

1 **A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge**

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27 **Abstract**

28 Mantle oxygen fugacity (fO_2) governs the physico-chemical evolution of the Earth, however current
29 estimates from commonly used basalt redox proxies are often in disagreement. In this study we
30 compare three different potential basalt fO_2 proxies: Fe^{3+}/Fe_{tot} , V/Sc and V isotopes, determined on
31 the same submarine lavas from a 700 km section of the Reykjanes Ridge, near Iceland. These samples
32 provide a valuable test of the sensitivities of fO_2 proxies to basalt petrogenesis, as they formed at
33 different melting conditions and from a mantle that towards Iceland exhibits increasing long-term
34 enrichment of incompatible elements. New trace element data were determined for 63 basalts with
35 known Fe^{3+}/Fe_{tot} . A subset of 19 lavas, covering the geographical spread of the ridge transect, was
36 selected for vanadium isotope analyses.

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38 Vanadium is a multi-valence element whose isotopic fractionation is theoretically susceptible to
39 redox conditions. Yet, the $\delta^{51}V_{AA}$ composition of basaltic glasses along the Reykjanes Ridge covers
40 only a narrow range ($\delta^{51}V_{AA} = -1.09$ to -0.86% ; $1SD = 0.02-0.09$) and does not co-vary with
41 fractionation-corrected Fe^{3+}/Fe_{tot} ($0.134-0.151$; $1SD = 0.005$) or V/Sc ($6.6-8.5$; $1SD = 0.1-1.3$) ratios.
42 However, on a global scale, basaltic $\delta^{51}V_{AA}$ may be controlled by the extent of melting. The V/Sc
43 compositions of primitive ($MgO > 7.5$ wt%) basalts show no systematic change along the entire
44 length of the Reykjanes Ridge. Typical peridotite melting models in which source Fe^{3+}/Fe_{tot} is
45 constant at 5% and that account for the increased mantle potential temperature nearer the plume center
46 and the fO_2 dependent partitioning of V, can reproduce the V/Sc data. However, while these melting
47 models predict that basalt Fe^{3+}/Fe_{tot} ratios should decrease with increasing mantle potential
48 temperature towards Iceland, fractionation-corrected Fe^{3+}/Fe_{tot} of Reykjanes Ridge lavas remain
49 nearly constant over the ridge length. This discrepancy is explained by source heterogeneity, where
50 an oxidized mantle pyroxenite component contributes to melting with increasing proximity to Iceland.

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52 Comparison of observed and modeled $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ indicate that source variation in $f\text{O}_2$ is present under
53 the Reykjanes Ridge, with higher $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ closer to Iceland. This source variability in $f\text{O}_2$ cannot be
54 resolved by V isotopes and redox-sensitive trace element ratios, which instead appear to record
55 magmatic processes.

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57 **Keywords**

58 mantle, oxygen fugacity, MORB, $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, vanadium, isotopes

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78 **Introduction**

79 Oxygen fugacity is an intensive thermodynamic property that dictates the oxidizing potential of a
80 system (e.g., Frost, 1991). In the Earth's mantle, fO_2 controls phase relations, elemental distributions
81 and magma genesis. As magmas rise, they retain an fO_2 inherited from their source, which controls
82 the speciation and solubility of volatile elements and thereby the composition and volume of gasses
83 they release to Earth's atmosphere (e.g., Frost and McCammon, 2008; Gaillard et al., 2011).
84 Knowledge of mantle fO_2 is thus fundamental for interpretation and understanding of the physico-
85 chemical processes that control the solid-Earth's interaction with the oceans and atmosphere.

86

87 One way to determine mantle fO_2 is through the study of mantle peridotites that are either tectonically
88 emplaced into the crust or magmatically delivered to the surface as xenoliths. Oxygen fugacity can
89 be quantitatively estimated from such rocks by application of a mineral oxybarometer, which
90 quantifies the thermodynamics of redox reactions between mineral phases present (e.g., olivine-
91 orthopyroxene-spinel, O'Neill & Wall, 1987). This approach has been used to demonstrate that in the
92 continental lithosphere, fO_2 decreases with depth, from ± 2 log units relative to the FMQ (fayalite-
93 magnetite-quartz) buffer in the spinel peridotite field to $-5 \Delta FMQ$ in the deeper garnet peridotite field
94 (Frost and McCammon, 2008 and references therein). However, the results from these studies are
95 primarily representative of the cratonic lithospheric mantle, from which most xenoliths derive. In
96 contrast to the cratons, the convecting mantle is poorly sampled by xenoliths, and its distinct chemical
97 and thermal regime means that its fO_2 may not be well described by observations of cratonic xenoliths.

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99 Basalts are more ubiquitous samples of the convecting mantle than xenoliths. Basalts that form in
100 equilibrium with their mantle source and subsequently remain a closed system during ascent and
101 surface emplacement will have an eruptive fO_2 related to their mantle fO_2 (Kress and Carmichael,
102 1991). A commonly used fO_2 proxy in basalts is their ferric iron content (Fe^{3+}/Fe_{tot}), which can be
103 precisely determined by micro-scale techniques such as X-ray absorption near edge structure

104 (XANES) spectroscopy (e.g., Berry et al., 2018; Cottrell et al., 2009). Through the determination of
105 the ferric content of basalts, mantle fO_2 can be estimated following empirical thermodynamic
106 calibrations and accounting for differentiation and degassing (e.g., Brounce et al., 2014, 2017; Helz
107 et al., 2017; Kelley and Cottrell, 2012; Kress and Carmichael, 1991; Moussallam et al., 2014, 2016;
108 Shorttle et al., 2015). Previous studies (see e.g., Brounce et al., 2014, 2015, 2017; Cottrell and Kelley,
109 2011, 2013; Hartley et al., 2017; Helz et al., 2017; Kelley and Cottrell, 2009; Moussallam et al., 2014,
110 2016; O'Neill et al., 2018; Shorttle et al., 2015) have indicated that the upper mantle is heterogeneous
111 in terms of Fe^{3+}/Fe_{tot} , with more oxidized conditions found at arc settings ($fO_2 \geq FMQ+1$) compared
112 to mid ocean ridges ($FMQ \leq fO_2 \leq FMQ+0.5$). Despite the prominence of using Fe^{3+}/Fe_{tot} in basalts
113 as a tool for estimating convecting mantle fO_2 , some work has also returned to the abyssal peridotite
114 record to investigate its preservation of mantle fO_2 . Birner et al. (2018) showed that peridotites and
115 basalts from mid-ocean ridge settings have good agreement in their estimates of mantle fO_2 , while
116 new experimental work also supports this conclusion (Davis and Cottrell, 2018).

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118 Importantly, different groups' XANES-derived estimates of Fe^{3+}/Fe_{tot} in mid ocean ridge basaltic
119 glasses have recently shown offsets from each other (e.g., Berry et al., 2018; Zhang et al., 2018; see
120 Results for a discussion of our data in this context). These differences reflect underlying decisions in
121 the interpretation of the Mössbauer spectra of glasses, in particular whether at highly reducing
122 conditions the spectra record the presence of ferric iron (Berry et al., 2018). As a result, the Berry et
123 al. (2018) XANES calibration, for a given sample, estimates lower ferric iron contents than the Zhang
124 et al. (2018) calibration. Debate continues around the correct choice of calibration (Berry et al., 2018;
125 Cottrell et al., 2009; Zhang et al., 2018; see Results). However, what is more significant for this study
126 is simply the thermodynamic basis for relating ferric iron abundances to fO_2 – i.e., that changes in
127 Fe^{3+}/Fe_{tot} within a sample suite of relatively constant major element chemistry relate to variation in
128 fO_2 , something which the question of XANES calibration does not directly affect.

129

130 Another potential tracer of mantle fO_2 in basalts is their V/Sc ratio, which uses the oxygen fugacity
131 dependence of the partition coefficients of V between minerals and melts $D_v^{min/melt}$ (e.g., Canil, 1997,
132 1999). Vanadium and Sc are mildly incompatible trace elements that behave similarly during melting,
133 but while Sc is homovalent in igneous systems (Sc^{3+}), V is multivalent (V^{2+} , V^{3+} , V^{4+} , V^{5+}). This
134 creates an fO_2 dependence to V partitioning during melting as the different valence states of V have
135 different partition coefficients: $D_v^{min/melt}$ decreases with increasing fO_2 whereas $D_{Sc}^{min/melt}$ remains
136 constant (e.g., Canil, 1997, 1999; Mallmann & O'Neill, 2009), resulting in higher V/Sc in basalts that
137 form at more oxidizing conditions (Lee et al., 2003, 2005; Li and Lee, 2004). Employing V/Sc to
138 estimate mantle fO_2 requires a correction for fractional crystallization, and therefore alternative ratios,
139 such as V/Yb, have been proposed (Laubier et al., 2014). Importantly, in contrast to Fe^{3+}/Fe_{tot} , V/Sc
140 ratios of MORBs and arc basalts have similar values, an observation which has been used to argue
141 that the convecting mantle, whether beneath arcs or ridges, has a relatively uniform fO_2 at $\sim FMQ-0.5$
142 (Lee et al., 2005). Thus, current estimates of mantle fO_2 determined by these two commonly used
143 proxies are in significant disagreement.

144

145 Mantle fO_2 might also be investigated by studying the stable isotopic composition of multivalent
146 transition metals in basaltic magmas (see review in Teng et al., 2017). This is because stable isotope
147 fractionation depends on valence state and coordination number. Vanadium is an element of interest
148 in this respect because of its multiple valence states. Also, V isotopic compositions are not disturbed
149 by secondary processes such as weathering or hydrothermal alteration (Prytulak et al., 2013; Wu et
150 al., 2018), which can affect other isotopic systems (e.g., Fe; Rouxel et al., 2003). However, the effects
151 of fO_2 , magmatic differentiation, partial melting and source heterogeneity need to be understood
152 before applying V isotopes as a mantle fO_2 proxy (Prytulak et al., 2013, 2017; Sossi et al., 2018; Wu
153 et al., 2018).

154

155 In this study, a suite of mantle-derived basalts from a ~ 700 km long segment of the Reykjanes Ridge

156 near Iceland was selected to investigate the behaviour of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, V/Sc and V isotopes to assess
157 their co-variation and suitability as $f\text{O}_2$ proxies. $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ data from Shorttle et al. (2015) were
158 recalibrated using the most recent values for the XANES reference standards (Zhang et al., 2018) and
159 combined with new trace element concentrations on 63 basalt glasses and V isotopic compositions
160 on a representative subset of 19 lavas (Fig. 1). The Reykjanes Ridge samples are well characterized
161 in terms of major and minor element concentration and display systematic variations of trace element
162 ratios and radiogenic isotopic composition with distance from Iceland (e.g., Murton et al., 2002;
163 Schilling, 1973). Pyroxenitic sources are inferred to be an important component feeding magmatism
164 on subaerial Iceland (e.g., Stapafell on the Reykjanes Peninsula where the ridge comes ashore; Fig.
165 1), and may also extend down the ridge and affect the genesis of Reykjanes Ridge basalts (Shorttle
166 and Maclennan, 2011; Shorttle et al., 2010). In addition, the crustal thickness along the Reykjanes
167 Ridge is well determined (e.g., Jones et al., 2014 and references therein) enabling precise constraints
168 on mantle melting conditions and potential temperature (T_p), which gradually rises by 60 °C towards
169 Iceland (see e.g., Matthews et al., 2016). The degree of basalt differentiation also increases along-
170 ridge, as the crust thickens. Thus, the Reykjanes Ridge is an excellent locality to evaluate the co-
171 variation of potential $f\text{O}_2$ proxies during mantle melting and the influence of both low-pressure
172 differentiation and lithological heterogeneity. In addition to comparison of potential proxies,
173 thermodynamic melting models were employed to further disentangle the interplay between source
174 $f\text{O}_2$, melting, and lithological heterogeneity.

175

176 **2. Methods**

177 **2.1 Vanadium isotopes**

178 Chemical isolation of vanadium was conducted in the MAGIC laboratories at the Department of Earth
179 Sciences and Engineering, Imperial College London. Clean glass shards without visible minerals,
180 air/fluid inclusions or weathering features were hand-picked under an optical microscope and ground
181 in an agate mortar to obtain a homogeneous, fine powder. Approximately 30 mg of each sample was

182 weighed to provide between 5 and 10 μg of total V. The samples were digested in a 2:1 mixture of
183 28M HF:15 M HNO_3 at 160 $^\circ\text{C}$ for at least 1 day. The samples were then evaporated and re-dissolved
184 in 15M HNO_3 . This step was repeated 3-5 times in order to ensure the complete destruction of the
185 fluorides that form during digestion. The dissolved basalts were processed through ion exchange
186 chromatography following the protocol of Nielsen et al. (2011). This technique describes a 7-column
187 procedure that allows for complete separation of V from the matrix and, in particular, quantitative
188 removal of Cr and Ti that can cause isobaric interferences on the minor isotope ^{50}V .

189

190 Vanadium isotopic compositions were measured with a Nu Plasma II multi collector inductively
191 coupled plasma mass spectrometer (MC-ICPMS) at Imperial College London following the
192 procedure outlined in Hopkins et al. (2019). Vanadium isotopic compositions were determined by
193 standard-sample bracketing, and are reported as permil variations relative to the Alpha Aesar (AA)
194 V standard solution (Nielsen et al., 2011) using the standard delta notation:

195

$$196 \quad \delta^{51}\text{V}_{\text{AA}} = 1000 \times [({}^{51}\text{V}/{}^{50}\text{V}_{\text{sample}} / {}^{51}\text{V}/{}^{50}\text{V}_{\text{AA}}) - 1].$$

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198 A secondary standard solution from BDH chemicals and the NIST 3165 solution were measured
199 during each session to monitor instrument stability. Samples and standards were diluted to a V
200 concentration of 600 ppb. Total procedural blanks were insignificant ($< 2\text{ng}$) compared to the amount
201 of V processed. Analysis of USGS reference materials (BIR-1a, BCR-2 and AGV-2) and the BDH
202 and NIST 3165 solution standards are in agreement with published literature (Table S1).

203

204 **2.2 Laser ablation inductively coupled plasma mass spectrometry**

205 Trace and rare earth element (REE) concentrations were measured by laser ablation inductively
206 coupled plasma mass spectrometry (LA-ICPMS) at the Department of Earth Sciences, the University
207 of Cambridge. This analytical setup combines a NWR193 excimer laser ablation systems with a

208 Perkin Elmer NexION 350D ICP mass spectrometer. The list of the trace elements analyzed and their
209 concentrations are reported in Table S2. Measurements were conducted on 63 polished glasses that
210 were previously analyzed by XANES to determine $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (Shorttle et al., 2015). Spot analyses of
211 100 μm diameter were conducted on clean portions of the glasses, avoiding potential sources of
212 contamination such as cracks or inclusions, using a laser power of 8 J/cm^2 and 10 Hz repetition rate.
213 These ablating conditions were optimized after testing international reference glass standards NIST-
214 612, BCR-2G, BIR-1G and ML3B-G and comparing with the preferred values from the GEOREM
215 database (available at <http://georem.mpch-mainz.gwdg.de>). The data were collected by the ICP-MS
216 using 1 sweep per reading, 50 readings and 1 replicate conditions. ICP-MS dwell time varied for the
217 different elements and it was typically between 10-20 ms for most trace elements, but this value was
218 increased up to 60 ms for some low concentrations REE. The Glitter Software (GEMOC, Australia)
219 was used to process raw data (signal intensity vs time), which allows to the user to select backgrounds
220 and signals and precisely calculate sample concentrations. The SiO_2 content of the glasses, previously
221 determined by electron microprobe analyses (Shorttle et al., 2015), was used as internal standard for
222 the normalization of trace element signals. BCR-2G was chosen as an external standard as it provided,
223 overall, better precision (RSD% generally <10%, 1SD) and accuracy (average percent error within
224 $\pm 15\%$) compared to other standards. These values of precision and accuracy were calculated
225 considering all individual analyses collected on a particular standard at the beginning, middle and end
226 of the session.

227

228 **2.3 Modelling rationale**

229 Two types of mantle melting scenarios were explored to reproduce the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and trace element
230 variation along the Reykjanes Ridge. The first approach was adopted to simulate adiabatic melting of
231 ambient mantle peridotite. The second was conducted to investigate the melting behavior of
232 pyroxenite and in particular the formation of enriched lavas, using the Stapafell eruption from
233 subaerial Iceland as an endmember (Fig. 1). Thermodynamic modelling was performed with the

234 pMELTS software operated through the alphaMELTS frontend (Ghiorso et al., 2002; Smith and
235 Asimow, 2005). pMELTS was used to predict the equilibrium phase assemblage of a mantle
236 composition at given conditions (P, T and fO_2). The chemical composition of the modelled
237 instantaneous melts was calculated from the phase equilibria and melting reactions. A general
238 description of the modelling rationale is provided below, while more details are reported in Table S3.
239

240 (1) *DMM melting*: Depleted MORB mantle (DMM) major element composition from Workman and
241 Hart (2005) was used as a starting composition, with varying initial Fe^{3+}/Fe_{tot} ratios (4-6%) calculated
242 maintaining constant total FeO_T . These Fe^{3+} contents are chosen such that the model produces melts
243 with a range of Fe^{3+}/Fe_{tot} close to that observed. A mantle Fe^{3+}/Fe_{tot} of 4-6% is slightly higher than
244 values predicted based on mantle xenolith studies ($Fe^{3+}/Fe_{tot} = 2\%$; e.g., Canil and O'Neill, 1996).
245 There may be two reasons for this: (1) model-based effects, whereby the treatment of ferric iron in
246 pMELTS is not accurately capturing its behavior in natural systems (e.g., the lack of ferric iron in
247 garnet in pMELTS, despite its presence in garnet solid solution as andradite); (2) the possibility that
248 cratonic xenoliths underestimate convecting mantle fO_2 values. However, this study is focused on
249 the *relative* changes in Fe^{3+}/Fe_{tot} rather than absolute values, so our choice of mantle Fe^{3+}/Fe_{tot} is less
250 important than how it translates to basalt Fe^{3+}/Fe_{tot} , given changing conditions of melt generation
251 along ridge.

252
253 Model simulations of decompression fractional melting were conducted for changing mantle potential
254 temperatures along the Reykjanes Ridge to account for the influence of the Icelandic plume on the
255 sub-ridge thermal structure. Potential temperatures increasing from 1404 °C at ~1100 km to 1468 °C
256 at ~400 km (Table S2), were constrained by matching the melt thickness produced by decompression
257 melting models of DMM with the crustal thickness reported by seismological surveys (e.g., Jones et
258 al., 2014 and references therein). Mantle fO_2 was not imposed in the models and was calculated using
259 the Fe^{3+}/Fe_{tot} ratio of the melts (Kress and Carmichael, 1991) with pMELTS considering that Fe^{3+} is

260 not incorporated in olivine and garnet. It is recognized, however, that in pMELTS fO_2 can be also
261 calculated based on solid phase equilibria (Asimow and Ghiorso, 1998) and that this method provides
262 systematically less oxidized values compared with the above calibration. The fO_2 determined with
263 the Kress and Carmichael (1991) calibration was used here for consistency with data from natural
264 samples.

265

266 Adiabatic decompression models were used to calculate the major element compositions (SiO_2 - TiO_2 -
267 Al_2O_3 - Fe_2O_3 - Cr_2O_3 - FeO - MgO - CaO - NaO) of progressive aggregate melts in a 2D triangular melting
268 region. Even though pMELTS allows for the direct calculation of trace element concentrations, their
269 behavior here was treated separately so that the effect of fO_2 on the distribution of V between minerals
270 and melts could be incorporated (e.g., Canil, 1997). Partition coefficients of V were calculated
271 following the parameterization of Mallmann and O'Neill (2009, 2013) while those for selected trace
272 elements (Sc, Ba, La, Nb, Zr, K) used the values of McKenzie & O'Nions (1991, 1995) and Mallmann
273 & O'Neill (2009). These particular elements were chosen to monitor the behavior of trace element
274 ratios in the models and track enrichment along the ridge (see discussion). The trace element
275 compositions of the melts were calculated assuming a depleted mantle source of Salters & Stracke
276 (2004), which provide concentrations for all elements of interest, and the phase compositions, modal
277 abundances and P, T and fO_2 from the pMELTS calculations.

278

279 (2) *Pyroxenite melting*: Modelling the composition of melts produced by melting of a bi-lithological
280 mantle, containing a mechanical mixture of peridotite and pyroxenite, is challenging due to the variety
281 of melt-rock reactions that can occur. pMELTS does not currently allow for direct calculation of
282 melting of a bi-lithological mantle and instead a multi-step approach, where the lithologies are
283 modelled separately and combined, needs to be followed (Rudge et al., 2013). A further complexity
284 for modelling pyroxenite melting is that its low solidus temperature means that melting begins above
285 4 GPa at the potential temperatures investigated here, which is outside the calibrated pressure range

286 of pMELTS. We therefore made a first-order investigation of pyroxenite's effect on the composition
287 of aggregate melts, discounting the full chemical and physical complexity a more complete model
288 would need to incorporate. Only an initial stage of isobaric melting of mantle pyroxenite was
289 modelled here, as described by Rudge et al. (2013). This approximates adiabatic decompression
290 melting by instead conducting isobaric melting calculations in the calibrated pressure range of
291 pMELTS. Assuming that the melt productivity (i.e., dF/dP) is known for the pyroxenite, the isobaric
292 calculations can be approximately related to a decompression interval. Low-degree model melts are
293 finally compared to Stapafell lavas in order to assess trace element enrichment of Reykjanes Ridge
294 basalts.

295

296 The pyroxenite chosen for modelling was KG1 from Kogiso et al. (1998), which compositionally
297 corresponds to a 1:1 peridotite:basalt mixture. The Fe^{3+}/Fe_{tot} of this lithology was set at 16% assuming
298 KG1 represents a peridotite with 5% Fe^{3+}/Fe_{tot} (DMM models) mixed with a Proterozoic basalt with
299 27% Fe^{3+}/Fe_{tot} ratio (e.g., Stolper and Keller, 2018). Proterozoic basalts can be envisaged as remnant
300 subducted slab in the mantle that were oxidized during seafloor weathering (Stolper and Keller,
301 2018). The trace element concentrations of KG1 were also calculated by mixing peridotite from
302 Salters and Stracke (2004) with recycled oceanic crust from Stracke et al. (2003). If not reported in
303 Stracke et al. (2003), the concentration of certain elements of the recycled oceanic crust were
304 calculated using the N-MORB mean of Gale et al. (2013) and the supercomposite altered MORB
305 composition from Bach et al. (2003). Concentrations of elements with high mobility were recalculated
306 using the dehydration model of Stracke et al. (2003). Model calculations were performed for a
307 pressure of 3 GPa, which corresponds to the onset of melt extraction of DMM source at the highest
308 T_p (approaching Iceland). Partition coefficients varying with P, T and composition were used and no
309 fixed fO_2 was imposed (Table S3).

310

311 **3. Results**

312 **3.1 Vanadium isotopic compositions**

313 The V isotopic composition of the Reykjanes Ridge basalts ranges between -1.09 and -0.86‰ (Table
314 S2), and extends towards lighter values from the global average for MORB ($-0.84‰ \pm 0.10$ 2SD, n=
315 22; Wu et al., 2018). No systematic variation is observed along the 700 km transect of the ridge (Fig.
316 2), with $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (Fig. 3a) or with V/Sc ratio (Fig. 3b). The average of all Reykjanes Ridge basalts
317 is $-0.97‰ \pm 0.17$ 2SD (n=19) and overlaps with the MORB average value of Wu et al. (2018). In
318 detail, the Reykjanes Ridge basalts are the light isotope end-member in the positive global correlation
319 between Na_8 and $\delta^{51}\text{V}$ determined by Wu et al. (2018) (Fig. 4).

320

321 **3.2 Trace elements**

322 Trace element concentrations are summarized in Table S2. The V/Sc ratios range between 6.5 and 10
323 and are displayed in Fig. 5 as a function of distance from Iceland and MgO content. The V/Sc ratio
324 increases approaching Iceland, however, this signal negatively correlates with MgO contents
325 indicating the strong effect of fractional crystallization (e.g., Li and Lee, 2004). Specifically, Fig. 6
326 shows that samples with $\text{V}/\text{Sc} > 8.5$ have $\text{CaO} < 11.9$ wt% and $\text{MgO} < 7.3$ wt%, demonstrating that
327 low pressure clinopyroxene fractionation is responsible for fractionating V from Sc (Fig. S1).
328 Primitive Reykjanes Ridge basalts with $\text{MgO} > 7.5$ wt%, however, are not affected by clinopyroxene
329 crystallization (Fig. 6 and S1) and show no systematic changes in V/Sc along the ridge ranging
330 between 6.5 and 8.5, in agreement with the average MORB value of 6.7 (Lee et al., 2005).

331

332 The incompatible trace element ratio Nb/Zr increases from 0.02 at 1100 km to 0.11 at 400 km distance
333 along the Reykjanes Ridge (Table S2), which has been interpreted to reflect a greater proportion of
334 plume-fed enriched material closer to Iceland (e.g., Murton et al., 2002; Schilling, 1973; Shorttle and
335 MacLennan, 2011). Short length scale heterogeneity along the Reykjanes Ridge is also shown by the
336 chemically anomalous seamount 14D, which has $\text{Nb}/\text{Zr} = 0.08$ at ~1100 km from the Icelandic plume

337 center (Table S2). This is 4 times above local background values and closer to the average crustal
338 composition of subaerial Iceland (Shorttle et al., 2015).

339

340 **3.3 Fe³⁺/Fe_{tot} ratios revisited from Shorttle et al. (2015)**

341 Shorttle et al. (2015) performed micro XANES on the same Reykjanes Ridge basalts that were
342 investigated in this study. Their work determined their Fe³⁺/Fe_{tot} ratios using the standards from the
343 Smithsonian NMNH (catalog #117393) described in Cottrell et al. (2009). By evaluating time-
344 resolved XANES spectra, Shorttle et al. (2015) ruled out beam damage causing oxidation effects.

345

346 However, since the work of Shorttle et al. (2015), cryogenic Mössbauer analyses were used to re-
347 determine the Fe³⁺/Fe_{tot} ratios of the standards developed by Cottrell et al. (2009), with the original
348 Mössbauer work having been performed at room temperature (Zhang et al., 2018). Zhang et al.'s
349 (2018) re-analysis of the standards provides lower Fe³⁺/Fe_{tot} estimates, with their work suggesting a
350 differential temperature-dependent response of the Fe³⁺ and Fe²⁺ Mössbauer doublets that has
351 compromised previous room-temperature Mössbauer work. As such, when the raw XANES spectra
352 of Shorttle et al. (2015) were reprocessed in this study using the Zhang et al. (2018) calibration, their
353 Fe³⁺/Fe_{tot} decreased (Table S2). Additionally, a more conservative measure of how to relate spectral
354 shape to Fe³⁺/Fe_{tot} was used in the quantifying of the XANES spectra here than had originally been
355 used by Shorttle et al. (2015) (who employed a principal component regression of the entire pre-edge
356 region). The peak area ratio was used in this study to form a calibration following Zhang et al. (2016),
357 as it showed the least compositional sensitivity. Although there is limited major element variability
358 in this sample suite, what variation there is co-varies with distance along ridge (via igneous
359 differentiation), so the peak area ratio approach minimizes that chance that this is aliased into
360 Fe³⁺/Fe_{tot} estimates.

361

362 Berry et al. (2018) and O'Neill et al. (2018) have recently argued for a different interpretation of the
363 Mössbauer spectra underpinning the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the XANES standards of Cottrell et al. (2009). This
364 interpretation would suggest that the recalibrated Shorttle et al. (2015) $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ should be
365 systematically lowered by a further 2-3% (absolute). However, the differences between the Berry et
366 al. (2018) and the Zhang et al. (2018) calibrations do not translate to significant differences in inferred
367 $f\text{O}_2$, because the Berry et al. (2018) calibration has been linked to a re-parameterization of how basalt
368 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ is related to $f\text{O}_2$ (O'Neill et al., 2018). The result is that either using Zhang et al. (2018)
369 with Kress and Carmichael (1991), or Berry et al. (2018) with O'Neill et al. (2018), the inferred
370 mantle $f\text{O}_2$ from basalts is nearly constant at ~FMQ.

371

372 Importantly, it is emphasized that this study is focused on understanding *relative* $f\text{O}_2$ variation along
373 the Reykjanes Ridge and how this is reflected in changes in the various $f\text{O}_2$ proxies. As such, further
374 comments on the cause of absolute discrepancies in Mössbauer-based XANES calibrations are not
375 developed.

376

377 The recalibrated $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ data of the Reykjanes Ridge basalts are reported in Table S2 and displayed
378 in Fig. 7a. The raw $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios range between 0.141 and 0.162, which is lower than the range of
379 0.155 to 0.175 previously reported by Shorttle et al. (2015). The highest values are observed in the
380 seamount samples 17D1 (0.158) and 14D (0.162) that are recognized as local heterogeneities (Murton
381 et al., 2002; Shorttle et al., 2015), with the rest of the Reykjanes Ridge basalts reaching a maximum
382 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.157. An error on $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.5% (absolute) is estimated from the long term
383 reproducibility of the standards used during the XANES sessions of Shorttle et al. (2015).

384

385 The effect of crystallization on the ferric iron content of the lavas (e.g., Cottrell and Kelley, 2011)
386 can be seen in Fig. 7a, where more evolved basalts with lower MgO have higher $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios. The
387 raw data calculated here were corrected for crystallization using the two-stage approach of Shorttle

388 et al. (2015), which combines a an empirical correction to 8 wt% MgO with olivine addition to 10
389 wt% MgO. Results are shown in Fig. 7b, where $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios corrected to 10 wt% MgO (MgO_{10})
390 are now shifted to lower values between 0.131 and 0.151. These $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios are in agreement
391 with recent MORB averages (0.143) determined by Zhang et al. (2018) using XANES. The
392 fractionation-corrected $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (Fig. 7b) are used in the discussion that follows and for comparison
393 with model results. Oxygen fugacities calculated using the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ MgO_{10} ratios and the calibration
394 of Kress and Carmichael (1991) at 2 kbar range between QFM+0.06 to QFM-0.32 (Fig. 7c). However,
395 it is remarked again that rather than absolute $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios, this study focuses on the differences
396 between natural and modelled observations.

397

398 **3.4 Melting models**

399 Given the restricted range of $\delta^{51}\text{V}$, the lack of systematic co-variation with other chemical parameters
400 (Fig. 2, 3) and the scarcity of isotopic mineral-melt fractionation factors, modelling focused on
401 reproducing the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, V/Sc and Nb/Zr ratio of the melts along the Reykjanes Ridge (Fig. 8, Table
402 S4).

403

404 In all DMM melting models, garnet is the first phase to disappear from the mantle residue during
405 decompression melting, followed by clinopyroxene. For example, for the DMM composition with
406 5% bulk $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and at the lowest T_p investigated (1404 °C), garnet disappears at approximately
407 2.2 GPa and clinopyroxene at 0.8 GPa. The same behavior is observed at higher T_p , with phases being
408 consumed in the solid assemblage at slightly higher pressures. At $T_p = 1404$ °C, melt is first produced
409 at approximately 1.9 GPa and is first extracted from the peridotite at slightly shallower depths, 1.8
410 GPa, when minimum porosity values of 0.5% (vol.) are reached (see constrains from e.g., Sims et al.,
411 1999). At the highest T_p investigated (1468 °C), melts begin to form at higher pressure, 3.4 GPa, and
412 begin separating from the residue at 3.0 GPa. Aggregate melt calculations stop at the base of the crust
413 (determined by pressure of the overlying melt-derived crust) at a particular T_p along the Reykjanes

414 Ridge. These pressures at the base of the crust range from 0.21 GPa in the south to 0.32 GPa at the
415 northern most section of the ridge, corresponding to crustal thicknesses of ~7 and 11 km, respectively
416 (assuming 2900 kg/m³ as an average crustal density). Over the 1404 °C to 1468 °C T_p range
417 considered, maximum extents of melting (F) increase from 25% to 29%.

418

419 Modelled Fe^{3+}/Fe_{tot} ratios of the aggregate melts decrease towards Iceland as higher potential
420 temperatures are encountered (Fig. 8a; Table S4). Depending on source Fe^{3+}/Fe_{tot} , decreases of
421 between 0.02 and 0.03 Fe^{3+}/Fe_{tot} in the modelled aggregate melt compositions are observed as T_p
422 increases by 64 °C (i.e., from 1404 °C to 1468 °C), with associated decrease in melt absolute fO_2
423 between 0.78 and 0.83. This result is consistent with the findings of Gaetani (2016), who also showed
424 that higher mantle temperatures produce more reduced aggregate melts. The calculated V/Sc ratio of
425 partial melts produced also reflects changes in fO_2 (Fig. 8b), indicating an increased average Dv/D_{Sc}
426 during melting towards Iceland (Table S4). However, V/Sc only exhibits a low amplitude response
427 to these changing melting conditions, varying by only 0.7-0.9 at a given Fe^{3+}/Fe_{tot} source
428 concentration over the investigated range of T_p (Fig. 8b). As expected for highly incompatible and
429 fO_2 insensitive elements, the calculated Nb/Zr ratio in the melts are near constant at ~0.03 along the
430 Reykjanes Ridge (Fig. 8c), regardless of the initial bulk Fe^{3+}/Fe_{tot} (Table S4).

431

432 The pyroxenite modelling focused on calculating Fe^{3+}/Fe_{tot} and trace element ratios, where disparities
433 between the melt concentrations from the DMM models and the Reykjanes Ridge basalts are observed
434 at distances < 700 km to Iceland (Fig. 8a, c). The low-degree (F% = 0.2 to ~20%) melt compositions
435 formed in the KG1 pyroxenite melting models are reported in Table S5. In the isobaric melting model
436 at 3 GPa, pyroxenite starts melting at 1384 °C and melts are extracted from the solid assemblage
437 (consisting of olivine + garnet + clinopyroxene + spinel) at 1394 °C, when the porosity is higher than
438 0.5% (vol.). With increasing temperature, orthopyroxene becomes a stable phase in the solid
439 assemblage with abundances increasing as melting proceeds. This is contrary to clinopyroxene

440 abundances, which decrease as it is consumed on melting. Spinel is the least abundant phase in the
441 solid assemblage and its abundance also slightly decreases with increasing temperature. As a result
442 of these melting reactions, the liquid's $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ increases with increasing extent of melting as
443 clinopyroxene (the dominant phase in the solid assemblage and major host of Fe^{3+}) and spinel
444 (another reservoir of Fe^{3+} in its magnetite component) are progressively consumed. Trace element
445 ratios used to indicate enrichment towards Iceland (e.g., Nb/Zr, La/Yb) are high in these melts (Table
446 S5). For example, the calculated Nb/Zr ratio of the isobaric melts produced by melting KG1
447 pyroxenite ranges between 0.12 and 0.04 at melt fractions 0.2 and 20%, respectively, which are higher
448 than the ratios produced in the DMM models at any T_p (Table S4).

449

450 **Discussion**

451 **4.1 Vanadium isotopes as an $f\text{O}_2$ proxy**

452 The $\delta^{51}\text{V}$ measured thus far in basaltic lavas with >4 wt% MgO have limited variation (Prytulak et
453 al., 2013, 2017; Wu et al., 2018). However, an increase of $\sim 2\text{‰}$ in $\delta^{51}\text{V}$ towards heavier $\delta^{51}\text{V}$ values
454 during progressive closed-system fractional crystallization of genetically related magmas has been
455 ascribed mainly to the crystallization of isotopically light iron oxides (Prytulak et al., 2017; Sossi et
456 al., 2018). The Reykjanes Ridge basalts investigated in this study all have MgO contents >6.3 wt%
457 (Shorttle et al., 2015), and thus fractional crystallization is not expected to influence their V isotopic
458 signatures. The Reykjanes Ridge basalts display coherent and significant variation in trace element
459 (e.g. Nb/Zr) and radiogenic isotopic compositions (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$; Murton et al.,
460 2002). Increasing enrichment along the Reykjanes Ridge on approach to Iceland is commonly
461 interpreted as the influence of the Icelandic mantle plume (e.g., Murton et al., 2002; Schilling, 1973).
462 Murton et al. (2002) explained the geochemical variations of the Reykjanes Ridge basalts by mixing
463 of six differently enriched mantle components. Thus, the data presented here suggest that V isotopes
464 are not sensitive to the chemical heterogeneities in the mantle source below the Reykjanes Ridge
465 documented by trace element and radiogenic isotope systems. This point is emphasized by the

466 unremarkable V isotopic composition of sample 14D of $\delta^{51}\text{V} = -1.09$ (Fig. 2), which in terms of its
467 trace elements and radiogenic isotopes clearly samples a local mantle compositional heterogeneity.

468

469 Wu et al. (2018) recently proposed that V isotope fractionation may be sensitive to the extent of
470 melting by demonstrating a positive correlation between $\delta^{51}\text{V}$ and Na_8 , an indicator of the degree of
471 melting (Klein and Langmuir, 1987). The Reykjanes Ridge basalts have Na_8 between 1.83 and 2.19,
472 and are displaced to isotopically lighter values compared with higher Na_8 MORB (Fig. 4). The
473 Reykjanes Ridge basalts follow the general trend established by Wu et al. (2018), supporting the
474 notion that the extent of melting may influence the V isotopic composition of MORBs on a global
475 scale.

476

477 Importantly, the V isotopic compositions of the Reykjanes Ridge basalts do not correlate with
478 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ or V/Sc (Fig. 3). This observation indicates that V isotopes of primitive basalts are not
479 sensitive to an $f\text{O}_2$ difference of ~ 0.3 log unit along the Reykjanes Ridge. However, primitive samples
480 not affected by fractional crystallization and equilibrated at more extreme $f\text{O}_2$ conditions, need to be
481 analyzed to further assess the sensitivity of V isotopes to redox conditions for their use as an $f\text{O}_2$
482 sensor.

483

484 **4.2 V/Sc as an $f\text{O}_2$ proxy**

485 The V/Sc ratio of the partial melts calculated by pMELTS are compared to the Reykjanes Ridge
486 compositions in Fig. 8b. The $D^{\text{peridotite/melt}}$ of trace elements is calculated based on $D^{\text{min/melt}}$ and the
487 modal abundances of the minerals in the solid residue, which change as a function of T_p and P during
488 decompression. The average V partition coefficients increase towards Iceland, where higher potential
489 temperatures are met and resultingly lower $f\text{O}_2$'s are calculated; the average Sc partition coefficient
490 only slightly increases towards Iceland due to the deeper onset of melting, meaning that garnet is
491 residual in the phase assemblage during proportionally more of the melting interval, and garnet has

492 the highest D_{Sc} (Table S4). The net effect of these processes is for D_V/D_{Sc} to increase towards Iceland,
493 resulting in the gently decreasing V/Sc ratio observed in the accumulated partial melts generated by
494 pMELTS (Fig. 8b). The melting model of DMM with initial 5% Fe^{3+}/Fe_{tot} reproduces, within error,
495 the V/Sc ratios of the primitive (>7.5 wt% MgO) Reykjanes Ridge basalts along the entire extent of
496 the ridge between 1100 and 400 km (Fig. 8b). The V/Sc of primitive basalts translates into fO_2 's
497 ranging between $\Delta FMQ = 0$ to -0.5 following the model of Lee et al. (2005). These fO_2 values are
498 consistent with those calculated from the Fe^{3+}/Fe_{tot} (Fig. 7c). However, interpretations of mantle fO_2
499 values determined by V/Sc proxy are model-dependent, as the V/Sc concentration of basalts depends
500 on both $D_V^{min/melt}$ and $D_{Sc}^{min/melt}$, the source concentrations and the fO_2 conditions. For example,
501 Prytulak et al. (2017) used batch melting calculations to illustrate that a less oxidized, fertile mantle
502 and a more oxidized, depleted mantle, with respectively higher and lower $D_V^{pdt/melt}$, can produce
503 similar V/Sc ratios in MORB and arc lavas, highlighting the limitations of V/Sc as a direct redox
504 proxy (see also Bucholz and Kelemen (2019) for this discussion in an arc context).

505

506 **4.3 Fe^{3+}/Fe_{tot} as an fO_2 proxy**

507 The ferric iron content of partial melts formed during adiabatic decompression of mantle peridotite
508 reflects both source Fe^{3+}/Fe_{tot} and T_p . At a fixed source Fe^{3+}/Fe_{tot} , the upwelling mantle peridotite
509 crosses fO_2 isopleths that become slightly more oxidized through the spinel stability field (Gaetani,
510 2016). Instantaneous melts may therefore become more oxidized as decompression proceeds.
511 However, aggregate melts are also sensitive to the onset of melting, and when melting begins in the
512 garnet field, at $T_p > 1447$ °C, the Fe^{3+}/Fe_{tot} of the aggregate melts decreases until garnet is exhausted
513 from the solid assemblage. The net effect is that the Fe^{3+}/Fe_{tot} of aggregate melts decreases with
514 increasing potential temperatures (Gaetani, 2016), as observed in the model runs as Iceland is
515 approached (Fig. 8a).

516

517 Melting models of DMM composition with 5% initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ reproduce the Reykjanes Ridge basalt
518 compositions between ~700 and 1100 km from the plume, in agreement with the V/Sc data (Fig. 8a-
519 b). The highest $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of seamounts 14D and 17D, which formed from particularly enriched
520 sources far from Iceland (Murton et al., 2002), are in agreement with the model, given the 0.01 2SD
521 uncertainty of XANES analyses of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. Notably, within ~700 km of the Icelandic plume, the
522 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of natural samples clearly deviate from that of modelled partial melts. While $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$
523 ratio in modelled partial melts decreases monotonically by 0.02-0.03 towards Iceland, the Reykjanes
524 Ridge basalts remain nearly constant (Fig. 7a-b). The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of the Reykjanes Ridge basalts
525 at 400 km distance can be reproduced by melting DMM with a higher initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ content (6%,
526 Fig. 8a). However, deviations from the models in both $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and trace element ratios at
527 approximately 700 km from Iceland require the mantle source heterogeneity, as is documented by
528 radiogenic isotopes (e.g., Murton et al., 2002). For example, a difference of 0.02 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ between
529 natural and modelled melts is reached at 400 km distance (Fig. 8a), which is twice the conservative
530 uncertainty of the XANES analyses (0.01 2SD). Shorttle et al. (2015) suggested that the presence of
531 recycled, oxidized oceanic crust in the mantle sampled by the Icelandic plume may explain the trace
532 element and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ signatures. The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of the Reykjanes Ridge basalts are therefore
533 sensitive to the melting conditions and, importantly, to the presence of chemical heterogeneities in
534 the mantle source as observed in the northern part of the ridge segment (Fig. 8a). The higher $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$
535 signal observed in the Reykjanes Ridge basalts near Iceland, compared to modelled concentrations
536 of DMM with 5% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, can be explained by the presence of pyroxenite in the source. Calculated
537 partial melts of KG1 pyroxenite have high $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (up to 0.187, Table S5), which if mixed with
538 melts produced from a nominal DMM peridotite will counterbalance the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ decrease predicted
539 from T_p effects alone. Notably, the more oxidized signature towards Iceland recognized by the
540 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ difference between the Reykjanes Ridge basalts and the DMM model prediction is not
541 recorded in the V/Sc ratios (Fig. 8b).

542

543 **4.4 The influence of a more oxidized and enriched source on the geochemistry of Reykjanes**
544 **Ridge basalts near Iceland**

545 The Nb/Zr concentrations of partial melts produced by DMM melting models (~0.03) are similar to
546 the Reykjanes Ridge basalts between 1100-700 km (Fig. 8c). However, Nb/Zr deviates from model
547 predictions at approximately 700 km and a ten-fold difference between the Reykjanes Ridge basalts
548 and the partial melts produced by DMM models is reached at 400 km (Fig. 8c). The deviation of
549 Nb/Zr ratios between the RR basalts and DMM models coincides with Fe^{3+}/Fe_{tot} mismatches (Fig.
550 S2), indicating the combined oxidized and enriched nature of the mantle source sampled by the
551 Reykjanes Ridge basalt close to Iceland.

552

553 In order to investigate the effect of lithological heterogeneity on Fe^{3+}/Fe_{tot} and trace elements used as
554 an indicator of enrichment, lavas from Stapafell were considered as a proxy for enriched melts.
555 Stapafell is one of the most enriched basalts on the Icelandic rift zone (Fig. 1) with high trace element
556 ratios (e.g., Nb/Zr= 0.157), high $^{87}Sr/^{86}Sr$ and low $^{143}Nd/^{144}Nd$ (e.g., Peate et al., 2009). Importantly,
557 Stapafell continues the geochemical trends towards Iceland set by the Reykjanes Ridge basalts in the
558 direction of progressively enriched compositions. Trace element concentrations of the Reykjanes
559 Ridge basalts range between partial melts produced by DMM melting models and Stapafell lavas
560 (Fig. 9), indicating that the apparent influence of an enriched source on approach to Iceland is possibly
561 the same that supplies Stapafell.

562

563 The composition of one of the Reykjanes Ridge basalts closest to Iceland at ~400 km (185D4, Table
564 S2), displays one of the highest deviations of Fe^{3+}/Fe_{tot} and Nb/Zr from the predictions of the DMM
565 melting models. The chemistry of 185D4 glass can be envisaged as a mixture of two melts, one
566 produced from ambient DMM and one from the enriched source of Stapafell lavas. This simplification
567 allows the composition of the enriched melt portion for sample 185D4 to be calculated through mass
568 balance, using the chemical composition of a Reykjanes Ridge basalt not influenced by the plume

569 (e.g., sample 12aD1 at ~1100 km; Table S2) as the melt produced by melting DMM and normalizing
570 the contributions from each melt to the crustal thickness. The enriched melt composition calculated
571 following this approach has a REE pattern that is similar to Stapafell basalt (Fig. 10), also validating
572 the choice of Stapafell to investigate enrichment along the Reykjanes Ridge.

573

574 Pyroxenite melting models conducted here can reproduce some of the trace element contents of
575 Stapafell lavas (Table S5), suggesting that KG1 pyroxenite or similar lithologies may cause the trace
576 element enrichment towards Iceland, in agreement with Shorttle and MacLennan (2011). Low-degree
577 melts ($F= 4-10\%$) have $Fe^{3+}/Fe_{tot}= 0.159-0.176$, which if mixed with melts produced by melting
578 DMM, in a 1:1 ratio, replicate the Fe^{3+}/Fe_{tot} of the Reykjanes Ridge basalts at 400 km from Iceland.
579 The models developed in this study confirm the increasing contribution from a pyroxenitic rich source
580 towards Iceland along the Reykjanes Ridge, which increases incompatible trace element
581 concentrations and is required to counterbalance the modelled decreasing Fe^{3+}/Fe_{tot} of the basalts
582 from a DMM source.

583

584 **5. Conclusions**

585 The behavior of V isotopes, V/Sc and Fe^{3+}/Fe_{tot} in the Reykjanes Ridge basalts can be summarized
586 as follow:

587

- 588 1. Vanadium isotopic compositions do not systematically vary along the Reykjanes Ridge ($\delta^{51}V= -$
589 $0.97\text{‰} \pm 0.17$, $n=19$). $\delta^{51}V$ is not sensitive to the small fO_2 differences observed along the
590 Reykjanes Ridge but may be controlled by the extent of melting when compared with global
591 decompression melts (Wu et al., 2018). More studies on pristine basalts equilibrated at more
592 extreme fO_2 conditions than those recorded along the Reykjanes Ridge are required to investigate
593 the sensitivity of V isotopes to mantle fO_2 . Vanadium isotopes appear insensitive to the presence
594 of pyroxenite in the Reykjanes Ridge mantle source.

595

596 2. V/Sc ratios show a general increase towards Iceland due to fractional crystallization of
597 clinopyroxene. High MgO basalts (> 7.5 wt%) not altered by crystallization show a minor decrease
598 of V/Sc ratios along the Reykjanes Ridge towards Iceland that agree with melts produced by DMM
599 melting models. However, V/Sc in the Reykjanes Ridge basalts does not increase towards Iceland
600 where enriched and more oxidized mantle source is sampled by the basalts, suggesting that this
601 proxy is not responsive to the presence of mantle chemical heterogeneities in these samples. The
602 use of V/Sc as a fO_2 proxy is highly model-dependent, requiring independent constraints on source
603 mineralogy, trace element abundance, extent of melting, and T_p . These parameters for Reykjanes
604 Ridge lavas are sufficiently uncertain at this time to permit non-unique fO_2 determinations from
605 measured V/Sc ratios.

606

607 3. Recalibrated Fe^{3+}/Fe_{tot} ratios, corrected for fractionation (MgO_{10}), remain virtually constant along
608 the Reykjanes Ridge. Thermodynamic melting models of DMM can reproduce Reykjanes Ridge
609 Fe^{3+} contents between 1100 and 700 km from the plume. However, melts produced upon melting
610 DMM need to be mixed with melts formed from an enriched source close to the plume, such as
611 pyroxenite, to replicate the Fe^{3+}/Fe_{tot} ratios observed between 400 and 700 km, which would
612 otherwise decrease under the influence of increased mantle potential temperature. Basalt Fe^{3+}/Fe_{tot}
613 both depends on melting conditions (T_p) and is responsive to bulk oxidation state alterations
614 associated with the presence of chemical heterogeneities in the mantle.

615

616 **Acknowledgments**

617 This study was funded by the Natural Environment Research Council NERC grant NE/N009568/1 to
618 J.M. and J.P. Katharina Kreissig and Barry Coles are thanked for their help in conducting the V
619 isotopes work. Thanks also to Jason Day for the support in performing the LA-ICPMS analyses. OS
620 acknowledges Diamond Light Source for time on beamline I18 under proposals SP9446, SP9456 and

621 SP12130 and the support during our analytical sessions from beamline scientist Konstantin Ignatyev
622 and principal beamline scientist Fred Mosselmans. This manuscript greatly benefitted from comments
623 of an anonymous reviewer and a very careful revision of Maryjo Brounce especially with regards to
624 the XANES and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ calibration debate.

625

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816

817 **Figure captions**

818 **Fig. 1:** Map showing the location of the Reykjanes Ridge basalts investigated in this study (dark blue
819 circles indicating samples with $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and V/Sc data, light blue circles showing those with
820 additional V isotopic compositions). Stapafell eruption on the Reykjanes Peninsula (coral circle) and
821 the plume center location (white star) proposed by Shorttle et al. (2010) are also shown. The map was
822 prepared with the software GeoMapApp (www.geomapapp.org).

823

824 **Fig. 2:** Vanadium isotopes along the investigated spread of the Reykjanes Ridge, reported as $\delta^{51}\text{V}$,
825 plotted as a function of MgO content (Shorttle et al., 2015). The grey horizontal bar indicates the
826 average MORB value of Wu et al. (2018) with calculated 2SD.

827

828 **Fig.3:** Vanadium isotopic composition plotted against (a) $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (corrected to MgO_{10} , see text)
829 and (b) V/Sc. Circles are color coded as a function of MgO content measured by electron microprobe
830 (Shorttle et al., 2015).

831

832 **Fig. 4:** Na_8 vs $\delta^{51}\text{V}$ of the Reykjanes Ridge lavas investigated in this study (circles). Ridge segments
833 data from Wu et al. (2018) and Prytulak et al. (2013) are also plotted as diamonds (Na_8 data reported
834 in Wu et al., 2018). Na_8 values for the Reykjanes Ridge samples were calculated from the regressed
835 melt compositions at ~8 wt% MgO (see text) using the formula of Shorttle et al. (2010). The grey
836 horizontal bar indicates the average MORB value of Wu et al. (2018) with calculated 2SD.

837

838 **Fig. 5:** The V/Sc ratio of the Reykjanes Ridge basalts as a function of distance from the Icelandic
839 plume. Samples are color coded with the MgO content (Shorttle et al., 2015), highlighting the effect
840 of fractional crystallization. Errors of the V/Sc ratios were calculated from the errors on V and Sc
841 (LA-ICPMS analyses; Supplementary Table S2) and range between 0.11 and 1.29 1SD.

842

843 **Fig. 6:** CaO vs MgO content of the Reykjanes Ridge basalts as a function of V/Sc ratio.

844

845 **Fig. 7:** $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio and oxygen fugacity along the Reykjanes Ridge. (a) Raw $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios
846 recalculated from the study of Shorttle et al. (2015) using the new calibration of the XANES standards
847 (Zhang et al., 2018; see text). Data are plotted as a function of MgO content of the glasses (Shorttle
848 et al., 2015). (b) $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of the same samples in (a) but now corrected for fractional
849 crystallization to MgO_{10} (see text), as a function of Nb/Zr. (c) Oxygen fugacity, as $\log f\text{O}_2$ relative to
850 the FMQ buffer (Frost, 1991), calculated from the data in (b) using the calibration of Kress and
851 Carmichael (1991) at 2 kb and 1200 °C. Data are plotted as a function of Nb/Zr of the glasses.

852

853 **Fig. 8:** Reykjanes Ridge basalt (blue circles) plotted as a function of distance from the Icelandic
854 plume along with partial melt compositions produced by the thermodynamic melting models of DMM
855 with 4, 5 and 6% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ in the source (grey circles). (a) $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of basalt corrected to
856 MgO_{10} . (b) V/Sc ratios, where light blue circles indicate more evolved basalts (< 7.5 wt% MgO) and
857 dark blue circles indicate more primitive compositions (> 7.5 wt% MgO). (c) Nb/Zr ratios, with
858 concentrations of the different models overlapping and being indistinguishable at the scale of the plot.
859 Pale red arrows in panel (a) and (c) highlight the disparity between Reykjanes Ridge basalts and
860 DMM modelled compositions near Iceland.

861

862 **Fig. 9:** Ba and La compositional trend of Reykjanes Ridge basalts (blue) between partial melts
863 produced by DMM melting model with 5% initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (grey) and Stapafell basalt from the
864 Reykjanes Peninsula (coral).

865

866 **Fig. 10:** Spider diagram reporting the trace element composition of Stapafell basaltic glass (Peate et
867 al., 2009), in coral, and the enriched melt forming at the point closest to the Icelandic plume along
868 the Reykjanes Ridge, in blue. In grey and yellow are also represented the compositions of Reykjanes
869 Ridge basalts 12aD1 (~1100 from Iceland) and 185D4 (~ 400 km from Iceland), respectively, used
870 to mass balance the enriched melt composition. See text for more details.

871

872 **Fig. S1:** Fractional crystallization model for Reykjanes Ridge basalt 153D3. The melt concentration
873 was calculated at an arbitrary low pressure of 0.6 kb using MELTS (Ghiorso et al., 2002; Smith and
874 Asimow, 2005). The model shows that V/Sc ratios in melts with MgO >7.5 wt% are not affected by
875 crystallization. Calculations employed D_V and D_{Sc} at FMQ from Mallmann and O'Neill (2009, 2013).
876 Between 9 and 7.5 wt% MgO only olivine crystallizes, while clinopyroxene (cpx) and plagioclase
877 (plag) start to crystallize at ~7.5 and ~6 wt% MgO, respectively.

878

879 **Fig. S2:** Difference in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ between the Reykjanes Ridge basalt and the partial melt composition
880 produced by DMM melting model with 5% initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ($\Delta\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$), calculated at a particular
881 distance, against the Nb/Zr ratio of the Reykjanes Ridge basalts.