

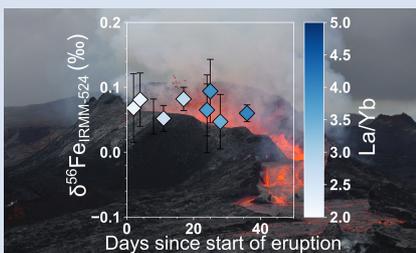
No V-Fe-Zn isotopic variation in basalts from the 2021 Fagradalsfjall eruption

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Abstract



The Earth's mantle is chemically heterogeneous in space and time, which is often reflected by variable isotopic compositions of mantle derived basalts. Basalts from the first 40 days of the 2021 Fagradalsfjall eruption, Reykjanes Peninsula, Iceland, display systematic temporal variations in the ratios of incompatible elements alongside resolvable variations in Sr, Nd and Pb radiogenic isotopes. These variations reflect progressive influx of magma derived from melting of a deeper, more enriched and potentially lithologically distinct source. We use this eruptive time series to conduct the first combined V-Fe-Zn isotope study, exploring the sensitivity of the combined isotopic approach, with particular focus on fingerprinting source lithological heterogeneity. We find no analytically resolvable change in V ($\delta^{51}\text{V}_{\text{AA}}$ between -0.95 ± 0.09 ‰ 2 s.d. and -0.86 ± 0.07 ‰ 2 s.d.), Fe ($\delta^{56}\text{Fe}_{\text{IRMM-524}}$ between $+0.047 \pm 0.042$ ‰ 2 s.d. and $+0.094 \pm 0.049$ ‰ 2 s.d.) and Zn ($\delta^{66}\text{Zn}_{\text{AA-ETH}}$ between -0.042 ± 0.003 ‰ 2 s.d. and $+0.013 \pm 0.027$ ‰ 2 s.d.) isotopic compositions. The lack of variability in V-Fe-Zn isotopes, despite the evolving trace element and radiogenic isotope ratios, suggests there is no significant contribution of melts from a lithologically distinct (pyroxenite) mantle component under the Reykjanes Peninsula.

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Introduction

It is widely accepted that crustal recycling has led to the formation of a chemically and isotopically heterogeneous upper mantle. Due to the relative inaccessibility of the mantle reservoir, most information about its composition comes from the study of mantle-derived basalts. Variations in the major, trace element and radiogenic isotopic composition of basalts require the presence of chemically enriched and depleted mantle domains (e.g., Hofmann, 1997). Enriched components can exist as pyroxene-rich (pyroxenite/eclogite) lithologies derived from subducted oceanic crust, which are more fusible and melt at a lower solidus temperature than peridotite (e.g., Pertermann and Hirschmann, 2003). Therefore, minor pyroxenite melting can dominate the trace element signature of basalts, making investigation of the spatial extent and characteristics of these heterogeneities challenging.

An emerging approach for investigating potential variation in mantle lithology is to use transition metal stable isotopes (TMI), the most well studied being Fe (e.g., Williams and Bizimis, 2014; Konter et al., 2016; Soderman et al., 2021). At equilibrium, stable isotope fractionation between phases is theoretically controlled by bond strength, with heavier isotopes concentrating in stronger

bonds where elements are present in higher oxidation state and lower bond coordination (e.g., Schauble, 2004). Analytically resolvable variations in the magnitude of TMI equilibrium mineral-mineral and mineral-melt isotopic fractionation at magmatic temperatures have been both theoretically predicted and directly documented (e.g., Prytulak et al., 2017; Sossi and O'Neill, 2017; Stow et al., 2022). For example, in the case of Fe, the difference in bonding environment and valence between pyroxene and olivine leads to heavier Fe isotopic composition in pyroxene-rich lithologies derived from subducted oceanic crust compared to olivine-rich peridotite (e.g., Williams and Bizimis, 2014). Thus, the transition metal stable isotopic composition of primitive basalts is an attractive prospect for fingerprinting magmatic source lithology.

Although TMI could theoretically track variations in mantle lithology, there is debate about their efficacy. Whether signals of mantle heterogeneity are preserved in primitive basalts depends on the contrast in isotopic composition between the different mantle sources and the proportions of each source melted (e.g., Soderman et al., 2022).

The 2021 Fagradalsfjall eruption on the Reykjanes Peninsula, Iceland, provides a unique opportunity to investigate

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the relationship between potential mantle lithological heterogeneity and the transition metal stable isotope composition of basalts. Continuous eruption and high-resolution sampling of basaltic material occurred from 19 March to 18 September 2021. The Fagradalsfjall time series is an ideal sample set for several reasons:

1. It is generally accepted that the mantle beneath Iceland, and the Reykjanes peninsula specifically, is lithologically heterogeneous and contains various depleted and enriched domains (e.g., Maclennan, 2008; Shorttle and Maclennan, 2011; Rasmussen *et al.*, 2020; Harðardóttir *et al.*, 2022).
2. The Fagradalsfjall basalts display systematic temporal variations in trace element compositions over the first 40 days of the eruption, which requires the melting of chemically, and potentially lithologically, distinct sources (Bindeman *et al.*, 2022; Halldórsson *et al.*, 2022). Increases in La/Yb and K₂O/TiO₂ suggest recharge of melts derived from a more enriched source during the eruption, consistent with increasing ²⁰⁶Pb/²⁰⁴Pb and ⁸⁷Sr/⁸⁶Sr, and decreasing ¹⁴³Nd/¹⁴⁴Nd (Halldórsson *et al.*, 2022).
3. The basalts have high MgO content (8.8–10 wt. %) and show no evidence for crustal assimilation or long-term crustal storage (Bindeman *et al.*, 2022; Halldórsson *et al.*, 2022; Kahl *et al.*, 2023). Therefore, the geochemical variability of these primitive basalts most likely reflects variation in the mantle source.

This work provides the first combined V, Fe and Zn stable isotope investigation of mantle-derived basalts. Iron, V and Zn are concentrated in different mineral phases with distinct equilibrium mineral-melt fractionation factors controlled by mineral bonding environment. Therefore, Fe, V and Zn should have distinctive responses to variations in mantle lithology. It follows that the combination of the three systems likely provides better constraint than any one system in isolation. Iron isotopes have been used to infer the presence of pyroxene-rich domains in mantle sources (e.g., Williams and Bizimis, 2014; Konter *et al.*, 2016; Nebel *et al.*, 2019; Soderman *et al.*, 2021). The influence of lithological heterogeneity on V isotopes is less well constrained; however, several studies report V isotopic compositions of Icelandic lavas, which can be compared to the Fagradalsfjall

data (Prytulak *et al.*, 2013, 2017; Novella *et al.*, 2020). It is debated whether Zn isotopes are fractionated during partial melting of distinct lithologies (e.g., Doucet *et al.*, 2016; Day *et al.*, 2022), or if variation is largely controlled by kinetic fractionation during melt or fluid percolation (Huang *et al.*, 2019; Fang *et al.*, 2022). Finally, Fe and V are redox sensitive elements whereas Zn is a monovalent element in terrestrial systems. Consequently, potential redox variations will not directly influence Zn isotopic fractionation, but may influence Fe and V (e.g., Stow *et al.*, 2022). Thus, a multi-isotope approach can address existing uncertainties by evaluating the relationships between the three isotope systems. The Fagradalsfjall basalts and their well-characterised secular chemical variations provide an opportunity to evaluate the sensitivity of V-Fe-Zn variations to potential changes in parameters such as oxygen fugacity, partial melting, and lithological heterogeneity.

Methods

We determined the V, Fe and Zn stable isotopic compositions of 10 glassy basalts erupted between 21 March and 24 April 2021, which capture the full breadth of trace element variability during the overall eruption. These are newly prepared aliquots of the same samples analysed by Halldórsson *et al.* (2022). Chemical separation and isotope ratio measurements were carried out in the Arthur Holmes Isotope Geology Laboratory, Durham University. The column chromatography procedure quantitatively separated V, Fe and Zn from the same sample digestion. See the [Supplementary Information](#) for a full description of the methods. Analytical uncertainties, reported as 2 s.d., are typically <0.1 ‰ for δ⁵¹V, <0.05 ‰ for δ⁵⁶Fe and <0.03 ‰ for δ⁶⁶Zn (see [Table S-1](#)).

Results and Discussion

The first order observation of this study is that there is no analytically resolvable temporal variation in V, Fe or Zn isotopic compositions of the Fagradalsfjall basalts over the first 40 days of the eruption (Fig. 1; [Table S-1](#)). There are limited published Icelandic V-Fe-Zn data for comparison, but the basalts have similar isotopic compositions to mafic samples (<50 wt. % whole rock SiO₂) from Hekla volcano (grey bars in [Fig. 1](#);

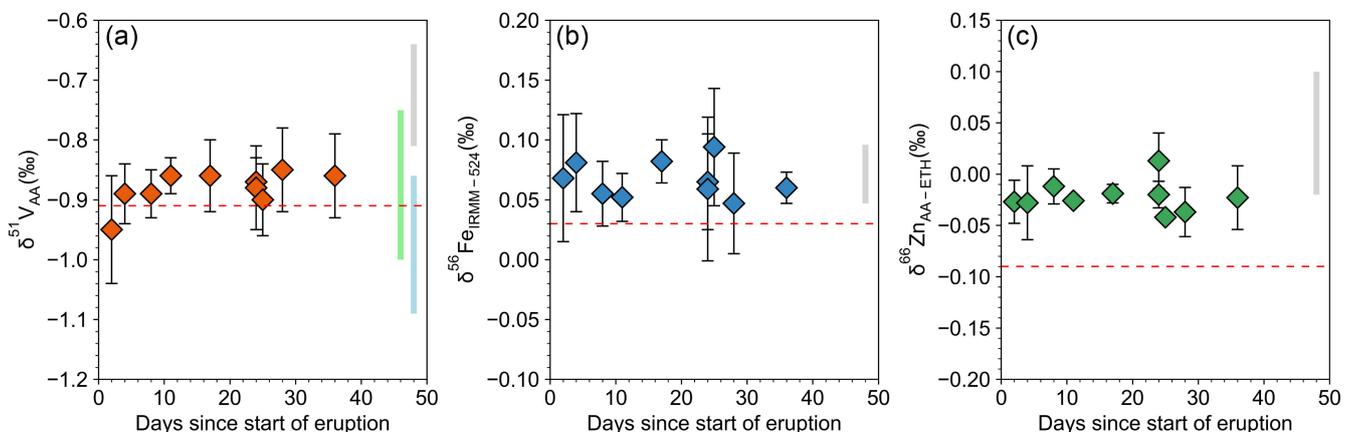


Figure 1 (a) Vanadium, (b) iron and (c) zinc isotopic compositions over the first 40 days of the eruption. Error bars are 2 s.d. of at least three measurements of each sample. Red dashed lines show estimates of the Bulk Silicate Earth (BSE); $\delta^{51}\text{V}_{\text{AA}} = -0.91 \pm 0.09$ ‰ (Qi *et al.*, 2019), $\delta^{56}\text{Fe}_{\text{IRMM-524}} = +0.030 \pm 0.007$ ‰ (Sossi *et al.*, 2016) and $\delta^{66}\text{Zn}_{\text{AA-ETH}} = -0.09 \pm 0.08$ ‰ (Fang *et al.*, 2022). Grey vertical bands indicate the ranges of V (Prytulak *et al.*, 2017), Fe (Schuessler *et al.*, 2009) and Zn (Chen *et al.*, 2013) isotopic compositions in lavas from Hekla volcano with whole rock SiO₂ < 50 wt. %. Vertical blue and green bars indicate the ranges of V isotopic compositions in basalts from the Reykjanes Ridge (Novella *et al.*, 2020) and Reykjanes Peninsula (Prytulak *et al.*, 2013).

Schuessler *et al.*, 2009; Chen *et al.*, 2013; Prytulak *et al.*, 2017). In addition, $\delta^{51}\text{V}$ values are within error of basalts from the Reykjanes Ridge (blue bar in Fig. 1a; Novella *et al.*, 2020) and Reykjanes Peninsula (green bar in Fig. 1a; Prytulak *et al.*, 2013).

The Fagradalsfjall basalts display a greater variation in major and trace element compositions over the first 40 days of the eruption than have been observed in historical lavas from the Reykjanes Peninsula (Halldórsson *et al.*, 2022). Bindeman *et al.* (2022) and Halldórsson *et al.* (2022) proposed similar models to explain these geochemical variations. A depleted melt sourced from shallow mantle melting is thought to dominate the initial eruptive products. Enriched melts derived from deeper and lower degrees of mantle melting became more significant as the eruption proceeded. Rapid mixing of depleted and enriched melts occurs in the deep magma reservoir which feeds the eruption, generating the linear trends observed in the trace elements (Halldórsson *et al.*, 2022). However, there is no correlation between V-Fe-Zn isotopes and $\text{K}_2\text{O}/\text{TiO}_2$ or La/Yb (Fig. 2), the parameters used to demonstrate progressive contribution

of melts derived from a deeper and/or more enriched source (Halldórsson *et al.*, 2022).

The Fagradalsfjall basalts also record resolvable variation in Sr, Nd and Pb isotopic compositions over the first 40 days of the eruption, which are likewise thought to reflect the presence of melts from distinct mantle sources (Halldórsson *et al.*, 2022). There is also no correlation between V-Fe-Zn isotopes and Sr, Nd or Pb isotopes (Figs. 2, S-4).

Although there is no variation in V-Fe-Zn isotopes at Fagradalsfjall, several previous studies of ocean island basalts have observed correlations between $\delta^{56}\text{Fe}$ and the ratios of trace elements and radiogenic isotopes. These studies suggest that heavy Fe isotope signatures are at least in part inherited from an isotopically heavy pyroxene-bearing source (*e.g.*, Konter *et al.*, 2016; Nebel *et al.*, 2019; Soderman *et al.*, 2021; Shi *et al.*, 2022). However, these studies often analyse samples erupted from multiple volcanic vents across different islands, and are therefore not directly comparable to the Fagradalsfjall eruption. To facilitate a more direct comparison, we plot a selection of the literature

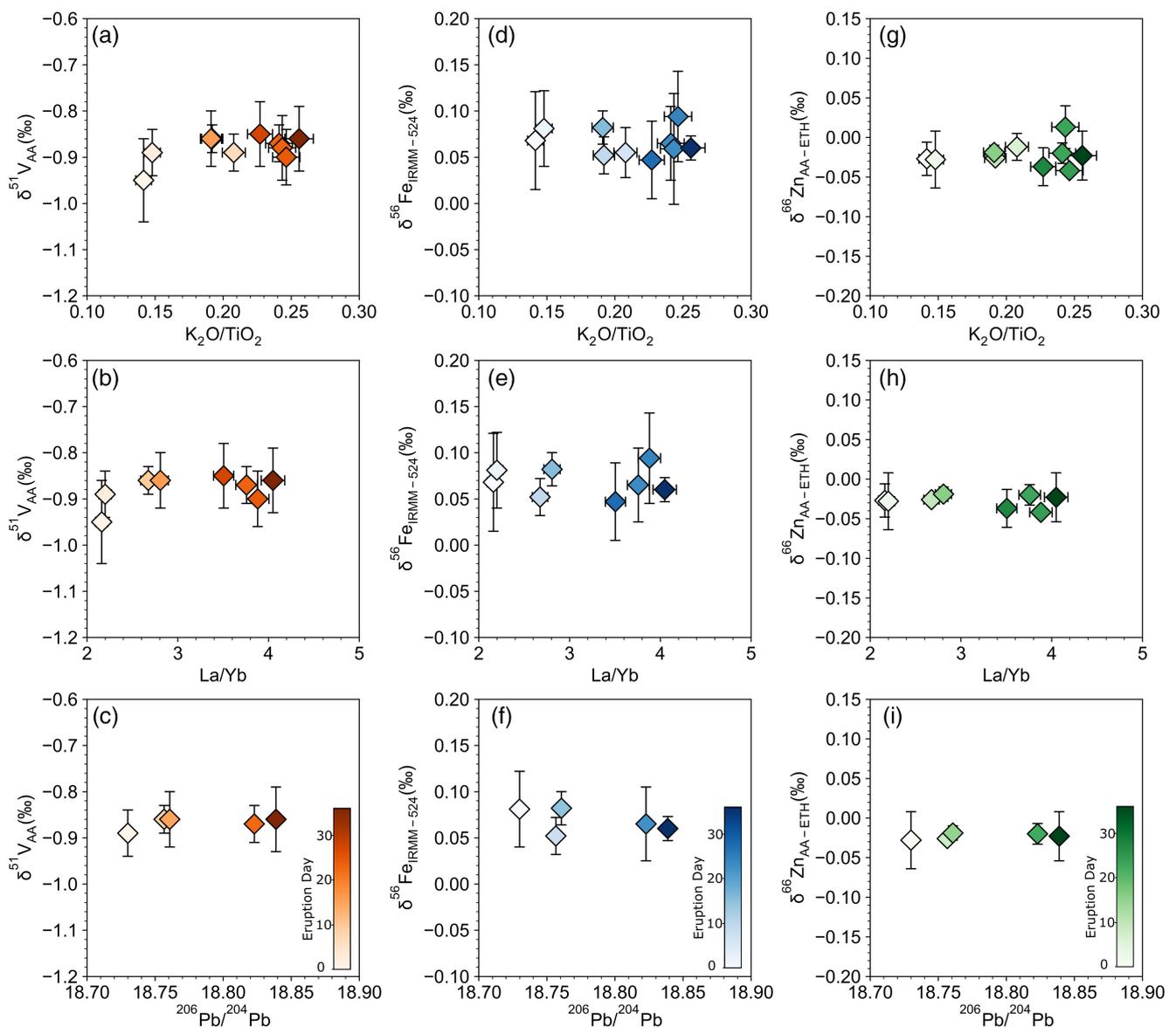


Figure 2 (a–c) Vanadium, (d–f) iron and (g–i) zinc isotopic compositions against whole rock (a, d, g) $\text{K}_2\text{O}/\text{TiO}_2$, (b, e, h) La/Yb and (c, f, i) $^{206}\text{Pb}/^{204}\text{Pb}$ from Halldórsson *et al.* (2022). The more enriched melts have higher La/Yb, $\text{K}_2\text{O}/\text{TiO}_2$ and $^{206}\text{Pb}/^{204}\text{Pb}$. The colour bar indicates the day the sample was erupted. Plots of isotopic composition against Sr and Nd isotopes are shown in Figure S-4.



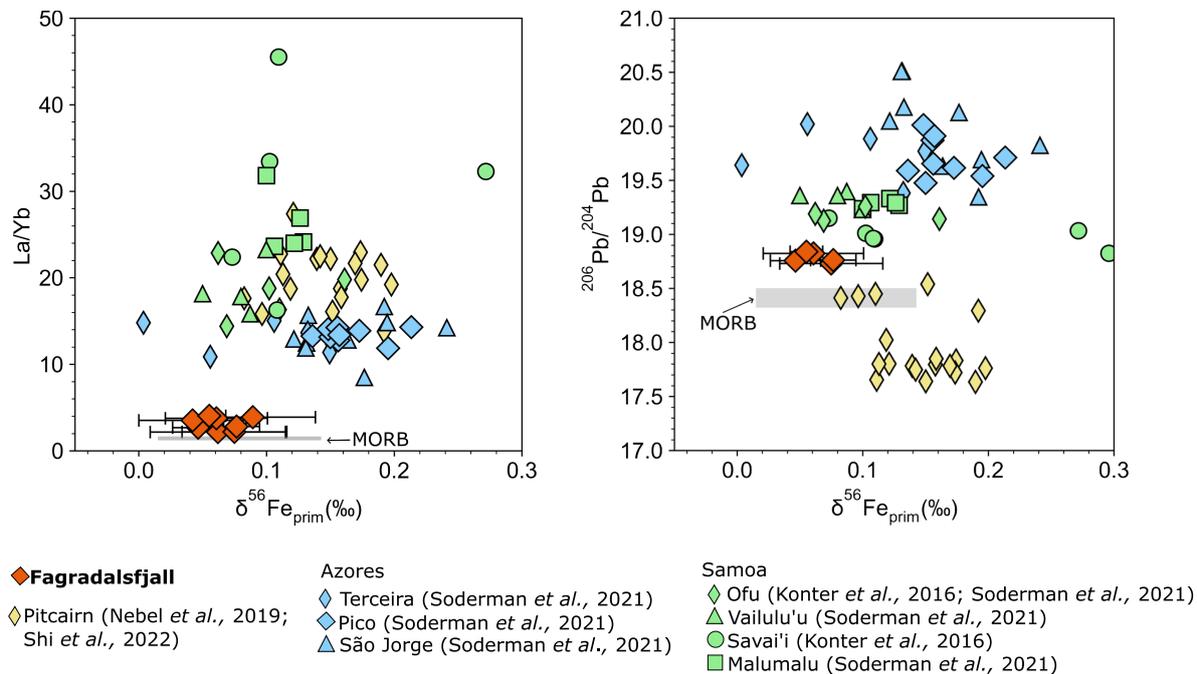


Figure 3 Iron isotopic compositions of selected ocean island basalts from the literature. The $\delta^{56}\text{Fe}_{\text{prim}}$ values are calculated as described in the [Supplementary Information](#). The MORB La/Yb and $^{206}\text{Pb}/^{204}\text{Pb}$ values are from Gale *et al.* (2013), and MORB $\delta^{56}\text{Fe}_{\text{prim}}$ values from Sossi *et al.* (2016).

data where at least four samples are from the same volcanic island, and where the presence of a pyroxene-bearing source has been proposed (Fig. 3). Although the Fagradalsfjall basalts do display resolvable variations in trace element and radiogenic isotope ratios, these ranges are much smaller than those observed in the other ocean island basalts. It is perhaps not surprising that the Fagradalsfjall basalts display no change in Fe isotopic composition. Although minor amounts of pyroxenite are required to explain some of the changes in the trace element and radiogenic isotope compositions of the basalts (*i.e.* <10–20 % pyroxenite melt; see [Supplementary Information](#)), this amount would be insufficient to drive changes in basalt $\delta^{56}\text{Fe}$. A binary mixing model (Fig. S-3) demonstrates that a contribution of at least 40–50 % enriched melt with $\delta^{56}\text{Fe} > 0.2$ ‰ is generally required to generate resolvable Fe isotopic variation. Therefore, the lack of variation in $\delta^{56}\text{Fe}$ in the Fagradalsfjall basalts is consistent with the lack of a volumetrically significant contribution of melts from a lithologically distinct source with a heavy Fe isotopic composition.

The controls on V and Zn isotope fractionation during mantle melting are not as well constrained as for Fe, but we can examine covariations between the three systems to investigate the drivers of isotopic fractionation. Previous empirical and modelling studies have suggested that V isotopes are insensitive to the presence of pyroxenite lithologies (Novella *et al.*, 2020; Soderman *et al.*, 2022). The lack of correlation between $\delta^{56}\text{Fe}$ and $\delta^{51}\text{V}$ in the Fagradalsfjall basalts supports this inference. In addition, the lack of correlation between these two redox sensitive elements suggests that there is no variation in mantle oxygen fugacity.

Previous studies suggest that Zn isotopic variability may be controlled by kinetic fractionation during percolation of melts and/or fluids through the mantle, and consequently hybridised mantle should have more variable $\delta^{66}\text{Zn}$ than peridotites (Huang *et al.*, 2019; Fang *et al.*, 2022). Therefore, the lack of covariation between Fe and Zn isotopes in the Fagradalsfjall basalts also supports the lack of a volumetrically significant contribution of melts from an enriched source.

This work has explored the sensitivity of a novel combination of three isotope systems (V, Fe and Zn) with contrasting chemical behaviours. In the case of the Fagradalsfjall high resolution eruptive time series, the lack of V-Fe-Zn isotopic variation suggests that there is no significant contribution of melts from a pyroxenite source. However, a multi-isotope approach still holds promise in identifying and disentangling processes and components involved in the generation of mantle-derived basalts.

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Data Access Statement

All data generated during this study are included in the published article and the [Supplementary Information](#).

Additional Information

[Supplementary Information](#) accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2335>.



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