
Experimental simulation of water formation on Earth from dry pebble rain

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Supplementary Information for **Experimental simulation of water formation on Earth from dry pebble rain**

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Sections S1-S3 show detailed calculations to estimate the D/H ratio of the present Earth, $f(H_2O)$ in an H_2 atmosphere, the fugacity of water in an H_2 atmosphere, and the reduction efficiency of our experimental run products, respectively. We show atmospheric pebble-melting duration versus different planet masses in Supplementary Fig. S1 and Rayleigh distillation in Supplementary Fig. S2. Supplementary Fig. S3 shows our experimental setups. Extended Data includes the Supplementary Tables. Supplementary Tables S1–S3 present the experimental data, whereas Supplementary Table S4 provides the input data used in the pebble models.

S1. Calculation of the evolved δD value of the Earth due to Rayleigh escape during atmospheric erosion

The δD value of the solar nebula was very low at ~ -850 ‰ (vs VSMOW)¹, corresponding to a D/H ratio of 3.11×10^{-5} , where VSMOW has a value of 1.5576×10^{-4} . Fractionation during conversion of this gas to H_2O by reaction (1) and incorporation into the magma ocean would raise the δD value of Earth to close to -800 ‰ due to the preferential incorporation of deuterium in H_2O (Table S3). Once the nebula had dissipated, hydrogen would be lost as H rather than H_2 due to heating and ionization by XUV radiation². The increase in the D/H ratio by loss to space can be

estimated using a simple Rayleigh fractionation equation where $\frac{D}{H}_{final} = \frac{D}{H}_{initial} f^{(\alpha-1)}$

$\frac{D}{H}_{final} = \frac{D}{H}_{initial} f^{(\alpha-1)}$. The initial D/H ratio in our calculations is 31×10^{-6} (corresponding to a δD value of -800 ‰). Assuming an α_{H_2-H} value of 1.57-2.03 for 200-400°C fractionation (ref³), the change in the D/H ratio as a function of f (fraction lost) is shown in Fig. S2. For a loss of 80-90% of the originally ingassed water, the present-day value of ~-80 to -40‰ is reached. Over 100 ocean equivalents of water may have been dissolved into the Earth during pebble accretion (Fig. 5c). Loss of 80-90% of this hydrogen would still lead to an estimate that is well within the range of estimates for Earth's present-day water (<12 ocean equivalents⁴).

S2. Calculation of $f(H_2O)$ in an H_2 atmosphere

The fugacity of water $f(H_2O)$ in an H_2 atmosphere is governed by the equation



The free energy for $FeO_{silicate}$ is taken from ref⁵ using the equation

$$\Delta G_{FeO \text{ in silicate melt}}^o = -244118 + 115.559 \times T - 8.474 \times T \ln(T). \quad (S2)$$

The free energy for the endmember reaction (equation S1) is given by

$$\Delta G_{reaction}^o = \Delta G_{Fe_{metal}}^o + \Delta G_{H_2O}^o - \Delta G_{FeO \text{ in silicate melt}}^o - \Delta G_{H_2}^o \quad (S3),$$

where free energy is relative to the elements at 1 bar. At 1600 K, $\Delta G_{Fe_{metal}}^o = 0$, $G_{H_2}^o = 0$, and $\Delta G_{H_2O}^o = -158569$ J. Equation (S2) yields $\Delta G_{FeO \text{ in silicate melt}}^o = -159254$ J. Now equation (S3) yields $\Delta G_{reaction}^o = 685$ J. The free energy of the reaction in an H_2 -rich atmosphere is

$$\Delta G_{reaction} = \Delta G_{reaction}^o + RT \ln \frac{[f(H_2O)] [a(Fe_{metal})]}{[f(H_2)] [a(FeO_{silicate\ melt})]}. \quad (S4)$$

At equilibrium, $\Delta G_{reaction} = 0$. The fugacity of H_2 gas $f(H_2)$ is equal to $P(H_2) \gamma(H_2)$ where $P(H_2)$ and $\gamma(H_2)$ are the partial pressure and the fugacity coefficient of the gas. R is the universal gas constant, T is the reaction temperature, and a is the activity of the endmember solid or melt. Using activity coefficients of ref⁶, we get

$$f(H_2O) = a(FeO_{silicate\ melt}) f(H_2) e^{-\frac{\Delta G_{reaction}^o}{RT}}. \quad (S5)$$

$X(FeO_{silicate\ melt})$ is the mass fraction of FeO in the melt, and $\gamma(FeO_{silicate\ melt})$ is the activity coefficient for $X(FeO_{silicate\ melt})$.

$a(FeO_{silicate\ melt}) = X(FeO_{silicate\ melt}) \gamma(FeO_{silicate\ melt}) = 1.7^5$ and $X(FeO_{silicate\ melt}) = 0.1$ for a 10% FeO in basalt; assuming $f(H_2) = 200$ bars, we get $f(H_2O)$ is 32 bars.

S3. Calculation of the FeO reduction efficiency as shown in Fig. 4

We are interested in estimating the amount of FeO reduction in each experiment, as functions of reduction time (or heating period as in Table S1) and temperatures. The efficiency of FeO reduction is then calculated by $\varepsilon = (1 - \frac{x_{FeO}^{Final}}{x_{FeO}^{initial}}) \times 100 \%$, where x_{FeO}^{Final} is the residue FeO present in the silicate melt after H_2 -reduction and $x_{FeO}^{initial}$ is the amount of FeO present in our starting compositions before H_2 -reduction.

For the experiments conducted using the SiC resistance heater, $x_{FeO}^{initial}$ and x_{FeO}^{Final} are measured by EMPA techniques on the silicate glass fraction as given in Table S2. The vertical

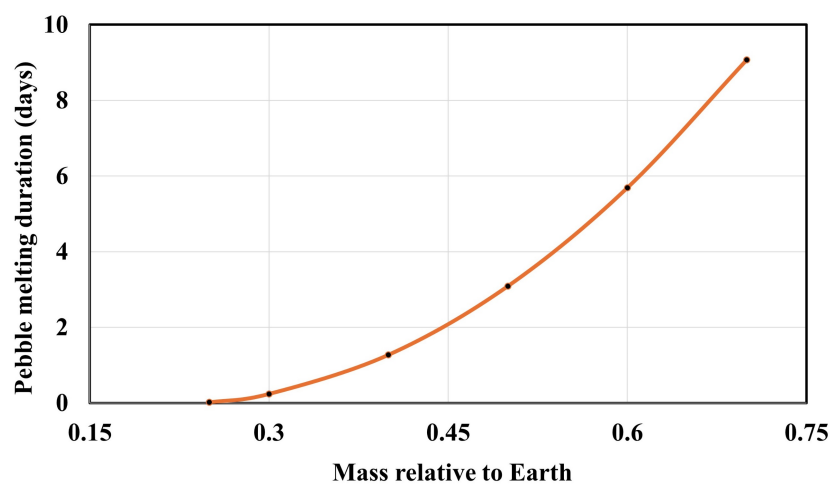
error bars in Fig. 4 represent the uncertainty in reduction efficiency arising from the standard deviation of the measured x_{Final}^{FeO} .

For the experiments with MORB and microbasalt conducted using the induction heater, we calculated the equivalent x_{Final}^{FeO} from the measured amount of water production (x^{H2O}) by H₂-reduction as $x_{Final}^{FeO} = x_{initial}^{FeO} - \text{the amount of FeO reduced}$. Therefore,

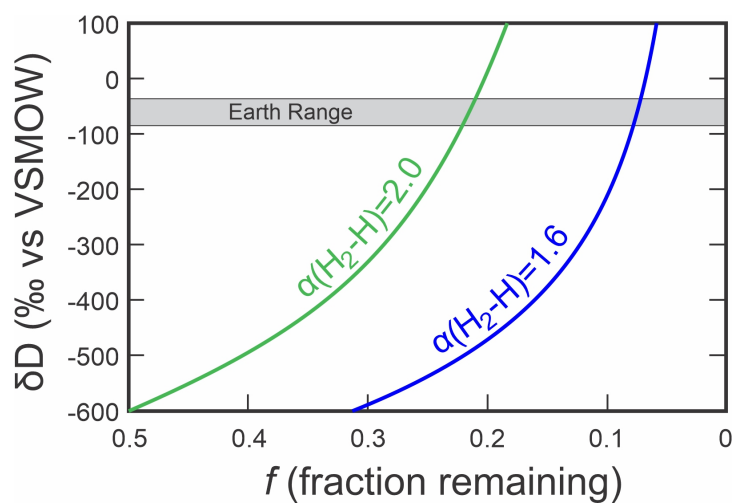
$$x_{Final}^{FeO} = x_{initial}^{FeO} - x^{H2O} * \frac{\text{molecular weight of FeO}}{\text{molecular weight of H2O}}.$$

Vertical error bars in Fig. 4 indicate the uncertainty in reduction efficiency from the measured water volume (final mass loss minus water collected) and final FeO_{silicate} content.

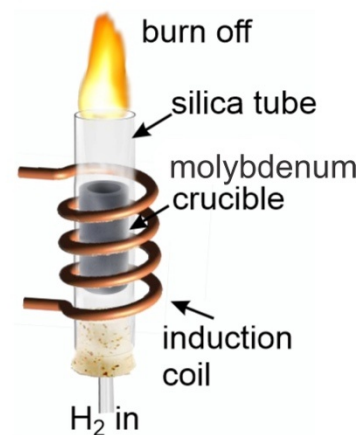
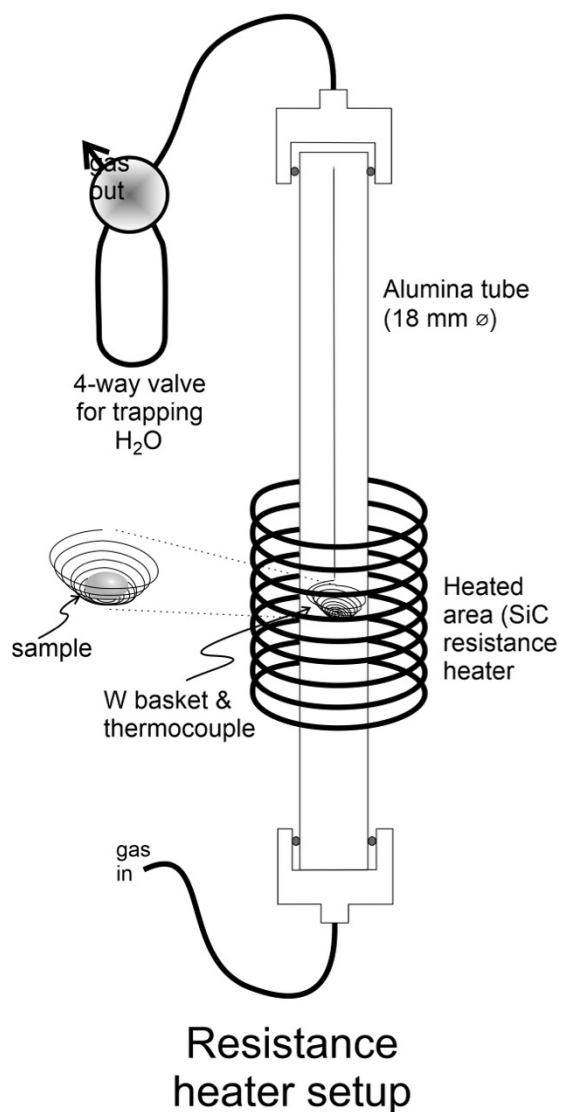
In Fig 5, we draw two orange contours that provide the observed uncertainty bounds in the primitive mantle Fe/Mg from ref⁷. In composition model A, the uncertainty arises in the reduction efficiency (Fig. 5a), and the ocean masses of water produced (Fig. 5c) are up to approximately 0.2% and 0.56 ocean masses of water, respectively. In composition model B, they are up to approximately 0.5% (Fig. 5b) and 0.56 ocean masses of water (Fig. 5d), respectively.



Supplementary Fig. S1: Time spent by pebbles above their rheological melting temperature as a function of planet mass relative to Earth. Extended from Figure 1b.



Supplementary Fig. S2: Rayleigh distillation demonstrating the change in δD during loss of H to space. Initial δD is assumed to be -800‰. f is the fraction of H remaining.



Induction furnace setup

Supplementary Fig. S3. Schematic illustration of the reaction setup for the heating experiments. **The left side** shows the system using a SiC resistance heater. Samples are placed in a W wire basket and suspended in a vertical alumina tube. A thermocouple is adjacent to the sample for precise temperature control. A custom O-ring coupling at the top and bottom allows for either He or H₂ gas to be admitted from the bottom and flow through the system at 200 mL/min. The exhaust gas is vented. **The right side** shows the induction heater setup. Samples are heated to higher temperatures (critical for the microbasalt composition). Water generated by reaction (1) is

quantitatively collected on a 4-way valve (1/8" stainless steel tubing) cooled with liquid nitrogen. After the experiment, the valve is switched, trapping the gas in the loop. The 4-way valve is then transferred to a vacuum line where the water is cryogenically transferred to a 6 mm borosilicate tube with Zn metal, sealed shut, and then heated at 500°C to produce H₂ gas⁸, which was analyzed in a mass spectrometer for D/H ratios relative to VSMOW/SLAP scale.

References

1. Geiss, J. & Gloeckler, G. Isotopic Composition of H, HE and NE in the Protosolar Cloud. *Space Science Reviews* **106**, 3–18 (2003).
2. Lammer, H. *et al.* Origin and loss of nebula-captured hydrogen envelopes from ‘sub’- to ‘super-Earths’ in the habitable zone of Sun-like stars. *Monthly Notices of the Royal Astronomical Society* **439**, 3225–3238 (2014).
3. Richer, P., Bottinga, Y. & Javoy, M. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Annu Rev Earth Planet Sci* **5**, 65–110 (1977).
4. Peslier, A. H., Schönbächler, M., Busemann, H. & Karato, S.-I. Water in the Earth’s Interior: Distribution and Origin. *Space Sci Rev* **212**, 743–810 (2017).
5. Holzheid, A., Palme, H. & Chakraborty, S. The activities of NiO, CoO and FeO in silicate melts. *Chemical Geology* **139**, 21–38 (1997).
6. Shaw, H. R. & Wones, D. R. Fugacity coefficients for hydrogen gas between 0 degrees and 1000 degrees C, for pressures to 3000 atm. *American Journal of Science* **262**, 918–929 (1964).
7. Wang, H. S., Lineweaver, C. H. & Ireland, T. R. The elemental abundances (with uncertainties) of the most Earth-like planet. *Icarus* **299**, 460–474 (2018).
8. Coleman, M. L., Shepherd, T. J., Durham, J. J., Rouse, J. E. & Moore, G. R. Reduction of water with zinc for hydrogen isotope analysis. *Analytical chemistry* **54**, 993–995 (1982).