomial (Table S3). Therefore, the 4-term and 3-term polynomials are taken to functionally fit the Centroid energy and the Edge energy, respectively:

$$\frac{Fe^{3+}}{\Sigma Fe_{calc}} = a_0 + a_1(Edge_{meas} - 7120) + a_2(Edge_{meas} - 7120)^2$$ (S2)
\[ \frac{\text{Fe}^{3+}}{\sum \text{Fe}_{\text{calc}}} = b_0 + b_1(Cent_{\text{meas}} - 7111) + b_2(Cent_{\text{meas}} - 7111)^2 + b_3(Cent_{\text{meas}} - 7111)^3 \]  

(S3)

Best fit values yield for \( a_0 = -0.0157, a_1 = 0.1495, a_2 = 0.0083 \) and for \( b_0 = -0.7594, b_1 = 1.4792, b_2 = -0.8300, b_3 = 0.2283 \). Once established, these expressions can be used in order to calculate the \( \text{Fe}^{3+}/\sum \text{Fe} \) ratios of the peridotite glasses from their measured Centroid and Edge energies.

However, the use of basaltic glasses to calibrate glasses of peridotitic composition is not necessarily substantiated \textit{a priori}, as XANES spectra are not only sensitive to the oxidation state of Fe, but also to its overall bonding environment, which is influenced by composition (83). The composition of the synthetic MORB glass used for the standards is given in ref. (31), and is SiO\(_2\) (52.0 wt. %), Al\(_2\)O\(_3\) (16.1 wt. %), CaO (12.4 wt. %), FeO\((T)\) (10.0 wt. %), MgO (8.2 wt. %) and TiO\(_2\) (1.3 wt.%), which differs notably in its higher Al\(_2\)O\(_3\), CaO and lower MgO contents compared to the peridotite glass (Table S2). Moreover, the Edge energy can be influenced by self-absorption depending on the mean atomic number of the medium through which the X-rays pass. However, the predominant contribution affecting this shift is the iron content of the glass itself, and typically only above the edge energy (84). Therefore, it may be expected that such a \( \text{Fe}^{3+}/\sum \text{Fe} \) edge/centroid energy calibration would hold for glasses with similar iron contents, as in the MORB glass (10.0 wt. % FeO\((T)\)) and peridotite glass (8.44 wt. % FeO\((T)\)).

**Fig. S5. Centroid vs. Edge energy of peridotite- and MORB glasses.** The Centroid energy plotted against the 0.8 Edge energy for both the unknown peridotite glasses (green circles) and the calibration MORB glasses (black). The concurrence of the two series indicates that there is no systematic effect of composition on the relationship between the two quantities, meaning their variation is solely a function of \( \text{Fe}^{3+}/\sum \text{Fe} \) ratio.

In order to evaluate the suitability of the MORB glasses as calibration standards for peridotite glasses, the relationship between measured Centroid- and Edge energies for each glass is plotted in Fig. S5. As evidenced from Fig. S5, the ‘unknown’ peridotite glasses fall on the same Centroid Energy – Edge Energy relationship defined by the MORB glasses of ref. (31). As such, the equations relating \( \text{Fe}^{3+}/\sum \text{Fe} \) to both Centroid energy and Edge energy can be used in tandem to more precisely determine
Fe$_{3+}$/$\sum$Fe in the peridotite glasses. These Fe$_{3+}$/$\sum$Fe ratios are then related to the log/O$_2$ calculated for the individual gas mixture at 1900°C, and are shown in Table S4.

**Table S4.** A summary of experimental conditions of peridotite and MORB glasses, together with their determined 0.8 Edge and Centroid energies measured at 13IDE, and the Fe$_{3+}$/$\sum$Fe ratios derived from eq. S2 and S3 (peridotite glasses) and reported in ref. (31), their Table 2 (MORB glasses).

| Sample  | Temperature (°C) | log/O$_2$ | 0.8 Edge Energy (eV) | Centroid Energy (eV) | Fe$_{3+}$/\sum$Fe |
|---------|------------------|-----------|----------------------|----------------------|------------------|
| Per-O$_2$ (1) | 1900±21 | 0.00 | 7122.624 | 7112.648 | 0.440±0.008 |
| Per-O$_2$ (2) | 1893±40 | -2.49 | 7121.833 | 7112.310 | 0.277±0.013 |
| Per-O$_2$ (3) | 1861±29 | -2.53 | 7121.792 | 7112.292 | 0.269±0.015 |
| Per-O$_2$ (6) | 1878±23 | -2.58 | 7121.547 | 7112.206 | 0.226±0.013 |
| Per-TS1 | 1851±13 | -2.72 | 7121.780 | 7112.291 | 0.267±0.013 |
| Per-O$_2$ (7) | 1866±13 | -2.72 | 7121.622 | 7112.235 | 0.240±0.013 |
| Per-TS2 | 1875±41 | -2.72 | 7121.460 | 7112.167 | 0.217±0.012 |
| Per-O$_2$ (8) | 1924±13 | -3.00 | 7121.184 | 7112.106 | 0.172±0.006 |
| Per-O$_2$ (9) | 1902±15 | -3.92 | 7120.885 | 7112.015 | 0.124±0.006 |
| Per-O$_2$ (10) | 1900±21 | -5.32 | 7120.335 | 7111.879 | 0.045±0.010 |
| Per-O$_2$ (11) | 1896±16 | -6.74 | 7120.085 | 7111.815 | 0.019±0.010 |
| Per-O$_2$ (12) | 1839±17 | -7.86 | 7120.079 | 7111.807 | 0.014±0.009 |

| MORB glasses (ref. (31))* |
|---------------------------|
| MORB0 | 1400±2 | 0.00 | 7124.353 | 7113.065 | 0.775±0.010 |
| MORB-1 | 1400±2 | -1.00 | 7123.685 | 7112.962 | 0.662±0.010 |
| MORB-2 | 1400±2 | -2.00 | 7123.010 | 7112.865 | 0.524±0.010 |
| MORB-3.07 | 1400±2 | -3.07 | 7122.433 | 7112.433 | 0.404±0.020 |
| MORB-4 | 1400±2 | -4.00 | 7121.610 | 7112.239 | 0.251±0.007 |
| MORB-5 | 1400±2 | -5.00 | 7121.120 | 7112.095 | 0.162±0.006 |
| MORB-6 | 1400±2 | -6.00 | 7120.756 | 7111.978 | 0.098±0.005 |
| MORB-7 | 1400±2 | -7.00 | 7120.491 | 7111.833 | 0.059±0.004 |
| MORB-8 | 1400±2 | -8.00 | 7120.326 | 7111.841 | 0.034±0.003 |
| MORB-9 | 1400±2 | -9.00 | 7120.268 | 7111.815 | 0.019±0.002 |
| MORB-10 | 1400±2 | -10.00 | 7120.180 | 7111.796 | 0.011±0.001 |
| MORB-11 | 1400±2 | -11.00 | 7120.132 | 7111.801 | 0.006±0.001 |

*Glasses are the same as those measured in ref. (31). XANES spectra were re-collected at the same time as the peridotite glass samples in order to determine the Edge- and Centroid energies. The Fe$_{3+}$/\sum$Fe contents are taken from ref. (31), as quantified by best fits to fO$_2$-Fe$_{3+}$/\sum$Fe systematics determined by Mössbauer spectroscopy.

Three experiments were run for different durations at the same temperature and under the same gas mixture in order to assess the effect of run time on the observed Fe$_{3+}$/\sum$Fe, and therefore the time for the melt to equilibrate with the gas mixture at high temperature. The samples subjected to the time series test were labelled Per-TS1 (10 s), Per-O$_2$ (7) (30 s) and Per-TS2 (120 s), and their calculated Fe$_{3+}$/\sum$Fe ratios are shown plotted against run duration (Fig. S6).
Fig. S6. Time series evolution of Fe$^{3+}$/ΣFe in peridotite glasses. Variation in the measured Fe$^{3+}$/ΣFe of quenched peridotite liquids as a function of time at constant temperature (1864±12) and log/$\text{O}_2$ (-2.72). The initial value of 0.440±0.008 comes from the fact that all glasses were first pre-equilibrated in pure $\text{O}_2$ at 2173 K prior to re-equilibration at the desired $\text{O}_2$.

Because all glasses were pre-melted first in pure oxygen, the initial Fe$^{3+}$/ΣFe of the starting glass is given by sample Per-$\text{O}_2$ (1), with Fe$^{3+}$/ΣFe = 0.440±0.008. Sample Per-TS1, run for 10 s, records resolvably higher Fe$^{3+}$/ΣFe, 0.267±0.011, than either of the longer duration experiments under the same conditions (Per-$\text{fO}_2$ (7) and Per-TS2), with 0.240±0.013 and 0.217±0.012, respectively. This value lies intermediate between those recorded by the starting glass and the longer run durations, and, importantly, is also higher than that determined in sample Per-$\text{fO}_2$ (6), 0.226±0.013, run at marginally higher oxygen fugacity (log/$\text{O}_2$ = -2.58). Taken together, these features are indicative of incomplete equilibration of the melt with the gas mixture after 10 s at ~2150 K in sample Per-TS1. By contrast, the experiments run at 30 s and 120 s have Fe$^{3+}$/ΣFe within uncertainty of one another, and within uncertainty of Per-$\text{fO}_2$ (6). This suggests the melt and gas mixture equilibrate after ~ 30 s.

In order to better quantify the expected equilibration time, the diffusion timescale can be estimated from:

$$t = \frac{r^2}{D}$$

where $t =$ time in (s), $r =$ the radius of the melt sphere (0.001 m), and $D =$ the diffusion coefficient of Fe. Experimental data suggest that $D$ should vary as a function of composition and temperature (85). Here, we obtain a value of $D_{Fe}$ from extrapolations based on basaltic compositions in air to 2173 K with an SiO$_2$ mole fraction of 0.4 for the peridotite liquid, yielding log$/D_{Fe}$ -6.73 (ref. (86); their eq. 86). Based on these models, full equilibration is achieved in ~6 s. However, our measurement times were counted from pyrometer temperatures measured at the surface of the bead, and hence the interior would have required longer timescales to reach the temperature measured at the surface. This thermal equilibration time, given the higher Fe$^{3+}$/ΣFe of sample Per-TS1, was likely of the order of 5 – 10 s. Once this temperature was reached throughout the bead, and considering that convection is also likely to play a role in melt homogenisation, sample run times > 15 s are sufficiently long to ensure complete equilibration of the melt with the imposed gas mixture.
4. Thermodynamic treatment of Fe$^{2+}$/Fe$^{3+}$ as a function of oxygen fugacity

The fugacity of any given gas species is traditionally reported relative to the standard state of the pure ideal gas at 1 bar and the temperature of interest. When defined relative to this standard state, numerical values of $f_{O_2}$ can change with temperature, for example in a silicate melt of constant composition including constant Fe$^{3+}$/Fe$^{2+}$, or in a H-C-N-O gas phase of constant composition. Therefore such numerical values of $f_{O_2}$ are meaningless unless the temperature is specified. To avoid this complication, it is customary to switch to a standard state defined by a simple univariant equilibrium. Here we use for the standard state the equilibrium $2\text{ Fe} + O_2 = 2\text{ FeO}$, for which $\Delta G^\circ$ (J/mol) = 488236 - 231.118T + 16.948Tln(T), where $T$ is in K, from ref. (87). These thermochemical data are for solid Fe metal but liquid FeO, and, following common usage, is abbreviated IW (for Iron – Wüstite, the latter being the mineral name for crystalline Fe$_{1-x}$O). Hence $\log_{10} f_{O_2}^{IW} = -572\text{ + }log_{10} f_{O_2}^{(O_2 \text{ standard state})} - log_{10} f_{O_2}^{(IW)}$. It is found empirically that values of $\Delta$IW do not change greatly with temperature in condensed systems of fixed composition, at least under conditions relevant to magmatic processes.

At 2173 K, we obtain a value for the IW buffer of $\log f_{O_2} = -6.47$. This compares with $\log f_{O_2}$ of -5.99 using our experimental calibration, $\log (\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.252\times \log f_{O_2} + 0.096$ for an Fe$^{3+}$/Fe$^{2+}$ = 0.0384 ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.037$). Hence, the terrestrial mantle’s Fe$^{3+}/\Sigma\text{Fe}$, were it to exist with the same ratio in liquid form, relates to an oxygen fugacity of $\Delta$IW+0.48.

In order to understand the solution behaviour of iron in peridotite melts, we relate the free energy of reaction of the FeO and FeO$_{1.5}$ components in the melt to that of their pure oxides. For the redox reaction in the silicate melt, we can write:

$$\text{FeO}(l) + \frac{1}{4} O_2 = \text{FeO}_{1.5}(l), (S4)$$

and for the reaction among pure oxides:

$$\text{FeO}(l) + \frac{1}{4} O_2 = \frac{1}{2} \text{Fe}_2\text{O}_3(l). (S5)$$

Thermodynamic data for the Gibbs free energy of formation of the pure oxides from the elements can be found in the JANAF (44) and IVTAN (88) databases, and are shown in Table S5, below. In these databases, O$_2$(g) is defined as the reference state for oxygen, and has $\Delta G^\circ = 0$ for all temperatures.

| Temperature (K) | IVTAN | JANAF |
|----------------|-------|-------|
|                 | Fe$_2$O$_3$ (l,s) | FeO (l) | Fe$_2$O$_3$ (l,s) | FeO (l) |
| 1700            | -388.65 | -165.24 | -384.03 | -163.83 |
| 1800            | -364.26 | -160.83 | -364.53 | -159.16 |
| 1900            | -342.77 | -155.94 | -343.65 | -153.83 |
| 2000            | -321.81 | -151.00 | -322.62 | -148.45 |
| 2100            | -300.93 | -146.07 | -301.59 | -143.09 |
| 2200            | -280.13 | -141.16 | -280.54 | -137.74 |
| 2300            | -259.40 | -136.27 | -259.49 | -132.41 |
| 2400            | -238.73 | -131.38 | -238.43 | -127.09 |

$T_m(\text{Fe}_2\text{O}_3) = 1812$ K

*Italic = $\Delta G^\circ$, calculated taking into account latent heat of fusion (eq. S6)*
The JANAF tables report only $\Delta G^\circ_f$ for crystalline Fe$_2$O$_3$ (hematite), and thus require a correction for the latent heat of fusion, which is performed according to the following relation:

$$ \Delta_{fus}^o G_f^o = T_m \Delta_{fus}^o H_f^o - T \Delta_{fus}^o H_f^o \quad (S6) $$

We determine the value of $\Delta_{fus}^o H_f^o$ by comparing the $\Delta G^\circ_f$ of the IVTAN and JANAF databases for solid hematite, and find $\Delta_{fus}^o H_f^o = 49$ J/molK for Fe$_2$O$_3$. This is in perfect agreement with the 24.5 J/molK inferred by ref. (38) for FeO$_{1.5}$ from the interpolation of data for the heats of fusion of AlO$_{1.5}$ and CrO$_{1.5}$.

Through the relation $\Delta G_r = -RT \ln K$, we calculate the equilibrium constant of the reaction $\Delta G_r = 0.5 \times \Delta G_f^o(\text{Fe}_2\text{O}_3) - \Delta G_f^o(\text{FeO})$ (eq. S5). At 2173 K and 1 bar, we obtain the value for $\log K_{\text{JANAF}} = 0.095$ and $\log K_{\text{IVTAN}} = 0.009$. When compared with the $\log K$ obtained from the experimental data on the basis of the correlation of $\log fO_2$ with $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ (Fig. 2 of the main text) in quenched peridotite liquid, 0.096±0.053, we can obtain $\gamma_{\text{FeO}_{1.5}}/\gamma_{\text{FeO}}$ by the following relation:

$$ \frac{\gamma_{\text{FeO}_{1.5}}}{\gamma_{\text{FeO}}} = \frac{\log K_{\text{experiment}}}{\log K_{\text{JANAF/IVTAN}}} \quad (S7) $$

We calculate values of 1.00±0.13 using the JANAF data and 1.22±0.15 using the IVTAN data.
5. Determination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of a terrestrial magma ocean

In order to inform models of possible secondary atmospheric compositions to have formed from outgassing of a terrestrial magma ocean, we exploit the present-day estimates for i) the mantle’s $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and hence O content, and ii) the abundances of the other three major volatile elements, H, C, and N in the Earth’s mantle. Specifically, their abundances in Earth’s fictive ‘primitive mantle’ or bulk silicate Earth (BSE) is most pertinent to this question, as it reflected the composition of Earth’s mantle prior its differentiation into crust and depleted mantle reservoirs (24, 89).

Use of mantle peridotites to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the magma ocean

Estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in peridotites derives from the weighted sum of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of its constituent minerals. The three most comprehensive studies to this end are refs. (40, 90) in xenolith suites and (41) in massif peridotites, in which $\text{Fe}^{3+}$ contents of each of the five relevant mantle minerals (olivine, orthopyroxene, clinopyroxene, spinel and garnet) are determined from $^{57}$Fe Mössbauer spectroscopy. Importantly, the 48 samples investigated by these authors cover a range of i) temperatures and pressures of equilibration [41]; ii) tectonic settings, and iii) fertility, that permit assessment of the degree to which these factors affect the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the whole rock (Table S6).

Table S6. Summary of data presented in refs. (40, 41, 90), showing selected features of whole rock peridotites from various localities and tectonic settings. Element oxides are presented in wt. %, T in °C and P in GPa. Refer to the original papers for methods.

| Sample | Rock type | Locality | MgO | FeO$^3+$ | FeO | CaO | NaO | T | P | $\text{Fe}^{3+}/\Sigma\text{Fe}$ |
|--------|-----------|----------|-----|----------|-----|-----|-----|---|---|------------------|
| Fr1    | spinel lherzolite | Landoz | 37.5 | 0.30     | 7.56 | 3.64 |     |    |    | 0.034            |
|        | Massif Central |         |      |          |      |      |      |    |    |                  |
|        |             | Southeastern Australia | | | | | | | | |
| 89-661 | garnet lherzolite, coarse | Lashaine | 48.1 | 0.07     | 6.8  | 0.94 |     |    |    | 0.009            |
| 89-669 | wehrlite, protogranular | Lashaine | 43.7 | 0.09     | 9.5  | 1.75 |     |    |    |                  |
| 89-680 | garnet harzburgite, coarse | Lashaine | 45.9 | 0.14     | 6.6  | 0.81 |     |    |    | 0.019            |
| 89-719 | garnet harzburgite, coarse | Lashaine | 47.7 | 0.07     | 6.8  | 0.55 |     |    |    | 0.009            |
| 89-772 | dunite, protogranular  | Olmani  | 46.1 | 0.039    | 12.5 | 0.66 |     |    |    | 0.003            |
| 89-777 | wehrlite, protogranular | Olmani  | 49.1 | 0.09     | 5.97 | 0.11 |     |    |    | 0.013            |
|        |             | Tanzania | | | | | | | | |
|        |             | Southern Africa | | | | | | | | |
| BD1140 | garnet lherzolite, coarse, low T | Bultfontein | 41.8 | 0.18     | 7.3  | 1.75 | 975 | 5  | 0.022 |
| BD1150 | garnet lherzolite, coarse, low T | Bultfontein | 37.6 | 0.39     | 7.1  | 3.49 | 1141 | 7 | 0.047 |
| BD1201 | garnet lherzolite, coarse, low T | Wesselton | 42.2 | 0.23     | 6.8  | 1.33 | 1007 | 6.3 | 0.030 |
| BD1354 | garnet websterite, coarse, low T | Matsoku | 29.3 | 0.77     | 11.2 | 4.38 | 1294 | 9 | 0.058 |
| F865  | garnet harzburgite, w/diamond | Finsch | 44.7 | 0.09     | 6.8  | 0.56 |     |    |    | 0.012            |
| F556  | garnet harzburgite, w/diamond | Finsch | 40.7 | 0.16     | 9.2  | 0.96 |     |    |    | 0.015            |
| FRB921 | garnet websterite, coarse, low T | Premier | 35.7 | 0.31     | 6.14 | 3.01 | 1055 | 4.2 | 0.043 |
| FRB1350 | sp-gt lherzolite, w/graphite | Premier | 42.6 | 0.14     | 6.8  | 1.43 | 722  | 2.5 | 0.018 |
| PHN5267 | garnet lherzolite, sheared, high T | Premier | 43.0 | 0.21     | 7.51 | 2.01 |     |    |    | 0.025            |
| FRB909 | garnet lherzolite, sheared, high T | Premier | 42.1 | 0.21     | 8.1  | 1.63 | 1395 | 6.2 | 0.023 |
From Fig. S7a, b, it is clear that there is no dependence of $\text{Fe}^{3+}/\Sigma\text{Fe}$ on either the temperature or pressure of equilibration, a conclusion that holds irrespective of whether the aluminous phase is spinel (P ~ 1.5 GPa) or garnet (P > 2 GPa). This is also true of samples that have similar chemical composition and equilibration temperature, such as sample 84-402 with $T (^\circ\text{C}) = 998$ and $P (\text{GPa}) = 1.5$, a spinel lherzolite with 44.5 wt. % MgO from Southeastern Australia and sample UV61/91 with $T (^\circ\text{C}) = 1239$ and $P (\text{GPa}) = 7.8$, a sheared garnet lherzolite with 44.6 wt. % MgO from Udachnaya, Siberian craton. The former sample has $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.019, whereas the latter has 0.017. The effect of temperature is difficult to isolate, as many continental xenoliths fall along geotherms with similar temperature gradients of ~40 mW/m$^2$. Nevertheless, the sample FRB1350, a spinel-garnet lherzolite containing graphite from the Kaapvaal craton, with an equilibration temperature of 722 °C and a pressure of 2.5 GPa, and an MgO content of 42.6 wt. % has $\text{Fe}^{3+}/\Sigma\text{Fe}$ identical to that of a spinel lherzolite from Southeastern Australia, 85-168, with $T = 1121 ^\circ\text{C}$, $P = 1.5$ GPa and MgO = 42.4 wt. %. It should also be noted that these xenoliths come from rather different tectonic settings; from the stable Archean shields of the Kaapvaal (FRB1350) and Siberian (UV61/91) cratons (91) and from the Tertiary Newer Volcanic Province erupting above lithosphere of accreted Phanerozoic arc terranes (85-168 and 84-402) (92).

| Sample | Description                  | Temperature | Pressure | MgO (%) | Fe$^{3+}$/ΣFe |
|--------|-----------------------------|-------------|----------|---------|---------------|
| PHN5239| garnet lherzolite, sheared, high T | Premier     | 44.2     | 0.17    | 7.2           |
| Siberia|                                    |             |          | 0.90    | 1431          |
| UV417/89| garnet lherzolite, coarse, low T | Udachnaya   | 39.2     | 0.21    | 8.3           |
| UV61/91| garnet lherzolite, sheared, high T | Udachnaya   | 44.6     | 0.14    | 7.3           |
| Massif Peridotites |                        |             | 1.68     | 1239    | 7.8           |
| Beni Bousera |                                |             |          | 0.021   | 0.017         |
| bbI-32e| spinel lherzolite              |             | 39.31    | 0.145   | 947           |
| bbI-36| spinel harzburgite             |             | 45.23    | 0.04    | 920           |
| bbI-37a| spinel lherzolite              |             | 41.35    | 0.137   | 950           |
| bbI-37b| spinel lherzolite              |             | 41.35    | 0.130   | 950           |
| bbI-43| spinel lherzolite              |             | 39.89    | 0.184   | 1110          |
| bbII-13| spinel lherzolite              |             | 39.20    | 0.077   | 1137          |
| bbII-14| spinel lherzolite              |             | 44.73    | 0.034   | 1084          |
| bbIV-11| spinel harzburgite             |             | 46.22    | 0.084   | 930           |
| Ronda |                                    |             |          | 1.5     |               |
| E3-126a| spinel lherzolite              |             | 44.59    | 0.051   | 915           |
| E3-126b| spinel lherzolite              |             | 44.59    | 0.054   | 915           |
| E3-208a| plagioclase lherzolite         |             | 42.24    | 0.088   | 929           |
| E3-208b| plagioclase lherzolite         |             | 42.24    | 0.098   | 929           |
| E3-227| spinel lherzolite              |             | 44.20    | 0.117   | 935           |
| E3-144| spinel lherzolite              |             | 39.07    | 0.224   | 948           |
| E3-148| spinel lherzolite              |             | 38.60    | 0.165   | 987           |
| Pyrenees |                                |             |          | 1.5     |               |
| Py-1  | spinel lherzolite              | Fontète Rouge | 40.39    | 0.190   | 958           |
| Py-18 | apatite-bearing sp lherzolite   | Lherz       | 40.49    | 0.263   | 986           |
| Py-30a| spinel lherzolite              | Lherz       | 40.28    | 0.197   | 833           |
| Py-30b| spinel lherzolite              | Lherz       | 40.28    | 0.198   | 833           |
| Py-34 | spinel lherzolite              | Lherz       | 39.74    | 0.220   | 903           |
| Py-25 | amphibole-bearing sp lherzolite | Caussou    | 40.71    | 0.279   | 849           |
Fig. S7. Variation of Fe$^{3+}/\Sigma$Fe of natural peridotite xenoliths with temperature and pressure.

Data of refs. (40, 41, 90) illustrating the variation of Fe$^{3+}/\Sigma$Fe in whole rock peridotites determined by measurements of individual minerals via Mössbauer spectroscopy with a) Temperature (°C) and b) Pressure (GPa). Samples are colour-coded according to their locality.

The observation that, for a given bulk composition, the temperature and pressure of equilibration (and tectonic setting) have no discernible effect on the Fe$^{3+}/\Sigma$Fe is crucial in establishing the insensitivity of the ratio to any potential redox exchange with other multivalent species (Cr, H, C, and S, in particular). This suggests that either i) the oxygen fugacities of samples in the upper mantle are such that redox reactions between other multivalent species do not occur (i.e., the equilibrium constant of the reaction $H_2O = H_2 + 1/2O_2$ at mantle $fO_2$s always has high $H_2O/H_2$ ratios) or that ii) any small change in the ratios of other redox-sensitive species (e.g. $H_2O/H_2$, $Cr_2O_3/CrO$, $CO_2/C$) is buffered by Fe$^{3+}/Fe^{2+}$ (cf. ref. (40)). On the basis of these observations, Fe$^{3+}/\Sigma$Fe can be taken as a faithful record of the oxygen content of peridotite.
Fig. S8. The variation of a) Fe$^{3+}$/ΣFe and b) Fe$_2$O$_3$ (wt. %) with MgO (wt. %) in whole rock peridotites. Shown is the line of best fit (dashed black line) and its 95% confidence envelope (grey curves). The MgO content of the BSE (24) is shown as a range demarcated by the grey vertical lines. The area of intersection gives the mean value and uncertainty thereof of the Fe$^{3+}$/ΣFe of the BSE (grey area). Data from refs. (40, 41, 90), see Table S6.

Examination of the dataset presented in Table S6 shows that Fe$^{3+}$/ΣFe covaries with indices of melt extraction; namely, the abundances of MgO, CaO and Na$_2$O in the peridotite whole rock (Fig. S8). Correlations with each of the element oxides defines an $r^2$~0.6 for the 20 pristine samples, with Fe$^{3+}$/ΣFe decreasing as the amount of basaltic component in the rock decreases (40, 90). Partial melting of the mantle produces melts with a higher Fe$^{3+}$/ΣFe ratio than in their source peridotite, due to the high contribution of clinopyroxene and spinel to the melting reactions at low pressures (93, 94) and the higher incompatibility of Fe$^{3+}$ relative to Fe$^{2+}$ in mantle minerals (71). By mass balance, therefore, Fe$^{3+}$/ΣFe in the residuum must decrease. These correlations can then be used to calculate the Fe$^{3+}$/ΣFe of a fictive BSE composition, and yield, based on MgO, Fe$^{3+}$/ΣFe = 0.035, for CaO, Fe$^{3+}$/ΣFe = 0.036 and for Na$_2$O, Fe$^{3+}$/ΣFe = 0.036, and hence an average of 0.036±0.001, n = 20. As all samples lie on the same trend, we use the entire dataset of ref. (40) to derive the relationship:

$$\frac{Fe^{3+}}{Fe^{2+}}(\%) = 13.7 \pm 1.1 - 0.27 \pm 0.03 \times MgO \ (wt.\%); \ r^2 = 0.80, n = 26 \quad (S8)$$

At the MgO content of the BSE, 36.77±0.44 wt. % (24), eq. (S10) gives Fe$^{3+}$/ΣFe of 0.037±0.005, propagating errors on both the BSE MgO content and the 95% confidence interval on the regression (Fig. S8).

With the inclusion of massif peridotite samples (41) allows for derivation of the relationship:

$$Fe_2O_3 \ (wt. \%) = 1.37 \pm 0.13 - 0.028 \pm 0.003 \times MgO \ (wt. \%); \ r^2 = 0.66, n = 48 \quad (S9)$$

Which, despite the greater number of samples, has a lower correlation coefficient. At the MgO content of the BSE, this expression yields Fe$_2$O$_3$ (wt. %) = 0.33±0.06. Given the well-known value of the FeO content of the BSE, 8.1±0.1 wt. %, this translates into an Fe$^{3+}$/ΣFe of 0.037±0.007, consistent with estimates from eq. (S8).

Use of Mid-Ocean Ridge Basalt (MORB) glasses to constrain the Fe$^{3+}$/Fe$^{2+}$ of their mantle sources

The Fe$^{3+}$/ΣFe ratios of MORB glasses have been determined by XANES spectroscopy (31) with results that are in agreement with previous wet-chemical determinations (51). The mean Fe$^{3+}$/ΣFe value is 0.11 and shows a weak negative correlation with the MgO content of the glass (39). Because MORB glasses have evolved from their parental magmas (i.e., they have Mg#s lower than that expected for equilibrium with Fo$_{90}$ olivine, their Fe$^{3+}$/ΣFe ratios cannot be directly be used to determine those of their mantle sources. Assuming the ‘Replenish-Fractionate-Tap’ model of MORB genesis gives a parental melt at 10.4 wt. % MgO with 0.61± wt. % Fe$_2$O$_3$ (39) (their Fig. 1). Alternatively, an empirical extrapolation to calculate their Fe$_2$O$_3$ contents at a melt Mg# of 0.72, yields values of 0.73±0.18 wt. % (31).

The corresponding Fe$_2$O$_3$ content of the mantle source can then be estimated by applying the non-modal batch melting equation, a fair approximation to the physically more realistic polybaric accumulated fractional melting. The equation for batch melting is

$$C_o = C_l(D + F(1 - P)) \quad (S10)$$

where $C_o$ and $C_l$ are the concentrations of Fe$_2$O$_3$ in the source, and liquid, respectively, $D$ is its bulk partition coefficient between solid and liquid, equated at each melt fraction $F$. Here, the non-modality of melting is applied by adopting $P$ according to the measured values as a function of $F$ from (39), yielding $C_o/C_l = 2.9$ at $F = 0.2$, giving $C_o = 0.21±0.06$ or 0.25±0.06 wt. % Fe$_2$O$_3$. 
Assuming the mantle source of MORB contains 8.1 wt. % FeO (T) (95), these FeO contents imply Fe^3+/ΣFe ratios of 0.028±0.007. For the ‘Replenish-Tap-Fractionate’ model of MORB genesis and the data of (31), a value of 0.21±0.06 wt. % FeO in the MORB source was estimated (39), yielding Fe^3+/ΣFe = 0.023±0.006. Because the MORB source mantle, on the basis of its trace element composition, is residual following ~3 – 5 % melt extraction (95), these Fe^3+/ΣFe are minimum estimates. Because of their agreement with direct measurements of Fe^3+/ΣFe in peridotites, whose composition enables determination of that in the BSE, we adopt Fe^3+/ΣFe = 0.037±0.005 as the nominal value of the terrestrial magma ocean.

6. Thermodynamic models of atmospheric composition

Use of the contemporary BSE abundances to calculate a primitive atmosphere implies that the Earth had already attained in present-day complement of H, C, N, and O by the time of the giant impact. By contrast, should the late veneer, thought to represent ~0.5 wt. % of the Earth’s mass, have delivered the bulk of the Earth’s volatile budget (4), then the post giant-impact magma ocean would have contained fewer volatiles, and likely in different ratios, than exist in the BSE today. However, due to the contrasting identities invoked for the chondritic meteoritic material (4, 70, 96) thought to have comprised the late veneer, back-calculating the volatile composition of a terrestrial magma ocean is uncertain. As such, while the equivalence of the present-day BSE volatile budget with that of the early Earth cannot be conclusively demonstrated, it remains our strongest constraint as to the composition of the Hadean Earth.

Recent estimates for the composition of the BSE converge relatively well upon the abundances of H, C and N (Table S7).

| Abundances (mass %) | BSE (24)       | BSE (53)       |
|---------------------|----------------|----------------|
| H                   | 0.0120±0.0024  | 0.0079±0.0010  |
| C                   | 0.0100±0.050   | 0.014±0.004    |
| N                   | 0.0002±0.0001  | 0.00028±0.00006|
| Ratios              |                |                |
| H/C (mass)          | 1.2            | 0.56           |
| H/C (moles)         | 14.4           | 6.76           |
| H/N (mass)          | 60             | 28.2           |
| H/N (moles)         | 840            | 395            |

Should the magma ocean quantitatively degas its entire H, C, and N budget, it would produce partial pressures (in bar) of \( p_{H_2O} = 832.6 \), \( p_{CO_2} = 282.7 \) and \( p_{N_2} = 1.54 \) for the BSE estimates of ref. (24), and \( p_{H_2O} = 547.4 \), \( p_{CO_2} = 395.8 \) and \( p_{N_2} = 2.16 \) for the more recent model of ref. (53). In both cases, however, H would be expected to be the dominant component, both by moles and by mass, in a terrestrial atmosphere, with \( N_2 \) contributing only as a minor component, at most ~2 bar of pressure. These estimates, however, assume negligible solubility of these elements in a silicate (i.e., peridotitic) magma ocean. In practice, each of these elements are soluble to varying degrees in silicate liquid and hence their associated partial pressures in the atmosphere will decrease accordingly.

Solubility laws depend on the speciation of the element in question, both in the liquid silicate and in the gaseous phase (8, 56). The oxygen fugacity of the magma ocean as constrained by Fe^3+/ΣFe of natural peridotites, combined with that determined by XANES spectroscopy of peridotite liquids, is equal to ΔIW+0.5. These mildly oxidising conditions allow some simplifying assumptions to be made as to the speciation of H, C and N in silicate melts. Ref. (97) showed that dissolved \( H_2 \) in basaltic silicate melts in equilibrium with a vapour phase with \( fH_2 \) between 166 and 68163 bar only becomes
important at oxygen fugacities below IW. By the same token, ref. (57) found evidence for the occurrence of Fe(CO)₅ and minor CH₄ in silicate melts of a lunar basaltic composition, but only at, or below, ΔIW-0.55. In a study of the solubility of N in silicate melts, dissolved N₂ was shown to be stable in a basaltic melt composition over a wide range of fO₂, down to the IW buffer (56).

Therefore, we presume that H dissolves as molecular H₂O and partially dissociates to OH in silicate melts (58):

\[ H₂O(g) = H₂O(l) \] (S11)

\[ H₂O(l) + O(l) = 2OH(l) \] (S12)

Because of the highly depolymerised melt composition, C is incorporated exclusively as the CO₃²⁻ anion (98):

\[ CO₂(g) + O²⁻(l) = CO₃²⁻(l) \] (S13)

and N is dissolved as molecular N₂ (56):

\[ N₂(g) = N₂(l) \] (S14)

The solubility of these elements in peridotite liquid can be estimated using expressions for the solubility of CO₃²⁻, H₂O and N₂ in basaltic melts. There are, however, two caveats to be mindful of, i) existing calibrations are performed over a limited temperature range (800 ≤ T °C ≤ 1400 °C) and ii) the compositions do not reflect those of a peridotite liquid. As such, extrapolation of existing solubility laws to the conditions of the magma ocean, at 2173 K for a peridotite liquid, should be treated with caution. Nevertheless, there are features of the behaviour of H₂O and CO₃²⁻ in basaltic liquids evident from existing data that suggest these laws should provide a good estimate of their solubility in peridotite liquids. First, the temperature dependence of their solubilities has been shown to be weak (H₂O; (99)) or undetectable within experimental uncertainty (CO₃²⁻; (100)). Furthermore, in the expression of (54) used to calculate water solubility, coefficients that take into account the mole fractions of the liquid oxides are included in order to account for the effect of composition of the silicate melt on H₂O solubility.

With these considerations in mind, the solubility of H₂O in peridotite liquid is calculated by (54):

\[ 2\ln X_{H₂O}^{melt} = \frac{a}{T} + \sum b_iX_i\left(\frac{P}{T}\right) + c\ln f_{H₂O}^{fluid} + d \] (S14)

where \( X_{H₂O}^{melt} \) and \( f_{H₂O}^{fluid} \) are the mole fraction and fugacity of water in the melt and fluid, respectively, \( a = 2565, b_{Al₂O₃} = -1.997, b_{FeO(T)} = -0.9275, b_{Na₂O} = 2.376, X_i \) refers to the oxide mole fraction, \( c = 1.171, d = -14.21, P \) is the total pressure in bars and \( T \) the temperature in Kelvin. We set \( X_{FeO(T)} = 0.08, X_{Na₂O} = 0 \) and \( X_{Al₂O₃} = 0.04 \).

The solubility of CO₃²⁻ in peridotite liquid is calculated following the model of (55):

\[ X_{CO₃²⁻}^{melt}(P, T) = X_{CO₃²⁻}^{fluid}(P_0, T_0) \frac{\frac{V_{CO₃²⁻}^{melt}(P, T)}{V_{CO₃²⁻}^{fluid}(P_0, T_0)}}{\exp\left(\frac{-\Delta V_{Y_{melt}}^{o}(P-P_0)}{RT_0}\right)} \] (S15)

where \( R \) is the gas constant, \( \Delta V_{Y_{melt}}^{o} \) is the standard molar volumes of CO₃²⁻ and O²⁻ in the silicate melt that are assumed to be independent of \( P \) and \( T \) over the range considered. Setting \( P_0 \) to 1 bar and \( T_0 = 1473 \text{ K} \), and \( \Delta V_{Y_{melt}}^{o} \) 23 cm³/mol the best fit value of \( X_{CO₃²⁻}^{melt} = 3.8 \times 10^{-7} \) or ~0.5 ppm (55).
The solubility of nitrogen as $N_2$ is the lowest of the three elements, and, above the IW buffer, is simply given according to Henry’s law (36):

$$N^{mol} (ppm) = f_{N_2}^{gas} (0.0611 \pm 0.0149). \quad (S16)$$

where $N^{mol}$ is the concentration of nitrogen in the melt in parts per million.

**Fig. S9. Solubilities of H$_2$O and CO$_2$ in a terrestrial magma ocean.** The solubility (in ppm) of H$_2$O and CO$_2$ as calculated by the equations of refs. (54) and (55), respectively. The grey lines represent the BSE estimates of H$_2$O according to (53) (H ’18) and (24) (P+O’N ’14), predicting $f_{H_2O}$ of ~2.5 bar and 5 bar, respectively. Conversely, the $f_{CO_2}$ calculated for a fully-degassing magma ocean of 62.5 bar and 41 bar yields 28.3 (ref. (53)) and 20.3 (ref. (24)) ppm CO$_2$ in the magma ocean. All fugacities by mass.

The H$_2$O solubility in the magma ocean is given by the point at which the BSE content of H$_2$O (Table S7) crosses the solubility curve defined by eq. S14 (Fig. S9). This occurs at only 2.5 bar H$_2$O for the composition of (53), and 5 bar for the composition of (24). At an $fO_2$ of $\Delta$IW+0.5, the H$_2$O/H$_2$ ratio is calculated according to the following equation:

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g) \quad (S17)$$

With a log$K$ of reaction at 2173 K of 3.21 assuming an ideal gas (43). This yields 0.2 bar of H$_2$ for 2.5 bar H$_2$O and 0.4 bar of H$_2$ for 5 bar H$_2$O (by mass). This equates to between 99.6 % and 99.4 % of the H$_2$O budget of the BSE being stored in the magma ocean. The final pressures of $\Sigma f$(H$_2$O; $x = 0$ or 1) are therefore between 2.7 and 5.4 bar (by mass).

For C, at $\Delta$IW+0.5, the gas phase is predicted to have $fCO_2/fCO_2 \sim 3.5$, according to the reaction:

$$CO(g) + \frac{1}{2}O_2(g) = CO_2(g) \quad (S18)$$

for which the log$K$ is calculated to be 2.30 at 2173 K (42). Hence, $fCO_2$ is significantly lower than $\Sigma f$(CO$_2$; $x = 1$ or 2). In this case, it is assumed that the oxygen buffering capacity of the mantle far exceeds that of the atmosphere, such that the atmospheric $fCO_2/fCO_2$ is fixed at 3.5 (or 4.8 by moles).
For an initial C abundance of 0.014% in the BSE, 62.5 bar of CO$_2$ and 221.1 bar of CO are present in a fully-degassed atmosphere of ref. (53) at ΔIW+0.5. This is equivalent to 287 ppm of CO and 81 ppm of CO$_2$ in the magma ocean. An f/CO$_2$ = 62.5 bar, eq. S15 predicts a CO$_2$ solubility in the magma ocean of 28.3 ppm, or 35% of the CO$_2$ budget. In order to maintain f/CO/CO$_2$ = 3.5, it must also dissolve an appropriate amount of CO (though its speciation in the magma ocean is CO$_3^{2-}$ given the excess buffering capacity of oxygen). There is some equilibrium amount of CO (likely in the form Fe(CO)$_5$) below ΔIW-0.55, but this is not considered here. This results in a final pressure of CO = 144 bar and CO$_2$ = 41 bar (by mass). An equivalent calculation for the BSE composition of ref. (24) yields 102.5 bar CO and 29 bar CO$_2$ (by mass).

For 2.16 bar of N$_2$, eq. S16 predicts an N content of the magma ocean of 0.13 ppm, or 5% of the total N budget. This quantity is smaller than the uncertainty in the abundance of N in the BSE (±0.6 ppm (53)), and so it is assumed that N$_2$ is present entirely in the atmosphere at f/N$_2$ of 2.16 bar (53) or 1.56 bar (24).

The resultant total pressures in an atmosphere in equilibrium with a magma ocean at 2173 K are 138.5 bar with the BSE of (24), and 189.5 bar for the BSE composition of (53). The molar H/C and H/N ratios are 0.23 and 6.79 for the model of (24) and 0.07 and 2.25 using the BSE abundances of (53).

**FactSage Atmosphere model**

With this information, the speciation of a model magma ocean atmosphere with molar H/C and H/N combining the estimates of (24, 53) estimates and a total pressure of 140 bar can be calculated using FactSage. The moles of all species are normalised to H = 1, yielding C = 4.3 and N = 0.17. The moles of O are adjusted such that the f/O$_2$ gives a value equivalent to ΔIW+0.5 at 2173 K (10$^6$ bar), and, for this composition, is found to be 5.3. The initial total pressure is set to 140 bar, to reflect the sum of the CO, CO$_2$, H$_2$, H$_2$O and N$_2$ species predicted to be present at 2173 K. The speciation and fugacities of the stable gas species, along with any condensed phases, are then calculated by minimising the Gibbs free energy of the system using FactSage 7.3 (61) at a given temperature and pressure. It should be noted that these conditions initially exceed the critical point of H$_2$O (647 K and 221 bar) and of mixed CO$_2$-H$_2$O systems (77).

As our treatment deals only with pure phases (i.e., no real or solid solutions), the calculations are necessarily simplified upon precipitation of graphite and water. Furthermore, the calculations are made so as to approximate a closed system, in which the bulk composition is held constant, and interactions of the atmosphere with the magma ocean, crystalline silicates, or other solids are ignored. As such, reactions of high water vapour pressures with condensed phases to form hydrous minerals, or the dissolution of CO$_3^{2-}$ into seawater are not treated and are beyond the scope of this work. Results of these calculations are discussed as Fig. 3 and in the main text.
| Temp. (K) | 2173 | 2123 | 2073 | 2023 | 1973 | 1923 | 1873 | 1823 | 1773 | 1723 | 1673 | 1623 | 1573 | 1523 | 1473 |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Gas (moles) | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 |
| CO | 101.8 | 101.7 | 101.6 | 101.5 | 101.4 | 101.3 | 101.1 | 101.0 | 100.8 | 100.7 | 100.5 | 100.3 | 100.1 | 99.9 | 99.7 |
| CO₂ | 21.3 | 21.4 | 21.5 | 21.6 | 21.7 | 21.8 | 21.9 | 22.1 | 22.2 | 22.4 | 22.6 | 22.8 | 23.0 | 23.2 | 23.4 |
| H₂O | 7.3 | 7.2 | 7.1 | 7.0 | 6.9 | 6.8 | 6.7 | 6.5 | 6.4 | 6.3 | 6.0 | 5.9 | 5.7 | 5.4 | 5.2 |
| H₂ | 6.9 | 7.0 | 7.1 | 7.2 | 7.4 | 7.5 | 7.6 | 7.8 | 7.9 | 8.1 | 8.3 | 8.5 | 8.7 | 8.9 | 9.1 |
| N₂ | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 |
| O₂ | 1.0E-06 | 5.1E-07 | 2.4E-07 | 1.1E-07 | 4.8E-08 | 2.0E-08 | 8.1E-08 | 3.1E-09 | 1.1E-09 | 3.8E-10 | 1.2E-10 | 3.5E-11 | 9.7E-12 | 2.2E-12 | 5.2E-13 |
| O | 2.3E-06 | 1.2E-06 | 5.6E-07 | 2.6E-07 | 1.2E-07 | 5.1E-08 | 2.1E-08 | 8.3E-09 | 3.1E-09 | 1.1E-09 | 3.6E-10 | 1.1E-10 | 3.2E-11 | 8.5E-12 | 2.1E-12 |
| CH₄ | 3.7E-09 | 5.2E-09 | 7.5E-09 | 1.1E-08 | 1.6E-08 | 2.5E-08 | 4.0E-08 | 6.4E-08 | 1.1E-07 | 1.8E-07 | 3.2E-07 | 5.8E-07 | 1.1E-06 | 2.2E-06 | 4.5E-06 |
| NH₃ | 3.2E-06 | 3.6E-06 | 3.9E-06 | 4.4E-06 | 4.9E-06 | 5.4E-06 | 6.1E-06 | 6.9E-06 | 7.9E-06 | 9.1E-06 | 1.1E-05 | 1.2E-05 | 1.5E-05 | 1.7E-05 | 2.1E-05 |
| Total P (bar) | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.9 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 |

Condensed phases
Graphite (moles)
Graphite (mass)
Water (moles)
Water (mass)
**Table S8-II.** Fugacities (bar), in moles, of species in a real gas calculated according to FactSage simulating closed system cooling of a magma ocean at ΔIW+0.5 from 2173 K to 273 K with initial molar ratios of H/C = 0.22 and H/N = 5.8. Part II – 1423 K – 773 K.

| Temp. (K) | 1423 | 1373 | 1323 | 1273 | 1223 | 1173 | 1123 | 1073 | 1023 | 998 | 973 | 923 | 873 | 823 | 773 |
|-----------|------|------|------|------|------|------|------|------|------|-----|------|------|------|------|------|
| Gas (moles) | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.88 | 4.6478 | 4.374 | 3.8739 | 3.506 | 3.2723 | 3.1361 |
| CO        | 99.4 | 99.2 | 98.9 | 98.6 | 98.3 | 97.9 | 97.6 | 97.2 | 96.8 | 84.1 | 69.2 | 52.2 | 22.9 | 11.2 | 4.9 |
| CO$_2$    | 23.7 | 23.9 | 24.2 | 24.5 | 24.8 | 25.1 | 25.5 | 25.9 | 26.3 | 32.4 | 39.5 | 42.2 | 61.1 | 66.1 | 68.5 |
| H$_2$O    | 5.0  | 4.7  | 4.4  | 4.1  | 3.8  | 3.5  | 3.1  | 2.8  | 2.4  | 2.9  | 3.7  | 5.2  | 6.9  | 8.5  | 9.9  |
| H$_2$     | 9.3  | 9.6  | 9.9  | 10.2 | 10.5 | 10.8 | 11.2 | 11.5 | 11.8 | 11.2 | 10.4 | 8.8  | 7.0  | 5.3  | 3.7  |
| N$_2$     | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  | 2.4  |
| O$_2$     | 1.1E-13 | 2.1E-14 | 3.3E-15 | 4.6E-16 | 5.3E-17 | 5.2E-18 | 4.1E-19 | 2.5E-20 | 1.2E-21 | 4.6E-22 | 1.7E-22 | 1.9E-23 | 1.3E-24 | 5.4E-26 | 1.4E-27 |
| O         | 4.5E-13 | 8.8E-14 | 1.5E-14 | 2.3E-15 | 2.9E-16 | 3.2E-17 | 2.8E-18 | 2.0E-19 | 1.1E-20 | 3.1E-21 | 8.9E-22 | 5.3E-23 | 2.1E-24 | 5.3E-26 | 7.9E-28 |
| CH$_4$    | 9.8E-06 | 2.3E-05 | 5.5E-05 | 1.5E-04 | 4.1E-04 | 1.3E-03 | 4.4E-03 | 1.7E-02 | 7.1E-02 | 9.4E-02 | 1.1E-01 | 1.6E-01 | 2.2E-01 | 2.9E-01 | 3.4E-01 |
| NH$_3$    | 2.6E-05 | 3.2E-05 | 4.0E-05 | 5.1E-05 | 6.7E-05 | 8.8E-05 | 1.2E-04 | 1.6E-04 | 2.3E-04 | 2.6E-04 | 3.0E-04 | 3.7E-04 | 4.4E-04 | 4.9E-04 | 5.0E-04 |
| Total P (bar) | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 | 139.8 |

Condensed phases

| Graphite (moles) | 0.23067 | 0.503 | 0.9996 | 1.3633 | 1.5928 | 1.7252 |
| Graphite (mass) | 2.7705 | 6.0413 | 12.006 | 16.374 | 19.13 | 20.721 |
| Water (moles) | |
| Water (mass) | |
Table S8-III. Fugacities (bar), in moles, of species in a real gas calculated according to FactSage simulating closed system cooling of a magma ocean at ΔIW+0.5 from 2173 K to 273 K with initial molar ratios of H/C = 0.22 and H/N = 5.8. Part III – 723 K – 273 K.

| Temp. (K) | 723 | 673 | 623 | 573 | 523 | 473 | 423 | 373 | 323 | 273 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Gas (moles) | 3.0611 | 3.0216 | 3.0015 | 2.9919 | 2.9876 | 2.9858 | 2.9852 | 2.985 | 2.8282 | 2.5 |
| CO | 1.9 | 0.6 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| CO₂ | 69.4 | 69.5 | 69.4 | 69.2 | 69.1 | 69.0 | 68.9 | 68.8 | 68.8 | 68.8 |
| H₂O | 11.2 | 12.1 | 12.9 | 13.3 | 13.7 | 13.9 | 14.1 | 14.2 | 9.8 | 0.4 |
| H₂ | 2.4 | 1.4 | 0.8 | 0.4 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| N₂ | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 |
| O₂ | 2.1E-29 | 1.6E-31 | 5.8E-34 | 7.6E-37 | 2.8E-40 | 2.0E-44 | 1.4E-49 | 4.4E-56 | 1.4E-64 | <1.0E-70 |
| O | 6.5E-30 | 2.6E-32 | 4.1E-35 | 2.2E-38 | 2.7E-42 | 5.2E-47 | 7.6E-53 | 3.1E-60 | 6.7E-70 | <1.0E-70 |
| CH₄ | 3.7E-01 | 3.8E-01 | 3.6E-01 | 3.1E-01 | 2.6E-01 | 1.9E-01 | 1.3E-01 | 7.7E-02 | 1.8E-02 | 1.2E-05 |
| NH₃ | 4.8E-04 | 4.2E-04 | 3.4E-04 | 2.6E-04 | 1.8E-04 | 1.1E-04 | 6.0E-05 | 2.7E-05 | 5.5E-06 | 1.2E-08 |
| Total P (bar) | 87.7 | 86.5 | 86.0 | 85.7 | 85.6 | 85.6 | 85.5 | 85.5 | 81.0 | 71.6 |

Condensed phases

| | Graphite (moles) | Graphite (mass) | Water (moles) | Water (mass) |
|---|----------------|----------------|--------------|--------------|
| | 1.7979 | 1.8369 | 1.8584 | 1.8711 | 1.8796 | 1.8858 | 1.8907 | 1.8946 | 1.8988 | 1.9 |
| | 21.594 | 22.063 | 22.321 | 22.474 | 22.575 | 22.65 | 22.709 | 22.755 | 22.805 | 22.82 |
| | 0.1568 | 0.48505 | 2.8247 | 8.7383 |
Effect of H/C ratio and log fO₂ on atmosphere speciation

Due to the uncertainty of the solubility of H and C in peridotite liquids, we explore the effect of the H/C ratio of the atmosphere on the stability of C- and H-bearing species at both high (2173 K) and low (300 K) temperatures. Here, we keep the molar quantities of C (4.3) and N (0.17) constant, and modify the number of moles of H from 0.05 to 61.85, in order to produce molar log(H/C) ratios between -0.73 and 1.16 (the BSE ratio of ref. (24)). The moles of O are modified in order to bracket the appropriate values relative to IW at 2173 K, between ΔIW-2.5 and ΔIW+2.5. For this exercise the total pressure is kept constant at 100 bar. In order to populate the parameter space densely enough to interpolate between individual point calculations, 21,000 Gibbs free energy minimisations were performed at both 300 K and 2173 K, and interpolated linearly to produce Fig. 4. An output of the calculation is available from the corresponding author upon request.

To explore how fO₂ evolves upon cooling, calculations were performed from 2173 K to 300 K at 50 K intervals, each starting with a fixed ΔIW (-1.25), with log(H/C) varying from -0.73 to 1.05 (Fig. S10) at 100 bar. Similar trends are observed for different starting fO₂, shifted to lower H/C (lower fO₂), and vice-versa. Graphite saturation is reached at progressively lower temperatures at increasing H/C (‘C in’ line in Fig. S10), and does not occur for log(H/C) > 0.8. Graphite precipitation increases the ΔIW of the atmosphere through the reaction CO(g) = C(s) + ½O₂(g). For high H/C atmospheres, the lack of graphite precipitation keeps the ΔIW relatively constant, until the condensation of liquid water. This occurs relatively isothermally (within the uncertainty of ±50 K calculation steps) across all H/C ratios. Depending on the pre-existing composition of the atmosphere, H₂O condensation produces an increase (log(H/C) < 0.4), a mild- to moderate decrease (0.4 < log(H/C) < 0.8) or a strong decrease for log(H/C) > 0.8. This occurs because, even though the reaction itself is independent of fO₂, H₂O (g) = H₂O (l), H is extracted at a constant molar ratio relative to O of 2:1, whereas the atmosphere contains a finite quantity of these two components. As such, removal of the minor amount of the abundant H present in a high H/C atmosphere, compared to the limited O budget of the atmosphere, has the effect of reducing O₂ even further (i.e., the mole fraction of O decreases at the expense of H). The situation is reversed for a low H/C atmosphere, where the removal of H increases the relative proportion of O in the atmosphere (XO increases whereas XH decreases), thus increasing ΔIW.

The above discussion highlights the causes for the observed distribution of atmospheric species as a function of ΔIW and log(H/C) displayed in Fig. 4.
Fig. S10. Relative oxygen fugacity as a function of temperature in a cooling magma ocean-generated atmosphere with variable H/C. Isochemical cooling calculations showing the variation of $f\text{O}_2$ (relative to the Iron-Wüstite buffer, $\Delta$IW) as a function of absolute temperature (K). Lines are colour-coded according to the log(H/C) of the starting gas, which all have a common $f\text{O}_2$ of $\Delta$IW-1.25 at 2173 K. Graphite precipitation (‘C in’) and liquid water condensation (‘H$_2$O in’) are demarcated by dashed black lines.
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