

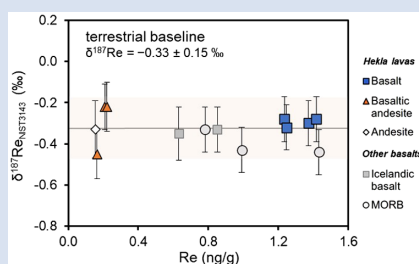
Rhenium elemental and isotopic variations at magmatic temperatures

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Abstract



Recent analytical advances in the measurement of rhenium (Re) isotope ratios allow its potential as a palaeoredox and chemical weathering proxy to be explored. However, a successful isotopic proxy must be grounded by an understanding of its composition and behaviour in the solid Earth. Here, we present Re concentrations and Re isotopic ($\delta^{187}\text{Re}$) compositions for a well-characterised sequence of lavas from Hekla volcano, Iceland. The concentration of Re varies from 0.02 to 1.4 ng/g, decreasing from basalt to more evolved lavas. We show that the crystallisation and removal of magnetite is responsible for the Re decrease in this system. By contrast, $\delta^{187}\text{Re}$ values for the same suite of samples show a relatively narrow range (-0.45 to -0.22 ‰), suggesting minimal resolvable Re isotope fractionation

between magnetite and the silicate melt. Together with other samples, including mid-ocean ridge basalts, these first igneous data can be used to estimate a baseline for terrestrial materials ($\delta^{187}\text{Re} = -0.33 \pm 0.15$ ‰, 2 s.d., $n = 14$), from which low-temperature Re isotope variations in Earth's surficial environments can be assessed, alongside the global isotope mass balance of Re.

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Introduction

Rhenium (Re) is one of the rarest elements in the Earth's crust, with an estimated abundance of ~ 0.93 ng/g and 0.2–2 ng/g in oceanic and continental crust, respectively (Peucker-Ehrenbrink and Jahn, 2001; Sun *et al.*, 2003a, 2003b). The Re concentration of the primitive mantle is ~ 0.28 ng/g, compared to 0.12–0.18 ng/g in the depleted mantle (McDonough and Sun, 1995; Hauri and Hart, 1997). There appears to be a “missing” Re component from the upper mantle (*e.g.*, Sun *et al.*, 2003b; Xue and Li, 2022), and there is a clear need for better constraints on the magmatic behaviour of Re. Whilst Re is known to be incompatible in most silicate phases, such as olivine and clinopyroxene (Richter *et al.*, 2004; Mallmann and O'Neill, 2007), the sulfur and oxygen fugacity (f_{S_2} and f_{O_2}) controls on Re partitioning appear to be complicated. For example, Re is predicted to behave as a lithophile element under sulfide-poor and/or relatively oxidised conditions (such as during differentiation of arc magmas), whereas Re behaves as a chalcophile in reduced mid-ocean ridge basalt (MORB) type mantle and becomes more compatible with lower f_{O_2} (Fonseca *et al.*, 2007; Mallmann and O'Neill, 2007); oxides such as magnetite can also potentially host Re (Richter *et al.*, 1998; Li, 2014).

Rhenium has two isotopes, ^{187}Re and ^{185}Re , which comprise ~ 63 % and 37 % of natural Re, respectively. The ^{187}Re isotope is radioactive, but decays with a very long half-life (4.12×10^{10} yr; Smoliar *et al.*, 1996), making the isotope ratio of ^{187}Re and ^{185}Re more analogous to a stable isotope system (Miller *et al.*, 2009). Rhenium is a redox-sensitive element (common valence states: 4+, 6+ and 7+), and because Re isotopes may be fractionated by redox and/or weathering processes (Miller *et al.*, 2015), the Re isotopic composition (denoted as $\delta^{187}\text{Re} = [({}^{187}\text{Re}/{}^{185}\text{Re})_{\text{sample}} / ({}^{187}\text{Re}/{}^{185}\text{Re})_{\text{NIST3143}} - 1] \times 1000$) of ancient sediments holds the potential to infer changes in seafloor redox and/or global weathering intensity (Dickson *et al.*, 2020; Dellinger *et al.*, 2021). There is a growing dataset of Re isotopic compositions of seawater and river waters (Dickson *et al.*, 2020; Dellinger *et al.*, 2021). However, due partly to analytical challenges, few $\delta^{187}\text{Re}$ measurements exist on igneous materials, limited to meteorites (Liu *et al.*, 2017) and standard reference materials (Dellinger *et al.*, 2020). No studies have investigated the behaviour of Re isotopes during magmatic processes on Earth. Additionally, our understanding of the Re isotopic composition of the mantle is currently limited. These features need to be resolved to establish a terrestrial baseline that can be compared with $\delta^{187}\text{Re}$ values of weathered materials, and to assess the global isotope mass balance of Re (Dickson *et al.*, 2020).

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Materials and Methods

We present Re concentrations and isotopic compositions for a well-characterised sequence of lavas from Hekla volcano, Iceland. The analysed Hekla lavas cover a compositional range from basalt to dacite (46–69 wt. % SiO₂), which have been interpreted as a differentiation sequence with or without contribution of minor amphibolite melting (Sigmarsson *et al.*, 1992, 2022; Savage *et al.*, 2011; Geist *et al.*, 2021; Supplementary Information). We also present results of Re isotope analysis for two unrelated Icelandic volcanic samples (RP80C-1 and BUR20-09) and three MORB samples spanning the Atlantic, Pacific and Indian Oceans (RDL DR30, CYP78 12-35 and MD57 D'10-1, respectively; Supplementary Information).

The Re concentrations of the samples were determined *via* isotope dilution and isoamylol liquid-liquid extraction method (Birck *et al.*, 1997). The low Re concentrations of these samples mean that a mass of 1–10 g is necessary for the precise determination of stable Re isotopes ($\delta^{187}\text{Re}$). Chemical separation of Re was conducted using a three-step AG1-X8 anion exchange column procedure, following newly established methods by Dellinger *et al.* (2020) and Dickson *et al.* (2020). Rhenium isotopes were measured using the multi-collector ICP-MS (Neptune Plus) instrument at Royal Holloway University of London. All the $\delta^{187}\text{Re}$ results are reported relative to the NIST SRM 3143 standard. Details of the analytical methods and all Re data for this study are given in Supplementary Information and Tables S-1 and S-2.

Results

The accuracy of the methods has been validated through the analysis of standard reference materials; the yielded $\delta^{187}\text{Re}$ values of BHVO-2, BIR-1, BCR-2 and MAG-1 are consistent with literature values (Table S-1). The measured Re concentrations of the Hekla suite were the highest in the basalt samples (1.23–1.42 ng/g), and sharply decreased with decreasing MgO from 0.17–0.23 ng/g in the basaltic andesite to 0.13–0.15 ng/g in the andesite and 0.021–0.026 ng/g in the dacite (Fig. 1a; Table S-2). The $\delta^{187}\text{Re}$ values of the Hekla lavas ranged from -0.28 ± 0.11 ‰ to -0.32 ± 0.11 ‰ and from -0.22 ± 0.11 ‰ to -0.45 ± 0.12 ‰ for the basalt and basaltic andesites, respectively, and a composition of -0.33 ± 0.14 ‰ (2 s.d.) was measured in an andesitic sample (Fig. 1b; Table S-2). It was not

possible to analyse dacitic samples for Re isotopes because of their extremely low Re concentrations. The $\delta^{187}\text{Re}$ values of two other Icelandic basalt samples, -0.35 ± 0.13 ‰ to -0.33 ± 0.11 ‰, were within the range of the Hekla suite. The three MORB samples exhibited Re concentrations of 0.78–1.43 ng/g and similar Re isotopic compositions of -0.33 ± 0.11 ‰ to -0.44 ± 0.11 ‰.

Discussion

Evolution of Re during magmatic processes at Hekla volcano. The co-variations of Re with vanadium (V) and TiO₂ provide a clue to the partitioning behaviour of Re within the Hekla suite. We demonstrate a concurrent removal of Re and V (Fig. 2a) during magmatic evolution; there is also a decreasing trend in Re concentrations with decreasing TiO₂ (from 4.5 to 0.3 wt. %; Fig. 2b). In the Hekla lavas, oxide minerals, such as (titano)magnetite, host the majority of V (Prytulak *et al.*, 2017). A self-consistent model of fractional crystallisation of cotectic phases (Fig. 3a), following Prytulak *et al.* (2017), shows that the evolution of Re concentrations in the Hekla lavas can be reproduced if the partition coefficient of Re in magnetite ($D_{\text{Re}}^{\text{mag}}$) is ~ 50 . Similar to this study, Righter *et al.* (1998) observed a sharp decrease in Re concentrations in samples from Volcán Alcedo (Galapagos), from 0.61 ng/g in icelandite to 0.026 ng/g in rhyolite along the FeO and TiO₂ depletion trend. These same authors measured an extremely high Re content in a magnetite separate (~ 40 ng/g) and concluded that magnetite is a significant host phase for Re, with an estimated $D_{\text{Re}}^{\text{mag}} = 20\text{--}50$ for a sulfide-free system. In support of this argument, Mallmann and O'Neill (2007) suggested that Re^{4+} has a partitioning behaviour similar to Ti^{4+} and could substitute for Ti^{4+} in the solid phase. Note that f_{O_2} (which is commonly reported in log units relative to the fayalite-magnetite-quartz buffer, FMQ) of the Icelandic magmas is close to FMQ (Moune *et al.*, 2007) so is relatively higher than in average MORB, while for the Alcedo (Galapagos) suite, the estimated f_{O_2} is more reducing, $\sim \text{FMQ}-3$ (Righter *et al.*, 1998). Lower f_{O_2} would result in higher fraction of Re as Re^{4+} , favouring dissolution of Re in common upper mantle minerals as well as in magnetite (Mallmann and O'Neill, 2007; Liu and Li, 2023). The similar $D_{\text{Re}}^{\text{mag}}$ estimated for the two suites regardless of varying f_{O_2} may be due to a compositional effect. In addition, it is possible that Re remains compatible in magnetite in anhydrous systems (*e.g.*, both the Hekla and the Alcedo suites; Geist *et al.*, 2021;

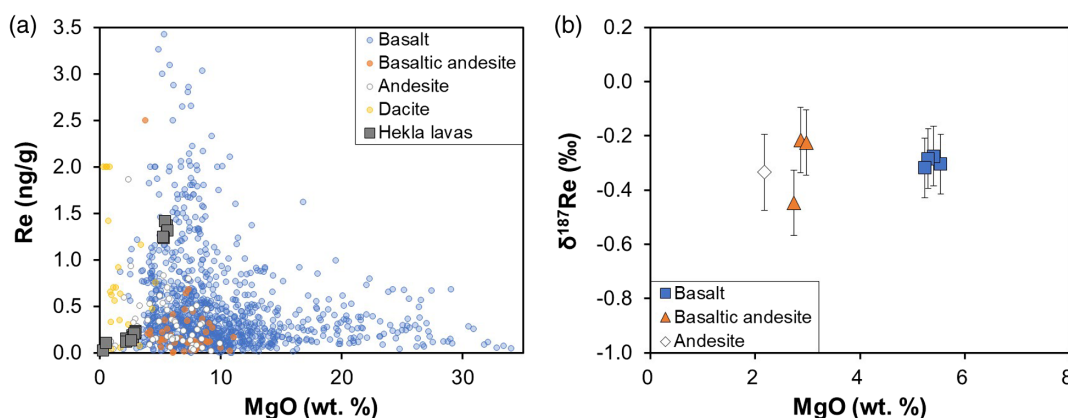


Figure 1 (a) A compilation of Re contents in igneous rock samples from the GEOROC database (<http://georoc.eu>; DIGIS Team, 2023) and from this study (Hekla lavas). (b) Re isotope ($\delta^{187}\text{Re}$) variations with MgO content in the Hekla lavas. Uncertainties on $\delta^{187}\text{Re}$ represent the 2 s.d. of repeat multi-collector ICP-MS measurements on the same sample (or 2 s.e. internal error if there was only one measurement), or the long-term reproducibility for the standard solution (ICP; 0.11 ‰), whichever is larger (Table S-2).

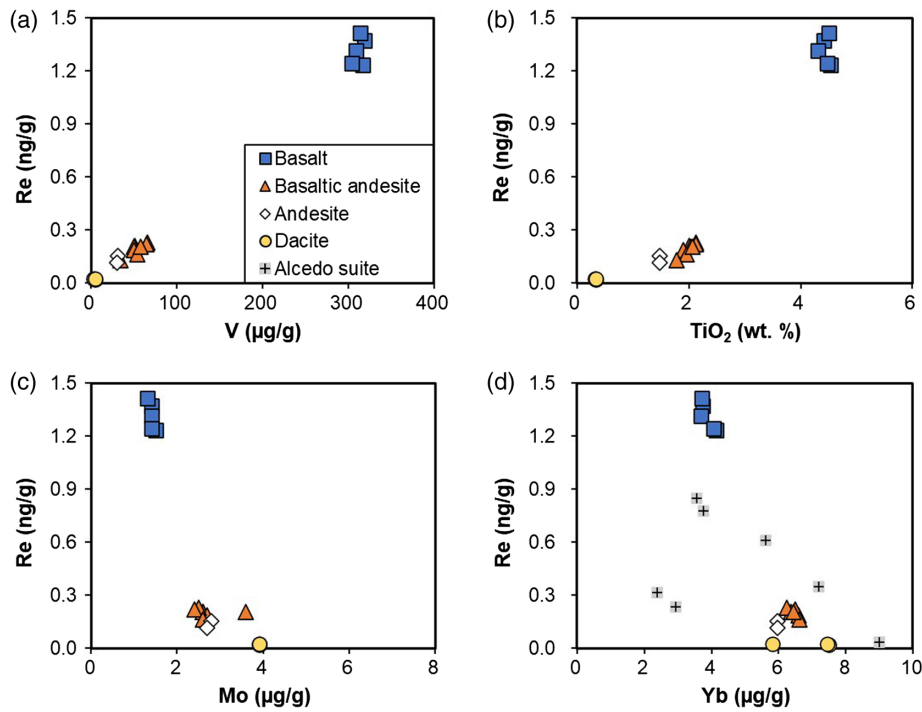


Figure 2 Re variations in the Hekla lavas with the concentrations of (a) V, (b) TiO₂, (c) Mo and (d) Yb. Ancillary major and trace element data are given in Table S-3. In (d), Alcedo suite data from Richter *et al.* (1998) are plotted in grey for comparison. Error bars on the data are smaller than the size of symbols.

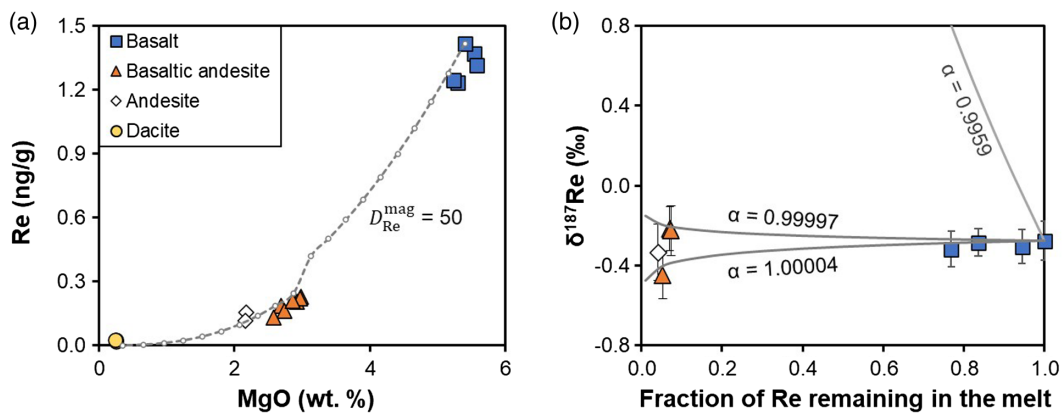


Figure 3 (a) Cotectic fractional crystallisation model (dashed line) for the evolution of Re in Hekla lavas. The fractionating assemblage at Hekla consists of orthopyroxene, plagioclase, clinopyroxene and (titano)magnetite (Sigmarsson *et al.*, 1992; Geist *et al.*, 2021). (b) Rayleigh fractionation model (solid lines) for assessing the extent of Re isotope fractionation during magma processes. Details of the modelling approach are given in Supplementary Information.

Richter *et al.*, 1998) but is incompatible in hydrous systems, analogous to some high field strength elements (Nielsen and Beard, 2000).

Although it is generally accepted that Re is compatible in sulfide minerals under relatively reduced environments (*e.g.*, Fonseca *et al.*, 2007), we found no evidence for the partitioning of Re into sulfides in the Hekla lavas. While some studies found traces of sulfide saturation and mineral formation in the Hekla lavas (Geist *et al.*, 2021), others did not (Moune *et al.*, 2007). The expected loss of molybdenum (Mo), another chalcophile element, due to sulfide extraction was also not observed (Yang *et al.*, 2015). High-pressure experiments conducted at ~FMQ–1.8 to FMQ+1.5 show a strong correlation between the partition coefficients of Re and Mo between sulfide liquid,

monosulfide solid solution and silicate melts (Feng and Li, 2019), suggesting similar partitioning behaviours of Re and Mo between these phases. In the Hekla lavas, however, we find that the concentration of Re decreases with increasing Mo (Fig. 2c). We note that Hekla lavas do show a pronounced drop in sulfur (S) concentrations through two orders of magnitude from the basalt to the andesite and dacite (Table S-3), but this is likely the result of sulfur degassing (Moune *et al.*, 2007).

Whether Re and ytterbium (Yb) share a similar degree of incompatibility during differentiation is debated. Although early studies on mantle-derived magmas (*e.g.*, Hauri and Hart, 1997; Sun *et al.*, 2003a) found roughly constant Yb/Re ratios, others suggested that the Re–Yb similarity is not ubiquitous (*e.g.*, Mallmann and O’Neill 2007; Li, 2014). We show clearly



that, in the Hekla lavas, Re is not enriched in evolved rocks (basaltic andesite, andesite, dacite) in the same way as Yb; Richter *et al.* (1998) observed a similar relationship between Re and Yb in their Galapagos icelandite to rhyolite sequence (Fig. 2d).

A compilation of Re concentrations in igneous rock samples (basalt, basaltic andesite, andesite and dacite) from the GEOROC database is presented in Figure 1a. Rhenium concentrations appear to increase with decreasing MgO, to a Re concentration peak at ~5 wt. % MgO, which could be primarily explained by the incompatibility of Re in common mafic phases, such as olivine and clinopyroxene. Whilst global igneous suites have varying degrees of sulfide saturation such that sequestration of Re by sulfide is plausible (*e.g.*, Feng and Li, 2019; Liu and Li, 2023), we propose that at lower MgO, crystallisation of oxide minerals also exerts a control on the behaviour of Re.

No resolvable Re isotope fractionation during magnetite crystallisation. Despite the very large range in Re concentrations, there is no statistically significant difference, within uncertainties, between the $\delta^{187}\text{Re}$ values for different types of rocks (basalt, basaltic andesite and andesite) of the Hekla suite. No clear trend or systematic variation in $\delta^{187}\text{Re}$ values is observed when plotted against concentrations of MgO, SiO₂, TiO₂, S, V, Mo, Yb or Re in the Hekla lavas. (Figs. 1b, S-1). The Hekla lava samples showed an average $\delta^{187}\text{Re}$ of -0.30 ± 0.14 ‰ (2 s.d., $n = 8$).

The relatively constant $\delta^{187}\text{Re}$ (despite systematically varying Re concentrations) during magmatic evolution implies minor Re isotope fractionation between the crystallising minerals and silicate melt. In general, the magnitude of equilibrium isotope fractionation in high-temperature geological environments depends on differences in bond strength, which are dominantly related to oxidation states and cation coordination. When the solid phase is an oxide, such as (titano)magnetite, Re likely occurs in the +4 state as ReO₂ (Richter *et al.*, 1998; Xiong and Wood, 1999). In the silicate melt, Re is mainly found as ReO₂ (Re⁴⁺) and ReO₃ (Re⁶⁺) species at typical terrestrial magma oxygen fugacities (Xiong and Wood, 1999; Ertel *et al.*, 2001); Re⁶⁺ is highly incompatible in mantle minerals (Mallmann and O'Neill, 2007; Liu and Li, 2023). No experimentally determined isotope fractionation factor between different Re molecules has been reported, but we adopt the electronic structure modelling by Miller *et al.* (2015) as a first approximation. Of all the Re⁴⁺ and Re⁷⁺ species investigated, excluding Re in the thiolated form, the net equilibrium fractionation factor (α) of Re, considering the combined mass dependent and nuclear volume effects at estimated Hekla magmatic temperatures of ~1000 °C (Geist *et al.*, 2021), is very close to unity: ~0.99997 to 1.00004 (Miller *et al.*, 2015; assuming $\alpha = e^{\delta^{187}\text{Re}_{\text{Re}^{6+}} - \delta^{187}\text{Re}_{\text{Re}^{7+}}}$). We may expect the equilibrium isotope fractionation between Re⁴⁺ and Re⁶⁺ oxides to be even smaller. If we apply 0.99997 and 1.00004 as an estimation for the bulk Re isotope fractionation factor, then a Rayleigh fractionation model suggests that crystallisation of magnetite would lead to only subtly heavier or lighter $\delta^{187}\text{Re}$ in the residual melt (Fig. 3b). The very subtle Re isotope fractionation in compositionally evolved lithologies may not be resolvable at current levels of precision.

The absence of significant Re isotope fractionation during magmatic processes at Hekla supports magnetite crystallisation as the dominant process instead of Re degassing. The volatility of Re has been reported in several magmatic systems (*e.g.*, Norman *et al.*, 2004), but kinetic isotope fractionation of Re is expected during degassing. The theoretical maximum Rayleigh fractionation coefficient (α) during vaporisation as Re₂O₇ gas can be calculated as the inverse square root of the mass of the Re isotopes ($\sqrt{481.899/485.905} = 0.9959$) (*e.g.*, Richter *et al.*, 2007).

If degassing of Re is the dominant process during the evolution of the Hekla lavas, we would expect the $\delta^{187}\text{Re}$ in the residual silicate melts to become progressively heavier; this model is illustrated in Figure 3b, which does not agree with the observed relatively narrow range (-0.45 to -0.22 ‰). Given the volatile behaviour of Re and that the Re isotope system is insensitive to fractional crystallisation, $\delta^{187}\text{Re}$ can potentially be used as a discriminant of Re degassing in magmatic processes.

Implications for a first estimate of a Re isotope terrestrial baseline. Whilst degassing of Re and post-eruption alteration have the potential to modify the Re isotope signature, we have been able to demonstrate that Re isotope fractionation between crystallising minerals (magnetite) and silicate melt during magmatic processes is not analytically resolvable at the current stage. Un-degassed and unaltered igneous rocks therefore have the potential to infer the Re isotopic composition of their source. Although sourced from different tectonic settings and mantle depths, our analysed other Icelandic basalts (RP80C-1 and BUR20-09) and MORBs (from the Atlantic, Pacific and Indian Oceans) also show limited Re isotopic variability (-0.44 to -0.33 ‰), overlapping with the Hekla lava $\delta^{187}\text{Re}$ (-0.45 to -0.22 ‰) (Table S-2; Fig. 4). We note that these Re isotope values are also indistinguishable within uncertainty from the $\delta^{187}\text{Re}$ of carbonaceous chondrite (-0.29 ± 0.03 ‰, CV3 Allende; Dellinger *et al.*, 2020; Fig. 4), as well as our analysed standard reference materials BHVO-2 (Hawaiian basalt), BIR-1 (Icelandic basalt) and BCR-2 (Columbia River Flood basalt) (Table S-1).

With the current data, the restricted range in $\delta^{187}\text{Re}$ values of the compositionally diverse igneous samples (eight Hekla lavas, two other Icelandic basalts, three MORBs, one chondrite) makes it possible to propose a first estimate of a terrestrial baseline for Re isotopes (-0.33 ± 0.15 ‰, 2 s.d., $n = 14$). Available Re isotope data (Fig. 4) suggest that the $\delta^{187}\text{Re}$ of Atlantic seawater (-0.17 ± 0.12 ‰, 2 s.d., $n = 12$; Dickson *et al.*, 2020) is isotopically heavy compared to this baseline. Whilst the only published $\delta^{187}\text{Re}$ values for river water (-0.29 ± 0.09 ‰, 2 s.d., $n = 10$; Dellinger *et al.*, 2021) are within the baseline range, sedimentary rock $\delta^{187}\text{Re}$ from New Albany shales (around -0.6 ‰;

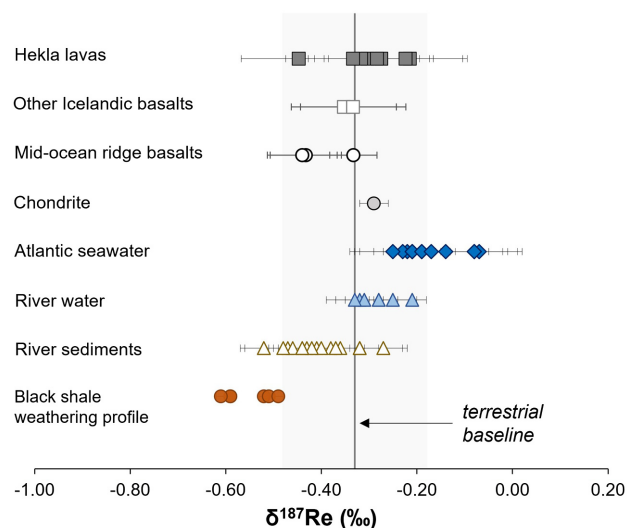


Figure 4 Available terrestrial Re isotope data (relative to NIST3143) measured to date. Data are from this study (Hekla lavas, other Icelandic basalts, MORBs; Table S-2), Dellinger *et al.* (2020; carbonaceous chondrite), Dickson *et al.* (2020; Atlantic seawater), Dellinger *et al.* (2021; Mackenzie River water and river sediments) and Miller *et al.* (2015; New Albany shale).

Miller *et al.*, 2015) and Mackenzie River sediments (around -0.52 to -0.27 ‰; Dellinger *et al.*, 2021) all exhibit offsets to lighter isotopic values. This illustrates notable isotopic variability during the surface cycling of Re, both in terms of weathering processes on land, likely *via* preferential oxidation of reactive phases with heavy $\delta^{187}\text{Re}$ (Dellinger *et al.*, 2021), and in terms of isotopically light sinks for Re in the oceans and/or input of Re to the oceans from other sources that are yet to be discovered (Dickson *et al.*, 2020). While there is a clear need for extending the analysis of stable Re isotopes in the Earth's igneous reservoirs, results from this study are pivotal for interpreting the causes of Re isotope variations in low-temperature natural environments.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2402>.



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Rhenium elemental and isotopic variations at magmatic temperatures

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Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- Tables S-1 to S-3
- Figure S-1
- Supplementary Information References

Materials and Methods

Hekla lavas

Hekla is a ridge shaped volcano in the South Iceland Volcanic Zone, and is, historically, one of the most active volcanoes on Iceland. It erupts a wide range of volcanic products with a range of SiO₂ from ~46 to 72 wt. %, covering basalts, basaltic andesites, andesites, dacites and rhyolites, from a cogenetic source (*e.g.*, Savage *et al.*, 2011).

It was generally considered that for the Hekla lavas: (1) basaltic magmas rise and trigger partial melting of the lower part of metabasaltic Icelandic crust to generate dacitic magma; (2) the basaltic magma and dacitic magma evolve by crystal fractionation, producing basaltic andesite and rhyolitic magma, respectively; (3) mixing of basaltic andesite and dacitic melts produces andesites (Sigmarsson *et al.*, 1992, 2022). However, it has recently been suggested that mineral compositional data are more consistent with the origin of the basaltic andesites and andesites by fractional crystallization (Geist *et al.*, 2021), arguing against the three-stage model.



This issue of the origin of the dacites—whether by fractional crystallisation of andesites or *via* partial melting of amphibolite—continues to be debated (*cf.* Sigmarsson, 2023; Geist *et al.*, 2023). However, the disagreement over the origin of the andesitic to silicic magma is not a concern for this study, as long as magmatic differentiation and/or remelting of cognate material link the production of the entire sequence of Hekla lavas. Furthermore, the origin of the basalt to basaltic andesites *via* fractional crystallisation is not contested, and it is this range where Re concentrations were high enough to determine Re isotopic compositions.

A previous study by Savage *et al.* (2011) on the same samples showed that silicon isotopic compositions correlate with SiO₂ content. Redox-sensitive isotope systems such as Fe and V also showed systematic isotopic fractionations during fractional crystallization (Schuessler *et al.*, 2009; Prytulak *et al.*, 2017). In contrast, for Li, Zn, Mo, Tl, K, N and Rb, no resolvable isotopic variation was found among the Hekla series of igneous rocks (Schuessler *et al.*, 2009; Chen *et al.*, 2013; Yang *et al.*, 2015; Prytulak *et al.*, 2017; Tuller-Ross *et al.*, 2019; Boocock *et al.*, 2023; Wang *et al.*, 2023).

Additional samples

Additional unrelated Icelandic samples are reported in this study. The sample RP80C-1 was dredged from 63° 49' N, 22° 39' W on the neovolcanic axis of the Reykjanes Ridge during the cruise CD80 of RRS Charles Darwin (Murton *et al.*, 2002); this sample has been previously analysed for strontium, lead and oxygen isotope ratios (Gee *et al.*, 1998; Thirlwall *et al.*, 2004, 2006). The samples BUR20-09 and RHY1-09 were collected from near Burfell, Iceland; their compositions have been widely reported in comparison to the Hekla lavas (*e.g.*, Yang *et al.*, 2015; Tuller-Ross *et al.*, 2019).

Three MORB samples from different mid-ocean ridge segments (one from the North Atlantic Ocean, one from the East Pacific Ocean, one from the Indian Ocean) were analysed in order to provide better constraints on Re isotopic composition of the upper mantle. Samples vary in chemical composition, with MgO ranging from ~6.8 to 7.8 wt. %. According to Marty and Zimmerman (1999), based on the measured K₂O/TiO₂ ratios, these MORB samples can be classified into two types: N-MORB (RDL DR30 and CYP 78 12-35; K₂O/TiO₂ < 0.08) and E-MORB (MD57 D'10-1; K₂O/TiO₂ > 0.15).



Rhenium concentration and isotope analysis

The Re concentrations of the samples were determined by isotope dilution following established methods (Birck *et al.*, 1997). Approximately 200 mg of sample powder was weighted into 7 mL PFA vials and ^{185}Re spike was added to each sample. Following equilibration, the digestion was achieved with 3:1 HF:HNO₃, and then 6 M HCl. Samples were subsequently taken up in 2 M HNO₃ and Re was extracted using 3-methyl-1-butanol (isoamylol) liquid-liquid extraction. The purified samples were re-dissolved in 0.4 mL 3 % HNO₃ containing 30 ppb W, and were measured on multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Neptune Plus) at Royal Holloway University of London. The Re concentration was calculated based on the known sample volume and the quantity of added spike.

The low Re concentration of these samples means that a mass of at least ~1 g (for the lowest Re concentration samples, up to ~10 g) is necessary for the precise determination of stable Re isotopes ($\delta^{187}\text{Re}$). Aliquots of sample powders (~1 g) were initially digested in 3:1 concentrated HF and HNO₃ in 30 mL PFA vials at 120 °C for at least 48 h; note that digestion in multiple vials is typically needed for one sample. The samples were slowly evaporated to dryness and re-dissolved in aqua regia and heated at 120 °C to destroy fluorides, before being evaporated again. The samples were then taken up in 6 M HCl. A pressure digestion system (PicoTrace) was further utilised if undissolved material remained (Jerram *et al.*, 2020). Finally, samples were re-dissolved in 1 M HCl (20–40 mL for every ~1 g sample aliquot); care was taken to ensure complete dissolution.

Prior to the isotopic analysis, the Re was purified using a three-step column procedure, adapted from Dellinger *et al.* (2020) and Dickson *et al.* (2020). First, 2 mL AG1-X8 (200–400 mesh) anion exchange resin was loaded into polypropylene BioRad columns, and was cleaned with 30 mL 7.5 M HNO₃ and pre-conditioned with, respectively, 10 mL 4 M and 3 mL 1 M HCl. Samples were loaded onto the columns in 1 M HCl, with a further addition of 20 mL 1 M HCl and 4 mL 3 M HNO₃ to remove matrix elements and transition metals. Thereafter, Re was eluted with 15 mL 7.5 M HNO₃. Note that some samples were dissolved in large volume of 1 M HCl (up to 200 mL, considering multiple aliquots/vials). In this case, in order to reduce the loading time, it was advisable to use multiple polypropylene BioRad columns for one same sample at this step; the collected fractions were then combined before loaded onto the micro-column (as below).

In the second step, samples were evaporated to dryness, re-dissolved in 1 mL 1 M HCl, and loaded onto 200 μL anion resin in Teflon micro-columns. Matrix elements were eluted with the additions of 1.5 mL 1 M HCl and 0.4 mL 3 M HNO₃. Re was then eluted with 2 mL 7.5 M HNO₃. This second step was repeated



one more time to purify the Re from the residual matrix. Samples were refluxed in concentrated HNO₃ at 120 °C for at least 24 h after each column step to destroy resin-derived organic residues.

The stable Re isotopic composition of the samples was determined by MC-ICP-MS (Neptune Plus) at Royal Holloway University of London, using the same methods as described in Dickson *et al.* (2020). The instrument was fitted with 10¹³ Ω amplifiers and was running in wet plasma mode with standard wet-plasma sample cones and ‘H’ skimmer cones. Purified samples with concentrations of ~1 to 3 ppb Re were introduced using a quartz SIS spray chamber and signals from ¹⁸⁴W, ¹⁸⁵Re, ¹⁸⁶W, ¹⁸⁷Re, ¹⁸⁹O_s and ¹⁹⁰O_s were quantified. Each analytical sequence consisted of repeat analyses of the NIST3143 and NIST989 standard reference materials (SRM) with every three samples. Each measurement comprised a single block of 40 × 8.5 s integrations, preceded by 10 integrations of 3 % HNO₃ blank solution.

The instrumental mass bias was corrected by doping each sample to 30 ppb tungsten (W) with NIST SRM 3163, and by using an exponential law with the measured ¹⁸⁶W/¹⁸⁴W (Miller *et al.*, 2015; Dellinger *et al.*, 2020; Dickson *et al.*, 2020). This method assumed that W and Re share the same degree of mass bias in the instrument (Poirier and Doucelance, 2009). The Re/W ratios for the measured samples were within ±10 % of that for the bracketing standards. The final Re isotope value of the samples was reported in delta notation relative to the NIST SRM 3143 and expressed as:

$$\delta^{187}\text{Re} (\text{‰}) = [({}^{187}\text{Re}/{}^{185}\text{Re})_{\text{sample}}/({}^{187}\text{Re}/{}^{185}\text{Re})_{\text{NIST3143}} - 1] \times 1000 . \quad (\text{S-1})$$

The overall procedure blank for the Re isotope analysis (digestion and purification) was below 10 pg Re, which was <2 % of the total Re analysed. Rhenium isotope fractionation can occur during column chromatography (Miller *et al.*, 2009; Liu *et al.*, 2017). The recovery of Re in this study was >60 % for all samples. As shown in Miller *et al.* (2009), when eluting the Re using 4 M HNO₃, a >60 % recovery will likely lead to <0.05 ‰ fractionation; this is smaller than the analytical error presented in this study. Furthermore, as discussed in Dellinger *et al.* (2020) and Dickson *et al.* (2020), column fractionation effects are likely negligible when eluting Re with higher molarity of HNO₃; consistent with Dellinger *et al.* (2020) and Dickson *et al.* (2020), in this study the elution was done with 7.5 M HNO₃, which should render any measurable fractionation minimal.



The precision and accuracy of the above methods were further validated through the analysis of (1) NIST 989 and ICP Re standard solutions, and (2) inter-comparison samples, including BHVO-2, BIR-1, BCR-2 and MAG-1; the results are summarised in Table S-1.

Modelling the evolution of Re and $\delta^{187}\text{Re}$

We aim to produce an internally consistent model for Re-MgO during magma differentiation, and undertook the same modelling approach as described Prytulak *et al.* (2017). The fractionating assemblage at Hekla consists of olivine (and later orthopyroxene), plagioclase, clinopyroxene and titanomagnetite (Sigmarsson *et al.*, 1992; Geist *et al.*, 2021). We use the most primitive (highest Re concentration) lavas as a starting point, and the modelling was performed at 5 % intervals of melt remaining (F). The Re partition coefficients for orthopyroxene and clinopyroxene are taken as 0.013 and 0.2, respectively, based on Li (2014) and references therein. The Re partition coefficient for magnetite is adjusted so as to best fit the data, and is derived to be $D_{\text{Re}}^{\text{Mag}} \approx 50$. This is nevertheless consistent with the MELTS modelling results by Righter *et al.* (1998) for a sulfide-free system.

A Rayleigh fractionation model is applied to assess the extent of Re isotope fractionation during crystallisation:

$$\delta^{187}\text{Re}_{\text{melt}} = \delta^{187}\text{Re}_{\text{bulk}} + \Delta^{187}\text{Re}_{\text{min-melt}} \ln(F_{\text{Re}}), \quad (\text{S-2})$$

where F_{Re} is the fraction of Re remaining in the liquid. Changes in the abundance of perfectly incompatible elements have been used to estimate the fraction of melt remaining in evolving magmatic systems; here we choose Rubidium (Rb) for the calculation (Prytulak *et al.*, 2017). We assume 1.00005 as the bulk Re isotope fractionation factor during crystallisation of magnetite, based on theoretical modelling by Miller *et al.* (2015). On the other hand, if kinetic fractionation occurs during degassing of Re, then the Re isotope fractionation factor would possibly be as large as ~ 0.9959 . The modelling results are illustrated in Figure 3.



Supplementary Tables

Table S-1 Re isotopic composition for standard solutions and method validation samples.

Sample	Measured values				Recommended values	
	Re (ng/g)	$\delta^{187}\text{Re}$ (‰)	2 s.d. (‰)	No. of measurements	Re (ng/g)	$\delta^{187}\text{Re}$ (‰)
<i>Standard solutions</i>						
NIST 989		-0.28	0.05	18		-0.29 ± 0.07 ‰ (Miller <i>et al.</i> , 2009), -0.28 ± 0.05 ‰ (Dellinger <i>et al.</i> , 2020), -0.27 ± 0.10 ‰ (Dickson <i>et al.</i> , 2020)
ICP Re		-0.16	0.11	15		-0.15 ± 0.07 ‰ to -0.19 ± 0.09 ‰ (Dickson <i>et al.</i> , 2020)
	Re (ng/g)	$\delta^{187}\text{Re}$ (‰)			Re (ng/g)	$\delta^{187}\text{Re}$ (‰)
	(1)	2 s.e.	(2)	2 s.e.		
<i>Inter-comparison samples</i>						
BHVO-2 (Hawaiian basalt)	0.55	-0.25	0.19			-0.34 ± 0.06 ‰ (Dellinger <i>et al.</i> , 2020)
BHVO-2 (Hawaiian basalt) (replicate)		-0.42	0.12			
BIR-1 (Icelandic basalt)	0.64	-0.28	0.09	-0.28	0.10	-0.34 ± 0.07 ‰ (Dellinger <i>et al.</i> , 2020)
BCR-2 (Columbia River Flood basalt)	11.0	-0.25	0.04	-0.26	0.10	-0.29 ± 0.04 ‰ (Dellinger <i>et al.</i> , 2020)
BCR-2 (Columbia River Flood basalt) (replicate)		-0.35	0.07	-0.36	0.06	
MAG-1 (marine mud)	3.10	-0.36	0.09	-0.38	0.09	-0.28 ± 0.05 ‰ (Dellinger <i>et al.</i> , 2020)

2 s.d. = 2 times standard deviations of replicated analyses of the sample; 2 s.e. is the internal error of each individual MC-ICP-MS measurement and reflects the analytical uncertainty. Numbers (1) and (2) represent up to two repeat MC-ICP-MS measurements on the same sample solution.



Table S-2 All Re data presented in this study.

Sample	Re (ng/g)		$\delta^{187}\text{Re}$ (‰)						Description	Age	
	Average	2 s.d.	(1)	2 s.e.	(2)	2 s.e.	Average	2 s.d.			
<i>Hekla lavas</i>											
HEK1-09	0.021	0.002								Dacite	2800 BP
HEK2-09	0.209	0.003	-0.22	0.11			-0.22	N.A.		Basaltic andesite	1970 AD
HEK3-09	0.206	0.004								Basaltic andesite	1970 AD
HEK4-09	1.372	0.006	-0.28	0.09	-0.33	0.10	-0.30	0.06		Basalt	1878 BP
HEK6-09	1.417	0.006	-0.28	0.10			-0.28	N.A.		Basalt	1913 AD
HEK7-09	1.317	0.006								Basalt	1878 AD
HEK8-09	0.187	0.005								Basaltic andesite	1970 AD
HEK9-09	1.234	0.007	-0.26	0.07	-0.31	0.06	-0.28	0.08		Basalt	1878 AD
HEK10-09	0.154	0.002	-0.33	0.14			-0.33	N.A.		Andesite	1947 AD
HEK11-09	0.117	0.003								Andesite	1947 AD
HEK12-09	1.246	0.005	-0.31	0.09	-0.33	0.08	-0.32	0.03		Basalt	1913 AD
HEK13-09	0.231	0.003								Basaltic andesite	1991 AD
HEK14-09	0.221	0.004	-0.22	0.12			-0.22	N.A.		Basaltic andesite	1991 AD
HEK16-09	0.165	0.004	-0.45	0.12			-0.45	N.A.		Basaltic andesite	1980 AD
HEK17-09	0.209	0.003								Basaltic andesite	1980 AD
HEK18-09	0.026	0.003								Dacite	2800 BP
HEK19-09	0.026	0.002								Dacite	2800 BP
HEK21-09	0.132	0.009								Basaltic andesite	1390 AD



Table S-2 continued

Sample	Re (ng/g)		$\delta^{187}\text{Re}$ (‰)						Description	Age
	Average	2 s.d.	(1)	2 s.e.	(2)	2 s.e.	Average	2 s.d.		
<i>Other Icelandic</i>										
RP80C-1	0.851	0.017	-0.30	0.11	-0.32	0.11	-0.33	0.08 (<i>n</i> = 5)	Basalt	8000–9000 BP
RP80C-1 (<i>replicate 1</i>)			-0.40	0.07	-0.33	0.06				
RP80C-1 (<i>replicate 2</i>)			-0.32	0.09						
BUR20-09	0.631	0.004	-0.40	0.10	-0.31	0.08	-0.35	0.13	Basalt	~1700 AD
RHY1-09	0.103	0.002							Dacite	Postglacial
<i>Mid-ocean ridge basalts</i>										
RDL DR30	0.781	0.015	-0.33	0.06			-0.33	N.A.	Atlantic Ocean (21° 82' N, 45° 22' W)	
CYP 78 12-35	1.431	0.029	-0.44	0.07			-0.44	N.A.	Pacific Ocean (20° 90' N, 109° 05' W)	
MD57 D'10-1	0.991	0.020	-0.43	0.08			-0.43	N.A.	Indian Ocean (06° 22' S, 68° 25' E)	

2 s.d. = 2 times standard deviations of repeat analyses of the sample; 2 s.e. is the internal error of each individual MC-ICP-MS measurement; N.A. = not available. Numbers (1) and (2) represent up to two repeat MC-ICP-MS measurements on the same sample solution.

In Figures 1 and 3, uncertainties on $\delta^{187}\text{Re}$ represent the 2 s.d. of repeat MC-ICP-MS measurements on the same sample (or 2 s.e. internal error if there was only one measurement), or the long-term reproducibility for the standard solution (ICP: 0.11 ‰; Table S-1), whichever is larger. Uncertainties on Re concentration represent the 2 s.d. of repeat measurements on the same sample; for the MORBs, a 2 % uncertainty is assigned as an estimate of the external reproducibility.



Table S-3 Ancillary data presented in this study.

Sample	SiO ₂ (wt. %)	MgO (wt. %)	TiO ₂ (wt. %)	S (µg/g)	Mo (µg/g)	V (µg/g)	Yb (µg/g)	Th (µg/g)	Rb (µg/g)
<i>Hekla lavas</i>									
HEK1-09	68.71	0.26	0.33	0	3.9	5	7.49	9.0	54.1
HEK2-09	53.92	2.86	2.01	31	2.6	50	6.48	3.7	24.8
HEK3-09	54.05	2.92	2.04	40	2.6	49	6.37	4.6	24.9
HEK4-09	46.97	5.53	4.42	123	1.4	319	3.73	2.1	12.1
HEK6-09	46.20	5.40	4.51	172	1.3	314	3.72	2.2	11.8
HEK7-09	46.64	5.57	4.31	124	1.4	309	3.69	2.7	12.7
HEK8-09	54.59	2.68	1.90	49	2.7	49	6.60	4.8	27.0
HEK9-09	47.01	5.30	4.53	122	1.5	317	4.14	2.3	12.3
HEK10-09	57.67	2.17	1.48	15	2.8	32	5.96	3.3	31.2
HEK11-09	58.09	2.16	1.47	6	2.7	30	5.98	5.3	31.2
HEK12-09	46.42	5.23	4.47	104	1.4	304	4.05	3.3	13.5
HEK13-09	53.90	2.98	2.12	57	2.5	66	6.25	4.5	23.8
HEK14-09	53.71	2.97	2.12	39	2.4	64	6.49	4.5	24.9
HEK16-09	54.81	2.74	1.96	42	2.6	53	6.61	4.7	25.7
HEK17-09	54.57	2.86	2.06	58	3.6	57	6.44	4.6	25.5
HEK18-09	68.41	0.25	0.31	2	3.9	2	7.49	9.2	53.2
HEK19-09	68.88	0.25	0.32	0	3.9	4	7.45	9.7	55.7
HEK21-09	55.64	2.58	1.77	26	2.7	34	6.74	4.9	28.6



Table S-3 continued

Sample	SiO ₂ (wt. %)	MgO (wt. %)	TiO ₂ (wt. %)	S (µg/g)	Mo (µg/g)	V (µg/g)	Yb (µg/g)	Th (µg/g)	Rb (µg/g)
<i>Other Icelandic</i>									
RP80C-1	N.A.	8.15	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
BUR20-09	49.05	7.57	1.47	0	0.3	300	2.38	0.3	2.9
RHY1-09	68.53	0.54	0.43	6	6.0	16	5.81	18.2	111
<i>Mid-ocean ridge basalts</i>									
RDL DR30	51.25	7.01	1.75	1540	0.2	390	4.84	0.2	1.1
CYP 78 12-35	50.61	7.81	1.46	1198	0.2	296	3.36	0.2	1.4
MD57 D'10-1	50.69	6.84	1.68	1127	0.4	316	3.36	0.6	5.3

Ancillary data for the Hekla lavas and other Icelandic samples are from: Savage *et al.* (2011) (major elements), Prytulak *et al.* (2017) (trace elements), Thirlwall *et al.* (2006) (RP80C-1); ancillary data for the MORBs are partly from Gannoun *et al.* (2007).



Supplementary Figures

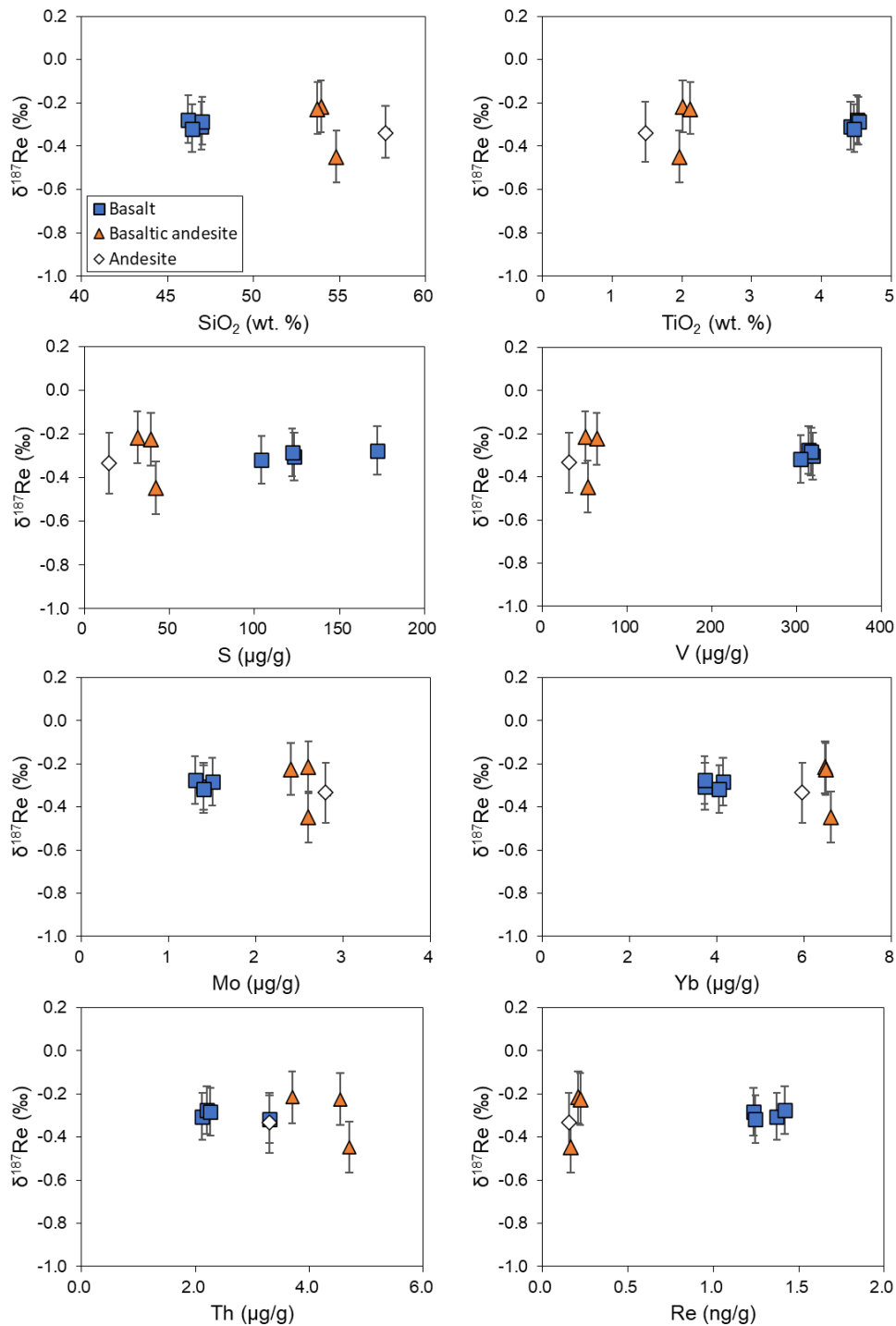


Figure S-1 Re isotope ($\delta^{187}\text{Re}$) variations with SiO_2 , TiO_2 , S, V, Mo, Yb, Th, and Re concentrations in the Hekla lavas. Error bars on $\delta^{187}\text{Re}$ represent the 2 s.d. of repeat MC-ICP-MS measurements on the same sample (or 2 s.e. internal error if there was only one measurement), or the long-term reproducibility for the standard solution (ICP: 0.11 ‰), whichever is larger.



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