

Table S1. Experimental conditions.

Oxygen fugacity	CO/CO ₂ mix	Nominal temperature	Measured temperature	Nature of the wire	Run duration
log(<i>f</i> O ₂)≈-0.7 (air)	N/A	1550 °C	1552°C	Platinum	2 h
log(<i>f</i> O ₂)≈-2.4 (QFM+2.5)*	CO: 0.41 %	1550 °C	1559°C	Pre-saturated platinum	2 h
log(<i>f</i> O ₂)≈-2.46 (QFM+2.5)**	CO: 0.43 %	1550 °C	1556°C	Pre-saturated platinum	3 h
log(<i>f</i> O ₂)≈-8 (IW+0.3)	CO: 72 %	1550 °C	1556°C	Rhenium	2 h

* Conditions used to prepare the tholeiitic basalt, andesite, dacite and rhyolite.

** Conditions used to prepare the basalt.

Table S2. Compositions of some olivine grains prepared by the hydrothermal method

	SiO ₂	FeO	MgO	Total
Olivine	41.20	17.80	41.85	100.85
Olivine	36.10	14.96	48.48	99.54
Olivine	40.25	17.43	43.80	101.48
Olivine	40.79	16.00	42.92	99.71
Olivine	38.49	16.77	45.23	100.49
Olivine	40.96	15.51	44.87	101.34
Olivine	43.41	17.07	38.93	99.41
Olivine	41.16	16.63	43.69	101.49
Olivine	39.61	17.38	43.78	100.77
Olivine	40.24	17.28	40.92	98.43
Olivine	39.40	17.56	41.78	98.73
Olivine	37.24	17.80	43.06	98.10

Table S3. Thermoelastic properties derived from NRXSD data

	Tholeitic basalt IW	Tholeitic basalt IW	Mean Tholeitic basalt IW	Tholeitic basalt INT	Tholeitic basalt AIR	Basalt INT	Basalt AIR	Andesite IW	Andesite INT	Andesite AIR
Parameters from S										
Temperature from detailed balance (K)	318	304	311	303	303	295	291	296	295	289
Lamb-Mössbauer factor from S	0.5777 ± 0.0016	0.6104 ± 0.0019	0.5912 ± 0.0013	0.6417 ± 0.0026	0.6679 ± 0.0025	0.6262 ± 0.0029	0.6611 ± 0.0027	0.5929 ± 0.0015	0.6254 ± 0.0018	0.6520 ± 0.0018
Mean square displacement <z ² > from S (Å ²)	0.01030 ± 0.00005	0.00926 ± 0.00006	0.00985 ± 0.00004	0.00833 ± 0.00007	0.00757 ± 0.00006	0.00878 ± 0.00008	0.00777 ± 0.00007	0.00981 ± 0.00005	0.00881 ± 0.00005	0.00803 ± 0.00005
Internal energy/atom from S (meV)	29.04 ± 0.65	28.78 ± 0.69	28.92 ± 0.48	29.17 ± 0.77	30.06 ± 0.80	28.92 ± 0.81	29.02 ± 0.77	28.23 ± 0.66	28.97 ± 0.72	28.83 ± 0.74
Kinetic energy/atom from S (meV)	14.52 ± 0.33	14.39 ± 0.35	14.46 ± 0.24	14.58 ± 0.39	15.03 ± 0.40	14.46 ± 0.40	14.51 ± 0.38	14.12 ± 0.33	14.49 ± 0.36	14.41 ± 0.37
Force constant from S (N/m)	189 ± 10	209 ± 13	197 ± 8	234 ± 16	292 ± 18	252 ± 23	275 ± 18	199 ± 11	256 ± 16	278 ± 18
⁵⁶ Fe/ ⁵⁴ Fe β coefficients from S										
1000 ln β=A ₁ /T ² +A ₂ /T+A ₃ /T ³ (T in K)										
A ₁	5.403E+05 ± 2.795E+04	5.955E+05 ± 3.606E+04	5.610E+05 ± 2.209E+04	6.675E+05 ± 4.641E+04	8.345E+05 ± 5.110E+04	7.199E+05 ± 6.583E+04	7.839E+05 ± 5.028E+04	5.692E+05 ± 3.243E+04	7.298E+05 ± 4.592E+04	7.931E+05 ± 5.066E+04
A ₂	-3.193E+09 ± 4.487E+08	-4.061E+09 ± 5.865E+08	-3.513E+09 ± 3.566E+08	-4.027E+09 ± 7.638E+08	-6.861E+09 ± 9.179E+08	-6.715E+09 ± 1.730E+09	-6.155E+09 ± 9.538E+08	-3.367E+09 ± 4.472E+08	-5.994E+09 ± 9.532E+08	-6.461E+09 ± 1.055E+09
A ₃	5.217E+13 ± 1.422E+13	7.257E+13 ± 1.740E+13	6.034E+13 ± 1.101E+13	5.124E+13 ± 2.273E+13	1.317E+14 ± 2.959E+13	1.831E+14 ± 7.843E+13	1.808E+14 ± 3.231E+13	4.561E+13 ± 1.100E+13	1.230E+14 ± 3.531E+13	1.201E+14 ± 3.881E+13
1000 ln β=B ₁ /F>T ² -B ₂ /F>T ⁴ (T in K)										
B ₁	2.853E+03	2.853E+03	2853	2.853E+03	2.853E+03	2.853E+03	2.853E+03	2.853E+03	2.853E+03	2.853E+03
B ₂	7.333E+04	7.525E+04	74290	6.347E+04	6.359E+04	7.474E+04	6.609E+04	7.224E+04	7.133E+04	6.684E+04
Parameters from g										
Lamb-Mössbauer factor from g	0.5757	0.6090	0.5923	0.6404	0.6666	0.6243	0.6598	0.5919	0.6239	0.6504
Mean square displacement <z ² > from g (Å ²)	0.01036	0.00931	0.00984	0.00837	0.00761	0.00884	0.00780	0.00984	0.00885	0.00807
d<z ² >/dT (Å ² /K)	3.29E-05	2.95E-05	3.12E-05	2.63E-05	2.38E-05	2.79E-05	2.44E-05	3.12E-05	2.79E-05	2.54E-05
Critical temperature (K)	571	637	604	713	790	673	768	602	672	740
Resilience (N/m)	42	47	44	52	58	50	56	44	49	54
Internal energy/atom from g (meV)	29.62	29.39	29.50	29.80	30.72	29.56	29.68	28.83	29.61	29.49
Kinetic energy/atom from g (meV)	14.81	14.70	14.75	14.90	15.36	14.78	14.84	14.41	14.80	14.74
Vibrational entropy (kb/atom)	1.35	1.28	1.32	1.21	1.14	1.20	1.12	1.26	1.19	1.11
Helmholtz free energy (meV)	-5.42	-3.78	-4.60	-1.49	-1.60	-1.50	-0.71	-3.84	-1.14	-0.72
Vibrational specific heat (kb/atom)	0.95	0.93	0.94	0.92	0.90	0.90	0.87	0.91	0.89	0.86
Lamb-Mössbauer factor at T=0	0.89	0.89	0.89	0.90	0.91	0.90	0.91	0.89	0.90	0.91
Kinetic energy/atom at T=0 (meV)	6.26	6.51	6.39	7.04	7.79	7.01	7.48	6.38	7.12	7.46
Force constant from g (N/m)	186	206	196	231	290	251	274	199	255	278
⁵⁶ Fe/ ⁵⁴ Fe β coefficients from g										
1000 ln β=A ₁ /T ² +A ₂ /T+A ₃ /T ³ (T in K)										
A ₁	5.300E+05	5.887E+05	5.594E+05	6.599E+05	8.263E+05	7.169E+05	7.827E+05	5.672E+05	7.270E+05	7.939E+05
A ₂	-3.156E+09	-4.041E+09	-3.598E+09	-3.982E+09	-6.840E+09	-6.691E+09	-6.136E+09	-3.362E+09	-5.973E+09	-6.449E+09
A ₃	5.256E+13	7.463E+13	6.360E+13	5.157E+13	1.371E+14	1.834E+14	1.100E+14	4.742E+13	1.251E+14	1.221E+14
Velocities from g										
Input density (g/cc)	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.57	2.57	2.57
Input bulk modulus (GPa)	63	63	63	63	63	63	63	52	52	52
Debye velocity (m/s)	3477 ± 86	3400 ± 167	3461 ± 77	4007 ± 164	3931 ± 228	3708 ± 71	3604 ± 165	3238 ± 165	3512 ± 158	3547 ± 91
p-wave velocity (m/s)	593 ± 56	591 ± 108	593 ± 50	631 ± 115	622 ± 159	611 ± 48	605 ± 110	593 ± 107	588 ± 62	589 ± 62
s-wave velocity (m/s)	3108 ± 82	3036 ± 159	3093 ± 73	3605 ± 156	3534 ± 217	3324 ± 68	3227 ± 157	2892 ± 157	3148 ± 150	3181 ± 87
Poisson ratio	0.313	0.321	0.317	0.259	0.267	0.290	0.301	0.318	0.289	0.286

	Dacite IW	Dacite INT	Dacite AIR	Rhyolite IW	Rhyolite IW	MeanRhyolite IW	Rhyolite INT	Rhyolite AIR	Olivine Fo82	Olivine Fo82	Mean Olivine
Parameters from S											
Temperature from detailed balance (K)	305	301	309	294	296	295	302	295	317	299	308
Lamb-Mössbauer factor from S	0.5832 ± 0.0028	0.6016 ± 0.0026	0.6092 ± 0.0029	0.5440 ± 0.0021	0.5285 ± 0.0021	0.5363 ± 0.0015	0.5673 ± 0.0026	0.5941 ± 0.0023	0.7178 ± 0.0059	0.7689 ± 0.0014	0.7662 ± 0.0014
Mean square displacement <z ² > from S (Å ²)	0.01077 ± 0.00009	0.00954 ± 0.00008	0.00930 ± 0.00009	0.01143 ± 0.00007	0.01197 ± 0.00007	0.01169 ± 0.00005	0.01064 ± 0.00008	0.00977 ± 0.00007	0.00202 ± 0.00014	0.00493 ± 0.00003	0.00499 ± 0.00003
Internal energy/atom from S (meV)	29.27 ± 0.74	29.58 ± 0.81	30.35 ± 0.89	28.89 ± 0.69	28.62 ± 0.68	28.75 ± 0.49	29.92 ± 0.77	30.41 ± 0.82	30.58 ± 0.97	28.13 ± 0.64	28.87 ± 0.53
Kinetic energy/atom from S (meV)	14.64 ± 0.37	14.79 ± 0.40	15.18 ± 0.45	14.44 ± 0.35	14.31 ± 0.34	14.38 ± 0.24	14.96 ± 0.39	15.20 ± 0.41	15.29 ± 0.49	14.07 ± 0.32	14.43 ± 0.27
Force constant from S (N/m)	206 ± 13	272 ± 19	296 ± 21	256 ± 14	241 ± 16	250 ± 10	308 ± 17	351 ± 20	190 ± 18	199 ± 12	197 ± 10
56Fe/54Fe β coefficients from S											
1000 ln β=A ₁ /T ² +A ₂ /T+A ₃ /T ³ (T in K)											
A ₁	5.872E+05 ± 3.825E+04	7.753E+05 ± 5.454E+04	8.440E+05 ± 6.072E+04	7.318E+05 ± 3.896E+04	6.890E+05 ± 4.556E+04	7.137E+05 ± 2.961E+04	8.798E+05 ± 4.774E+04	1.002E+06 ± 5.675E+04	5.426E+05 ± 5.205E+04	5.690E+05 ± 3.298E+04	5.615E+05 ± 2.786E+04
A ₂	-3.523E+09 ± 5.158E+08	-6.946E+09 ± 1.081E+09	-8.457E+09 ± 1.102E+09	-5.493E+09 ± 6.011E+08	-6.977E+09 ± 1.242E+09	-5.775E+09 ± 5.411E+08	-7.110E+09 ± 7.424E+08	-8.959E+09 ± 1.091E+09	-2.091E+09 ± 5.985E+08	-3.195E+09 ± 6.615E+08	-2.587E+09 ± 4.444E+08
A ₃	4.922E+13 ± 1.296E+13	1.510E+14 ± 3.795E+13	1.031E+14 ± 3.489E+13	8.535E+13 ± 1.632E+13	2.072E+14 ± 6.185E+13	9.328E+13 ± 1.578E+13	1.113E+14 ± 2.006E+13	1.609E+14 ± 3.653E+13	2.285E+13 ± 1.267E+13	6.220E+13 ± 2.610E+13	3.035E+13 ± 1.140E+13
1000 ln β=B ₁ /F>T ² -B ₂ /F>T ⁴ (T in K)											
B ₁	2.853E+03	2.853E+03	2853	2853	2853	2853	2853	2853	2.853E+03	2.853E+03	2853
B ₂	7.065E+04	7.200E+04	6.107E+04	69502	81270	75386	62347	58559	5.101E+04	6.346E+04	57255
Parameters from g											
Lamb-Mössbauer factor from g	0.5620	0.5999	0.6075	0.5431	0.5228	0.5330	0.5659	0.5917	0.7176	0.7686	0.7431
Mean square displacement <z ² > from g (Å ²)	0.01081	0.00959	0.00935	0.01146	0.01217	0.01181	0.01069	0.00985	0.00623	0.00494	0.00558
d<z ² >/dT (Å ² /K)	3.44E-05	3.04E-05	2.95E-05	3.66E-05	3.89E-05	3.78E-05	3.40E-05	3.12E-05	1.90E-05	1.49E-05	1.70E-05
Critical temperature (K)	546	619	635	513	482	498	552	601	987	1260	1124
Resilience (N/m)	40	46	47	38	35	37	41	44	73	93	83
Internal energy/atom from g (meV)	29.84	30.19	30.97	29.45	29.21	29.33	30.51	31.02	31.27	28.89	30.08
Kinetic energy/atom from g (meV)	14.92	15.10	15.49	14.73	14.60	14.67	15.25	15.51	15.64	14.44	15.04
Vibrational entropy (kb/atom)	1.33	1.21	1.17	1.20	1.26	1.23	1.14	1.08	1.30	1.12	1.21
Helmholtz free energy (meV)	-4.57	-1.16	-0.64	-1.58	-3.54	-2.56	-0.91	-3.04	-2.46	-1.02	-1.29
Vibrational specific heat (kb/atom)	0.94	0.90	0.91	0.88	0.89	0.89	0.88	0.86	1.02	0.91	0.96
Lamb-Mössbauer factor at T=0	0.89	0.90	0.90	0.89	0.89	0.89	0.90	0.90	0.90	0.92	0.91
Kinetic energy/atom at T=0 (meV)	7.30	6.51	7.30	7.85	7.10	6.86	6.66	6.88	6.44	6.88	6.83
Force constant from g (N/m)	202	270	292	256	241	249	307	350	181	198	190
56Fe/54Fe β coefficients from g											
1000 ln β=A ₁ /T ² +A ₂ /T+A ₃ /T ³ (T in K)											
A ₁	5.773E+05	7.694E+05	8.340E+05	7.313E+05	6.882E+05	7.098E+05	8.766E+05	9.983E+05	5.169E+05	5.658E+05	5.414E+05
A ₂	-3.506E+09	-6.937E+09	-6.408E+09	-5.510E+09	-6.964E+09	-6.237E+09	-7.142E+09	-8.948E+09	-2.043E+09	-3.162E+09	-2.602E+09
A ₃	5.158E+13	1.562E+14	1.057E+14	8.958E+13	2.092E+14	1.494E+14	1.192E+14	1.666E+14	2.434E+13	6.234E+13	4.334E+13
Velocities from g											
Input density (g/cc)	2.48	2.48	2.48	2.33 ± 2.33	2.33 ± 2.33	2.33	2.33 ± 2.33	2.33 ± 2.33	3.43	3.43	3.43
Input bulk modulus (GPa)	46	46	46	37.8 ± 37.8	37.8 ± 37.8	37.8	37.8 ± 37.8	37.8 ± 37.8	129	129	129
Debye velocity (m/s)	3353 ± 469	3440 ± 118	3428 ± 118	3							

Modeling of partial mantle melting and granitoid differentiation

Partial mantle melting. Dauphas et al. (2009) had derived analytical expressions to calculate the iron isotopic composition of mantle partial melts when the isotopic fractionation is entirely controlled by redox conditions in the melt. We have modified these equations to account for the possibility that there could be some equilibrium isotopic fractionation between Fe^{2+} in minerals and Fe^{2+} in melt, and between Fe^{2+} and Fe^{3+} in minerals.

The following notations are used:

- $\delta_i = [({}^{56}\text{Fe}/{}^{54}\text{Fe})_i / ({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{std}} - 1] \times 1,000$, where $i=0, 2l, 2s, 3l$, and $3s$ stand for initial, Fe^{2+} in liquid, solid, Fe^{3+} in liquid, and solid, respectively,
- f is the degree of partial melting,
- $K_2 = [\text{Fe}^{2+}]_l / [\text{Fe}^{2+}]_s$, and $K_3 = [\text{Fe}^{3+}]_l / [\text{Fe}^{3+}]_s$,
- $\Delta_j^i = \delta_i - \delta_j$.
- $R = \text{Fe}^{3+} / \text{Fe}^{2+}$

Batch melting

We start by writing the following mass balance,

$$[{}^{56}\text{Fe}]_0 = f([\text{Fe}^{2+}]_l + [\text{Fe}^{3+}]_l) + (1-f)([\text{Fe}^{2+}]_s + [\text{Fe}^{3+}]_s). \quad (\text{S1})$$

Introducing $[{}^{56}\text{Fe}] = ({}^{56}\text{Fe}/{}^{54}\text{Fe})[{}^{54}\text{Fe}]$, we have,

$$\begin{aligned} & \left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_0 [f([\text{Fe}^{2+}]_l + [\text{Fe}^{3+}]_l) + (1-f)([\text{Fe}^{2+}]_s + [\text{Fe}^{3+}]_s)] \\ &= f[\text{Fe}^{2+}]_l \left(\frac{{}^{56}\text{Fe}^{2+}}{{}^{54}\text{Fe}^{2+}} \right)_l + f[\text{Fe}^{3+}]_l \left(\frac{{}^{56}\text{Fe}^{3+}}{{}^{54}\text{Fe}^{3+}} \right)_l + (1-f)[\text{Fe}^{2+}]_s \left(\frac{{}^{56}\text{Fe}^{2+}}{{}^{54}\text{Fe}^{2+}} \right)_s + (1-f)[\text{Fe}^{3+}]_s \left(\frac{{}^{56}\text{Fe}^{3+}}{{}^{54}\text{Fe}^{3+}} \right)_s. \quad (\text{S2}) \end{aligned}$$

We can bring the term on the left side to the right side, divide by $({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{std}}$, and multiply everything by 1,000 to reformulate this expression in δ or Δ notation,

$$f[\text{Fe}^{2+}]_l \Delta_0^{2l} + f[\text{Fe}^{3+}]_l \Delta_0^{3l} + (1-f)[\text{Fe}^{2+}]_s \Delta_0^{2s} + (1-f)[\text{Fe}^{3+}]_s \Delta_0^{3s} = 0, \quad (\text{S3})$$

or relative to the isotopic composition of Fe^{2+} in the solid Δ_0^{2s} ,

$$f[\text{Fe}^{2+}]_l (\Delta_0^{2s} + \Delta_{2s}^{2l}) + f[\text{Fe}^{3+}]_l (\Delta_0^{2s} + \Delta_{2s}^{2l} + \Delta_{2l}^{3l}) + (1-f)[\text{Fe}^{2+}]_s \Delta_0^{2s} + (1-f)[\text{Fe}^{3+}]_s (\Delta_0^{2s} + \Delta_{2s}^{3s}) = 0. \quad (\text{S4})$$

This can be rewritten as,

$$f K_2 [\text{Fe}^{2+}]_s (\Delta_0^{2s} + \Delta_{2s}^{2l}) + f K_3 [\text{Fe}^{3+}]_s (\Delta_0^{2s} + \Delta_{2s}^{2l} + \Delta_{2l}^{3l}) + (1-f)[\text{Fe}^{2+}]_s \Delta_0^{2s} + (1-f)[\text{Fe}^{3+}]_s (\Delta_0^{2s} + \Delta_{2s}^{3s}) = 0. \quad (\text{S5})$$

Given that to a very good approximation ${}^{54}\text{Fe}^{3+} / {}^{54}\text{Fe}^{2+} \simeq \text{Fe}^{3+} / \text{Fe}^{2+}$, the previous equation takes the form,

$$f K_2 (\Delta_0^{2s} + \Delta_{2s}^{2l}) + f K_3 R_s (\Delta_0^{2s} + \Delta_{2s}^{2l} + \Delta_{2l}^{3l}) + (1-f) \Delta_0^{2s} + (1-f) R_s (\Delta_0^{2s} + \Delta_{2s}^{3s}) = 0, \quad (\text{S6})$$

where Δ_{2s}^{2l} , Δ_{2l}^{3l} , and Δ_{2s}^{3s} are taken to be known constants. We now have to estimate R_s as a function of R_0 . Using the fact that,

$$\begin{aligned} [\text{Fe}^{2+}]_0 &= f[\text{Fe}^{2+}]_l + (1-f)[\text{Fe}^{2+}]_s \\ [\text{Fe}^{3+}]_0 &= f[\text{Fe}^{3+}]_l + (1-f)[\text{Fe}^{3+}]_s, \quad (\text{S7}) \end{aligned}$$

it follows,

$$\begin{aligned} R_s &= R_0 (f K_2 + 1 - f) / (f K_3 + 1 - f) \\ R_l &= R_0 [f + (1-f)/K_2] / [f + (1-f)/K_3]. \quad (\text{S8}) \end{aligned}$$

Using this expression for R_s , it is possible to solve Eq. S6 for Δ_0^{2s} and then calculate Δ_0^{2l} , Δ_0^{3s} , and Δ_0^{3l} . The bulk Fe isotopic compositions of solids and liquids are combinations of the two oxidation states of iron,

$$\begin{aligned} \Delta_0^l &= (R_l \Delta_0^{3l} + \Delta_0^{2l}) / (R_l + 1) \\ \Delta_0^s &= (R_s \Delta_0^{3s} + \Delta_0^{2s}) / (R_s + 1). \quad (\text{S9}) \end{aligned}$$

Deriving the final expressions poses no difficulty other than being cumbersome,

$$\delta_l = \delta_0 + \frac{1-f}{1+R_0} \left\{ \frac{1-f+R_0+f(K_3+R_0K_2-R_0)}{(1-f+fK_2)(1-f+fK_3)} \Delta_{2s}^{2l} + \frac{K_3R_0[1-f+R_0+f(K_3+R_0K_2-R_0)]}{(1-f+fK_3)[(1-f)K_3R_0+K_2(1-f+fK_3+fK_3R_0)]} \Delta_{2l}^{3l} - \frac{R_0}{(1-f+fK_3)} \Delta_{2l}^{3l} \right\}, \quad (S10)$$

$$\delta_s = \delta_0 + \frac{f}{R_0+1} \left[\frac{(f-1)K_3R_0-K_2(1-f+fK_3+fK_3R_0)}{(1-f+fK_2)(1-f+fK_3)} \Delta_{2s}^{2l} - \frac{K_3R_0}{1-f+fK_3} \Delta_{2l}^{3l} + \frac{R_0(K_2-fK_2+fK_2K_3+K_3R_0-fK_3R_0+fK_2K_3R_0)}{(1-f+fK_3)(1-f+fK_3+R_0-fR_0+fK_2R_0)} \Delta_{2s}^{3s} \right]. \quad (S11)$$

If $\Delta_{2s}^{2l} = 0$ and $\Delta_{2l}^{3l} = \Delta_{2s}^{3s} = \Delta_2^3$, we recover Eq. 20 and 21 in Appendix A of Dauphas et al. (2009).

Fractional melting

Let us first calculate the Fe^{3+} and Fe^{2+} ratios in the solid and cumulative liquid (cl). For each increment of melt removal (m denotes the mass of solid residue and l denotes the instantaneous liquid in equilibrium with solid) we have,

$$\begin{aligned} d(m[\text{Fe}^{2+}]_s) &= [\text{Fe}^{2+}]_l dm = K_2[\text{Fe}^{2+}]_s dm, \\ d(m[\text{Fe}^{2+}]_s) &= K_2[\text{Fe}^{2+}]_s dm. \end{aligned} \quad (S12)$$

After some rearrangement, it is straightforward to show that,

$$\begin{aligned} [\text{Fe}^{2+}]_s &= [\text{Fe}^{2+}]_0 (1-f)^{K_2-1}, \\ [\text{Fe}^{3+}]_s &= [\text{Fe}^{3+}]_0 (1-f)^{K_3-1}. \end{aligned} \quad (S13)$$

Therefore we have,

$$R_s = R_0 (1-f)^{K_3-K_2}. \quad (S14)$$

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the cumulative liquid can be estimated by using the following mass balance,

$$R_0[\text{Fe}^{2+}]_0 = fR_{cl}[\text{Fe}^{2+}]_{cl} + (1-f)R_s[\text{Fe}^{2+}]_s. \quad (S15)$$

We also have,

$$[\text{Fe}^{2+}]_0 = f[\text{Fe}^{2+}]_{cl} + (1-f)[\text{Fe}^{2+}]_s. \quad (S16)$$

Using Eq. S13 and solving Eq. S16 for $[\text{Fe}^{2+}]_{cl}$, we get (and similarly for Fe^{3+}),

$$\begin{aligned} [\text{Fe}^{2+}]_{cl} &= [\text{Fe}^{2+}]_0 [1 - (1-f)^{K_2}] / f, \\ [\text{Fe}^{3+}]_{cl} &= [\text{Fe}^{3+}]_0 [1 - (1-f)^{K_3}] / f. \end{aligned} \quad (S17)$$

Therefore it follows,

$$R_{cl} = R_0 [1 - (1-f)^{K_3}] / [1 - (1-f)^{K_2}]. \quad (S18)$$

Let us now examine the isotopic fractionation between the solid residue and the instantaneous liquid, which are in equilibrium. We have for the liquid,

$$\left({}^{56}\text{Fe}/{}^{54}\text{Fe} \right)_l = ({}^{56}\text{Fe}_l^{2+} + {}^{56}\text{Fe}_l^{3+}) / ({}^{54}\text{Fe}_l^{2+} + {}^{54}\text{Fe}_l^{3+}). \quad (S19)$$

This can be rewritten as,

$$\left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_l = \frac{({}^{56}\text{Fe}^{2+}/{}^{54}\text{Fe}^{2+})_l + ({}^{56}\text{Fe}^{3+}/{}^{54}\text{Fe}^{3+})_l ({}^{54}\text{Fe}^{3+}/{}^{54}\text{Fe}^{2+})_l}{1 + ({}^{54}\text{Fe}^{3+}/{}^{54}\text{Fe}^{2+})_l}. \quad (S20)$$

Given that isotopic variations are small, we have $({}^{54}\text{Fe}^{3+}/{}^{54}\text{Fe}^{2+})_l \approx R_l$. Factorizing $({}^{56}\text{Fe}^{2+}/{}^{54}\text{Fe}^{2+})_l$ the previous equation takes the form,

$$\left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_l = \left(\frac{{}^{56}\text{Fe}^{2+}}{{}^{54}\text{Fe}^{2+}} \right)_l \frac{1 + \alpha_{2l}^{3l} R_l}{1 + R_l} = \alpha_{2s}^{2l} \left(\frac{{}^{56}\text{Fe}^{2+}}{{}^{54}\text{Fe}^{2+}} \right)_s \frac{1 + \alpha_{2l}^{3l} (K_3/K_2) R_s}{1 + (K_3/K_2) R_s}. \quad (S21)$$

Using a similar development for the solid as that used for the instantaneous liquid, it is easy to show that,

$$\left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_s = \left(\frac{{}^{56}\text{Fe}^{2+}}{{}^{54}\text{Fe}^{2+}} \right)_s \frac{1 + \alpha_{2s}^{3s} R_s}{1 + R_s}. \quad (S22)$$

Dividing Eq. S21 by Eq. S22, we obtain the isotopic fractionation between liquid and solid as a function of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the solid residue,

$$\frac{({}^{56}\text{Fe}/{}^{54}\text{Fe})_l}{({}^{56}\text{Fe}/{}^{54}\text{Fe})_s} = \alpha_{2s}^{2l} \left(\frac{1 + \alpha_{2l}^{3l} (K_3/K_2) R_s}{1 + (K_3/K_2) R_s} \right) \left(\frac{1 + R_s}{1 + \alpha_{2s}^{3s} R_s} \right). \quad (S23)$$

We can now derive the differential equation that controls Fe iron isotopic fractionation in solid and cumulative liquid. It starts with the following distillation equation,

$$d(m[{}^{56}\text{Fe}]_s) = [{}^{56}\text{Fe}]_l dm, \quad (S24)$$

Given that isotopic variations are small, this can be rewritten as,

$$d\{m(^{56}\text{Fe}/^{54}\text{Fe})_s[\text{Fe}]_s\} = (^{56}\text{Fe}/^{54}\text{Fe})_l[\text{Fe}]_l dm. \quad (\text{S25})$$

After dividing by $m(^{56}\text{Fe}/^{54}\text{Fe})_s[\text{Fe}]_s$ and rearranging the result, we have,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left\{ \frac{(^{56}\text{Fe}/^{54}\text{Fe})_l[\text{Fe}]_l}{(^{56}\text{Fe}/^{54}\text{Fe})_s[\text{Fe}]_s} - 1 \right\} d \ln m - d \ln[\text{Fe}]_s. \quad (\text{S26})$$

The partition of iron between solid and instantaneous liquid is,

$$\frac{[\text{Fe}]_l}{[\text{Fe}]_s} = \frac{[\text{Fe}^{2+}]_l + [\text{Fe}^{3+}]_l}{[\text{Fe}^{2+}]_s + [\text{Fe}^{3+}]_s} = \frac{[\text{Fe}^{2+}]_l}{[\text{Fe}^{2+}]_s} \left(\frac{1 + R_l}{1 + R_s} \right) = \frac{K_2 + K_3 R_s}{1 + R_s}. \quad (\text{S27})$$

By injecting Eq. S23 and S27 into Eq. S26, it follows,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left[\alpha_{2s}^{2l} \left(\frac{K_2 + \alpha_{2l}^{3l} K_3 R_s}{1 + \alpha_{2s}^{3s} R_s} \right) - 1 \right] d \ln m - d \ln[\text{Fe}]_s. \quad (\text{S28})$$

Let us now examine the second term in this equation. We have $[\text{Fe}]_s = [\text{Fe}^{2+}]_s(1 + R_s)$ and therefore,

$$d \ln[\text{Fe}]_s = d \ln[\text{Fe}^{2+}]_s + d \ln(1 + R_s). \quad (\text{S29})$$

Using Eq. S13 and S14, this can be rewritten as,

$$d \ln[\text{Fe}]_s = (K_2 - 1) d \ln m + \frac{(K_3 - K_2) R_s}{1 + R_s} d \ln m = \frac{K_2 + K_3 R_s - 1 - R_s}{1 + R_s} d \ln m. \quad (\text{S30})$$

Equation S28 now takes the form,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left[\alpha_{2s}^{2l} \left(\frac{K_2 + \alpha_{2l}^{3l} K_3 R_s}{1 + \alpha_{2s}^{3s} R_s} \right) - \frac{K_2 + K_3 R_s}{1 + R_s} \right] d \ln m. \quad (\text{S31})$$

Let us introduce the notation $\gamma = \alpha - 1$. This equation can be rewritten as,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left\{ \frac{K_3 R_s (1 + R_s) \gamma_{2l}^{3l} (1 + \gamma_{2s}^{2l}) + (K_2 + K_3 R_s) [-R_s \gamma_{2s}^{3s} + (1 + R_s) \gamma_{2s}^{2l}]}{[1 + (1 + \gamma_{2s}^{3s}) R_s] (1 + R_s)} \right\} d \ln m. \quad (\text{S32})$$

Given that $1 + \gamma \approx 1$, we have to a good approximation,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left\{ \frac{K_3 R_s (1 + R_s) \gamma_{2l}^{3l} + (K_2 + K_3 R_s) [-R_s \gamma_{2s}^{3s} + (1 + R_s) \gamma_{2s}^{2l}]}{(1 + R_s)^2} \right\} d \ln m. \quad (\text{S33})$$

Writing $x = m/m_0$ and using Eq. S14, the previous equation can be rewritten as,

$$d \ln(^{56}\text{Fe}/^{54}\text{Fe})_s = \left\{ \frac{K_3 R_0 x^{K_3 - K_2 - 1}}{1 + R_0 x^{K_3 - K_2}} \gamma_{2l}^{3l} - \frac{R_0 x^{K_3 - K_2 - 1} (K_2 + K_3 R_0 x^{K_3 - K_2})}{(1 + R_0 x^{K_3 - K_2})^2} \gamma_{2s}^{3s} + \frac{K_2 + K_3 R_0 x^{K_3 - K_2}}{x(1 + R_0 x^{K_3 - K_2})} \gamma_{2s}^{2l} \right\} dx. \quad (\text{S34})$$

This differential equation can be resolved analytically between $x = 1$ (initial, before melting) and $x = 1 - f$. In δ notation, this yields,

$$\delta_s = \delta_0 + \ln \left[\frac{(1 - f)^{K_2} + R_0 (1 - f)^{K_3}}{1 + R_0} \right] \Delta_{2s}^{2l} + \frac{K_3}{K_2 - K_3} \ln \left[\frac{(1 + R_0)(1 - f)^{K_2 - K_3}}{(1 - f)^{K_2 - K_3} + R_0} \right] \Delta_{2l}^{3l} + \left\{ \frac{R_0}{1 + R_0} \left[\frac{(1 - f)^{K_3 - K_2} - 1}{1 + R_0 (1 - f)^{K_3 - K_2}} \right] - \frac{K_3}{K_2 - K_3} \ln \left[\frac{(1 + R_0)(1 - f)^{K_2 - K_3}}{(1 - f)^{K_2 - K_3} + R_0} \right] \right\} \Delta_{2s}^{3s}. \quad (\text{S35})$$

If $\Delta_{2s}^{2l} = 0$ and $\Delta_{2l}^{3l} = \Delta_{2s}^{3s}$, we recover Eq. 48 in Appendix A of Dauphas et al. (2009). If one sets $R_0 = 0$, we recover a standard Rayleigh distillation equation. The isotopic composition of the cumulative liquid is most easily obtained by mass balance,

$$\delta_{cl} = \delta_0 - \frac{(1 - f)[\text{Fe}]_s}{[\text{Fe}]_0 - (1 - f)[\text{Fe}]_s} (\delta_s - \delta_0). \quad (\text{S36})$$

Using Eq. S13 to calculate $[\text{Fe}]_s/[\text{Fe}]_0$ we can rewrite this equation as,

$$\delta_{cl} = \delta_0 - \frac{(1 - f)^{K_2} + R_0 (1 - f)^{K_3}}{1 + R_0 - (1 - f)^{K_2} - R_0 (1 - f)^{K_3}} (\delta_s - \delta_0), \quad (\text{S37})$$

where $\delta_s - \delta_0$ is given by Eq. S35.

We have calculated the isotopic composition of the liquid during partial melting of the mantle using Eqs. S10 (batch), S35, and S37 (fractional). We use $K_2 = 1$, $K_3 = 4.5$ (Canil et al. 1994; Mallmann and O'Neill 2009; Cottrell and Kelley 2011), $f = 0.1$ (Klein and Langmuir 1987), and $R_0 = 0.043$, which is required to explain the MORB $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.16

(Cottrell and Kelley 2011) at 10 % partial melting. The temperature is taken to be 1300 °C (McKenzie and Bickle, 1988). The force constants of Fe^{2+} and Fe^{3+} in basaltic magma are 199 ± 15 and 351 ± 29 N/m, respectively. The force constants of Fe^{2+} and Fe^{3+} in mantle minerals are estimated to be 197 ± 10 (olivine) and 255 ± 24 N/m (Fig. S1), respectively. The value for Fe^{3+} in minerals is estimated based on an extrapolation to $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}=1$ of silicate and oxide NRXS data in Fig. S1 (Table 1; Polyakov et al. 2007; Dauphas et al. 2012; Sinmyo et al. 2014; and references therein). The value for Fe^{3+} thus estimated is close to the values obtained in silicates by conventional Mössbauer spectroscopy (Polyakov and Mineev, 2000) and has little influence on the calculation. The MORB $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.16 (Cottrell and Kelley, 2011) is attained when $\delta^{56}\text{Fe}_{\text{melt-initial}} = +0.023 \pm 0.020$ ‰.

Granitoid differentiation. The chemical and isotopic evolution of an andesite melt affected by fractional crystallization under a fixed oxygen fugacity of QFM was calculated using the Rhyolite-MELTS software (Gualda et al., 2012). The chemical composition of the starting andesite was in wt% SiO_2 58.23, TiO_2 0.94, Al_2O_3 16.94, Cr_2O_3 0.03, FeO 7.31, MgO 3.99, CaO 7.08, Na_2O 3.47, K_2O 1.57, P_2O_5 0.24, H_2O 0.20. The pressure remained constant at 1 kbar. The temperature decreased from the liquidus temperature of 1176.95 °C to 851.95 °C in increments of 5 °C. These conditions are appropriate to model the formation of an A-type granite (Clemens et al. 1986). The program calculates at each step the nature and abundance of minerals that are removed from the system. The iron isotopic evolution is simulated by calculating at each step the isotopic fractionation between the minerals removed and the remaining magma. For Fe^{2+} and Fe^{3+} in minerals, we use force constants of 197 N/m (olivine) and 255 N/m (Fig. S1), respectively. For Fe^{3+} in melts, we adopt a force constant of 351 N/m (Fig. 1). For Fe^{2+} in melt, we use a sigmoid function that passes through the data, $\langle F \rangle = 199 + 41/(1 + e^{34 - \text{SiO}_2/2})$ with SiO_2 in wt.% (Fig. 7). Fig. 8 shows which minerals influence the iron isotopic evolution of the magma.

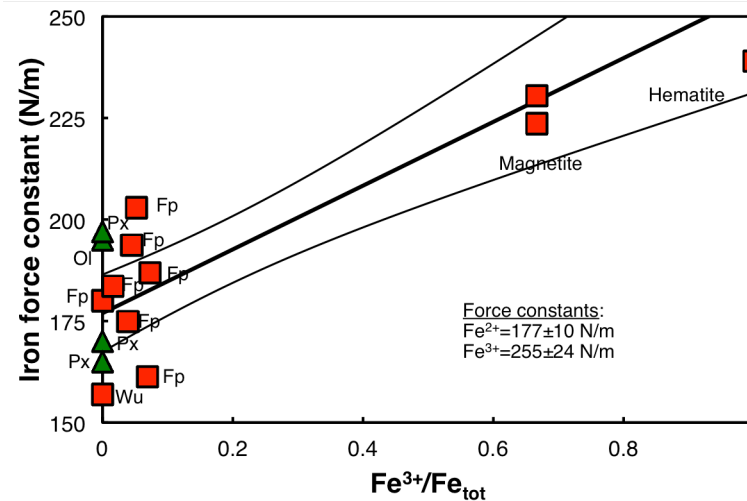


Fig. S1. Iron force constants measured in silicate and oxide minerals by NRVS. Olivine is from this study (Table 1). The other values are from Polyakov et al. (2007), Dauphas et al. (2012), Sinmyo et al. (2014) and references therein. In all these minerals, iron is in 6-fold coordination with oxygen except magnetite, which contains iron in both 4-fold and 6-fold coordinations. A linear regression gives force constants of 177 ± 10 and 255 ± 24 N/m for the Fe^{2+} and Fe^{3+} end-members, respectively.

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