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# Rhenium elemental and isotopic variations at magmatic temperatures

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Wenhao Wang<sup>1</sup>, Alexander J. Dickson<sup>1</sup>, Madeleine A. Stow<sup>2</sup>, Mathieu Dellinger<sup>3,4</sup>, Kevin W. Burton<sup>3</sup>, Paul S. Savage<sup>5</sup>, Robert G. Hilton<sup>2</sup>, Julie Prytulak<sup>3</sup>

<sup>1</sup> Centre of Climate, Ocean and Atmosphere, Department of Earth Sciences, Royal Holloway University of London, Egham, UK

<sup>2</sup> Department of Earth Sciences, University of Oxford, Oxford, UK

<sup>3</sup> Department of Earth Sciences, Durham University, Durham, UK

<sup>4</sup> Environnements Dynamiques et Territoires de la Montagne (EDYTEM), CNRS – Université Savoie Mont-Blanc, Le Bourget du Lac, France

<sup>5</sup> School of Earth and Environmental Sciences, University of St. Andrews, Bute Building, Queen's Terrace, St Andrews, UK

## Abstract

Recent analytical advances in the measurement of rhenium (Re) isotope ratios allow its potential as a paleoredox 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 0.02–1.4 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 ( $\delta^{187}\text{Re} = -0.33 \pm 0.15 \text{ ‰}$ , 2SD, 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.

**Key words:** rhenium isotopes, Hekla, magmatic processes, terrestrial baseline, geochemical cycling of rhenium

## 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 (Sun *et al.*, 2003a,b; Peucker-Ehrenbrink and Jahn, 2001). 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.*, 2003a; Xue and Li, 2021) 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 (Righter *et al.*, 2004; Mallmann and O'Neill, 2007), the sulphur and oxygen fugacity ( $fS_2$  and  $fO_2$ ) controls on Re partitioning appear to be complicated. For example, Re is predicted to behave as a lithophile element under sulphide-poor and/or relatively oxidised conditions (such as during differentiation of arc magmas), whereas Re behaves chalcophile in reduced mid-ocean ridge basalt (MORB) type mantle and becomes more compatible with lower  $fO_2$  (Fonseca *et al.*, 2007; Mallmann and O'Neill, 2007); oxides such as magnetite can also potentially host Re (Righter *et al.*, 1998; Li, 2014).

Rhenium has two isotopes,  $^{187}\text{Re}$  and  $^{185}\text{Re}$ , which comprise ~ 63 % and 37 % of natural Re respectively. The  $^{187}\text{Re}$  isotope is radioactive, but decays with a very long half-life ( $4.12 \times 10^{10}$  yr; Smoliar *et al.*, 1996), making the isotope ratio of  $^{187}\text{Re}$  and  $^{185}\text{Re}$  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.*, 2016) and standard reference materials (Dellinger *et al.*, 2020). No studies have investigated the behavior 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).

## **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.%  $\text{SiO}_2$ ) 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, MD57 D'10-1; [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 concentration of these samples means 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 [Table S-1, 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  $-0.28 \pm 0.11$  to  $-0.32 \pm 0.11$  ‰, and from  $-0.22 \pm 0.11$  to  $-0.45 \pm 0.12$  ‰ for the basalt and basaltic andesites respectively, and a composition of  $-0.33 \pm 0.14$  ‰ (2SD) 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,  $-0.35 \pm 0.13$  to  $-0.33 \pm 0.11$  ‰, 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,  $-0.33 \pm 0.11$  to  $-0.44 \pm 0.11$  ‰.

## Discussion

## Evolution of Re during magmatic processes at Hekla volcano

The co-variations of Re with vanadium (V) and TiO<sub>2</sub> 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 TiO<sub>2</sub> (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 ( $D^{\text{mag}}_{\text{Re}}$ ) is  $\sim 50$ . Similar to this study, Richter *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 TiO<sub>2</sub> depletion trend. These same authors measured an extremely high Re content in a magnetite separate ( $\sim 40$  ng/g) and concluded that magnetite is a significant host phase for Re, with an estimated  $D^{\text{mag}}_{\text{Re}} = 20\text{--}50$  for a sulphide-free system. In support of this argument, Mallmann and O'Neill (2007) suggested that Re<sup>4+</sup> has a partitioning behaviour similar to Ti<sup>4+</sup> and could substitute for Ti<sup>4+</sup> in the solid phase. Note that  $f\text{O}_2$  (which is commonly reported in log units relative to the fayalite-magnetite-quartz (FMQ) buffer) 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  $f\text{O}_2$  is more reducing,  $\sim \text{FMQ}-3$  (Richter *et al.*, 1998). Lower  $f\text{O}_2$  would result in higher fraction of Re as Re<sup>4+</sup>, favouring dissolution of Re in common upper mantle minerals as well as in magnetite (Mallmann and O'Neill, 2007; Liu and Li, 2003). The similar  $D^{\text{mag}}_{\text{Re}}$  estimated for the two suites regardless of varying  $f\text{O}_2$  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;

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 sulphide minerals under relatively reduced environments (*e.g.*, Fonseca *et al.*, 2007), we found no evidence for the partitioning of Re into sulphides in the Hekla lavas. While some studies found traces of sulphide saturation and mineral formation in the Hekla lavas (Geist *et al.*, 2021), others do not (Moune *et al.*, 2007). The expected loss of molybdenum (Mo), another chalcophile element, due to sulphide extraction was also not observed (Yang *et al.*, 2015). High-pressure experiments conducted at  $fO_2$  of  $\sim$  FMQ-1.8 to FMQ+1.5 show a strong correlation between the partition coefficients of Re and Mo between sulphide liquid, monosulphide 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 sulphur (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 sulphur 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.*, 2003b) 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 Fig. 1a. Rhenium concentrations appear to increase with decreasing MgO, to a Re concentration peak at around ~ 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 sulphide saturation such that sequestration of Re by sulphide 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, SiO<sub>2</sub>, TiO<sub>2</sub>, S, V, Mo, Yb, or Re in the Hekla lavas. (Fig. 1b; Fig. S-1). The Hekla lava samples showed an average  $\delta^{187}\text{Re}$  of  $-0.30 \pm 0.14$  ‰ (2SD, 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 ReO<sub>2</sub> (Richter *et al.*, 1998; Xiong and Wood, 1999). In the silicate melt, Re is mainly found as ReO<sub>2</sub> (Re<sup>4+</sup>) and ReO<sub>3</sub> (Re<sup>6+</sup>) species at typical terrestrial magma

oxygen fugacities (Xiong and Wood, 1999; Ertel *et al.*, 2001);  $\text{Re}^{6+}$  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  $\text{Re}^{4+}$  and  $\text{Re}^{7+}$  species investigated, excluding Re in the thiolated form, the net equilibrium fractionation factor ( $\alpha$ ) of Re considering the combined mass dependent and nuclear volume effects at estimated Hekla magmatic temperatures of  $\sim 1000^\circ\text{C}$  (Geist *et al.*, 2021) is very close to unity:  $\sim 0.99997$  to  $1.00004$  (Miller *et al.*, 2015; assuming  $\alpha = e^{\delta^{187}\text{Re}_{\text{Re}^{4+}} - \delta^{187}\text{Re}_{\text{Re}^{7+}}}$ ). We may expect the equilibrium isotope fractionation between  $\text{Re}^{4+}$  and  $\text{Re}^{6+}$  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 ( $\alpha$ ) during vaporisation as  $\text{Re}_2\text{O}_7$  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 heavy; this model is illustrated in Fig. 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 ( $-0.29 \pm 0.03$  ‰, 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 ( $-0.33 \pm 0.15$ ‰, 2SD, n=14). Available Re isotope data (Fig. 4) suggest that the  $\delta^{187}\text{Re}$  of Atlantic seawater ( $-0.17 \pm 0.12$ ‰, 2SD, 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 ( $-0.29 \pm 0.09$ ‰, 2SD, n=10; Dellinger *et al.*, 2021) are within the baseline range, sedimentary rock  $\delta^{187}\text{Re}$  from New Albany shales ( $\sim -0.6$ ‰; Miller

*et al.*, 2015) and Mackenzie River sediments (~ -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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## References

- Birck, J.L., Barman, M.R., Capmas, F. (1997) Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards Newsletter* 21(1), 19-27. <https://doi.org/10.1111/j.1751-908X.1997.tb00528.x>
- Dellinger, M., Hilton, R.G., Nowell, G.M. (2020) Measurements of rhenium isotopic composition in low-abundance samples. *Journal of Analytical Atomic Spectrometry* 35(2), 377-387. <https://doi.org/10.1039/C9JA00288J>
- Dellinger, M., Hilton, R.G., Nowell, G.M. (2021) Fractionation of rhenium isotopes in the Mackenzie River basin during oxidative weathering. *Earth and Planetary Science Letters* 573, 117131. <https://doi.org/10.1016/j.epsl.2021.117131>
- Dickson, A.J., Hsieh, Y.T., Bryan, A. (2020). The rhenium isotope composition of Atlantic Ocean seawater. *Geochimica et Cosmochimica Acta* 287, 221-228. <https://doi.org/10.1016/j.gca.2020.02.020>
- Ertel, W., O'Neill, H.S.C., Sylvester, P.J., Dingwell, D.B., Spettel, B. (2001) The solubility of rhenium in silicate melts: Implications for the geochemical properties of rhenium at high temperatures. *Geochimica et Cosmochimica Acta* 65(13), 2161-2170. [https://doi.org/10.1016/S0016-7037\(01\)00582-8](https://doi.org/10.1016/S0016-7037(01)00582-8)
- Feng, L., Li, Y. (2019) Comparative partitioning of Re and Mo between sulfide phases and silicate melt and implications for the behavior of Re during magmatic processes. *Earth and Planetary Science Letters* 517, 14-25. <https://doi.org/10.1016/j.epsl.2019.04.010>
- Fonseca, R.O., Mallmann, G., CO'Neill, H.S., Campbell, I.H. (2007) How chalcophile is rhenium? An experimental study of the solubility of Re in sulphide mattes. *Earth and Planetary Science Letters* 260(3-4), 537-548. <https://doi.org/10.1016/j.epsl.2007.06.012>
- Geist, D., Harpp, K., Oswald, P., Wallace, P., Bindeman, I., Christensen, B. (2021) Hekla revisited: fractionation of a magma body at historical timescales. *Journal of Petrology* 62(8), egab001. <https://doi.org/10.1093/petrology/egab001>
- Hauri, E.H., Hart, S.R. (1997) Rhenium abundances and systematics in oceanic basalts. *Chemical Geology* 139(1-4), 185-205. [https://doi.org/10.1016/S0009-2541\(97\)00035-1](https://doi.org/10.1016/S0009-2541(97)00035-1)

262 Li, Y. (2014) Comparative geochemistry of rhenium in oxidized arc magmas and MORB and  
 263 rhenium partitioning during magmatic differentiation. *Chemical Geology* 386, 101-114.  
 264 <https://doi.org/10.1016/j.chemgeo.2014.08.013>

265 Liu, R., Hu, L., Humayun, M. (2017) Natural variations in the rhenium isotopic composition of  
 266 meteorites. *Meteoritics & Planetary Science* 52(3), 479-492. <https://doi.org/10.1111/maps.12803>

267 Liu, Z., Li, Y. (2023) Experimental constraints on the behavior of Pt and Re in oxidized arc  
 268 magmas. *Earth and Planetary Science Letters* 603. <https://doi.org/10.1016/j.epsl.2022.117986>

269 Mallmann, G., O'Neill, H.S.C. (2007) The effect of oxygen fugacity on the partitioning of Re  
 270 between crystals and silicate melt during mantle melting. *Geochimica et Cosmochimica*  
 271 *Acta* 71(11), 2837-2857. <https://doi.org/10.1016/j.gca.2007.03.028>

272 McDonough, W.F., Sun, S.S. (1995) The composition of the Earth. *Chemical Geology* 120(3-4),  
 273 223-253. [https://doi.org/10.1016/0009-2541\(94\)00140-4](https://doi.org/10.1016/0009-2541(94)00140-4)

274 Miller, C.A., Peucker-Ehrenbrink, B., Ball, L. (2009) Precise determination of rhenium isotope  
 275 composition by multi-collector inductively-coupled plasma mass spectrometry. *Journal of*  
 276 *Analytical Atomic Spectrometry* 24(8), 1069-1078. <https://doi.org/10.1039/B818631F>

277 Miller, C.A., Peucker-Ehrenbrink, B., Schauble, E.A. (2015) Theoretical modeling of rhenium  
 278 isotope fractionation, natural variations across a black shale weathering profile, and potential as a  
 279 paleoredox proxy. *Earth and Planetary Science Letters* 430, 339-348.  
 280 <https://doi.org/10.1016/j.epsl.2015.08.008>

281 Moune, S., Sigmarsson, O., Thordarson, T., Gauthier, P.J. (2007) Recent volatile evolution in the  
 282 magmatic system of Hekla volcano, Iceland. *Earth and Planetary Science Letters* 255(3-4), 373-  
 283 389. <https://doi.org/10.1016/j.epsl.2006.12.024>

284 Norman, M.D., Garcia, M.O., Bennett, V.C. (2004) Rhenium and chalcophile elements in basaltic  
 285 glasses from Ko'olau and Moloka'i volcanoes: Magmatic outgassing and composition of the  
 286 Hawaiian plume. *Geochimica et Cosmochimica Acta* 68(18), 3761-3777.  
 287 <https://doi.org/10.1016/j.gca.2004.02.025>

288 Prytulak, J., Sossi, P.A., Halliday, A.N., Plank, T., Savage, P.S., Woodhead, J.D. (2017) Stable  
 289 vanadium isotopes as a redox proxy in magmatic systems. *Geochemical Perspectives Letters* 3,  
 290 75-84. <https://doi.org/10.7185/geochemlet.1708>

291 Richter, F.M., Janney, P.E., Mendybaev, R.A., Davis, A.M., Wadhwa, M. (2007) Elemental and  
 292 isotopic fractionation of Type B CAI-like liquids by evaporation. *Geochimica et Cosmochimica*  
 293 *Acta* 71(22), 5544-5564. <https://doi.org/10.1016/j.gca.2007.09.005>  
 294 Richter, K., Campbell, A.J., Humayun, M., Hervig, R.L. (2004) Partitioning of Ru, Rh, Pd, Re, Ir,  
 295 and Au between Cr-bearing spinel, olivine, pyroxene and silicate melts. *Geochimica et*  
 296 *Cosmochimica Acta* 68(4), 867-880. <https://doi.org/10.1016/j.gca.2003.07.005>  
 297 Richter, K., Chesley, J.T., Geist, D., Ruiz, J. (1998) Behavior of Re during magma fractionation:  
 298 an example from Volcan Alcedo, Galapagos. *Journal of Petrology* 39(4), 785-795.  
 299 <https://doi.org/10.1093/petroj/39.4.785>  
 300 Savage, P.S., Georg, R.B., Williams, H.M., Burton, K.W., Halliday, A.N. (2011) Silicon isotope  
 301 fractionation during magmatic differentiation. *Geochimica et Cosmochimica Acta* 75(20), 6124-  
 302 6139. <https://doi.org/10.1016/j.gca.2011.07.043>  
 303 Sigmarsson, O., Bergþórsdóttir, I.A., Devidal, J.L., Larsen, G., Gannoun, A. (2022) Long or short  
 304 silicic magma residence time beneath Hekla volcano, Iceland? *Contributions to Mineralogy and*  
 305 *Petrology* 177(1), 13. <https://doi.org/10.1007/s00410-021-01883-5>  
 306 Sigmarsson, O., Condomines, M., Fourcade, S. (1992) A detailed Th, Sr and O isotope study of  
 307 Hekla: differentiation processes in an Icelandic volcano. *Contributions to Mineralogy and*  
 308 *Petrology* 112, 20-34. <https://doi.org/10.1007/BF00310953>  
 309 Smoliar, M.I., Walker, R.J., Morgan, J.W. (1996) Re-Os ages of group IIA, IIIA, IVA, and IVB  
 310 iron meteorites. *Science* 271(5252), 1099-1102. <https://doi.org/10.1126/science.271.5252.1099>  
 311 Sun, W., Arculus, R.J., Bennett, V.C., Eggins, S.M., Binns, R.A. (2003b) Evidence for rhenium  
 312 enrichment in the mantle wedge from submarine arc-like volcanic glasses (Papua New  
 313 Guinea). *Geology* 31(10), 845-848. <https://doi.org/10.1130/G19832.1>  
 314 Sun, W., Bennett, V.C., Eggins, S.M., Arculus, R.J., Perfit, M.R. (2003a). Rhenium systematics  
 315 in submarine MORB and back-arc basin glasses: laser ablation ICP-MS results. *Chemical Geology*  
 316 196(1-4), 259-281. [https://doi.org/10.1016/S0009-2541\(02\)00416-3](https://doi.org/10.1016/S0009-2541(02)00416-3)  
 317 Xiong, Y., Wood, S.A. (1999) Experimental determination of the solubility of ReO<sub>2</sub> and the  
 318 dominant oxidation state of rhenium in hydrothermal solutions. *Chemical Geology* 158(3-4), 245-  
 319 256. [https://doi.org/10.1016/S0009-2541\(99\)00050-9](https://doi.org/10.1016/S0009-2541(99)00050-9)

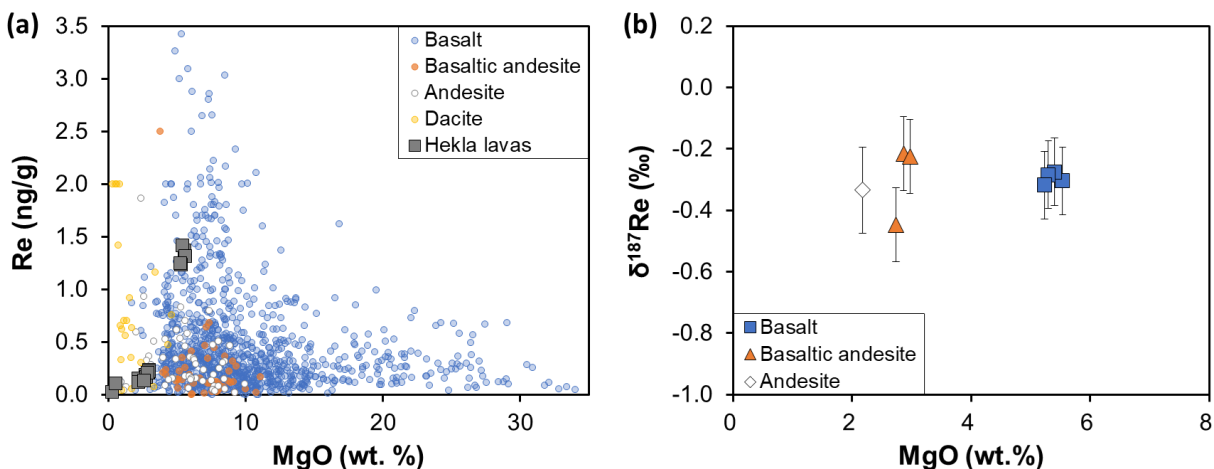
320 Xue, S., Li, Y. (2022) Pyrrhotite–silicate melt partitioning of rhenium and the deep rhenium cycle  
321 in subduction zones. *Geology* 50(2), 232-237. <https://doi.org/10.1130/G49374.1>

322 Yang, J., Siebert, C., Barling, J., Savage, P., Liang, Y.H., Halliday, A.N. (2015) Absence of  
323 molybdenum isotope fractionation during magmatic differentiation at Hekla volcano,  
324 Iceland. *Geochimica et Cosmochimica Acta* 162, 126-136.  
325 <https://doi.org/10.1016/j.gca.2015.04.011>

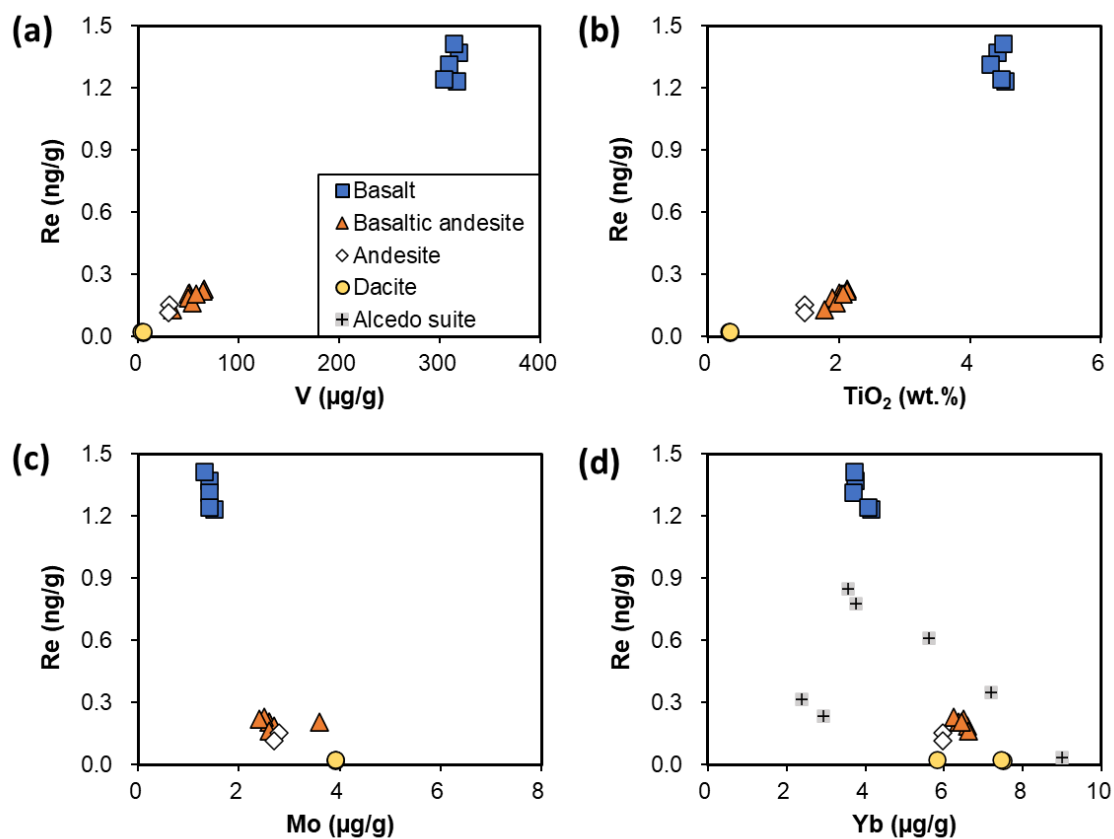
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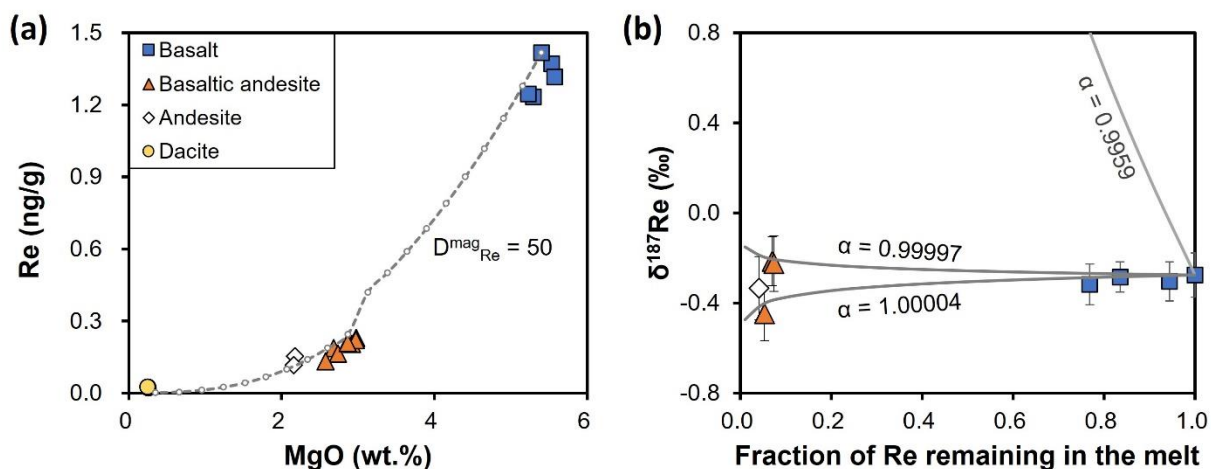




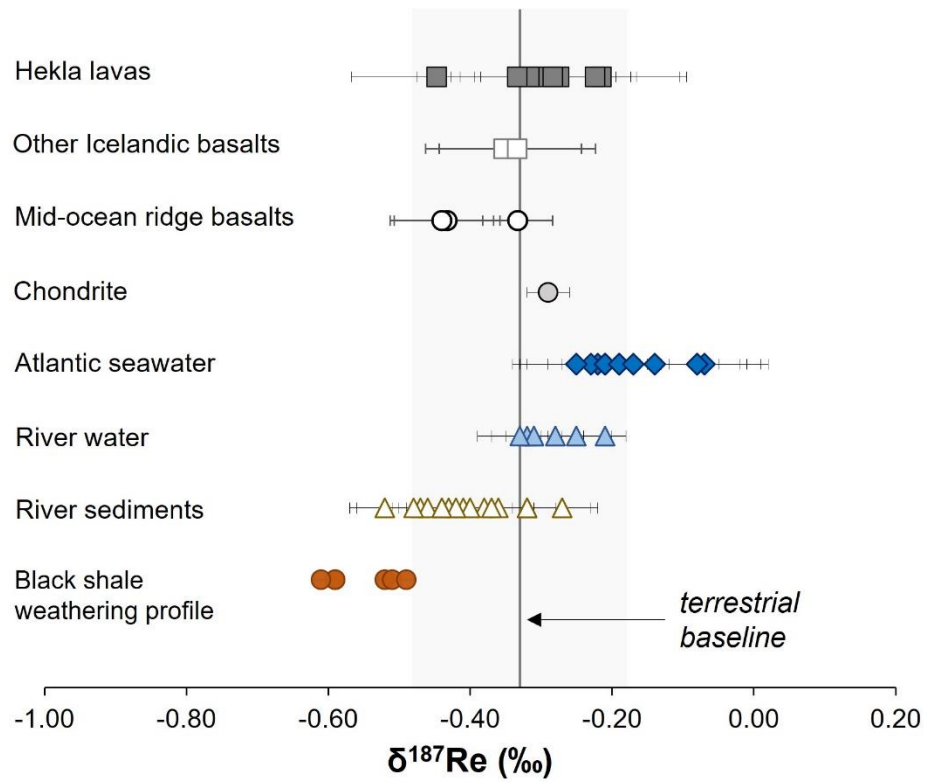
**Fig. 1 (a)** A compilation of Re contents in igneous rock samples from the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc>), and from this study (Hekla lavas). **(b)** Re isotope ( $\delta^{187}\text{Re}$ ) variations with MgO content in the Hekla lavas. Uncertainties on  $\delta^{187}\text{Re}$  represent the 2SD of repeat MC-ICP-MS measurements on the same sample (or 2SE 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).



**Fig. 2** Re variations in the Hekla lavas with the concentrations of (a) V, (b) TiO<sub>2</sub>, (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.



**Fig. 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](#).



**Fig. 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); Miller *et al.* (2015) (New Albany shale).