No V-Fe-Zn isotopic variation in basalts from the 2021 Fagradalsfjall eruption


Supplementary Information

The Supplementary Information includes:

- 1. Analytical Methods
- 2. Results
- 3. Correcting Fe Isotopes for Fractional Crystallisation
- 4. Fe Isotope Modelling During Mantle Melting
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1. Analytical Methods

Chemical purification and isotopic analysis were performed at the Arthur Holmes Isotope Geology Laboratory, Durham University.

Sample Digestion

Whole rock samples were ground into homogeneous powders by hand using an agate pestle and mortar, which was cleaned with low-Fe quartz sand between samples to avoid contamination. Approximately 30–50 mg of each powder was digested in 3 mL Teflon Distilled (TD) 29 M HF and 1 mL TD 16 M HNO₃ on a hotplate at 160 °C for 48 hours. Samples were evaporated at 120 °C to incipient dryness, then the residues were repeatedly covered with TD 16 M HNO₃ and evaporated at 180 °C until dark brown, indicating that insoluble fluorides were destroyed. Samples were dissolved in 1 mL TD 6 M HCl for the first column chromatography procedure.

Column Chromatography

The following column chromatography procedure quantitatively separates V, Fe and Zn from the same sample digestion. The first column follows the method of Sossi et al. (2015). Samples were loaded in 1 mL TD 6 M HCl onto Savillex
PFA columns containing 2 mL of pre-cleaned Bio-Rad AG1-X8 resin (200–400 mesh). The V fraction was collected as the samples were loaded, and with a further 4 mL TD 6 M HCl. Vanadium was eluted with most other matrix elements at this stage, and four further column chromatography procedures were required to fully purify the V fraction. The V fraction was evaporated and the residue was covered with TD 16 M HNO₃ and evaporated at 160 °C. This step was carried out twice between every column procedure to destroy any organic resin which may have passed through the frits.

After a 10 mL TD 6 M HCl wash, Fe was collected in 6 mL TD 0.5 M HCl and Zn was collected in 4 mL TD 3 M HNO₃. The Zn fraction was processed through the entire column procedure a second time. The Fe and Zn fractions were then evaporated and dissolved in 1 mL TD 3 % HNO₃ for isotopic analysis.

The procedure for further V separation is adapted from Nielsen et al. (2011) and Wu et al. (2016). The underlying principle is that V$^{5+}$ forms anionic V-peroxide complexes with hydrogen peroxide (H₂O₂) in mildly acidic solutions, and these complexes will partition strongly onto AG1-X8 resin (Nielsen et al., 2011). However, before H₂O₂ can be used, all Fe and Ti must be removed, because Fe and Ti can catalyse the dissociation of H₂O₂ to water and oxygen (Nielsen et al., 2011). The first column procedure separates Fe, and the second column procedure, from Wu et al. (2016), removes Ti. The third column procedure, from Nielsen et al. (2011) then uses H₂O₂ and separates V from remaining matrix elements.

Column 2 (Wu et al., 2016) uses 2 mL of pre-cleaned AG50W-X12 cation resin (200–400 mesh) in Savillex PFA columns. Samples were loaded in 1 mL 1 M HNO₃. 4 mL TD 1 M HNO₃ + 0.1 M HF was used to elute Ti and Al. The V fraction was then collected in 20 mL TD 1.2 M HNO₃.

Column 3 (Nielsen et al., 2011) uses 1 mL of pre-cleaned AG1-X8 resin in quartz glass columns. Samples were dissolved in 1 mL 0.01 M HCl, and 33 μL H₂O₂ (1 % v/v) was added to cool samples immediately before loading, to form the V-peroxide complexes which partition onto the resin. Most matrix elements were eluted with 21 mL TD 0.01 M HCl + 1 % v/v H₂O₂ and V was then collected with 8 mL TD 1 M HCl.

The final two columns, from Nielsen et al. (2011) are small-scale clean-up columns designed to remove all remaining Ti and Cr from samples, because $^{50}$Ti and $^{50}$Cr are direct interferences on the minor $^{51}$V isotope (Nielsen et al., 2011). These columns were typically repeated twice each, with a Cr clean-up column always being the final column before isotopic analysis. For both procedures, Teflon micro-columns containing 100 μL AG1-X8 resin were used.

For the Ti clean-up column, samples were loaded in 1 mL TD 2 M HF. Vanadium was collected as the sample was loaded, and with a further 1.2 mL TD 2 M HF and 1.4 mL TD 0.5 M HF/HCl mixture. For the Cr clean-up column, which is a scaled down version of column 3, samples were dissolved in 1 mL TD 0.01 M HCl and 33 μL H₂O₂ was added to cool samples immediately before loading. After a wash of 0.6 mL TD 0.01 M HCl + 1 % H₂O₂, V was collected in 0.8 mL TD 1 M HCl. Samples were then re-dissolved in TD 3 % HNO₃ for isotopic analysis.

Isotope Ratio Measurements

All isotope ratio measurements were undertaken on Neptune or NeptunePlus MC-ICP-MS at Durham University. The USGS reference material BIR-1a was processed alongside unknowns, and gave Fe, V and Zn isotopic compositions which agree with previous measurements.

Vanadium. Vanadium isotope ratio measurements were made in medium resolution mode ($m/Δm ≈ 6000–8000$), which allows V to be resolved from isobaric interferences. The sample introduction system consisted of a PFA concentric flow nebuliser (uptake rate 50 μL/min) coupled to an Aridis 2 desolvating nebuliser system, giving typical sensitivity of >100 V/ppm on $^{51}$V. 2 mL sample aliquots were diluted with TD 3 % HNO₃ to a concentration of 1 μg/g V. Masses $^{48}$Ti, $^{49}$Ti, $^{50}$V, $^{51}$V, $^{52}$Cr and $^{53}$Cr were measured in Faraday cups L4, L2, L1, C, H1 and H3 respectively, with a $1×10^{10}$ Ω resistor connected to the centre cup to measure signals $>50$ V on $^{51}$V. Standard sample bracketing with the AA standard (Nielsen et al., 2011) was used to correct for mass bias. $^{48}$Ti, $^{49}$Ti, $^{53}$Cr and $^{53}$Cr were used to correct for interferences of $^{50}$Ti and $^{50}$Cr on $^{50}$V, using the exponential law ($R_I = R_M × (m_i/m_M)^β$). Two BDH solutions (Nielsen et al., 2011) were doped with 100 ppb Ti and Cr, respectively, and measured during every sequence. The β factor was then varied iteratively until $^{51}$V matched the long-term average BDH value of approximately −1.19 % to −1.23 % (Nielsen...
et al., 2011; Wu et al., 2016). These β factors were then used to correct for the interferences of $^{50}\text{Ti}$ and $^{50}\text{Cr}$ on all samples in the sequence, after Wu et al. (2016). USGS reference material BIR-1a gave a $\delta^{51}\text{V}_{AA}$ value of $-0.87 \pm 0.03$ ‰ (2 s.d., $n = 3$).

**Iron.** Iron isotope ratio measurements were made in medium resolution mode ($m/\Delta m \approx 6000–8000$), which allows Fe to be resolved from isobaric oxide and nitride interferences. The sample introduction system consisted of a Savillex CF50 concentric flow nebuliser and ESI SIS spray chamber, giving a sensitivity of 5–8 V/ppm on $^{56}\text{Fe}$. 2 mL sample aliquots were diluted with TD 3 % HNO$_3$ to a concentration of 10 μg/g Fe, and doped with 8 μg/g Ni. Masses $^{53}\text{Cr}$, $^{54}\text{Fe}$, $^{56}\text{Fe}$, $^{57}\text{Fe}$, $^{60}\text{Ni}$ and $^{61}\text{Ni}$ were measured on Faraday cups L4, L2, L1, C, H2 and H4. A 10$^{10}$ Ω resistor was connected to L1 to measure signals of >50 V on $^{56}\text{Fe}$. The isobaric interference of $^{54}\text{Cr}$ on $^{54}\text{Fe}$ was corrected by monitoring $^{53}\text{Cr}$ and assuming an exponential law. A combination of standard sample bracketing and external element doping with Ni was used to correct for mass bias (e.g., Gong et al., 2020). Samples were bracketed using the IRMM-524 standard, which is isotopically indistinguishable from IRMM-014 (Craddock and Dauphas, 2011). USGS reference material BIR-1a gave a $\delta^{56}\text{Fe}_{IRMM-524}$ value of 0.065 ± 0.043 ‰ (2 s.d., $n = 6$).

**Zinc.** Zinc isotope ratio measurements were made in low resolution mode ($m/\Delta m \approx 400$). The sample introduction system consisted of a Savillex CF50 concentric flow nebuliser and ESI SIS spray chamber, giving typical sensitivity of 6–7 V/ppm on $^{64}\text{Zn}$. 2 mL sample aliquots were diluted with TD 3 % HNO$_3$ to a concentration of 750 ng/g Zn, and doped with 375 ng/g Cu. Masses $^{62}\text{Ni}$, $^{63}\text{Cu}$, $^{64}\text{Zn}$, $^{65}\text{Cu}$, $^{66}\text{Zn}$, $^{67}\text{Zn}$ and $^{68}\text{Zn}$ were measured in Faraday cups L3, L2, L1, C, H1, H2, and H3, and 10$^{11}$ Ω resistors were used on all cups. The isobaric interference of $^{64}\text{Ni}$ on $^{64}\text{Zn}$ was corrected by monitoring $^{62}\text{Ni}$ and assuming an exponential law. A combination of standard sample bracketing with the AA-ETH Zn solution (Archer et al., 2017) and external element doping with Cu was used to correct for mass bias. Data in this study is reported relative to AA-ETH, which is offset relative to the commonly used reference standard JMC Lyon (Maréchal et al., 1999) by +0.28 ± 0.02 ‰ (Archer et al., 2017). This correction can be used to recast the data in this study relative to JMC-Lyon. USGS reference material BIR-1a gave a $\delta^{66}\text{Zn}_{AA-ETH}$ value of $-0.033 \pm 0.010$ ‰ (2 s.d., $n = 3$), which is equivalent to a $\delta^{66}\text{Zn}_{JMC-Lyon}$ value of +0.247 ± 0.010 ‰ (2 s.d., $n = 3$).
2. Results

Table S-1  Vanadium, iron and zinc isotopic compositions of Fagradasfjall lavas. Errors are given as 2 standard deviations of at least three measurements of an individual sample. Sample names and eruption day are from Halldórsson et al. (2022), where the eruption day is the best estimate of the day the material was erupted from the vent. The eruption day for sample G20210404-1 is unknown, but is between days 4 and 11. This sample is plotted as day 8 in all figures, which is the midpoint of this time period. Zinc isotopic compositions are expressed relative to the AA-ETH standard (Archer et al., 2017). Data is recast relative to the JMC-Lyon standard using the correction of +0.28 ‰ (Archer et al., 2017).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Eruption Day</th>
<th>$^{51}$V$_{AA}$ (‰)</th>
<th>2 s.d.</th>
<th>$^{56}$Fe$_{IRMM-524}$ (‰)</th>
<th>2 s.d.</th>
<th>$^{57}$Fe$_{IRMM-524}$ (‰)</th>
<th>2 s.d.</th>
<th>$^{66}$Zn$_{AA-ETH}$ (‰)</th>
<th>2 s.d.</th>
<th>$^{66}$Zn$_{JMC-Lyon}$ (‰)</th>
<th>2 s.d.</th>
<th>$^{67}$Zn$_{AA-ETH}$ (‰)</th>
<th>2 s.d.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>G20210321-2</td>
<td>2</td>
<td>−0.95</td>
<td>0.09</td>
<td>5</td>
<td>0.068</td>
<td>0.053</td>
<td>0.108</td>
<td>0.086</td>
<td>3</td>
<td>−0.027</td>
<td>0.253</td>
<td>0.021</td>
<td>−0.059</td>
<td>0.027</td>
</tr>
<tr>
<td>G20210323-1</td>
<td>4</td>
<td>−0.89</td>
<td>0.05</td>
<td>3</td>
<td>0.081</td>
<td>0.041</td>
<td>0.116</td>
<td>0.051</td>
<td>3</td>
<td>−0.028</td>
<td>0.252</td>
<td>0.036</td>
<td>−0.074</td>
<td>0.029</td>
</tr>
<tr>
<td>G20210330-2</td>
<td>11</td>
<td>−0.86</td>
<td>0.03</td>
<td>3</td>
<td>0.052</td>
<td>0.020</td>
<td>0.086</td>
<td>0.050</td>
<td>3</td>
<td>−0.026</td>
<td>0.254</td>
<td>0.003</td>
<td>−0.052</td>
<td>0.050</td>
</tr>
<tr>
<td>G20210404-1</td>
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<td>0.04</td>
<td>3</td>
<td>0.055</td>
<td>0.027</td>
<td>0.089</td>
<td>0.048</td>
<td>3</td>
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<td>0.268</td>
<td>0.017</td>
<td>+0.002</td>
<td>0.047</td>
</tr>
<tr>
<td>G20210405-1</td>
<td>17</td>
<td>−0.86</td>
<td>0.06</td>
<td>3</td>
<td>0.082</td>
<td>0.018</td>
<td>0.108</td>
<td>0.029</td>
<td>3</td>
<td>−0.019</td>
<td>0.261</td>
<td>0.009</td>
<td>−0.024</td>
<td>0.013</td>
</tr>
<tr>
<td>G20210412-1</td>
<td>24</td>
<td>−0.87</td>
<td>0.04</td>
<td>3</td>
<td>0.065</td>
<td>0.040</td>
<td>0.096</td>
<td>0.045</td>
<td>5</td>
<td>−0.020</td>
<td>0.260</td>
<td>0.013</td>
<td>−0.038</td>
<td>0.048</td>
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<td>G20210412-2</td>
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<td>−0.88</td>
<td>0.07</td>
<td>3</td>
<td>0.059</td>
<td>0.060</td>
<td>0.106</td>
<td>0.089</td>
<td>5</td>
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<td>0.293</td>
<td>0.027</td>
<td>−0.013</td>
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<td>G20210416-3</td>
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<td>0.07</td>
<td>3</td>
<td>0.047</td>
<td>0.042</td>
<td>0.086</td>
<td>0.075</td>
<td>3</td>
<td>−0.037</td>
<td>0.243</td>
<td>0.024</td>
<td>−0.066</td>
<td>0.043</td>
</tr>
<tr>
<td>G20210416-4</td>
<td>25</td>
<td>−0.90</td>
<td>0.06</td>
<td>3</td>
<td>0.094</td>
<td>0.049</td>
<td>0.135</td>
<td>0.059</td>
<td>6</td>
<td>−0.042</td>
<td>0.238</td>
<td>0.003</td>
<td>−0.058</td>
<td>0.087</td>
</tr>
<tr>
<td>G20210424-5</td>
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<td>−0.86</td>
<td>0.07</td>
<td>3</td>
<td>0.060</td>
<td>0.013</td>
<td>0.093</td>
<td>0.048</td>
<td>4</td>
<td>−0.023</td>
<td>0.257</td>
<td>0.031</td>
<td>−0.028</td>
<td>0.031</td>
</tr>
<tr>
<td>BIR-1a</td>
<td></td>
<td>−0.87</td>
<td>0.03</td>
<td>3</td>
<td>0.065</td>
<td>0.043</td>
<td>0.085</td>
<td>0.067</td>
<td>6</td>
<td>−0.033</td>
<td>0.247</td>
<td>0.010</td>
<td>−0.078</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Table S-2  Compilation of data from Halldórsson et al. (2022) presented in this study.

| Sample Name | Eruption Day | TiO$_2$ (wt. %) | K$_2$O (wt. %) | K$_2$O/TiO$_2$ | La (µg/g) | Yb (µg/g) | La/Yb | $^{206}$Pb/$^{204}$Pb | 2 s.e. (Abs) | $^{87}$Sr/$^{86}$Sr | 2 s.e. (Abs) | $^{141}$Nd/$^{144}$Nd | 2 s.e. (Abs) |
|--------------|--------------|----------------|----------------|----------------|------------|-----------|--------|----------------|-------------|----------------|-------------|----------------|-------------|-------------|
| G20210321-2  | 2            | 0.96           | 0.136          | 0.142          | 4.3        | 1.99      | 2.16   | 18.7328        | 0.0012      | 0.703109       | 0.000005   | 0.513010       | 0.000003   |
| G20210323-1  | 4            | 0.97           | 0.144          | 0.148          | 4.3        | 1.96      | 2.20   | 18.7567        | 0.0013      | 0.703108       | 0.000008   | 0.513017       | 0.000003   |
| G20210330-2  | 11           | 1.01           | 0.194          | 0.192          | 5.1        | 1.89      | 2.68   | 18.7607        | 0.0019      | 0.703135       | 0.000007   | 0.512991       | 0.000003   |
| G20210404-1  | 4–11         | 1.03           | 0.213          | 0.208          | 6.4        | 2.26      | 2.81   | 18.8229        | 0.0014      | 0.703139       | 0.000006   | 0.512984       | 0.000003   |
| G20210405-1  | 17           | 1.01           | 0.193          | 0.191          | 8.0        | 2.13      | 3.76   | 18.8389        | 0.0016      | 0.703183       | 0.000006   | 0.512949       | 0.000004   |
| G20210412-1  | 24           | 1.08           | 0.259          | 0.241          | 2.7        | 1.94      | 3.88   | 18.8389        | 0.0016      | 0.703183       | 0.000006   | 0.512949       | 0.000004   |
| G20210412-2  | 24           | 1.08           | 0.263          | 0.243          |            |           |        |                |             |                |             |                |             |
| G20210416-3  | 28           | 1.04           | 0.236          | 0.227          | 7.0        | 2.00      | 3.51   |                |             |                |             |                |             |
| G20210416-4  | 25           | 1.08           | 0.266          | 0.246          | 7.5        | 1.94      | 3.88   |                |             |                |             |                |             |
| G20210424-5  | 36           | 1.10           | 0.282          | 0.256          | 8.3        | 2.04      | 4.05   | 18.8389        | 0.0016      |                |             |                |             |
3. Correcting Fe Isotopes for Fractional Crystallisation

Many studies correct the Fe isotopic composition of basalts for the effect of olivine crystallisation, in order to determine the Fe isotopic composition of the primary magma at the time of mantle melting ($\delta^{56}\text{Fe}_{\text{prim}}$).

The method, first presented in Sossi et al. (2016), is a mass balance calculation where olivine (with a composition in equilibrium with the current melt), is progressively added back into the melt until a Mg# of 0.74 is reached. This is assumed to reflect the composition of a primary mantle derived magma. The resulting change in the Fe isotopic composition of the melt is then also calculated by a mass balance calculation, assuming an appropriate $\Delta^{56}\text{Fe}_{\text{ol}-\text{melt}}$ value.

For the calculation, the FeO, MgO and $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the uncorrected basalt must be known (or assumed), and used to calculate an initial Mg# (Mg# = Mg$^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$). The number of moles of Mg$^{2+}$ and Fe$^{2+}$ can be calculated using the atomic masses of MgO (40.3 amu) and FeO (71.8 amu) and the weight percent concentrations of MgO and FeO in the basalt (i.e. moles Mg$^{2+}$ = MgO (wt. %)/40.3).

Following Sossi et al. (2016), for each 1% incremental addition of olivine:

1) **Calculate the composition of the olivine in equilibrium with the melt.** We assume a Fe/Mg partition coefficient for olivine of 0.3 (Roeder and Emslie, 1970). Therefore, the Fe/Mg ratio of the olivine is given as:

$$\left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{Ol}} = K_{\text{D}}^{\text{Fe-Mg}} \times \left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{melt}}. \quad (S-1)$$

From olivine stoichiometry, we know that the number of moles of Fe + Mg must equal 2, which can be substituted into Equation S-1 to calculate the moles of Mg$^{2+}$ and Fe$^{2+}$ in the olivine. This can then be transformed into a concentration in wt. % using the atomic masses of the elements using Equations S-5 and S-7 as:

$$\text{Fe}^{2+} + \text{Mg}^{2+} = 2, \quad (S-2)$$

$$\left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{Ol}} = \frac{\text{Mg}^{2+} - 2}{\text{Mg}^{2+}}, \quad (S-3)$$

moles Mg$^{2+}$ = $\frac{2}{(1-(\text{Fe}/\text{Mg})_{\text{Ol}})}$ and MgO$_{\text{Ol}}$ (wt. %) = moles Mg$^{2+} \times 40.3$, \quad (S-4, S-5)

Fe$^{2+}$ = 2 - Mg$^{2+}$ and FeO$_{\text{Ol}}$ (wt. %) = moles Fe$^{2+} \times 71.8$. \quad (S-6, S-7)

2) **Calculate the new melt composition after olivine addition.** For 1% (0.01) incremental additions of olivine, this is given as:

$$\text{FeO}_{\text{melt}}^{\text{new}} = (1 - 0.01)\text{FeO}_{\text{melt}}^{\text{previous}} + (0.01)\text{FeO}_{\text{Ol}}, \quad (S-8)$$

$$\text{MgO}_{\text{melt}}^{\text{new}} = (1 - 0.01)\text{MgO}_{\text{melt}}^{\text{previous}} + (0.01)\text{MgO}_{\text{Ol}}. \quad (S-9)$$

3) **Calculate the change in melt $\delta^{56}\text{Fe}$ following olivine addition.** The proportion of Fe in olivine and melt is calculated as:

$$\Delta F(\text{Fe}) = (0.01) \times \frac{\text{Fe}_{\text{Ol}}}{\text{Fe}_{\text{melt}}}. \quad (S-10)$$
Then a mass balance equation is used to calculate the change in Fe isotopic composition of the melt:

\[
\delta^{56}\text{Fe}_{\text{Ol}} = \delta^{56}\text{Fe}_{\text{melt}} + \Delta^{56}\text{Fe}_{\text{Ol-melt}},
\]

(S-11)

\[
\delta^{56}\text{Fe}_{\text{melt}} = (1 - \Delta F(\text{Fe}))\delta^{56}\text{Fe}_{\text{melt}}^{\text{previous}} + \Delta F(\text{Fe})\delta^{56}\text{Fe}_{\text{Ol}}.
\]

(S-12)

This is repeated incrementally until Mg# reaches 0.74 and olivine forsterite content reaches 90, which is assumed to represent a primary melt.

There are several different ways that \(\Delta^{56}\text{Fe}_{\text{Ol-melt}}\) can be calculated, which is a large source of uncertainty with the fractional crystallisation corrections. For this study, we used two separate methods:

- **Method 1:**

  From Sossi and O’Neill (2017), the olivine-melt fractionation factor can be expressed as:

  \[
  \Delta^{56}\text{Fe}_{\text{Ol-melt}} = 2904 \times \frac{F_{\text{Ol}} - F_{\text{melt}}}{T^2},
  \]

  (S-13)

  where \(F_{\text{Ol}}\) has a value of 197 N/m (Dauphas et al., 2014), \(F_{\text{melt}}\) varies depending on melt Fe\(^{3+}/\Sigma\text{Fe}\) but has a value of approximately 222 N/m when Fe\(^{3+}/\Sigma\text{Fe}\) is near 0.15 (since \(F_{\text{Fe}^{3+}} = 199\) N/m and \(F_{\text{Fe}^{3+}} = 351\) N/m; Dauphas et al., 2014). Temperature is calculated using the expression from Nisbet (1982):

  \[
  T(\text{K}) = [1000 + 20 \times \text{MgO (wt.%) + 273}].
  \]

  (S-14)

- **Method 2:**

  The maximum correction which has been proposed so far in the literature is \(\Delta^{57}\text{Fe}_{\text{Ol-melt}} = -0.4 \times 10^6/T^2\) (Nebel et al., 2019) which is equivalent to \(\Delta^{56}\text{Fe}_{\text{Ol-melt}} = -0.276 \times 10^6/T^2\). We use this expression to calculate the maximum magnitude of possible fractional crystallisation correction.

  For the Fagradalsfjall data, the corrected Fe isotopic compositions (\(\delta^{56}\text{Fe}_{\text{prim}}\)) are shown in Figure S-1 by the red bars. Correction Method 1 gives a \(\Delta^{56}\text{Fe}_{\text{Ol-melt}}\) value of approximately \(-0.03\) ‰, and a minimum \(\delta^{56}\text{Fe}\) correction. We consider this to be a realistic correction because it is based on fractionation factors directly determined using NRIXS. Correction Method 2 gives a \(\Delta^{56}\text{Fe}_{\text{Ol-melt}}\) value of approximately \(-0.10\) ‰, which we suspect may be an overcorrection of the data.
Iron isotopic compositions of the Fagradalsfjall basalts corrected for olivine crystallisation. The red bar spans the range of the $\delta^{56}\text{Fe}_{\text{prim}}$ values calculated using two separate methods, as described in the text.

The Fagradalsfjall lavas are relatively primitive, with high Mg# between 64 and 67, and olivine cores with Fo content between 80 and 90 % (Halldórsson et al., 2022), which suggests they have experienced limited fractional crystallisation. For both correction methods, the $\delta^{56}\text{Fe}_{\text{prim}}$ values are still within analytical uncertainty.

There are many uncertainties with fractional crystallisation corrections, the largest being which olivine-melt fractionation factors are selected. If different fractionation factors are chosen, discrepancies in the corrections are accentuated in those samples which have undergone the most olivine crystallisation. While this is less of an issue in the Fagradalsfjall samples, it becomes an increasingly important issue to consider in less primitive basalts, and those that crystallise phases other than olivine. In addition, there are uncertainties with assuming a $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the melt, and in estimating accurate crystallisation temperatures.

For the above reasons, we chose to report and plot the uncorrected $\delta^{56}\text{Fe}$ values in this paper, as the correction had no effect on our Fe isotope trends or interpretations, and could instead increase uncertainty.

4. Fe Isotope Modelling During Mantle Melting

The variations in major and trace element composition in the Fagradalsfjall basalts is thought to be caused by changes in the proportions of melt contributed by depleted and enriched mantle domains over the course of the eruption, with melts from a geochemically enriched source becoming more significant with time (Halldórsson et al., 2022). However, it is uncertain if this source is lithologically distinct (i.e. pyroxenitic). The aim of the Fe isotope modelling in this section is to investigate the source required to generate the trace element and Fe isotopic compositions of the Fagradalsfjall basalts.

We use a batch melting model after Sossi and O’Neill (2017) to model the trace element and Fe isotopic composition of melts produced from batch melting spinel lherzolite, garnet lherzolite, and pyroxenite sources (Fig. S-2). A full explanation of the calculations is given below. The parameters used are listed in Tables S-3 to S-6.
Batch Melting Models

Trace element concentrations in the melt ($C_l$) are calculated using a batch melting equation:

$$\frac{C_l}{C_0} = \frac{1}{(D+F(1-P))}. \quad (S-15)$$

The Fe isotope modelling follows the approach outlined in Sossi and O’Neill (2017), and calculates the concentrations of the isotopes $^{54}$Fe and $^{56}$Fe in the melt ($l$). Equation S-16 is the general form of this equation, where $i$ is the isotope being calculated, $j$ denotes the normalising isotope ($^{54}$Fe), and $C_o$ is the initial concentration in the bulk solid. $F$ is the melt fraction, and is varied in steps of 0.02.

$$\frac{C_i}{C_j} = \frac{1}{\left(\frac{D_i^{1-2} \alpha E_j^{1-2}}{D_j} + F(1-P)\right)}. \quad (S-16)$$

The term $\alpha E_j^{1-2}$ is the isotopic fractionation factor of element $E$, and is equivalent to the ratio of the two partition coefficients $D_i^{1-2}/D_j^{1-2}$. For example, Fe isotopes fractionation between the melt ($l$) and mantle ($o$) is expressed as:

$$\alpha_{Fe}^{56} = \frac{D_{56}^{1-o}}{D_{54}^{1-o}} = \frac{^{56}\text{Fe}_l}{^{54}\text{Fe}_l}/\frac{^{56}\text{Fe}_o}{^{54}\text{Fe}_o}. \quad (S-17)$$

However, since at high temperatures, $\alpha$ is approximately equal to 1, the partition coefficients for $D_i$ and $D_j$ are approximately equal. It is assumed that the partition coefficient for the normalising isotope $D_j^{54}$Fe is equal to the bulk partition coefficient for Fe (see Sossi and O’Neill, 2017, for the full derivation). The partition coefficient for $D_j^{56}$Fe can then be calculated from Equation S-18, where $K$ is the force constant of Fe-O bonds in the minerals and melt and $x$ is a constant equal to 2904 which considers the difference in mass between the two isotopes (see Equation B-13 in Sossi and O’Neill, 2017, for the equation to calculate $x)$:

$$D_{56}^{54}\text{Fe}_{\text{min-melt}} = \left(\frac{D_{54}\text{Fe}_{\text{min-melt}}}{D_{56}\text{Fe}_{\text{min-melt}}}\right) e^{\left(x\left(K_{\text{Fe-O}}^{\text{min}}-K_{\text{Fe-O}}^{\text{melt}}\right)/T\right)}. \quad (S-18)$$

The force constants for the minerals are given in Tables S-4 to S-6, and remain constant throughout the model. We select force constants determined by the same method (NRIXS) for consistency. The force constant for the melt scales with melt Fe$^{3+}/\Sigma$Fe, and is calculated at each model step using Equation S-19, from the Dauphas et al. (2014) regression for force constants in basaltic, andesitic and dacitic glasses ($a = 152$ and $b = 199$):

$$K_{\text{Fe-O}}^{\text{melt}} = a \times \frac{\text{Fe}^{3+}}{\Sigma \text{Fe}} + b \quad (S-19)$$
Therefore, for $^{56}$Fe, Equation S-16 reduces to:

$$\frac{C_i^{56}}{C_0^{56}} = \frac{1}{(D_{\text{min}}^{56}\text{melt}) + F(1-P)},$$  \hspace{1cm} \text{(S-20)}

and for $^{54}$Fe, Equation S-16 reduces to:

$$\frac{C_i^{54}}{C_0^{54}} = \frac{1}{(D_{\text{min}}^{54}\text{melt}) + F(1-P)},$$  \hspace{1cm} \text{(S-21)}

Dividing $\frac{C_i^{56}}{C_0^{56}}$ by $\frac{C_i^{54}}{C_0^{54}}$ gives the Fe isotope fractionation factor between the melt and the mantle ($\alpha_{Fe}^{56}$; Eq. S-17). Therefore, the Fe isotopic composition of the melt can be calculated using Equation S-22, where $\delta^{56}$Fe$_0$ is the initial Fe isotopic composition of the mantle source.

$$\delta^{56}\text{Fe}_1 = \delta^{56}\text{Fe}_0 + 1000 \ln \left(\frac{(^{56}\text{Fe})_1 / (^{56}\text{Fe})_0}{(^{54}\text{Fe})_1 / (^{54}\text{Fe})_0}\right) = \delta^{56}\text{Fe}_0 + 1000 \ln \left(\alpha_{Fe}^{56}\right).$$  \hspace{1cm} \text{(S-22)}

Model Parameters

Table S-3  Initial Parameters for non-modal batch melting models for spinel peridotite, garnet peridotite and MORB-like pyroxenite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Spinel Peridotite</th>
<th>Reference</th>
<th>Garnet Peridotite</th>
<th>Reference</th>
<th>Pyroxenite</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO (wt. %)</td>
<td>8.18</td>
<td>Workman and Hart (2005), DMM</td>
<td>8.18</td>
<td>Workman and Hart (2005), DMM</td>
<td>9.35</td>
<td>Lambart (2017), G2 pyroxenite</td>
</tr>
<tr>
<td>Fe$^{3+}$/ΣFe</td>
<td>0.036</td>
<td>Sossi and O’Neill (2017), intermediate value</td>
<td>0.036</td>
<td>Sossi and O’Neill (2017), intermediate value</td>
<td>0.16</td>
<td>Cottrell and Kelley (2011), average MORB</td>
</tr>
<tr>
<td>$\delta^{56}$Fe</td>
<td>0.026</td>
<td>Craddock et al. (2013), DMM</td>
<td>0.026</td>
<td>Craddock et al. (2013), DMM</td>
<td>0.105</td>
<td>Teng et al. (2013), average MORB</td>
</tr>
<tr>
<td>La (µg/g)</td>
<td>0.192</td>
<td>Workman and Hart (2005), DMM</td>
<td>0.192</td>
<td>Workman and Hart (2005), DMM</td>
<td>2.695</td>
<td>Lambart (2017), G2 pyroxenite</td>
</tr>
<tr>
<td>Yb (µg/g)</td>
<td>0.365</td>
<td>Workman and Hart (2005), DMM</td>
<td>0.365</td>
<td>Workman and Hart (2005), DMM</td>
<td>3.4</td>
<td>Lambart (2017), G2 pyroxenite</td>
</tr>
<tr>
<td>Nb (µg/g)</td>
<td>0.1485</td>
<td>Workman and Hart (2005), DMM</td>
<td>0.1485</td>
<td>Workman and Hart (2005), DMM</td>
<td>6.13</td>
<td>Lambart (2017), G2 pyroxenite</td>
</tr>
<tr>
<td>Zr (µg/g)</td>
<td>5.082</td>
<td>Workman and Hart (2005), DMM</td>
<td>5.082</td>
<td>Workman and Hart (2005), DMM</td>
<td>65</td>
<td>Lambart (2017), G2 pyroxenite</td>
</tr>
</tbody>
</table>
**Table S-4** Input parameters for melting a spinel-bearing depleted peridotite. Modal proportions are from Workman and Hart (2005). Melting coefficients are from Kinzler and Grove (1992). Partition coefficients for Fe$^{2+}$ and Fe$^{3+}$ are from Mallmann and O’Neill (2009). Trace element partition coefficients are from Gibson and Geist (2010). Force constants are from (a) Dauphas et al. (2014; forsterite value) and (b) Roskosz et al. (2015; median value for spinel). Due to the lack of NRIXS measurements for pyroxene, we assume olivine, orthopyroxene and clinopyroxene have equal force constants. In reality, Fe$^{3+}$ bearing pyroxene will have a higher force constant than Fe$^{2+}$ bearing olivine.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Modal Proportion</th>
<th>Melting Coefficient</th>
<th>D(Fe$^{2+}$)</th>
<th>D(Fe$^{3+}$)</th>
<th>D(La)</th>
<th>D(Yb)</th>
<th>D(Nb)</th>
<th>D(Zr)</th>
<th>Force Constant (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine</td>
<td>0.57</td>
<td>0.4</td>
<td>0.57</td>
<td>0.68</td>
<td>0.005</td>
<td>0.02</td>
<td>0.005</td>
<td>0.0033</td>
<td>197$^a$</td>
</tr>
<tr>
<td>orthopyroxene</td>
<td>0.28</td>
<td>0.82</td>
<td>0.23</td>
<td>0.453</td>
<td>0.049</td>
<td>0.08</td>
<td>0.015</td>
<td>0.119</td>
<td>197$^a$</td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>0.13</td>
<td>0.08</td>
<td>0.175</td>
<td>0.453</td>
<td>0.049</td>
<td>0.4</td>
<td>0.015</td>
<td>0.119</td>
<td>264$^b$</td>
</tr>
<tr>
<td>spinel</td>
<td>0.02</td>
<td>0.08</td>
<td>0.02</td>
<td>0.08</td>
<td>0.001</td>
<td>0.015</td>
<td>0.015</td>
<td>0.27</td>
<td>110</td>
</tr>
</tbody>
</table>

**Table S-5** Input parameters for melting a garnet-bearing depleted peridotite. Modal proportions are from Hirschmann and Stolper (1996). Melting coefficients are from Walter (2003; garnet lherzolite at 3 GPa). Partition coefficients for Fe$^{2+}$ and Fe$^{3+}$ are from Mallmann and O’Neill (2009). Trace element partition coefficients are from Gibson and Geist (2010). The force constant for garnet is from Nie et al. (2021), and those for olivine and pyroxenes are as above.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Modal Proportion</th>
<th>Melting Coefficient</th>
<th>D(Fe$^{2+}$)</th>
<th>D(Fe$^{3+}$)</th>
<th>D(La)</th>
<th>D(Yb)</th>
<th>D(Nb)</th>
<th>D(Zr)</th>
<th>Force Constant (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine</td>
<td>0.525</td>
<td>0.05</td>
<td>0.14</td>
<td>0.18</td>
<td>0.001</td>
<td>0.4</td>
<td>0.015</td>
<td>0.27</td>
<td>110</td>
</tr>
<tr>
<td>orthopyroxene</td>
<td>0.23</td>
<td>0.15</td>
<td>0.60</td>
<td>0.453</td>
<td>0.049</td>
<td>0.4</td>
<td>0.015</td>
<td>0.119</td>
<td>197$^a$</td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>0.175</td>
<td>0.96</td>
<td>0.60</td>
<td>0.453</td>
<td>0.049</td>
<td>0.4</td>
<td>0.015</td>
<td>0.119</td>
<td>197$^a$</td>
</tr>
<tr>
<td>garnet</td>
<td>0.07</td>
<td>0.14</td>
<td>0.872</td>
<td>0.287</td>
<td>0.049</td>
<td>0.4</td>
<td>0.015</td>
<td>0.27</td>
<td>197</td>
</tr>
</tbody>
</table>

**Table S-6** Input parameters for melting a MORB-like pyroxenite. Melting coefficients are from Pertermann and Hirschmann (2003). Modal proportions selected to represent an average pyroxenite. Partition coefficients for Fe$^{2+}$ and Fe$^{3+}$ for clinopyroxene are from Mallmann and O’Neill (2009), and assume that values are similar for garnet and orthopyroxene after Sossi and O’Neill (2017). Trace element partition coefficients are from Gibson and Geist (2010). The force constant for garnet is from Nie et al. (2021) and that for clinopyroxene is as above.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Modal Proportion</th>
<th>Melting Coefficient</th>
<th>D(Fe$^{2+}$)</th>
<th>D(Fe$^{3+}$)</th>
<th>D(La)</th>
<th>D(Yb)</th>
<th>D(Nb)</th>
<th>D(Zr)</th>
<th>Force Constant (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>clinopyroxene</td>
<td>0.8</td>
<td>0.872</td>
<td>0.287</td>
<td>0.453</td>
<td>0.049</td>
<td>0.4</td>
<td>0.015</td>
<td>0.119</td>
<td>197</td>
</tr>
<tr>
<td>garnet</td>
<td>0.2</td>
<td>0.173</td>
<td>0.60</td>
<td>0.18</td>
<td>0.001</td>
<td>0.6</td>
<td>0.015</td>
<td>0.27</td>
<td>110</td>
</tr>
</tbody>
</table>
Modelling Results

Figure S-2  Batch melting models of trace element and Fe isotopic composition, and binary mixing between end-member melts. La and Yb data are from Halldórsson et al. (2022). The Nb and Zr data for the Fagradalsfjall samples are for a different sample set from Bindeman et al. (2022), so are shown as a range.

Figure S-2 shows that if melting occurs within the spinel stability field, a minor proportion (~10–20 %) of pyroxenite melt is required to explain the La/Yb ratios of the lavas. However, if melting is >3 GPa and garnet is present in the mantle source, melting a garnet bearing peridotite at different pressures and melt fractions can explain the range of La/Yb and δ56Fe in the Fagradalsfjall lavas. However, in order to explain the Nb/Zr ratios of the lavas (as reported in Bindeman et al., 2022), a minor pyroxenite contribution (~10–20 % pyroxenite melt) is required. However, such a low proportion of pyroxenite does not cause resolvable variations in the major element or Fe isotopic composition of the melt.

In order to investigate the proportion and Fe isotopic composition of enriched end member melts which are required to cause a resolvable variation in basalt Fe isotopic composition, we construct a simple binary mixing model
using Equation S-23, where \( p \) is the proportion of end member A. For simplicity, the FeO content of the end member melts is assumed to be equal, although in reality this will vary with depth and degree of melting:

\[
\delta^{56}\text{Fe}_{\text{melt}} = \frac{p \cdot \text{FeO}_A \cdot \delta^{56}\text{Fe}_A + (1-p) \cdot \text{FeO}_B \cdot \delta^{56}\text{Fe}_B}{p \cdot \text{FeO}_A + (1-p) \cdot \text{FeO}_B}. \tag{S-23}
\]

Assuming a spinel lherzolite has initial \( \delta^{56}\text{Fe} \) similar to the depleted MORB mantle (0.026‰; Craddock et al., 2013), a depleted melt would have \( \delta^{56}\text{Fe} \approx 0.05 \text{‰} \) (e.g., see Fig. S-2). For the enriched melt, if a pyroxenite source has initial \( \delta^{56}\text{Fe} \) similar to average MORB (0.105‰; Teng et al., 2013), the melt would have \( \delta^{56}\text{Fe} \approx 0.150 \text{‰} \) (e.g., see Fig. S-2). However, pyroxenite xenoliths with \( \delta^{56}\text{Fe} \) up to 0.20‰ have been measured previously (Zhao et al., 2017). If the bulk melt-mantle fractionation factor is approximately 0.04–0.06‰ during pyroxenite melting, then a melt with \( \delta^{56}\text{Fe} \approx 0.25 \text{‰} \) could hypothetically be produced.

In reality, enriched melts are not sourced directly from the melting of subducted ocean crust. Instead, silica rich melts sourced from melting of recycled crust react with the peridotite mantle, consuming olivine and orthopyroxene and forming a hybrid source containing pyroxenite. Soderman et al. (2021) propose melts from reaction zone pyroxenites could be as heavy as \( \delta^{57}\text{Fe} = 0.30 \text{‰} \) (or \( \delta^{56}\text{Fe} \approx 0.2 \text{‰} \)), although these are likely rare heavy values. Therefore, we use a geologically feasible range of enriched end member compositions from 0.10‰ to 0.25‰.

**Figure S-3**  Binary mixing model of depleted and enriched end members. The blue shaded area is the typical analytical uncertainty of Fe isotope measurements, which here is the average 2 s.d. measured in this study. Values for the depleted and enriched end members are discussed in the text.

The binary mixing model (Fig. S-3) shows that at current analytical uncertainty, at least 40–50% enriched melt with \( \delta^{56}\text{Fe} > 0.2 \text{‰} \) is generally required to generate resolvable Fe isotopic variation. This therefore suggests that at Fagradalsfjall there is no significant contribution of melts from a lithologically distinct (pyroxenite) mantle component, or the melting signal of enriched lithologies is masked by more significant peridotite melting.
Additional Figures

Figure S-4     Whole rock (a–c) vanadium, (d–f) iron and (g–i) zinc isotopic compositions plotted against (a, d, g) $^{87}\text{Sr}/^{86}\text{Sr}$, (b, e, h) $^{143}\text{Nd}/^{144}\text{Nd}$ and (c, f, i) $^{206}\text{Pb}/^{204}\text{Pb}$ from Halldórsson et al. (2022). The colour bars indicate the day the samples were erupted.
Supplementary Information References


Iron, magnesium, and titanium isotopic fractionations between garnet, ilmenite, fayalite, biotite, and tourmaline: Results from NRIXS, ab initio, and study of mineral separates from the Moosilauke metapelite. *Geochemica et Cosmochimica Acta* 302, 18–45. [https://doi.org/10.1016/j.gca.2021.05.014](https://doi.org/10.1016/j.gca.2021.05.014)


