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1 **Rhenium elemental and isotopic variations at magmatic temperatures**

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3

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14

15

16 **Abstract**

17 Recent analytical advances in the measurement of rhenium (Re) isotope ratios allow its potential
18 as a paleoredox and chemical weathering proxy to be explored. However, a successful isotopic
19 proxy must be grounded by an understanding of its composition and behaviour in the solid Earth.
20 Here we present Re concentrations and Re isotopic ($\delta^{187}\text{Re}$) compositions for a well characterised
21 sequence of lavas from Hekla volcano, Iceland. The concentration of Re varies from 0.02–1.4 ng/g,

22 decreasing from basalt to more evolved lavas. We show that the crystallisation and removal of
23 magnetite is responsible for the Re decrease in this system. By contrast, $\delta^{187}\text{Re}$ values for the same
24 suite of samples show a relatively narrow range (-0.45 to -0.22 ‰), suggesting minimal resolvable
25 Re isotope fractionation between magnetite and the silicate melt. Together with other samples
26 including mid-ocean ridge basalts, these first igneous data can be used to estimate a baseline for
27 terrestrial materials ($\delta^{187}\text{Re} = -0.33 \pm 0.15 \text{ ‰}$, 2SD, n=14) from which low-temperature Re isotope
28 variations in Earth's surficial environments can be assessed, alongside the global isotope mass
29 balance of Re.

30

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

33

34

35 **Introduction**

36 Rhenium (Re) is one of the rarest elements in the Earth's crust, with an estimated abundance of ~
37 0.93 ng/g and 0.2–2 ng/g in oceanic and continental crust respectively (Sun *et al.*, 2003a,b;
38 Peucker-Ehrenbrink and Jahn, 2001). The Re concentration of the primitive mantle is ~ 0.28 ng/g,
39 compared to 0.12–0.18 ng/g in the depleted mantle (McDonough and Sun, 1995; Hauri and Hart,
40 1997). There appears to be a “missing” Re component from the upper mantle (*e.g.*, Sun *et al.*,
41 2003a; Xue and Li, 2021) and there is a clear need for better constraints on the magmatic behaviour
42 of Re. Whilst Re is known to be incompatible in most silicate phases such as olivine and
43 clinopyroxene (Righter *et al.*, 2004; Mallmann and O'Neill, 2007), the sulphur and oxygen
44 fugacity (fS_2 and fO_2) controls on Re partitioning appear to be complicated. For example, Re is
45 predicted to behave as a lithophile element under sulphide-poor and/or relatively oxidised
46 conditions (such as during differentiation of arc magmas), whereas Re behaves chalcophile in
47 reduced mid-ocean ridge basalt (MORB) type mantle and becomes more compatible with lower
48 fO_2 (Fonseca *et al.*, 2007; Mallmann and O'Neill, 2007); oxides such as magnetite can also
49 potentially host Re (Righter *et al.*, 1998; Li, 2014).

50 Rhenium has two isotopes, ^{187}Re and ^{185}Re , which comprise ~ 63 % and 37 % of natural Re
51 respectively. The ^{187}Re isotope is radioactive, but decays with a very long half-life (4.12×10^{10} yr;
52 Smoliar *et al.*, 1996), making the isotope ratio of ^{187}Re and ^{185}Re more analogous to a stable isotope
53 system (Miller *et al.*, 2009). Rhenium is a redox-sensitive element (common valence states: 4+,
54 6+, and 7+) and because Re isotopes may be fractionated by redox and/or weathering processes
55 (Miller *et al.*, 2015), the Re isotopic composition (denoted as $\delta^{187}\text{Re} =$
56 $[(^{187}\text{Re}/^{185}\text{Re})_{\text{sample}} / (^{187}\text{Re}/^{185}\text{Re})_{\text{NIST3143}} - 1] \times 1000$) of ancient sediments holds the potential to
57 infer changes in seafloor redox and/or global weathering intensity (Dickson *et al.*, 2020; Dellinger

58 *et al.*, 2021). There is a growing dataset of Re isotopic compositions of seawater and river waters
59 (Dickson *et al.*, 2020; Dellinger *et al.*, 2021). However, due partly to analytical challenges, few
60 $\delta^{187}\text{Re}$ measurements exist on igneous materials, limited to meteorites (Liu *et al.*, 2016) and
61 standard reference materials (Dellinger *et al.*, 2020). No studies have investigated the behavior of
62 Re isotopes during magmatic processes on Earth. Additionally, our understanding of the Re
63 isotopic composition of the mantle is currently limited. These features need to be resolved to
64 establish a terrestrial baseline that can be compared with $\delta^{187}\text{Re}$ values of weathered materials, and
65 to assess the global isotope mass balance of Re (Dickson *et al.*, 2020).

66

67 **Materials and methods**

68 We present Re concentrations and isotopic compositions for a well-characterised sequence of lavas
69 from Hekla volcano, Iceland. The analysed Hekla lavas cover a compositional range from basalt
70 to dacite (46–69 wt.% SiO_2) which have been interpreted as a differentiation sequence with or
71 without contribution of minor amphibolite melting (Sigmarsson *et al.*, 1992, 2022; Savage *et al.*,
72 2011; Geist *et al.*, 2021; [Supplementary Information](#)). We also present results of Re isotope
73 analysis for two unrelated Icelandic volcanic samples (RP80C-1 and BUR20-09) and three MORB
74 samples spanning the Atlantic, Pacific and Indian oceans (RDL DR30, CYP78 12-35, MD57 D'10-
75 1; [Supplementary Information](#)).

76 The Re concentrations of the samples were determined via isotope dilution and isoamylol liquid-
77 liquid extraction method (Birck *et al.*, 1997). The low Re concentration of these samples means
78 that a mass of 1–10 g is necessary for the precise determination of stable Re isotopes ($\delta^{187}\text{Re}$).
79 Chemical separation of Re was conducted using a three-step AG1-X8 anion exchange column

80 procedure, following newly established methods by Dellinger *et al.* (2020) and Dickson *et al.*
81 (2020). Rhenium isotopes were measured using the multi-collector ICP-MS (Neptune Plus)
82 instrument at Royal Holloway University of London. All the $\delta^{187}\text{Re}$ results are reported relative to
83 the NIST SRM 3143 standard. Details of the analytical methods and all Re data for this study are
84 given in [Supplementary Information](#) and [Table S-1, S-2](#).

85

86 **Results**

87 The accuracy of the methods has been validated through the analysis of standard reference
88 materials, the yielded $\delta^{187}\text{Re}$ values of BHVO-2, BIR-1, BCR-2 and MAG-1 are consistent with
89 literature values ([Table S-1](#)). The measured Re concentrations of the Hekla suite were the highest
90 in the basalt samples (1.23–1.42 ng/g), and sharply decreased with decreasing MgO from 0.17–
91 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
92 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
93 ± 0.11 ‰, and from -0.22 ± 0.11 to -0.45 ± 0.12 ‰ for the basalt and basaltic andesites respectively,
94 and a composition of -0.33 ± 0.14 ‰ (2SD) was measured in an andesitic sample ([Fig. 1b](#); [Table](#)
95 [S-2](#)). It was not possible to analyse dacitic samples for Re isotopes because of their extremely low
96 Re concentrations. The $\delta^{187}\text{Re}$ values of two other Icelandic basalt samples, -0.35 ± 0.13 to -0.33
97 ± 0.11 ‰, were within the range of the Hekla suite. The three MORB samples exhibited Re
98 concentrations of 0.78–1.43 ng/g and similar Re isotopic compositions, -0.33 ± 0.11 to $-0.44 \pm$
99 0.11 ‰.

100

101 **Discussion**

102 Evolution of Re during magmatic processes at Hekla volcano

103 The co-variations of Re with vanadium (V) and TiO₂ provide a clue to the partitioning behaviour
104 of Re within the Hekla suite. We demonstrate a concurrent removal of Re and V (Fig. 2a) during
105 magmatic evolution; there is also a decreasing trend in Re concentrations with decreasing TiO₂
106 (from 4.5 to 0.3 wt.%; Fig. 2b). In the Hekla lavas, oxide minerals such as (titano)magnetite host
107 the majority of V (Prytulak *et al.*, 2017). A self-consistent model of fractional crystallisation of
108 cotectic phases (Fig. 3a) following Prytulak *et al.* (2017) shows that the evolution of Re
109 concentrations in the Hekla lavas can be reproduced if the partition coefficient of Re in magnetite
110 ($D^{\text{mag}}_{\text{Re}}$) is ~ 50 . Similar to this study, Righter *et al.* (1998) observed a sharp decrease in Re
111 concentrations in samples from Volcán Alcedo (Galapagos), from 0.61 ng/g in icelandite to 0.026
112 ng/g in rhyolite along the FeO and TiO₂ depletion trend. These same authors measured an
113 extremely high Re content in a magnetite separate (~ 40 ng/g) and concluded that magnetite is a
114 significant host phase for Re, with an estimated $D^{\text{mag}}_{\text{Re}} = 20\text{--}50$ for a sulphide-free system. In
115 support of this argument, Mallmann and O'Neill (2007) suggested that Re⁴⁺ has a partitioning
116 behaviour similar to Ti⁴⁺ and could substitute for Ti⁴⁺ in the solid phase. Note that $f\text{O}_2$ (which is
117 commonly reported in log units relative to the fayalite-magnetite-quartz (FMQ) buffer) of the
118 Icelandic magmas is close to FMQ (Moune *et al.*, 2007) so is relatively higher than in average
119 MORB, while for the Alcedo (Galapagos) suite, the estimated $f\text{O}_2$ is more reducing, $\sim \text{FMQ-3}$
120 (Righter *et al.*, 1998). Lower $f\text{O}_2$ would result in higher fraction of Re as Re⁴⁺, favouring
121 dissolution of Re in common upper mantle minerals as well as in magnetite (Mallmann and O'Neill,
122 2007; Liu and Li, 2003). The similar $D^{\text{mag}}_{\text{Re}}$ estimated for the two suites regardless of varying $f\text{O}_2$
123 may be due to a compositional effect. In addition, it is possible that Re remains compatible in
124 magnetite in anhydrous systems (*e.g.*, both the Hekla and the Alcedo suites: Geist *et al.*, 2021;

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

127 Although it is generally accepted that Re is compatible in sulphide minerals under relatively
128 reduced environments (*e.g.*, Fonseca *et al.*, 2007), we found no evidence for the partitioning of Re
129 into sulphides in the Hekla lavas. While some studies found traces of sulphide saturation and
130 mineral formation in the Hekla lavas (Geist *et al.*, 2021), others do not (Moune *et al.*, 2007). The
131 expected loss of molybdenum (Mo), another chalcophile element, due to sulphide extraction was
132 also not observed (Yang *et al.*, 2015). High-pressure experiments conducted at fO_2 of \sim FMQ-1.8
133 to FMQ+1.5 show a strong correlation between the partition coefficients of Re and Mo between
134 sulphide liquid, monosulphide solid solution, and silicate melts (Feng and Li, 2019), suggesting
135 similar partitioning behaviours of Re and Mo between these phases. In the Hekla lavas, however,
136 we find that the concentration of Re decreases with increasing Mo (Fig. 2c). We note that Hekla
137 lavas do show a pronounced drop in sulphur (S) concentrations through two orders of magnitude
138 from the basalt to the andesite and dacite (Table S-3), but this is likely the result of sulphur
139 degassing (Moune *et al.*, 2007).

140 Whether Re and ytterbium (Yb) share a similar degree of incompatibility during differentiation is
141 debated. Although early studies on mantle-derived magmas (*e.g.*, Hauri and Hart, 1997; Sun *et al.*,
142 2003b) found roughly constant Yb/Re ratios, others suggested that the Re-Yb similarity is not
143 ubiquitous (*e.g.*, Mallmann and O'Neill 2007; Li, 2014). We show clearly that, in the Hekla lavas,
144 Re is not enriched in evolved rocks (basaltic andesite, andesite, dacite) in the same way as Yb;
145 Righter *et al.* (1998) observed a similar relationship between Re and Yb in their Galapagos
146 icelandite to rhyolite sequence (Fig. 2d).

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

155

156 **No resolvable Re isotope fractionation during magnetite crystallisation**

157 Despite the very large range in Re concentrations, there is no statistically significant difference,
158 within uncertainties, between the $\delta^{187}\text{Re}$ values for different types of rocks (basalt, basaltic
159 andesite and andesite) of the Hekla suite. No clear trend or systematic variation in $\delta^{187}\text{Re}$ values
160 is observed when plotted against concentrations of MgO, SiO₂, TiO₂, S, V, Mo, Yb, or Re in the
161 Hekla lavas. (Fig. 1b; Fig. S-1). The Hekla lava samples showed an average $\delta^{187}\text{Re}$ of $-0.30 \pm$
162 0.14 ‰ (2SD, n=8).

163 The relatively constant $\delta^{187}\text{Re}$ (despite systematically varying Re concentrations) during magmatic
164 evolution implies minor Re isotope fractionation between the crystallising minerals and silicate
165 melt. In general, the magnitude of equilibrium isotope fractionation in high-temperature geological
166 environments depends on differences in bond strength, which are dominantly related to oxidation
167 states and cation coordination. When the solid phase is an oxide, such as (titano)magnetite, Re
168 likely occurs in the +4 state as ReO₂ (Richter *et al.*, 1998; Xiong and Wood, 1999). In the silicate
169 melt, Re is mainly found as ReO₂ (Re⁴⁺) and ReO₃ (Re⁶⁺) species at typical terrestrial magma

170 oxygen fugacities (Xiong and Wood, 1999; Ertel *et al.*, 2001); Re^{6+} is highly incompatible in
171 mantle minerals (Mallmann and O'Neill 2007; Liu and Li, 2023). No experimentally determined
172 isotope fractionation factor between different Re molecules has been reported, but we adopt the
173 electronic structure modelling by Miller *et al.* (2015) as a first approximation. Of all the Re^{4+} and
174 Re^{7+} species investigated, excluding Re in the thiolated form, the net equilibrium fractionation
175 factor (α) of Re considering the combined mass dependent and nuclear volume effects at estimated
176 Hekla magmatic temperatures of $\sim 1000^\circ\text{C}$ (Geist *et al.*, 2021) is very close to unity: ~ 0.99997 to
177 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
178 equilibrium isotope fractionation between Re^{4+} and Re^{6+} oxides to be even smaller. If we apply
179 0.99997 and 1.00004 as an estimation for the bulk Re isotope fractionation factor, then a Rayleigh
180 fractionation model suggests that crystallisation of magnetite would lead to only subtly heavier or
181 lighter $\delta^{187}\text{Re}$ in the residual melt (Fig. 3b). The very subtle Re isotope fractionation in
182 compositionally evolved lithologies may not be resolvable at current levels of precision.

183 The absence of significant Re isotope fractionation during magmatic processes at Hekla supports
184 magnetite crystallisation as the dominant process instead of Re degassing. The volatility of Re has
185 been reported in several magmatic systems (*e.g.*, Norman *et al.*, 2004), but kinetic isotope
186 fractionation of Re is expected during degassing. The theoretical maximum Rayleigh fractionation
187 coefficient (α) during vaporisation as Re_2O_7 gas can be calculated as the inverse square root of the
188 mass of the Re isotopes ($\sqrt{481.899/485.905} = 0.9959$) (*e.g.*, Richter *et al.*, 2007). If degassing
189 of Re is the dominant process during the evolution of the Hekla lavas, we would expect the $\delta^{187}\text{Re}$
190 in the residual silicate melts to become progressively heavy; this model is illustrated in Fig. 3b,
191 which does not agree with the observed relatively narrow range (-0.45 to -0.22 ‰). Given the

192 volatile behaviour of Re and that the Re isotope system is insensitive to fractional crystallisation,
193 $\delta^{187}\text{Re}$ can potentially be used as a discriminant of Re degassing in magmatic processes.

194

195 **Implications for a first estimate of a Re isotope terrestrial baseline**

196 Whilst degassing of Re and post-eruption alteration have the potential to modify the Re isotope
197 signature, we have been able to demonstrate that Re isotope fractionation between crystallising
198 minerals (magnetite) and silicate melt during magmatic processes is not analytically resolvable at
199 the current stage. Un-degassed and unaltered igneous rocks therefore have the potential to infer
200 the Re isotopic composition of their source. Although sourced from different tectonic settings and
201 mantle depths, our analysed other Icelandic basalts (RP80C-1 and BUR20-09) and MORBs (from
202 the Atlantic, Pacific and Indian Oceans) also show limited Re isotopic variability (-0.44 to -
203 0.33 ‰), overlapping with the Hekla lava $\delta^{187}\text{Re}$ (-0.45 to -0.22 ‰) (Table S-2; Fig. 4). We note
204 that these Re isotope values are also indistinguishable within uncertainty from the $\delta^{187}\text{Re}$ of
205 carbonaceous chondrite (-0.29 ± 0.03 ‰, CV3 Allende, Dellinger *et al.*, 2020; Fig. 4), as well as
206 our analysed standard reference materials BHVO-2 (Hawaiian basalt), BIR-1 (Icelandic basalt)
207 and BCR-2 (Columbia River Flood basalt) (Table S-1).

208 With the current data, the restricted range in $\delta^{187}\text{Re}$ values of the compositionally diverse igneous
209 samples (eight Hekla lavas, two other Icelandic basalts, three MORBs, one chondrite) makes it
210 possible to propose a first estimate of a terrestrial baseline for Re isotopes (-0.33 ± 0.15 ‰, 2SD,
211 $n=14$). Available Re isotope data (Fig. 4) suggest that the $\delta^{187}\text{Re}$ of Atlantic seawater ($-0.17 \pm$
212 0.12 ‰, 2SD, $n=12$; Dickson *et al.*, 2020) is isotopically heavy compared to this baseline. Whilst
213 the only published $\delta^{187}\text{Re}$ values for river water (-0.29 ± 0.09 ‰, 2SD, $n=10$; Dellinger *et al.*, 2021)
214 are within the baseline range, sedimentary rock $\delta^{187}\text{Re}$ from New Albany shales (~ -0.6 ‰; Miller

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

223

224

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232

233

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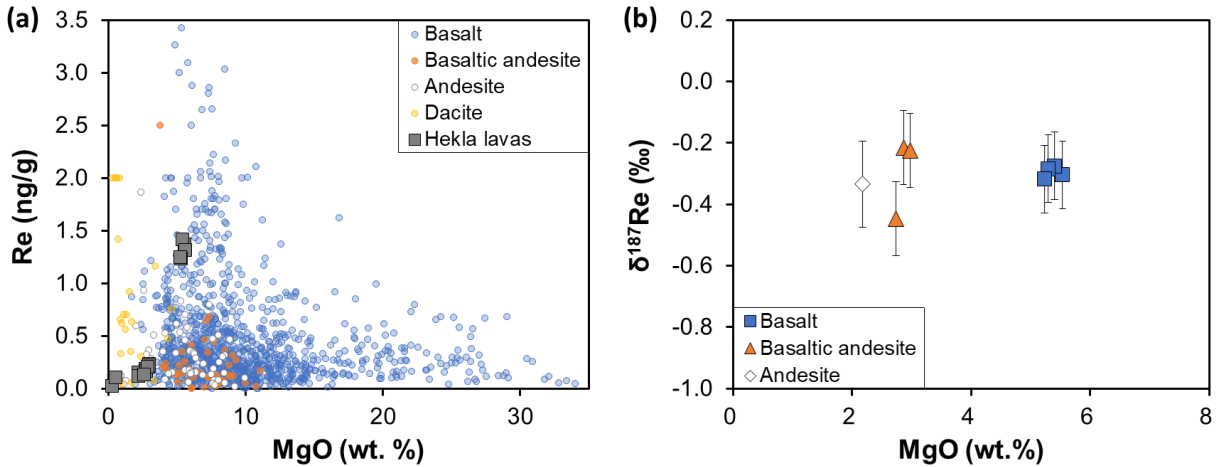
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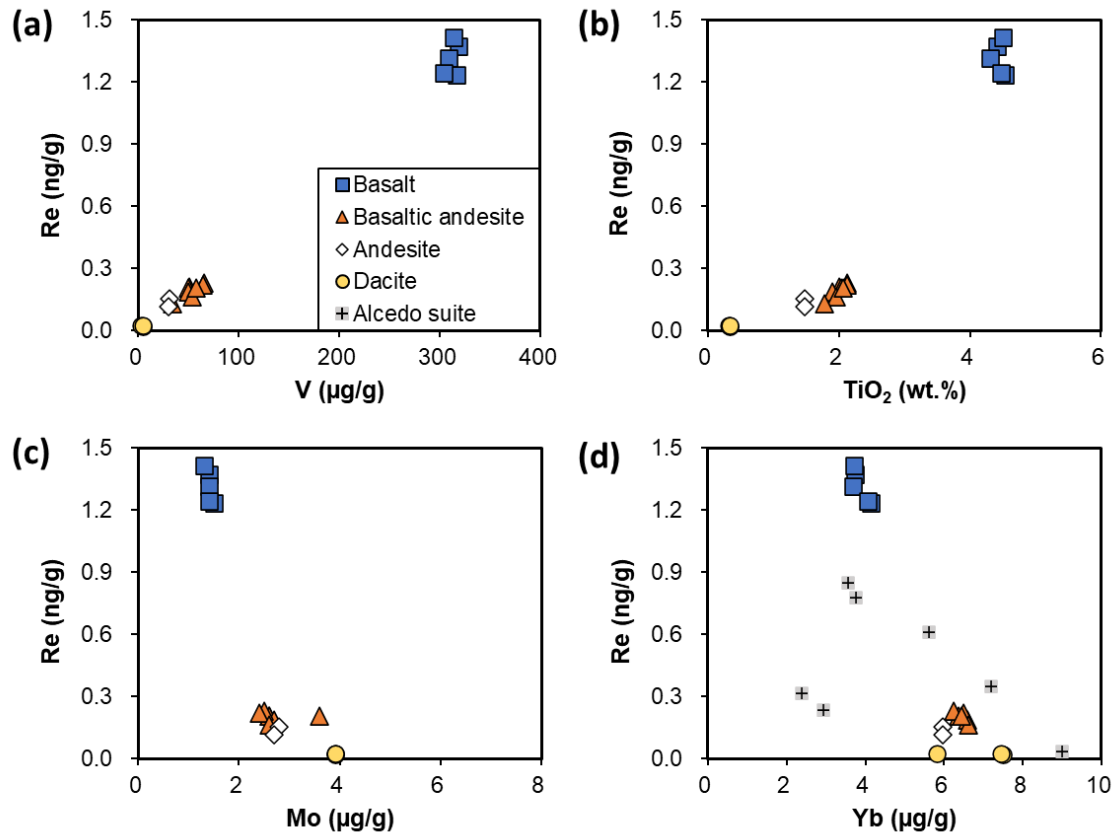
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329 **Fig. 1 (a)** A compilation of Re contents in igneous rock samples from the GEOROC database
 330 (<http://georoc.mpch-mainz.gwdg.de/georoc>), and from this study (Hekla lavas). **(b)** Re isotope
 331 ($\delta^{187}\text{Re}$) variations with MgO content in the Hekla lavas. Uncertainties on $\delta^{187}\text{Re}$ represent the
 332 2SD of repeat MC-ICP-MS measurements on the same sample (or 2SE internal error if there was
 333 only one measurement), or the long-term reproducibility for the standard solution (ICP; 0.11%),
 334 whichever is larger (Table S-2).

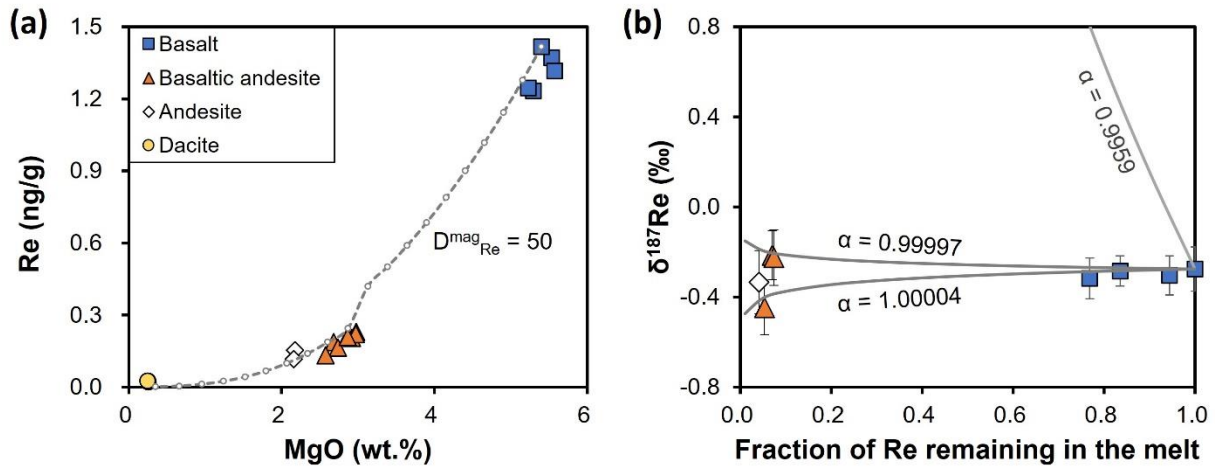
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337 **Fig. 2** Re variations in the Hekla lavas with the concentrations of (a) V, (b) TiO₂, (c) Mo and (d)
 338 Yb. Ancillary major and trace element data are given in [Table S-3](#). In (d), Alcedo suite data from
 339 Righter *et al.* (1998) are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

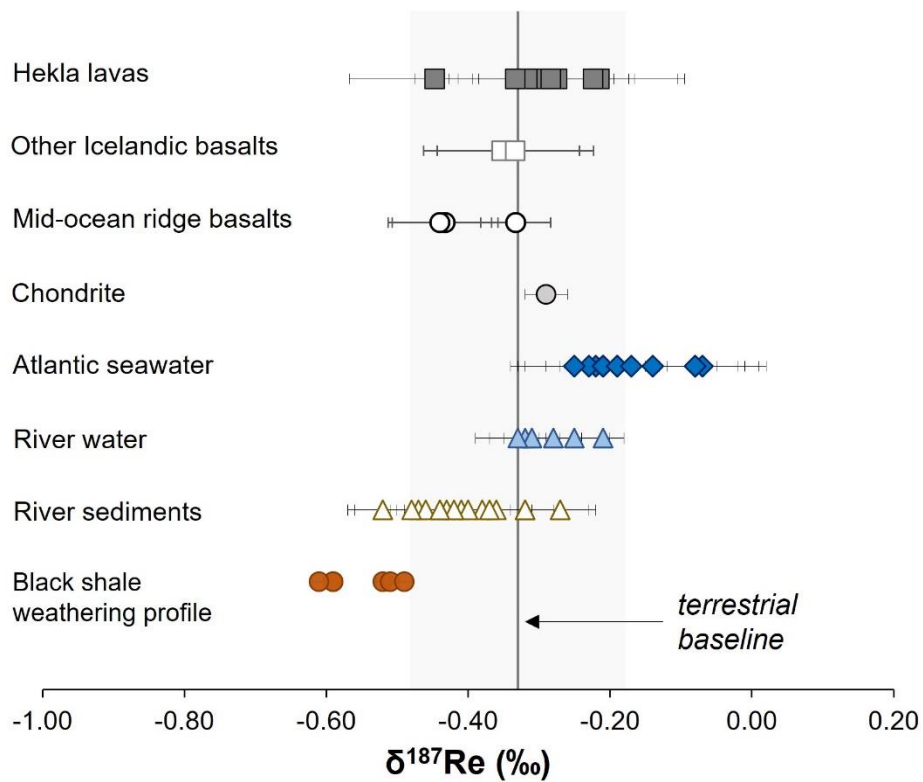
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343 **Fig. 3 (a)** Cotectic fractional crystallisation model (dashed line) for the evolution of Re in Hekla
 344 lavas. The fractionating assemblage at Hekla consists of orthopyroxene, plagioclase,
 345 clinopyroxene and (titano)magnetite (Sigmarsson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

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

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