

13 **Abstract**

14 Ocean Island Basalts (OIBs) are generated by mantle plumes, with their geochem-
 15 istry controlled by a combination of source composition, temperature, and thickness of
 16 overlying lithosphere. For example, OIBs erupting onto thicker, older oceanic lithosphere
 17 are expected to exhibit signatures indicative of higher average melting pressures. Here,
 18 we quantitatively investigate this relationship using a global dataset of Neogene and younger
 19 OIB compositions. Local lithospheric thicknesses are estimated using theoretical plate-
 20 cooling models and Bayes factors are applied to identify trends. Our findings provide com-
 21 pelling evidence for a correlation between OIB geochemistry and lithospheric thickness,
 22 with some variables (SiO_2 , Al_2O_3 , FeO , Lu, Yb and λ_2) showing linear trends that can
 23 be attributed to increasing average melting pressure, whereas others (λ_0 and λ_1 , CaO)
 24 require a bi-linear fit with a change in gradient at ~ 55 km. Observed variations in highly
 25 incompatible elements are consistent with melt fractions that decrease with increasing
 26 lithospheric thickness, as expected. Nevertheless, at thicknesses beyond ~ 55 km, the
 27 implied melt fraction does not decrease as rapidly as suggested by theoretical expecta-
 28 tions. This observation is robust across different lithospheric thickness estimates, includ-
 29 ing those derived from seismic constraints. We interpret this result as weak plumes fail-
 30 ing to effectively thin overlying lithosphere and/or producing insufficient melt to erupt
 31 at the surface, in combination with a ‘memory effect’ of incomplete homogenisation of
 32 melts during their ascent. This view is supported by independent estimates of plume buoy-
 33 ancy flux, indicating that OIB magmatism on older lithosphere may be biased towards
 34 hotter plumes.

35 **Plain Language Summary**

36 Most of Earth’s volcanoes occur at tectonic plate boundaries, but some emerge within
 37 plate interiors in so-called intra-plate settings. These volcanoes are believed to mark the
 38 surface expression of mantle plumes: hot, buoyant columns that rise from the core-mantle-
 39 boundary towards the surface. As they rise, lower pressures near the surface facilitate
 40 melting. However, the lithosphere – Earth’s rigid outermost shell – limits plume ascent,
 41 and therefore controls the final (lowest) melting pressure of mantle plumes (the ‘lid ef-
 42 fect’). Here, we collate and analyse a global geochemical dataset of oceanic island basalts
 43 – the products of plume melting – to test this hypothesis. Using a range of diagnostics
 44 and a novel probabilistic analytical approach, we find that some geochemical paramet-
 45 ers either linearly increase or decrease with lithospheric thickness, whereas other trends
 46 exhibit abrupt changes. We propose potential explanations for these patterns, focusing
 47 on factors such as the melt fraction (which is sensitive to temperature and pressure) and
 48 variations in mantle mineralogy at different depths. Notably, we suggest that there is
 49 a higher chance of observing volcanism above hotter plumes in regions of thicker litho-
 50 sphere and identify a ‘memory effect’, whereby their geochemistry to some extent pre-
 51 serves information from the initial melting process.

52 **1 Introduction**

53 While the majority of Earth’s volcanism is concentrated at tectonic plate bound-
 54 aries, there are many volcanic activities that occur within plate interiors and/or extend
 55 across plate boundaries. Although some of this volcanism has been attributed to edge-
 56 driven convection, shear-driven upwelling and bursts in slab flux (e.g., King & Ander-
 57 son, 1998; Conrad et al., 2011; D. R. Davies & Rawlinson, 2014; Rawlinson et al., 2017;
 58 Mather et al., 2020; Duvernay et al., 2021), the majority displays characteristics that im-
 59 ply an association with mantle plumes – hot, buoyant columns that rise from the core-
 60 mantle boundary towards the surface (e.g., Morgan, 1971; Griffiths & Campbell, 1990,
 61 1991; Duncan & Richards, 1991; Campbell, 2007; D. R. Davies & Davies, 2009, Figure 1).
 62 As they rise into the shallow mantle, plumes undergo partial melting, with voluminous

63 plume heads giving rise to Large Igneous Provinces and their tails producing lower frac-
 64 tion melts, termed *Ocean Island Basalts* (OIBs) in oceanic settings (e.g. White & McKen-
 65 zie, 1989). The geological, geophysical and geochemical characteristics of OIBs have been
 66 widely studied (e.g., White & McKenzie, 1989; Weaver, 1991; Courtillot et al., 1999; Li
 67 et al., 2014; D. R. Davies, Goes, & Sambridge, 2015; Jones et al., 2016; Iaffaldano et al.,
 68 2018; P. W. Ball et al., 2019; Nebel et al., 2019; Jones et al., 2019; Bao et al., 2022). Nev-
 69 ertheless, despite mantle-plume theory being well established, our understanding remains
 70 incomplete concerning the interaction between plumes and overlying lithosphere – Earth’s
 71 rigid outermost shell – and its reflection in the geochemistry of OIBs.

72 The lithospheric mantle is cool and refractory. Accordingly, it is unlikely to melt
 73 and generate magmas (e.g., Katz et al., 2003). In addition, the lithosphere is highly vis-
 74 cous and is therefore difficult to mechanically deform (e.g., Burov et al., 2007; Camp-
 75 bell, 2007; Burov & Gerya, 2014; Jones et al., 2017; Duvernay et al., 2021, 2022). As a
 76 consequence, it is expected to act as a lid that limits plume ascent and thereby dictate
 77 the lowest melting pressure for plume-derived melts (Figure 1). This behaviour is the
 78 so-called ‘*lid effect*’, first proposed by Watson and McKenzie (1991) and subsequently
 79 examined in several studies at both global (e.g. Ellam, 1992; Humphreys & Niu, 2009;
 80 Dasgupta et al., 2010; Niu et al., 2011; Niu, 2021) and regional scales (e.g. Gibson & Geist,
 81 2010; D. R. Davies, Rawlinson, et al., 2015; Hole & Millett, 2016; Liu et al., 2016; Klöcking
 82 et al., 2018). Despite this extensive body of work, a complete and statistically rigorous
 83 assessment of the relationship between lithospheric thickness and the geochemistry of
 84 plume-derived magmas has not yet been established: previous studies have either described
 85 this relationship qualitatively or only made use of simple linear statistics (e.g. Ellam,
 86 1992; Humphreys & Niu, 2009; Niu et al., 2011; D. R. Davies, Rawlinson, et al., 2015;
 87 Niu, 2021). Several important questions remain, including:

- 88 1. Do available geochemical data statistically support existence of a lid effect?
- 89 2. Are observed trends consistent with theoretical expectations for partial melting
 90 at different pressures?
- 91 3. What other processes might be affecting observed trends?

92 The last few years have seen progress in several areas that are pertinent to answering
 93 these questions. There has been a steady increase in the quantity and accessibility of high-
 94 quality data available on melt geochemistry, improvements in the accuracy and resolu-
 95 tion of lithospheric thickness datasets, and the advent of comprehensive statistical tech-
 96 niques to examine any potential relationship between the two. There is, therefore, an
 97 opportunity to undertake a critical reevaluation of evidence for the lid effect.

98 Our study exploits an extensive and carefully curated dataset of geochemical anal-
 99 yses for OIBs, extracted from the ever-growing open-source **GeoRoc** database (<https://georoc.eu>).
 100 The dataset is filtered to eliminate those samples whose geochemistry has been strongly
 101 altered after initial magma generation. Alongside the geochemical parameters examined
 102 by previous studies, we analyse geochemical diagnostics on Rare Earth Elements (REEs)
 103 that have been recently proposed by O’Neill (2016) and are expected to show a clear pres-
 104 sure signal owing to their sensitivity to melt fraction and the spinel-garnet phase tran-
 105 sition. The latter, a pressure-sensitive aluminium-rich phase change, induces a substan-
 106 tial change to the peridotite mineral assemblage, with different REEs exhibiting vary-
 107 ing compatibility between the two phases (e.g., Sun & Liang, 2013; Wood et al., 2013).
 108 Furthermore, we exploit new estimates of lithospheric thickness, based upon both the-
 109 oretical models of oceanic spreading and observational constraints from seismic data (Richards,
 110 Hoggard, Crosby, et al., 2020; Hoggard, Czarnota, et al., 2020). Using a probabilistic Bayesian
 111 approach that is capable of detecting sharp changes in geochemical trends, we investi-
 112 gate the role of lithospheric thickness in controlling OIB geochemistry and explore the
 113 mechanisms that underpin the trends that we observe.

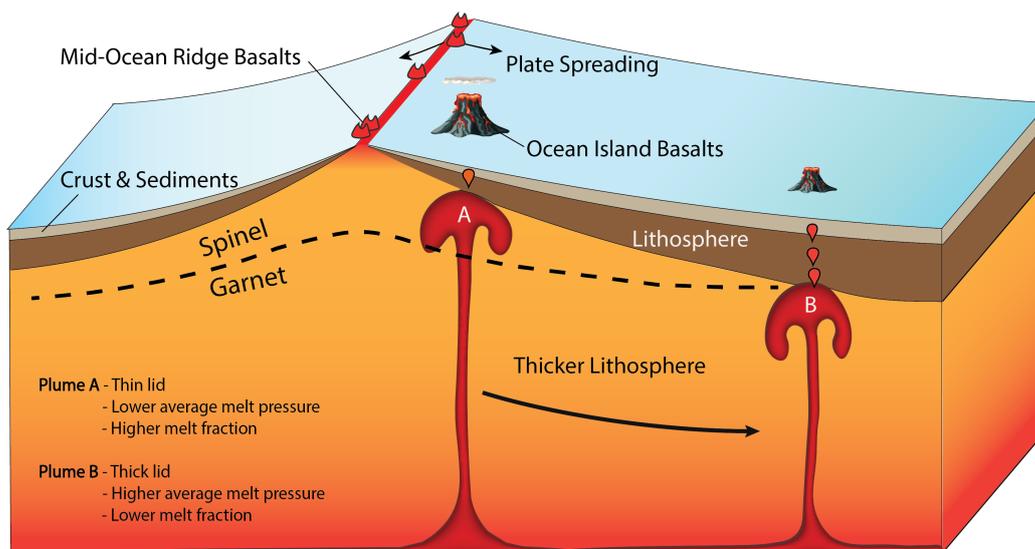


Figure 1. Schematic cartoon illustrating how oceanic lithosphere acts as a lid, hindering the ascent of mantle plumes. The dashed line represents the spinel-garnet transition. When a plume rises beneath thin lithosphere, large melt volumes will be produced with more melts generated within the spinel stability field, thus exhibiting a low-pressure signature. Conversely, when a plume rises beneath thick lithosphere, melt volumes are smaller and melting will principally occur within the garnet stability field, displaying a high-pressure signature.

114 The remainder of our paper is structured as follows. In Section 2.1, we introduce
 115 our OIB database, our approach to filtering this data, and the geochemical diagnostics
 116 examined. In Section 2.2, we describe the lithospheric thickness estimates at each indi-
 117 vidual island, derived using both plate-cooling models and local constraints from surface-
 118 wave tomography models. In Section 2.3 we present a probabilistic Bayesian approach
 119 developed and utilised to analyse relationships between geochemistry and lithospheric
 120 thickness. Our results are presented in Section 3, with their sensitivities, implications
 121 for our understanding of the lid-effect, the role of the lithosphere in modulating plume
 122 melting, and other processes affecting OIB chemistry, discussed in Section 4.

123 2 Methods

124 2.1 Geochemical Dataset

125 In compiling our geochemical database of the products of plume melting in oceanic
 126 settings, we have chosen to focus solely on OIB data and neglect data associated with
 127 Large Igneous Provinces (LIPs). This omission is because LIPs are the melt-products
 128 of plume heads and are also often associated with continental break-up. They regularly
 129 occur in the vicinity of the continent-ocean boundary and consequently often display a
 130 strong crustal signature (e.g., Chung & Jahn, 1995; Owen-Smith et al., 2017; J. H. F. L. Davies
 131 et al., 2021). It is also therefore difficult to estimate lithospheric thickness at the time
 132 of eruption (e.g., Hill, 1991; Courtillot et al., 1999).

133 2.1.1 Source of Analyses

134 Geochemical data for major and trace element concentrations are compiled from
 135 OIB data in the GeoRoc database. As the number of high-quality glass samples is lim-

136 ited, the data are derived principally from analyses of bulk rocks (with some additional
 137 glass analyses where available). The GeoRoc database contains geochemical information
 138 from over 20,000 OIB samples from the Atlantic, Indian and Pacific Oceans, with their
 139 locations mapped in Figure 2 and listed in Tables S1 and S2. Our database incorporates
 140 concentrations of major (SiO_2 , Al_2O_3 , MgO , FeO , TiO_2 , Na_2O , K_2O , CaO , P_2O_5) and
 141 trace elements (REEs, U, Nb, Ba, Th), as well as derivative parameters describing REE
 142 patterns (λ_0 , λ_1 and λ_2 , from O'Neill, 2016). Major elements with high concentrations
 143 are likely influenced by the stabilities of minerals under varying pressure and their com-
 144 patibilities in mantle peridotite. We expect that major elements with lower concentra-
 145 tions (usually < 5 wt. %) and trace elements are sensitive to phase changes and the melt
 146 fraction, which, in turn, are sensitive to pressure. The combined use of both major and
 147 trace element parameters can therefore offer a more complete picture of the impact of
 148 the lithospheric lid on mantle melting processes.

149 **2.1.2 Database Filtering**

150 Melts generated from peridotite melting are subject to various physiochemical pro-
 151 cesses during their ascent and whilst residing in magma chambers, such as fractional crys-
 152 tallisation and crustal assimilation (e.g., Sisson & Grove, 1993; Class & Goldstein, 1997;
 153 Straub et al., 2013; Ubide et al., 2022). Additionally, post-eruptive hydrothermal alter-
 154 ation can substantially alter the original chemical signature of basalts (e.g., Saito et al.,
 155 2015; Khogenkumar et al., 2016). Some previous studies of the lid effect have chosen to
 156 use all available OIB geochemical data without attempting to screen samples that are
 157 heavily impacted by these additional processes (e.g., Humphreys & Niu, 2009). In our
 158 analyses, however, we have filtered OIB samples to isolate those that exhibit a compo-
 159 sition most similar to that of the primitive magma. We therefore restrict our dataset to
 160 samples that have not undergone excessive alteration or fractional crystallization after
 161 initial generation. We do so by applying the following filters to the data:

- 162 1. Only those samples with SiO_2 43–54 wt.% are accepted in order to exclude melts
 163 that fall outside of the basalt field (Figure 3a);
- 164 2. Only samples with MgO 7–16 wt.% are accepted. Values with $\text{MgO} < 7$ wt.% are
 165 likely to have been subjected to extensive fractional crystallisation (e.g., Sisson
 166 & Grove, 1993) and may contain clinopyroxene and/or plagioclase phenocrysts or
 167 have experienced clinopyroxene and plagioclase crystallisation, complicating in-
 168 terpretation of major element trends. Samples with $\text{MgO} > 16$ wt.% are rejected
 169 because they are likely to contain olivine phenocrysts (Figures 3a and 3b, e.g., Al-
 170 barède et al., 1997);
- 171 3. Samples with a loss on ignition (LOI) > 3 wt.% are rejected to eliminate basalts
 172 subjected to excessive levels of post-eruptive hydrothermal alteration (e.g., Green-
 173 berger et al., 2012);
- 174 4. Samples with $\text{Nb/U} < 30$, $\text{La/Nb} > 1.2$, or La/Ba and Nb/U values outside of the
 175 ellipse of Fitton et al. (1991) are rejected because they are likely to have been con-
 176 taminated by continental crust (e.g., Rudnick, 1995; Condie, 1999; Hofmann, 2003,
 177 Figures 3c and 3d).

178 Applying these filters to the global OIB dataset results in a subset of 1,737 samples, each
 179 consisting of concentrations of major elements, trace elements and REEs.

180 **2.1.3 Correction for Fractional Crystallisation**

181 When magma travels through the lithosphere or remains in a magma chamber, any
 182 fractional crystallisation that occurs alters the concentration of major and trace elements
 183 in the remaining melt (e.g., Jackson et al., 2012; Ubide et al., 2022). Provided that the
 184 mineral phases that have crystallised are not complex, we can ‘revert’ this process to es-

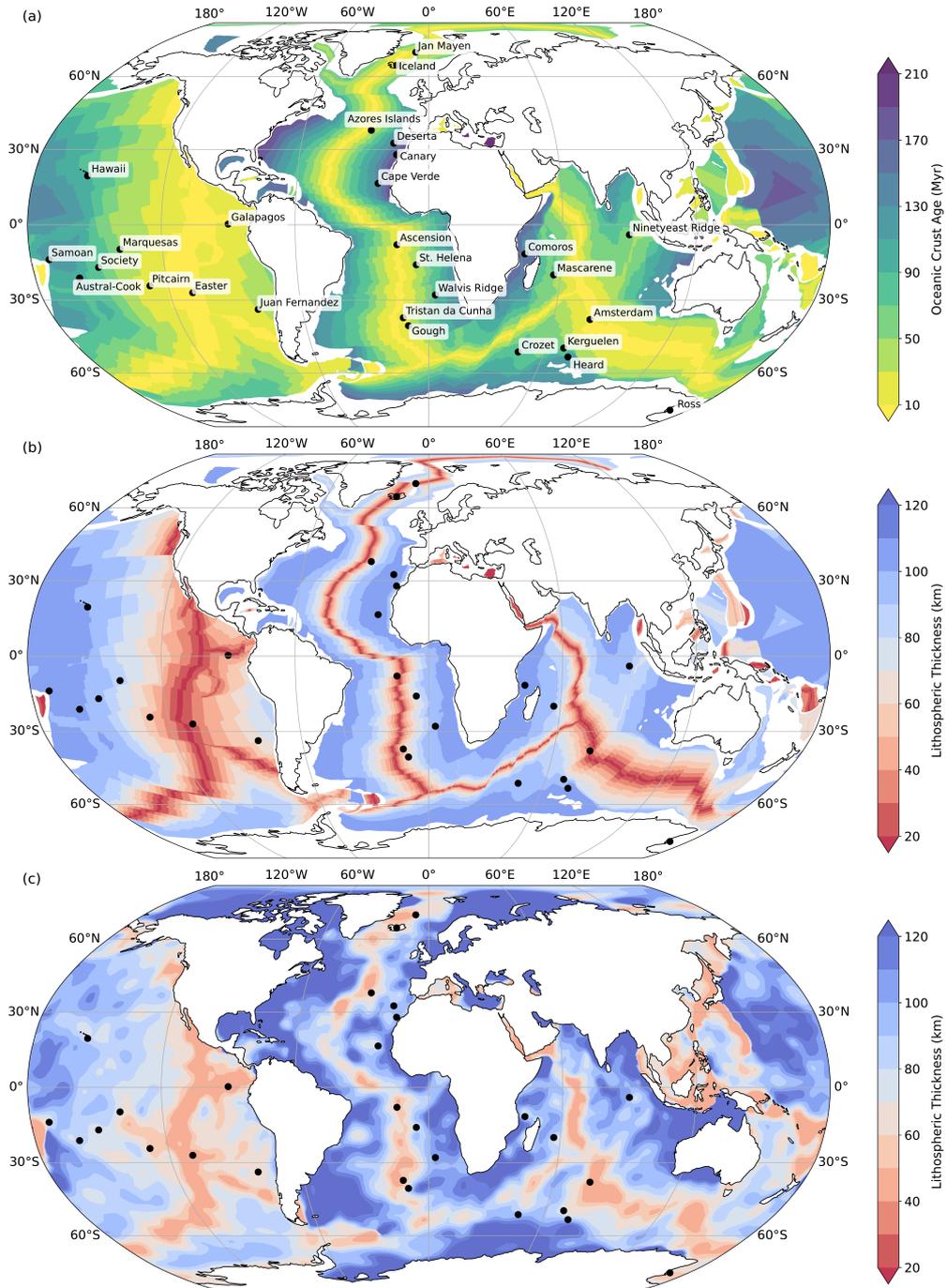


Figure 2. (a) Present-day oceanic lithospheric age from Seton et al. (2020) with locations of selected OIB samples (black dots). Only the name of the archipelago for each island group is displayed, but each individual island's lithospheric age and thickness are considered separately during the analysis. (b) Present-day oceanic lithospheric thickness based on a global plate-cooling model (Richards, Hoggard, Crosby, et al., 2020). (c) Present-day oceanic lithospheric thickness constrained by surface-wave tomography (Hoggard, Czarnota, et al., 2020).

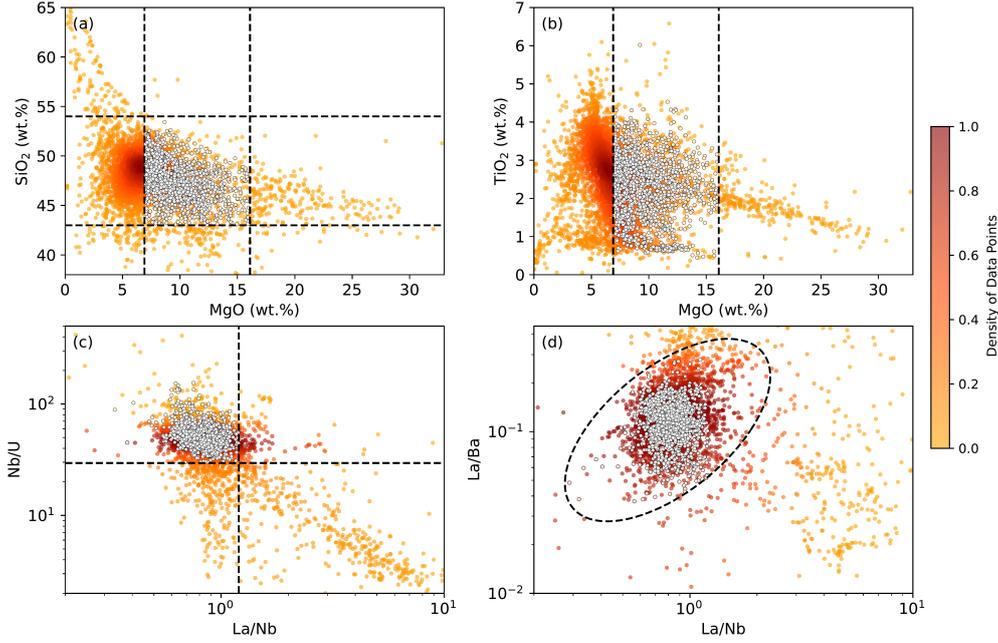


Figure 3. OIB database and sample filtering criteria. (a) SiO_2 versus MgO ; coloured dots = original samples coloured by Gaussian kernel density estimation, normalised from 0 to 1; dashed lines = filtering criteria corresponding to SiO_2 43–54 wt.% and MgO 7–16 wt.%; white circles = subset of data that pass all filtering criteria. (b) Same for TiO_2 versus MgO . (c) Same for Nb/U versus La/Nb , where criteria of > 30 and < 1.2 , respectively, are applied. (d) Same for La/Ba versus La/Nb , where only samples inside the ellipse of Fitton et al. (1991) are accepted.

185 timate concentrations of both major and trace elements in the primary magma. To do
 186 so, we use the `Petrolog3` software (Danyushevsky & Plechov, 2011) to reintroduce olivine
 187 into evolved OIBs until MgO concentrations reach 16 wt.%, which is the assumed MgO
 188 content of magma that is in equilibrium with the mantle (e.g., Norman & Garcia, 1999).
 189 Despite some studies showing that minerals fractionate throughout magma ascent (e.g.,
 190 Lundstrom et al., 2003; Liu et al., 2016), we make the simplifying assumption that this
 191 olivine did not crystallise until melts reached a magma chamber at ~ 0.3 GPa (~ 9 km
 192 depth). This choice of depth roughly coincides with the Moho, where the drop in den-
 193 sity from mantle to crustal rocks results in melts becoming neutrally buoyant, allowing
 194 magma to remain in the chamber for a more extended period of time (Ryan, 1988, 1994).
 195 In the continuous, pure fractional crystallisation process, we assume that partition co-
 196 efficients for trace elements in olivine remain constant. For each individual OIB sample,
 197 we use the major element calculations of `Petrolog3` to determine how much olivine to ‘add
 198 back in’ to obtain the composition of the primitive magma. Accordingly, the concentra-
 199 tion of each trace element in the primitive magma (c_p) is calculated via

$$200 \quad c_p = \frac{c_1}{(1 - X)^{D-1}}, \quad (1)$$

201 where c_1 is the measured concentration of each element in the sample, X is the fraction
 202 of olivine crystallised, and D is the associated partition coefficient (Shaw, 1970).

203 **2.1.4 Shape of REE patterns**

204 Due to their high charge and large ionic radii, REEs behave as incompatible ele-
 205 ments in most mantle minerals. Moreover, the consistency of REE chemical valence makes
 206 their ionic radius systematically decrease with increasing atomic number (so-called lan-
 207 thanide contraction; Ahrens, 1952). Since REEs occupy identical crystal lattice positions,
 208 their partition coefficients therefore exhibit a systematic dependence on atomic number,
 209 with lower atomic number REEs (Light Rare Earth Elements; LREEs) possessing larger
 210 radii and being more incompatible. Accordingly, during partial melting, REEs with a
 211 smaller atomic number more preferentially enter the melt than their heavier counterparts,
 212 an imbalance that is particularly pronounced at low degrees of melting. A caveat to this
 213 basic behaviour is that heavy rare earth elements (HREEs) readily substitute for Al^{3+}
 214 in garnet and, hence, can be compatible in garnet. As such, low-fraction melts gener-
 215 ated within the garnet stability field will have lower HREE concentrations than equiv-
 216 alent melts generated in the spinel stability field. Many laboratory experiments have been
 217 conducted to constrain the partition coefficients of REEs, with results consistent with
 218 these aforementioned theoretical predictions (e.g., Fujimaki et al., 1984; McKenzie & O’Nions,
 219 1991; Johnson, 1994, 1998). It is also worth noting that, due to the general incompat-
 220 ibility of REEs in all low-pressure mineral phases, their relative proportions are gener-
 221 ally unaffected by fractional crystallisation at low pressure.

222 The systematic variation in REE behavior is best illustrated by plotting the log
 223 of their relative abundances as a function of atomic size: as demonstrated by O’Neill (2016),
 224 such patterns can be fit by polynomials with different shape coefficients. Given current
 225 analytical precision, third-order polynomials are usually sufficient to fit measured REE
 226 patterns. Their coefficients are denoted as λ_i (where $i = 0, 1, 2$) and can vary indepen-
 227 dently of one another. λ_i values also have a physical significance: (i) λ_0 measures the
 228 average log concentration of REEs (excluding Eu) normalized to their chondritic con-
 229 centrations, with higher λ_0 indicating higher average REE concentrations; (ii) λ_1 mea-
 230 sures the linear slope of the pattern (with increasing values for larger slopes), where pos-
 231 itive λ_1 values indicate LREE enrichment relative to HREE and negative λ_1 values in-
 232 dicate HREE enrichment relative to LREE; (iii) λ_2 describes the quadratic curvature of
 233 the pattern (with increasing absolute values for larger curvatures), where positive and
 234 negative λ_2 indicate concave or convex REE patterns, respectively. In contrast to the
 235 simple ratios between two REEs, such as Ce/Y and La/Sm, that have been extensively
 236 used in previous studies (e.g., Ellam, 1992; Humphreys & Niu, 2009; Niu, 2021), λ_i con-
 237 sider all REEs except Eu and is more robust to the idiosyncrasies of individual element
 238 behavior.

239 **2.2 Lithospheric Thickness and Eruptive Age**

240 The thickness of oceanic lithosphere as a function of ocean floor age is commonly
 241 approximated through one of two theoretical cooling models: (i) the half-space model,
 242 in which lithospheric thickness is proportional to the square root of lithospheric age (Turcotte
 243 & Oxburgh, 1967); and (ii) the plate model, where lithospheric thickness increases with
 244 plate age, but asymptotes towards a constant value beyond a certain age due to heat re-
 245 supply from below (McKenzie, 1967). Plate-model predictions have been shown to pro-
 246 vide an improved match to heat flow and bathymetry observations in older ocean floor
 247 and also inferences of lithosphere-asthenosphere boundary (LAB) depth obtained from
 248 seismology (McKenzie, 1967; Parsons & Sclater, 1977; Richards et al., 2018; Richards,
 249 Hoggard, Crosby, et al., 2020). Accordingly, the plate model is our preferred reference
 250 and we test two different versions of it: one derived from globally averaged subsidence
 251 and heatflow data and the second providing optimal fits to subsets of these data from
 252 each individual oceanic basin (Atlantic, Indian and Pacific Oceans; Richards, Hoggard,
 253 Crosby, et al., 2020). We present results for the latter in the main text and also conduct
 254 assessments of the sensitivity of our results to this choice, with a summary presented in

255 the Supplementary Information. In all cases, the potential temperature in the model is
 256 fixed to 1333°C and the base of the lithosphere is assumed to follow the $1175 \pm 50^\circ\text{C}$
 257 isotherm (Richards, Hoggard, Crosby, et al., 2020).

258 A limitation of theoretical cooling models is that they assume oceanic lithospheric
 259 thickness varies solely as a function of ocean-floor age and, hence, cannot capture local
 260 deviations away from this average behaviour. Seismological observations, particularly
 261 from surface-wave tomography, provide a way of mapping these local variations in litho-
 262 spheric thickness, including those potentially induced by the impingement of mantle plumes
 263 (Ballmer et al., 2011; Schaeffer & Lebedev, 2013; Richards, Hoggard, White, & Ghelichkhan,
 264 2020; Duvernay et al., 2022). Accordingly, to complement our plate-model derived es-
 265 timates of lithospheric thickness and explore the sensitivity of our results to regional litho-
 266 spheric thickness variations, we also make use of a seismologically derived model of litho-
 267 spheric thickness from Hoggard, Czarnota, et al. (2020).

268 We separate ocean islands into two categories: products from off-axis and on-axis
 269 plumes. For off-axis islands, we estimate lithospheric thickness using the aforementioned
 270 plate-cooling and seismologically derived models. Unfortunately, neither theoretical cool-
 271 ing models nor global-scale seismic estimates are good at constraining lithospheric thick-
 272 ness above on-axis plumes. The former do not capture the consequences of increased melt
 273 generation and hence thicker crust above plumes, while the latter suffer from the lim-
 274 ited resolution of surface waves at depths shallower than ~ 75 km (White & McKen-
 275 zie, 1989; Priestley & McKenzie, 2006). For on-axis islands, we therefore obtain litho-
 276 spheric thickness from local estimates of crustal thickness, assuming that melting extended
 277 to the top of the underlying mantle as is observed in ophiolites (e.g., Pallister & Hop-
 278 son, 1981). Seismic estimates for Moho depths are as follows: Iceland ~ 20 – 30 km (White
 279 et al., 1996); Ninetyeast Ridge, ~ 15 – 25 km (Grevemeyer et al., 2001); Walvis Ridge \sim
 280 10 – 25 km (for lithosphere that is now aged between 60 Ma and 100 Ma; Goslin & Sibuet,
 281 1975; Graça et al., 2019). At each of these sites, we calculate average lithospheric thick-
 282 ness according to $\frac{1}{2}(h_{\max} + h_{\min})$, where h_{\max} and h_{\min} are the maximum and minimum
 283 estimates of Moho depth, respectively.

284 Estimating lithospheric thickness at the time of eruption requires knowledge of litho-
 285 spheric age at that time, which can be obtained by subtracting the OIB age from the
 286 present-day lithospheric age (Figure 2a). Present-day lithospheric age for each island is
 287 obtained from the global grid of Seton et al. (2020), with the age range of OIBs on each
 288 island constrained, where possible, by the onset and termination of the shield stage of
 289 volcanism or, in cases where geological constraints on the shield period are unavailable
 290 or unclear, the maximum and minimum age of OIB samples (Tables S1 and S2).

291 To estimate lithospheric thickness at the time of eruption for off-axis plumes, we
 292 assume that both the present-day lithospheric age (t_{crust}) and the OIB age (t_{OIB}) on each
 293 island follow a Gaussian distribution as

$$294 \quad t_{\text{crust}} \sim \mathcal{N}(\mu_1, \sigma_1^2), \quad (2)$$

$$295 \quad t_{\text{OIB}} \sim \mathcal{N}(\mu_2, \sigma_2^2), \quad (3)$$

297 where μ_1 is the oceanic crustal age, σ_1 is half of the age misfit, μ_2 is the mean of max-
 298 imum and minimum OIB eruption ages, and σ_2 is a quarter of the length of the OIB ma-
 299 jor eruption period. t_{crust} and t_{OIB} can be considered as independent random variables,
 300 thus the age of oceanic lithosphere at the time of OIB volcanism (t_{erupt}) should also fol-
 301 low a Gaussian distribution given by

$$302 \quad t_{\text{erupt}} \sim \mathcal{N}(\mu_1 - \mu_2, \sigma_1^2 + \sigma_2^2). \quad (4)$$

303 Lithospheric thickness is estimated from the theoretical cooling models by assuming that
 304 it lies between the 1125°C and 1225°C isotherms. We assume that lithospheric thick-

ness (z) at a given time follows a Gaussian distribution according to

$$z \sim \mathcal{N}(\mu_3, \sigma_3^2), \quad (5)$$

in which μ_3 is the mean of the lithospheric thickness obtained from the 1125°C and 1225°C isotherms and σ_3 is a quarter of the difference in depth between them. For each island, we randomly choose a t_{erupt} based on Equation (4) and calculate the corresponding lithospheric thickness using Equation (5). Iteratively repeating this process until reaching a stable distribution of thickness estimates yields the plate-model-derived mean value of lithospheric thickness beneath each ocean island.

For the seismically constrained estimates of lithospheric thickness, we test two end-member scenarios: (i) lithospheric thickness at the time of eruption is equivalent to that of the present day; and (ii) following eruption and movement away from the location of the plume tail, the lithosphere has re-thickened to its present-day value by conductive cooling following a half-space model. The true scenario likely falls between these two assumptions. Both assumptions yield similar results, likely because the majority of OIBs in our dataset are young (< 10 Ma) and the lithosphere cannot substantially rethicken over such a short time frame. Correcting for this process makes no appreciable difference to our results (< 5 km thickness change; see Supplementary Tables S4 and S5) and the size of this correction is generally smaller than the depth range covered by the 1175 \pm 50°C isotherms. When using seismically derived estimates of lithospheric thickness, we therefore adopt the first option above.

Estimated lithospheric thickness at the time of eruption, based on either the basin-specific plate models (Richards, Hoggard, Crosby, et al., 2020) or seismological constraints (Hoggard, Czarnota, et al., 2020), are tabulated in Supplementary Tables S4 and S5. Plate model thicknesses for the Atlantic basin are slightly greater than those derived from the global-average model, whereas in the Indian and Pacific basins, lithospheric thickness estimates from basin-based models are similar to, or thinner than, those of the global model (Supplementary Figure S1).

2.3 Bayesian Model Selection

To investigate the variation of each geochemical parameter with lithospheric thickness, we have plotted and parameterised OIB geochemical data against lithospheric thickness at the time of eruption. To understand whether a particular dataset suggests a trend, or a change in gradient, we make use of Bayes factors: the ratio of the evidence or marginal likelihood between two competing statistical models (Jeffreys, 1935; Kass & Raftery, 1995). The evidence represents the integral of the likelihood over the prior for a given model choice. In our case, it quantitatively evaluates how likely it is to generate the observed geochemical dataset, based on a specified model (i.e., a function that describes the trend of the geochemical parameters against lithospheric thickness). Therefore, given two or more competing models, the model with the larger evidence is preferred. Computing the evidence is difficult, particularly for large dimension models, but for this problem we use Dynamic Nested Sampling (Skilling, 2006; Speagle, 2020), which gives both posterior and evidence estimates in a single analysis.

The geochemical data include the raw and fractional crystallisation-corrected concentrations of major elements, trace elements and λ values calculated from REE concentrations. To determine whether a given geochemical parameter is sensitive to lithospheric thickness or influenced by any potential sudden changes in mantle composition, such as the phase change from spinel to garnet peridotite, three models were compared: (i) a constant value model (which would imply no sensitivity to lithospheric thickness); (ii) a linear model (which suggests a lid effect); and (iii) a bi-linear model that permits a change in gradient at some depth determined by the data (Figure 4). We choose not to examine exponential models since they are monotonous, so incapable of describing a

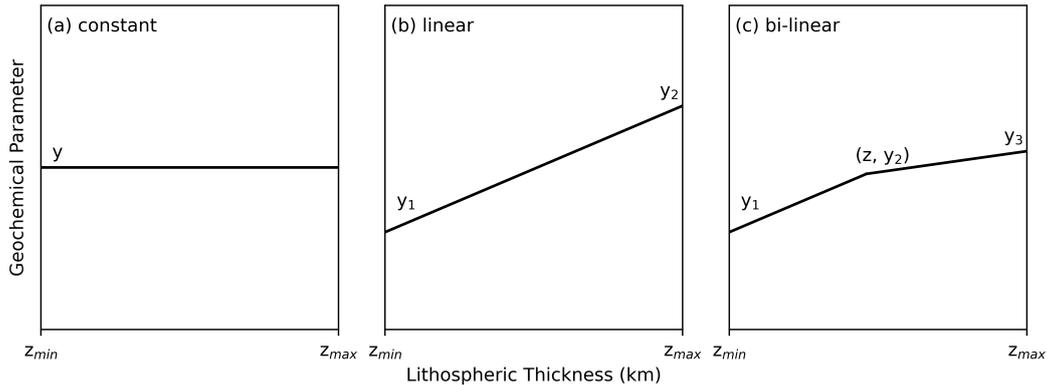


Figure 4. Schematic cartoon showing (a) a constant model with one unknown parameter; (b) a linear model with two unknown parameters; and (c) a bi-linear model with four unknown parameters. Associated model variables are labelled.

355 reverse in a trend or detecting the depth of a potential trend change. To estimate pos-
 356 terior probability densities of the model parameters for each candidate model, we choose
 357 an independent Gaussian likelihood which is written as

$$358 \quad L(\mathbf{p}|\mathbf{d}) \propto \exp \left[-\frac{1}{2} \sum_{i=1}^M \sum_{j=1}^{N_i} \frac{(p_i - d_j)^2}{\sigma^2} \right], \quad (6)$$

359 where M is the number of islands, N_i the number of samples for each island i , p_i is the
 360 model prediction of the geochemical concentration for island i , d_j is the observed data
 361 value for each sample from that island, and σ is the overall standard error. This formu-
 362 lation assumes that the data follows the standard normal distribution at each lithospheric
 363 thickness.

364 We fix values for the minimum and maximum lithospheric thicknesses (z_{min} and
 365 z_{max} in Figure 4), resulting in one, two and four unknown parameters for the constant,
 366 linear and bi-linear models, respectively. The use of Bayes factors to test the relative sup-
 367 port of competing models is subtly affected by the choice of priors. Regarding priors for
 368 the y values (i.e., the geochemical data), we adopt an empirical Bayes approach and set
 369 the prior to be Gaussian with mean and standard deviation equal to that of the over-
 370 all data. The mean and standard deviation of z (i.e., the lithospheric thickness of a pu-
 371 tative transition in the trend for the bi-linear model) are assumed to be 60 km and 5 km
 372 respectively, close to the average of all thickness data. To test the sensitivity of evidence
 373 calculations, we ran repeated tests that changed the standard deviation of the prior by
 374 $\pm 10\%$, which resulted in an average change of \log_{10} evidence values of ± 0.14 . Similarly,
 375 changing the standard deviation by $\pm 50\%$ (a comparatively large change in the prior)
 376 resulted in an average change in the \log_{10} evidence of ± 0.18 . We are therefore confident
 377 that the choice of priors for our Bayesian evidence calculations are reasonable and that
 378 sensitivity to the choice of priors is minor. Nonetheless, in the Bayesian evidence results
 379 herein, a reasonable error bound on the numerical \log_{10} evidence values would be ± 0.2 .

380 The evidences for constant, linear and bi-linear models are denoted as E_0 , E_1 , and
 381 E_2 , respectively. Since evidence values are typically vanishingly small numbers, they are
 382 usually represented by their logarithms. A candidate model with a larger evidence value
 383 is to be preferred, for example, model ‘‘A’’ with a \log_{10} evidence of -1000 is a hundred
 384 times more likely than a competing model ‘‘B’’ with a \log_{10} evidence of -1002. Gener-
 385 ally, a difference in the \log_{10} evidence greater than 2 is taken to be statistically signif-

386 icant (Jeffreys, 1935; Kass & Raftery, 1995). We note that model evidence values can
 387 only be compared for the same geochemical parameter, as they are influenced by the range
 388 of values in the data and sample sizes. As a reminder, the constant model implies that
 389 a geochemical parameter is insensitive to changes in lithospheric thickness. The linear
 390 model can detect an overall trend but is incapable of describing a change or reversal in
 391 trend. The bi-linear model can be useful for identifying a change point in a trend and
 392 even detecting a reversal of the trend, but is more sensitive to outliers. For a given geo-
 393 chemical parameter, if $\log_{10}E_1 - \log_{10}E_0 > 2$, we are confident in saying that it varies
 394 with lithospheric thickness. Furthermore, if $\log_{10}E_2 - \log_{10}E_1 > 2$, we can say that a
 395 change point or kink can be found in the data trend. In these cases, we provide histograms
 396 of the depth of the likely kink in the model and calculate its mean and standard devi-
 397 ation.

398 2.4 Sensitivity to Sites with Large Numbers of Samples

399 Due to the form of our likelihood function in Equation (6), clusters of large num-
 400 bers of measurements from a single site could potentially bias the results. Two notable
 401 examples of this are the large OIB sample sizes of Iceland and Hawaii. To test the ro-
 402 bustness of our results to potential biasing from these two localities, we repeat the cal-
 403 culation of posterior probability densities and evidence values for each geochemical pa-
 404 rameter using: (i) all data (i.e. our reference case); and (ii) the dataset with samples from
 405 both Iceland and Hawaii excluded. Removal of Hawaiian samples is of particular rele-
 406 vance because they represent the only OIBs located on thick lithosphere that are dom-
 407 inated by tholeiites (e.g., MacDonald & Katsura, 1964). All other OIBs at and beyond
 408 these lithospheric thicknesses consist predominantly or exclusively of alkali basalts (e.g.,
 409 Schmincke, 1982; Fisk et al., 1988; Gautier et al., 1990).

410 3 Results

411 To provide a relatively simple overview that gets at the essence of our results, we
 412 have chosen to focus in the main text on a preferred reference case. This case includes
 413 the initial correction of geochemical concentrations for the effects of fractional crystalli-
 414 sation, uses data from all OIB localities within our database, and adopts lithospheric thick-
 415 nesses from basin-specific plate-cooling models. While we discuss any important differ-
 416 ences that arise from changes to this reference setup in the main text, the full suite of
 417 associated figures and results are presented in the Supplementary Information.

418 3.1 Geochemical Histograms

419 Raw histograms of major element concentrations for all OIB data, before applica-
 420 tion of sample filters, display slightly skewed Gaussian-like distributions with peaks at
 421 approximately 7 wt.% for MgO, 48 wt.% for SiO₂, 3 wt.% for TiO₂, and 14 wt.% for Al₂O₃
 422 (blue bars in Figure 5a–d). The MgO peak at 7 wt.% broadly coincides with the mini-
 423 mum in magma density at 7–8 wt.% MgO calculated using *Petrolog3* at 0.1 GPa, which
 424 is consistent with expectations that the lightest magmas are the most likely to erupt at
 425 the surface (see Supplementary Figure S2; Danyushevsky & Plechov, 2011). The con-
 426 tinuous distribution of major element concentrations is consistent with expectations for
 427 mixing of distinct, end-member reservoirs to varying extents, which is also supported by
 428 isotopic evidence (e.g., Hart et al., 1992). Filtering the raw data according to the cri-
 429 teria outlined in Section 2.1.2 has limited impact on distributions for SiO₂, Al₂O₃ and
 430 TiO₂, but the filtered MgO histogram retains only the right-hand side of the distribu-
 431 tion due to the sharp cut-off of samples with MgO < 7 wt.% (green bars in Figure 5a–
 432 d). Histograms of the REE shape parameters for filtered OIB samples exhibit more scat-
 433 ter and less clean unimodal behaviour (Figure 5e–g). Nevertheless, λ_0 has a clear peak
 434 at ~ 3.3 . λ_1 is left skewed, with a peak around 10 and more than 80% of samples have

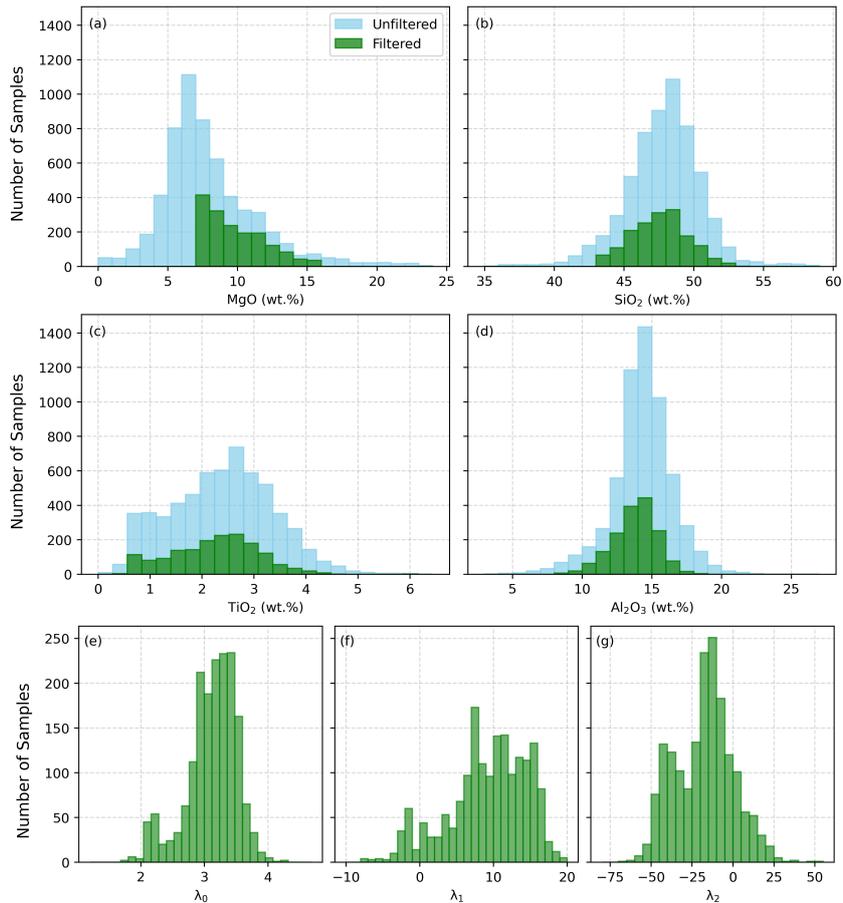


Figure 5. Concentration histograms of (a) MgO; (b) SiO₂; (c) TiO₂; and (d) Al₂O₃ in our OIB dataset. Original, unfiltered data are colored blue, while data in green represent the subset of data remaining following application of screening filters outlined in Section 2.1.2. For simplicity, histograms of (e) λ_0 , (f) λ_1 , and (g) λ_2 values are shown only for filtered OIB samples.

435 $\lambda_1 > 5$. λ_2 is somewhat bimodal, with a central peak at approximately -15 and a sub-
 436 sidiary peak at -40.

437 3.2 Evidence Results

438 3.2.1 Example of Statistical Results

439 To illustrate our procedure for quantifying the relationship between lithospheric
 440 thickness and various geochemical parameters, we present two examples for Al₂O₃ and
 441 λ_1 in Figure 6. Both use our reference setup, in which the global OIB dataset is filtered
 442 and corrected for fractional crystallisation, with lithospheric thickness evaluated via the
 443 basin-specific plate model. Black crosses represent individual OIB samples and log₁₀ of
 444 the evidence is provided for each of the three types of model.

445 For both Al₂O₃ and λ_1 , we find that the evidence increases by ~ 160 when mov-
 446 ing from constant to linear models (compare Figure 6a with 6b, and 6e with 6f), sup-
 447 porting the existence of a lid effect for both Al₂O₃ and λ_1 . However, we see contrast-
 448 ing results when the bi-linear model is introduced. For Al₂O₃, evidence values for lin-

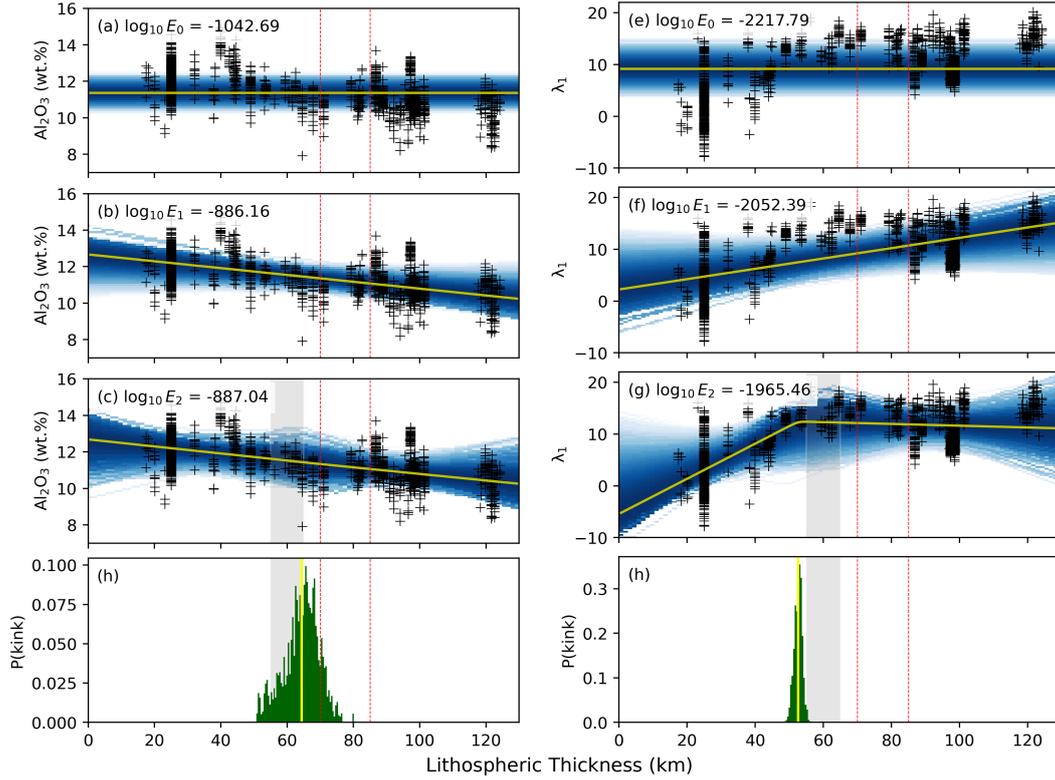


Figure 6. Statistical evidence evaluation results for Al_2O_3 and λ_1 under our reference setup. (a) Al_2O_3 as a function of lithospheric thickness fitted using a constant model; black crosses = individual samples; blue shading = probability density; yellow line = mean model; red dotted lines = expected spinel-garnet transition depths for typical mantle potential temperatures expected in plumes (e.g. Robinson & Wood, 1998; Klemme & O’Neill, 2000; Tomlinson & Holland, 2021); inset gives \log_{10} evidence value. (b) Same for a linear model. (c) Same for a bi-linear model; grey band = prior distribution for kink depth with one standard deviation width. (d) Probability distribution of kink depths, shown as a green histogram; grey band = prior; yellow line = mean value. (e–h) Same as a–d, albeit for λ_1 .

ear and bi-linear models are similar (Figure 6b–c), implying the absence of any obvious transition in the trend as a function of lithospheric thickness. The resulting probability distribution of potential kink depths is therefore broad and poorly constrained in Figure 6d, and we infer that Al_2O_3 in OIBs decreases linearly with increasing lithospheric thickness, with no definitive kink. On the other hand, λ_1 shows a clear preference for a bi-linear model, with an increase in the \log_{10} evidence value of ~ 87 over a linear model (Figure 6f–g). The associated probability distribution for the kink is tightly constrained in the depth range of 49–56 km, with an average of ~ 52 km (Figure 6h). Based on this preferred bi-linear model, the most likely trend for λ_1 is that it increases with lithospheric thickness until a depth of ~ 52 km, before subsequently remaining approximately constant.

3.2.2 Summary of Evidence Evaluation Results

Values of $\log_{10} E_1 - \log_{10} E_0$ and $\log_{10} E_2 - \log_{10} E_1$ have been determined for each geochemical parameter, under our reference setup. As a reminder, when greater than a

Constant															
Linear						✓	✓	✓			✓	✓			✓
Bi-linear	✓	✓	✓	✓	✓				✓	✓			✓	✓	
	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	SiO ₂	Al ₂ O ₃	FeO	La	Th	Yb	Lu	λ ₀	λ ₁	λ ₂

Figure 7. Optimal model type for each geochemical parameter under our reference setup. Ticks denote optimal model; strength of colour fill indicates level of preference for that model type (i.e., when a simpler model has an evidence value that is within 20 but less than 2 of the optimal model, it is filled with colour that linearly increases in intensity).

463 key threshold value of two (i.e. more than hundred-fold increase in the likelihood), the
 464 former indicates statistical preference for a linear model over a constant one, while the
 465 latter indicates a bi-linear rather than linear relationship.

466 The preferred model for each geochemical parameter is shown in Figure 7, with fur-
 467 ther details in Figures 8–11, and can be summarised as follows:

- 468 1. All geochemical parameters prefer either a linear or bi-linear model over a con-
 469 stant model, indicating universal sensitivity to lithospheric thickness.
- 470 2. For major elements Al₂O₃, FeO, and SiO₂, data are optimally fitted by linear mod-
 471 els (Figure 8). Conversely, TiO₂, Na₂O, K₂O, CaO, and P₂O₅ data are optimally
 472 fitted by bi-linear models (Figure 9c–g);
- 473 3. For trace elements, the highly incompatible elements La and Th are best fitted
 474 by bi-linear models (Figure 9a–b), whereas the less incompatible Yb and Lu are
 475 best fitted by linear models (Figure 10);
- 476 4. For parameters describing REE patterns, λ₀ and λ₁ are optimally fitted by bi-linear
 477 models (Figure 11a–b), whereas λ₂ prefers a linear model (Figure 11c).
- 478 5. For geochemical parameters that prefer a bi-linear model, kink depths generally
 479 occur at lithospheric thicknesses of 50–60 km.

480 4 Discussion

481 4.1 Existence of a Lid Effect

482 Lithospheric thickness dictates the minimum pressure of plume melting through
 483 the so-called ‘lid effect’. It affects OIB chemistry in two ways (e.g., Watson & McKen-
 484 zie, 1991; Humphreys & Niu, 2009; Niu, 2021). First, by inhibiting upwelling beyond a
 485 certain depth, lithospheric thickness limits the maximum melt fraction (F). We there-
 486 fore expect F to be inversely proportional to lithospheric thickness, which will have a
 487 substantial impact on the concentrations of highly incompatible trace elements. Second,
 488 the pressure at which melting occurs has strong implications for the mineral phases present
 489 in the residue following partial melting. In particular, over the depth range of interest
 490 here, the stable aluminium-rich phase converts from garnet (Mg₃Al₂Si₃O₁₂) to spinel (MgAl₂O₄)
 491 with decreasing pressure, subsequently becoming plagioclase (CaAl₂SiO₈) at shallow depths
 492 beneath mid-oceanic spreading centers (e.g., Masaaki, 1980). Despite our analyses be-
 493 ing subject to uncertainty, particularly in relation to estimates of lithospheric thickness
 494 and assumptions on uniform source composition, the data support a linear or bi-linear
 495 trend between all geochemical parameters and lithospheric thickness, providing univer-

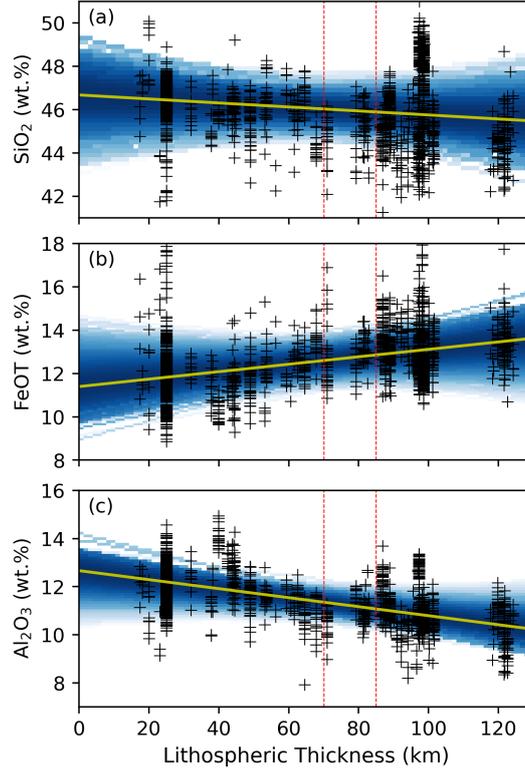


Figure 8. Statistical evidence evaluation results for major elements optimally fitted by linear models, under our reference setup. (a) Results for SiO_2 for all localities; black crosses = individual samples; blue shading = probability density; yellow line = mean model; red dotted lines = spinel-garnet transition depths (e.g., Robinson & Wood, 1998; Klemme & O’Neill, 2000; Tomlinson & Holland, 2021). (b) Same for FeOT. (c) Same for Al_2O_3 .

496 sal evidence for the lid effect and corroborating the conclusions of, for example, Humphreys
 497 and Niu (2009), Dasgupta et al. (2010) and Niu (2021).

498 Nonetheless, it is clear from our results that different geochemical parameters exhibit
 499 distinct responses to the lid effect. Some trends (e.g., Al_2O_3) show a linear relationship
 500 with lithospheric thickness, whereas others show a bi-linear relationship with
 501 an abrupt change at a certain depth (e.g., λ_0 , λ_1). In the following sections, we discuss
 502 potential explanations for these behaviours. We start with major element trends that
 503 are best fitted by linear models, with an emphasis on the relationship to pressure-dependent
 504 mineral assemblages. We then discuss the remaining major and trace elements, relating
 505 observed trends to the influence of variations in melt fraction and the spinel-garnet
 506 phase transition. Although Yb and Lu are best fitted by linear models, we include them
 507 in this section because their behaviour is associated with an interplay between F and
 508 the spinel-garnet phase transition. We finish by discussing REE trends, described by λ_i ,
 509 drawing on the lessons learned from the interpretation of trace elements trends.

510 4.2 Major Elements with Linear Trends

511 Concentrations of the major elements SiO_2 , FeOT and Al_2O_3 in OIBs show a linear
 512 dependence on lithospheric thickness (Figure 8). In mantle melts, these components
 513 are known to be buffered by the mineral assemblage of the mantle residue and the ob-

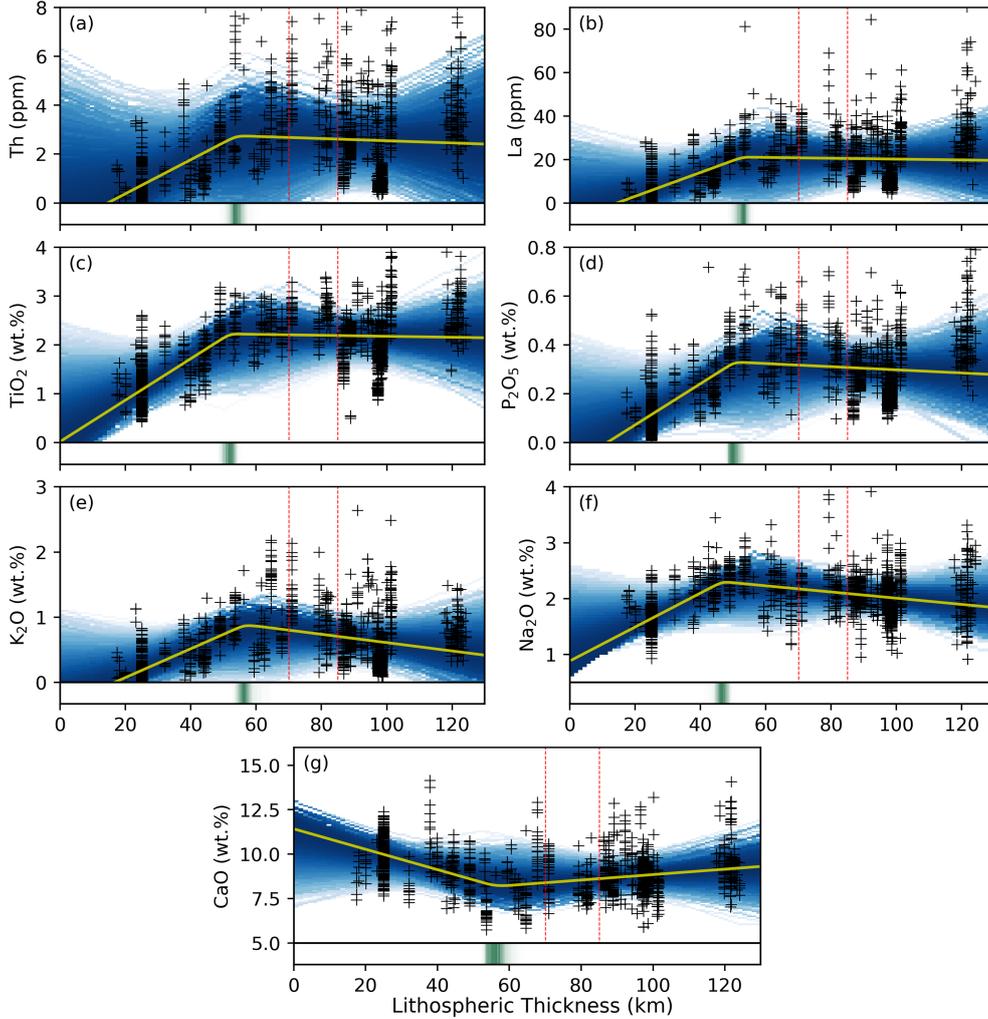
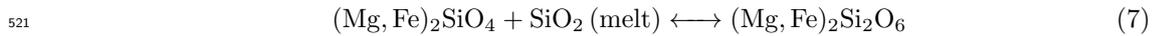


Figure 9. Statistical evidence evaluation results for geochemical parameters optimally fitted by bi-linear models. Data and panel contents same as for Figure 8 but for (a) Th, (b) La, (c) TiO₂, (d) P₂O₅, (e) K₂O, (f) Na₂O, and (g) CaO. The horizontal bar below panel (d) shows the probability distribution of the likely kink depth, with more opaque colors indicating that a kink is more likely at that depth.

514 served trends are consistent both with experimental studies on the Calcium, Magnesium,
 515 Aluminium, Silicon (CMAS) system (e.g., Walter & Presnall, 1994) and with the results
 516 of previous observational studies (e.g., Humphreys & Niu, 2009; Niu et al., 2011; Niu,
 517 2021).

518 SiO₂ exhibits a moderate decrease with increasing lithospheric thickness (Figure
 519 8a). Its concentration in mantle melts is buffered by the two most abundant minerals
 520 in the upper mantle, olivine and orthopyroxene, according to the reaction



522 Increasing pressure drives this reaction to the right, expanding the stability field of or-
 523 thopyroxene at the expense of olivine (e.g., Campbell & Nolan, 1974; Walter & Presnall,
 524 1994). As a consequence, as the average melting pressure increases beneath thicker litho-
 525 sphere, the residue contains more SiO₂-rich orthopyroxene and the corresponding melts

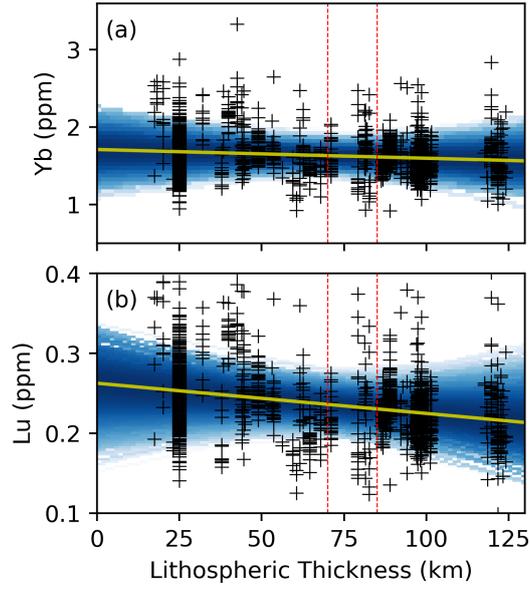


Figure 10. Statistical evidence evaluation results for HREEs, which are optimally fitted by linear models. Data and panel contents same as for Figure 9 but for (a) Yb and (b) Lu.

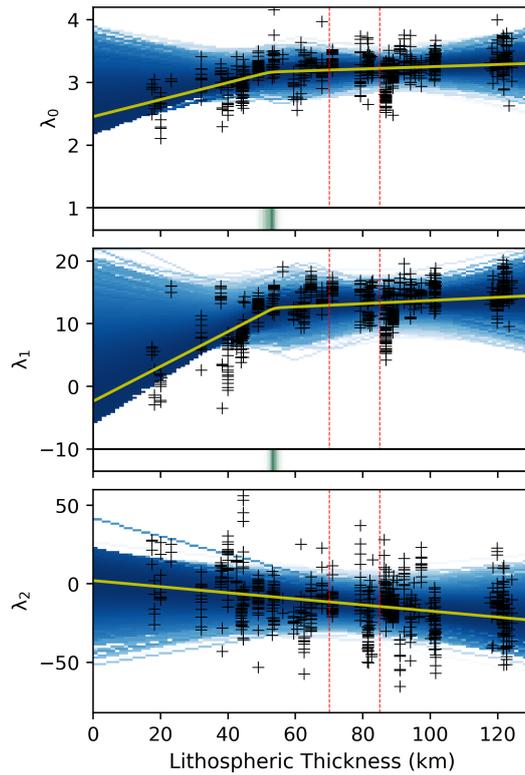
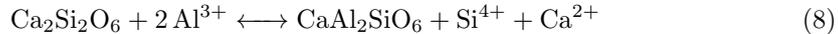


Figure 11. Statistical evidence evaluation results for REE shape parameters. Data and panel contents same as for Figure 9, but for (a) λ_0 , (b) λ_1 and (c) λ_2 . Note that λ_0 and λ_1 are optimally fitted by bi-linear models, whereas λ_2 is optimally fitted by a linear model.

526 produced are increasingly SiO₂-poor (e.g., Bohlen et al., 1980; Bohlen & Boettcher, 1981).
 527 We note that Herzberg (1992) further proposed that the decrease in SiO₂ with increas-
 528 ing melt pressure stops at ~ 45 wt.% SiO₂ due to low melt fractions in the presence of
 529 garnet, but this cut-off behaviour is not observed in either our analyses or in previous
 530 studies (e.g., Scarrow & Cox, 1995; Dasgupta et al., 2010). We therefore suggest that
 531 the spinel-garnet transition has limited influence on the SiO₂ content of OIBs, with re-
 532 action (7) and associated buffering of the silica content by olivine and orthopyroxene be-
 533 ing the key control.

534 We also attribute the linear increase in FeOT with increasing lithospheric thick-
 535 ness (Figure 8b) to the relative stabilities of olivine and orthopyroxene as a function of
 536 pressure. Olivine contains more Fe than orthopyroxene and increasing the pressure stabilizes
 537 orthopyroxene at the expense of olivine. As a consequence, for similar melt frac-
 538 tions, high-pressure melts contain more Fe than low-pressure melts. The relative abun-
 539 dance of olivine and orthopyroxene in the residue was also used by Niu (2016) to explain
 540 the increase in FeOT in mid-ocean ridge basalts (MORB) with increasing ridge axial depth.
 541 Analysis of our OIB dataset suggests that this trend can be extended over a greater depth
 542 range than is possible with the MORB data alone.

543 Al₂O₃ linearly decreases with increasing lithospheric thickness (Figure 8c), which
 544 we believe can be attributed to an increase in the Al content of clinopyroxene and, to
 545 a lesser extent, orthopyroxene, with increasing pressure. Al³⁺ can occupy either the tetra-
 546 hedral or octahedral sites within the pyroxene crystal lattice. The two tetrahedral sites
 547 are characterised by a central cation (usually Si⁴⁺) surrounded by four oxygen atoms,
 548 whereas the two larger octahedral sites are positions in which the central cation is sur-
 549 rounded by six oxygen atoms and are usually occupied with cations that have greater
 550 ionic radii, such as Ca²⁺. Increasing pressure shrinks the octahedral M1 and M2 sites
 551 in both pyroxenes and allows more Al³⁺ to enter the M1 site, which is the smaller of the
 552 two octahedral sites (Colson & Gust, 1989). The octahedral Al³⁺ can either be charge
 553 balanced by additional Al³⁺ replacing Si⁴⁺ in an adjacent tetrahedral site according to
 554 the reaction



556 or by Na⁺ or K⁺ replacing a divalent ion on the larger M2 site (Campbell & Borley, 1974;
 557 Safonov et al., 2011), according to reaction



559 As a consequence, the Al₂O₃ content of the residual pyroxenes increases with increas-
 560 ing pressure and the Al₂O₃ concentration in the melt correspondingly decreases. This
 561 simple interpretation may be complicated, however, by Al³⁺ being buffered by reactions
 562 between spinel and pyroxene in the spinel stability field and between garnet and pyrox-
 563 ene in the garnet stability field. We might therefore have also expected a dependence
 564 on the spinel-garnet transition. The fact that our Al₂O₃ trends do not require a bi-linear
 565 model in our reference setup suggests that this is not the case, perhaps because both spinel
 566 and garnet contain two Al³⁺ ions and the increasing Al content of pyroxenes with pres-
 567 sure is therefore not affected by the spinel-garnet transition.

568 In summary, we infer that variations in the concentration of major elements SiO₂,
 569 FeOT, and Al₂O₃ in OIBs are dominated by gradual changes in mineral assemblage as
 570 a function of pressure rather than variations in F or effects arising from the spinel-garnet
 571 phase transition.

572 4.3 Major and Trace Elements with Bi-linear Trends

573 The behavior of trace elements, which do not form stoichiometric components in
 574 minerals, can be understood using the distribution coefficient, D , for the partitioning of
 575 the element between a mineral and the melt. During partial melting of mantle peridotite,

576 the concentration of a given element in the aggregate melt (C_1) during batch melting is
 577 given by

$$578 \quad C_1 = \frac{1}{D'(1-F) + F} C_s, \quad (10)$$

579 and, in the case of fractional melting, is

$$580 \quad C_1 = \frac{1}{F} \left[1 - (1-F)^{\frac{1}{D'}} \right] C_s, \quad (11)$$

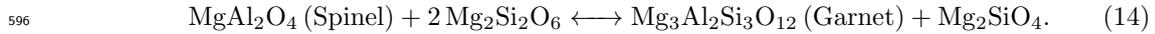
581 where D' is the bulk partition coefficient, F is the melt fraction and C_s is the concen-
 582 tration of the element in the source before melting (Shaw, 1970, 1979). C_1 is therefore
 583 controlled by the combined effect of D' and F . Nevertheless, for incompatible trace el-
 584 ements where D' is low (usually < 0.01), these equations can be simplified to

$$585 \quad C_1 \approx \frac{1}{F} C_s, \quad (12)$$

586 indicating that C_1 is proportional to $\frac{1}{F}$, regardless of the melting mechanism. The lower
 587 the value of D' , the more reliable this approximation becomes. Similarly for moderately
 588 low values of D' (i.e. < 0.2), given that melt fractions for OIBs are never higher than
 589 ~ 0.2 , we can simplify Equations (10) and (11) to

$$590 \quad C_1 \approx \frac{1}{D' + F} C_s. \quad (13)$$

591 In cases where $D' > 0.2$ and differences in the partition coefficients for different
 592 minerals are large, which can occur, for example, across the spinel-garnet phase tran-
 593 sition, C_1 is influenced by both pressure and the phase change. The case of spinel-garnet
 594 can be represented by a reaction between spinel and pyroxene to give garnet and olivine
 595 according to



597 The transition is abrupt and temperature dependent (e.g. Klemme & O'Neill, 2000). For
 598 temperatures appropriate for mantle plumes, the transition occurs over a ~ 5 km depth
 599 range somewhere between 70–85 km, depending on the mantle composition (e.g. Robin-
 600 son & Wood, 1998; Klemme & O'Neill, 2000; Wood et al., 2013; Tomlinson & Holland,
 601 2021). Note that the shallower plagioclase-spinel transition in peridotite is not relevant
 602 to this study because the plagioclase stability field extends only to pressures of 0.8 GPa
 603 in fertile lherzolite and to 0.6 GPa in depleted lherzolite, corresponding to depths of 24 km
 604 and 18 km, respectively (Borghini et al., 2010).

605 For geochemical parameters that are best fitted by bi-linear models, we divide them
 606 into two groups: (i) elements exhibiting low partition coefficients ($D' < 0.2$), includ-
 607 ing Th, La, Ti, P, K and Na, which we propose can be interpreted primarily in terms
 608 of melt fraction F (although Na and K may be further influenced by D values for py-
 609 roxenes at high pressure); and (ii) Ca, which requires consideration of both F and the
 610 spinel-garnet phase change. These bi-linear trends were not identified in previous stud-
 611 ies (e.g., Ellam, 1992; Humphreys & Niu, 2009; Dasgupta et al., 2010; Niu et al., 2011;
 612 Niu, 2021) and we discuss their likely origin.

613 **4.3.1 Incompatible elements**

614 D' values for the incompatible elements investigated in this study decrease in the
 615 following order: $\text{Ti} \approx \text{P} \approx \text{Na} > \text{La} > \text{K} > \text{Th}$. All are optimally fitted by bi-linear mod-
 616 els, in which their concentrations initially increase rapidly with increasing lithospheric
 617 thickness, before remaining flat or increasing at a significantly reduced rate in the cases
 618 of Th, La, Ti, P, or slightly decreasing in the cases of K and Na. The kinks in slopes all
 619 occur at 50–60 km depth (Supplementary Figure S3).

Table 1. Partition coefficients for incompatible elements in the main peridotite minerals. D'_{sprd} and D'_{gprd} are bulk partition coefficients for spinel peridotite (assuming model abundances of 59% Ol, 28% Cpx, 8% Opx, 5% Sp) and garnet peridotite (55% Ol, 23% Cpx, 15% Opx, 7% Grt), respectively. D in each mineral can vary as a function of mineral composition, temperature and pressure.

	Ol	Opx	Cpx	Sp	Grt	D'_{sprd}	D'_{gprd}
Th	0.0001	0.0001	0.00026	0.00001	0.0001	0.00014	0.00014
K	0.00018	0.001	0.002	0.0001	0.001	0.00075	0.00078
La	0.0004	0.002	0.054	0.01	0.01	0.016	0.014
Ti	0.02	0.1	0.18	0.15	0.28	0.078	0.087
P	0.1	0.03	0.05	0	0.1	0.075	0.078
Na	0.006	0.05	0.2	0	0.04	0.064	0.060
Lu	0.0015	0.06	0.28	0.01	7.7	0.085	0.61
Yb	0.0121	0.1036	0.5453	0.01	6.9	0.17	0.63

620 La, K and Th are highly incompatible in peridotites, regardless of whether the ma-
621 jor aluminum-rich phase is spinel or garnet ($D' \leq 0.01$; Table 1). Following on from
622 our interpretation of Equations (12) and (13) for such elements, at constant potential
623 temperature, we expect variations in their concentration to be proportional to $\frac{1}{F}$ as a
624 function of lithospheric thickness and insensitive to the spinel-garnet phase transition
625 (dashed line in Figure 12a). This behaviour should impart an increase in incompatible
626 trace element concentrations at larger thicknesses, with a steeper rate of increase at greater
627 thicknesses. This prediction is consistent with the observed increase in incompatible el-
628 ement concentrations with increasing lithospheric thickness beneath thinner lithosphere.
629 When lithospheric thickness exceeds 50–60 km, however, it is not consistent with the slightly
630 increasing, flat or decreasing concentrations observed. We can further demonstrate this
631 aspect by converting our observed concentrations of La into estimates of F as a func-
632 tion of lithospheric thickness (solid purple line in Figure 12a) and comparing it to the
633 predicted F curves (note that the resulting F curve is insensitive to the choice of La or
634 Th). There is an agreement between the shapes of the two curves for lithospheric thick-
635 ness < 55 km but they become inconsistent at larger thicknesses, implying that another
636 process modulates concentrations of incompatible elements beyond thicknesses of ~ 55 km.
637 The most important conclusion that can be drawn from the analyses of highly incom-
638 compatible Th and La is that F remains nearly constant for lithosphere thickness > 55 km.

639 The moderately incompatible elements Na, P and Ti have $D' \sim 0.06 - 0.08$ in
640 both the spinel and garnet stability fields and follow similar trends. For these elements,
641 D' cannot be neglected and Equation (13) should be used to interpret changes in their
642 concentrations. Since D' varies little with mineralogy for these elements, it can be re-
643 garded as a constant and F becomes the dominant variable. As a consequence, exper-
644 imental and theoretical constraints imply that these moderately incompatible element
645 concentrations should again increase with increasing lithospheric thickness, with steeper
646 rates of increase at greater thicknesses. The contribution from D' should reduce the ef-
647 fect of F , diluting the concentration ratio of these elements between the melts and residue
648 at higher pressures without altering the underlying trend. This prediction is consistent
649 with observations for lithospheric thicknesses less than 55 km, but it is inconsistent with
650 thicker lithosphere trends, which again suggest minimal changes in F at larger thicknesses.
651 This aspect is important to keep in mind for the following interpretations.

652 Our analyses demonstrate that the concentrations of Na and K differ from other
653 incompatible elements in that they show a slight decrease with increasing lithospheric
654 thickness beyond the kink (Figure 9e and f). At these pressures, F is expected to be small

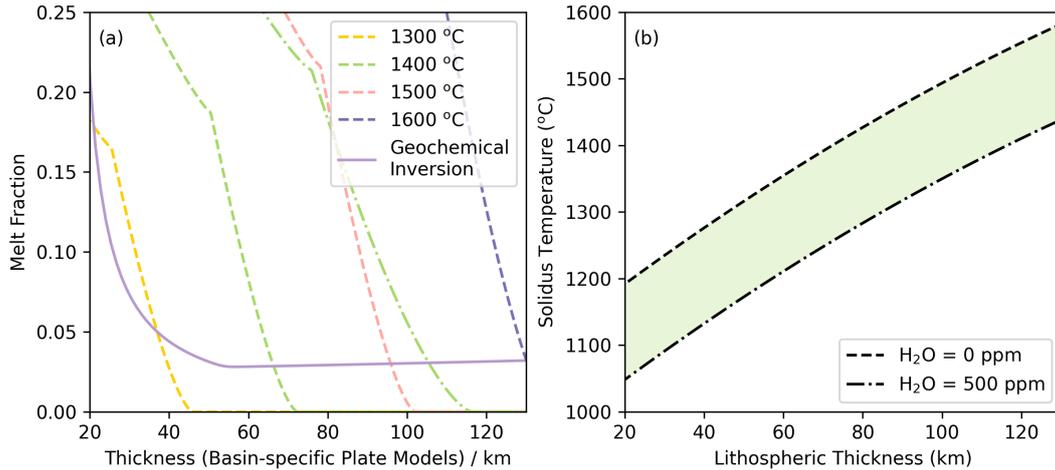


Figure 12. (a) Solid line = melt fraction (F) as a function of lithospheric thickness inferred from Equation (10) and the bi-linear trends for La concentrations, with basin-specific plate model-derived estimates of lithospheric thickness; dashed lines = theoretical melt fraction for decompression melting of dry, primitive peridotite at different potential temperatures from the parameterisation of Katz et al. (2003), as modified by P. W. Ball et al. (2022); dash-dotted line = same for a wet 1400°C source with H₂O = 500 ppm, which is thought to be an upper bound for water content in plume source regions (e.g., Wallace, 1998; Asimow & Langmuir, 2003). (b) Solidi for peridotite with 0–500 ppm water contents.

655 and to remain nearly constant with increasing lithospheric thickness. The observed trends
 656 in Na and K may therefore indicate that variations in D' are playing a role. As discussed
 657 in Section 4.2, increasing pressure allows entry of Al³⁺ into the clinopyroxene M1 site.
 658 Via reaction (9), this substitution can be charge balanced by replacing a X²⁺
 659 in the larger M2 site with Na⁺ and/or K⁺, resulting in an increase of D' for K⁺ and Na⁺
 660 with increasing pressure. With minimal changes in F , this effect may explain their ob-
 661 served decrease in concentration with increasing lithospheric thickness, relative to highly
 662 incompatible La and Th, although we note that Na⁺ is expected to have a stronger affin-
 663 ity for the M2 site than K⁺ because its ionic size is closer to the size of the site (Safonov
 664 et al., 2011).

665 4.3.2 CaO

666 Calcium is the element most likely to be affected by the spinel-garnet transition
 667 because garnet contains stoichiometric Ca, whereas spinel does not. The principal repos-
 668 itories for Ca²⁺ in garnet peridotites are, in order of decreasing affinity, clinopyroxene
 669 > garnet > orthopyroxene > olivine. Beneath shallow lithosphere, there is a steady de-
 670 crease in CaO concentration with increasing lithospheric thickness up to ~ 55 km (Fig-
 671 ure 9m–n). We attribute this behaviour to the continuous decrease in F , previously de-
 672 duced from analyses of incompatible element trends: as F decreases, less clinopyroxene
 673 melts and the resulting melt has a lower Ca concentration. Our interpretation of the in-
 674 compatible element trends suggests that, beyond the kink, F should remain approximately
 675 constant or continue to decrease, but at a reduced rate. Therefore, we would expect a
 676 further decrease in CaO (albeit at a lower rate), rather than the increase that is observed.
 677 The cause of this increase is unclear, but assuming that F is not changing (as suggested
 678 by the most incompatible elements), it requires that, with increasing pressure, a Ca-rich
 679 phase (presumably Ca-rich pyroxene) melts in preference to moderately Ca-poor garnet

680 and orthopyroxene. We note that previous studies, which applied linear regression to the
 681 data, found no discernible trend between CaO and lithospheric thickness (e.g., Humphreys
 682 & Niu, 2009), probably because the reversal in trends from decreasing to increasing CaO
 683 counteract each other.

684 **4.3.3 Yb and Lu**

685 Concentrations of Yb and Lu change little with increasing lithospheric thickness,
 686 showing only a slight, linear decrease (Figure 10). This behaviour occurs even though
 687 these elements exhibit an order of magnitude difference in compatibility between spinel
 688 (incompatible) and garnet (compatible; Table 1), from which we might expect to see a
 689 kink in their trends.

690 Within the spinel stability field, the decrease in F with increasing pressure, required
 691 by the incompatible trace element trends, is offset by increasing D' due to an increas-
 692 ing amount of clinopyroxene in the residue at higher pressures (e.g., Green & Ringwood,
 693 1967). Within the garnet stability field, the constant or slight decrease in F with increas-
 694 ing lid thickness is initially offset by an increase in D' as garnet replaces spinel and, sub-
 695 sequently, as pressure continues to increase, by garnet partially replacing pyroxene ac-
 696 cording to reaction (14).

697 Superimposed on these changes is the migration of low Yb-Lu melt from the gar-
 698 net zone into the spinel zone, where it partially offsets the potential increase in the con-
 699 centration of these elements due to their lower D' in the spinel zone. This behaviour is
 700 termed the ‘memory effect’, whereby erupted melts preserve a geochemical memory of
 701 high-pressure melting despite melting continuing to shallower depths (e.g. Elliott et al.,
 702 1991). The relative proportions of melt from the spinel and garnet zone are also criti-
 703 cal in determining melt composition: increasing pressure can increase Yb-Lu concentra-
 704 tions in melts within the spinel zone while simultaneously reduce the melt volume within
 705 that zone, thus limiting low-pressure melts’ impact on determining the final average Yb-
 706 Lu concentration and resulting in an decrease of Yb-Lu with increasing lithospheric thick-
 707 ness. Overall, the combined impact of the competing influences of increasing F , espe-
 708 cially within the spinel zone, changes in D' as garnet is replaced by spinel, and the sys-
 709 tematic decrease in the proportion of melt coming from the spinel zone with increasing
 710 pressure, can plausibly explain the slight decrease in Yb and Lu concentrations with in-
 711 creasing lithosphere thickness. Taken together, this result implies that the absence of a
 712 kink in Yb-Lu trends, which might be expected from the spinel-garnet phase transition,
 713 is obscured by the memory effect.

714 **4.4 Shape of REEs**

715 We next discuss the shape parameters, λ_i , for REE concentration patterns (O’Neill,
 716 2016). λ_0 is the average of the logarithmic concentration of all REEs except Eu, normalised
 717 by each element’s concentration in chondrites. Increasing lid thickness reduces the melt
 718 fraction, thereby elevating the concentration of highly incompatible LREEs (Figure 9)
 719 while having a limited effect on the concentration of HREEs (Figure 10). It is therefore
 720 not surprising that λ_0 follows trends defined by the highly incompatible elements, with
 721 a kink at ~ 55 km (Figures 11a).

722 λ_1 measures the enrichment of LREEs relative to HREEs and has a bi-linear trend,
 723 similar to λ_0 (Figure 11b). Previous studies described variations in REE trends using
 724 ratios, such as La/Yb and Sm/Yb, and related observed changes to an increasing abun-
 725 dance of garnet in the residue as the melting pressure increases (e.g., Ellam, 1992; Humphreys
 726 & Niu, 2009). However, these studies did not recognise either a kink or the influence of
 727 changes in F on LREE and, hence, the slope of the REE pattern. As noted in connec-
 728 tion with λ_0 , the LREEs initially increase with increasing lithospheric thickness to ~ 55 km

(Section 4.3.1), driven by changes in F , then remain nearly constant, while HREE concentrations change little throughout (Section 4.3.3). Therefore, the combined behaviour of LREEs and HREEs accounts for the observed variation in λ_1 .

λ_2 quantifies the curvature of the REE pattern. As outlined by O'Neill (2016), values are positive if amphibole remains in the residue following melting and transitions from positive to negative if more garnet remains. OIBs are dry relative to arc magmas, so amphibole is not expected to play a role in their genesis (e.g., O'Neill, 2016). To examine the sensitivity of λ_2 to melting depth, we consider a two-stage melting model (Supplementary Table S6), in which partial melting begins in the garnet zone and extends into the spinel zone, with mixing permitted between melts from both zones. For melting in the garnet zone, λ_2 becomes more negative as both F and the amount of garnet in the residue increase. For melting in the spinel zone, λ_2 is positive when F is low, but decreases as F increases. When melts from both zones mix, the effect is cumulative. λ_2 is also sensitive to source composition: melts generated from a primitive mantle source have higher λ_2 values than those from a depleted mantle source (Supplementary Table S6). These insights imply that interpretations of λ_2 are complex, although certain inferences can be made.

Figure 11c shows that λ_2 linearly decreases with increasing lithospheric thickness. At lithospheric thicknesses greater than ~ 55 km, the majority of λ_2 values are negative and the trend becomes increasingly negative as the lithosphere thickens. Assuming that total F changes little after the kink, as is implied by the trends identified for highly incompatible elements, and there is no mixing of melts from the spinel and garnet zones (which is plausible given that the lid should act as a barrier to melting above the spinel-garnet transition depth), based on the two-stage model outlined above, we infer that the amount of garnet in the source increases with pressure at lithospheric thicknesses exceeding those of the kink, as expected. When lithospheric thickness is less than 55 km, assuming all melts are generated in the spinel zone and there is no mixing with melts from the garnet zone, as the lithosphere thickens, F will decrease and λ_2 will increase. This is inconsistent with the trend that we have identified for λ_2 (Figure 11c), which decreases across all lithospheric thicknesses. This can be plausibly explained if a larger proportion of garnet melts mixed with a smaller proportion of spinel melts as lithospheric thickness and pressure increase (decreasing total F – e.g., primitive mantle starting to melt from 4 GPa, if $F(0.06) = F_{\text{grt}}(0.01) + F_{\text{spl}}(0.05)$, $\lambda_2 = 7.26$; if $F(0.04) = F_{\text{grt}}(0.03) + F_{\text{spl}}(0.01)$, $\lambda_2 = 1.86$), providing further evidence for the memory effect when melts are generated under thin lithosphere (e.g., Elliott et al., 1991).

4.5 Trend Robustness

To analyse the robustness of our results to initial OIB processing steps, potential bias towards heavily sampled localities, and/or choice of lithospheric thickness model, we evaluate Bayes factors for a suite of additional scenarios including: (i) filtered OIB data prior to- and post-corrections for fractional crystallisation; (ii) a sub-sample of the OIB dataset, where a percentage of samples are randomly removed; (iii) datasets where Iceland and Hawaii samples are included/excluded; and (iv) lithospheric thickness obtained from the basin-specific plate-cooling models versus a model derived from seismic tomography. A summary of these results are presented in Figure 13, with further plots presented in Supplementary Figures S4–S5.

4.5.1 Correction for Fractional Crystallisation

Our reverse-fractionation calculations in Petrolog3 suggest that primitive OIB melts commonly undergo 5–25% fractional crystallisation in the magma chamber (Supplementary Figure S6). Correcting for fractional crystallisation does alter absolute geochemical concentrations, but the preference for a linear over constant dependence on litho-

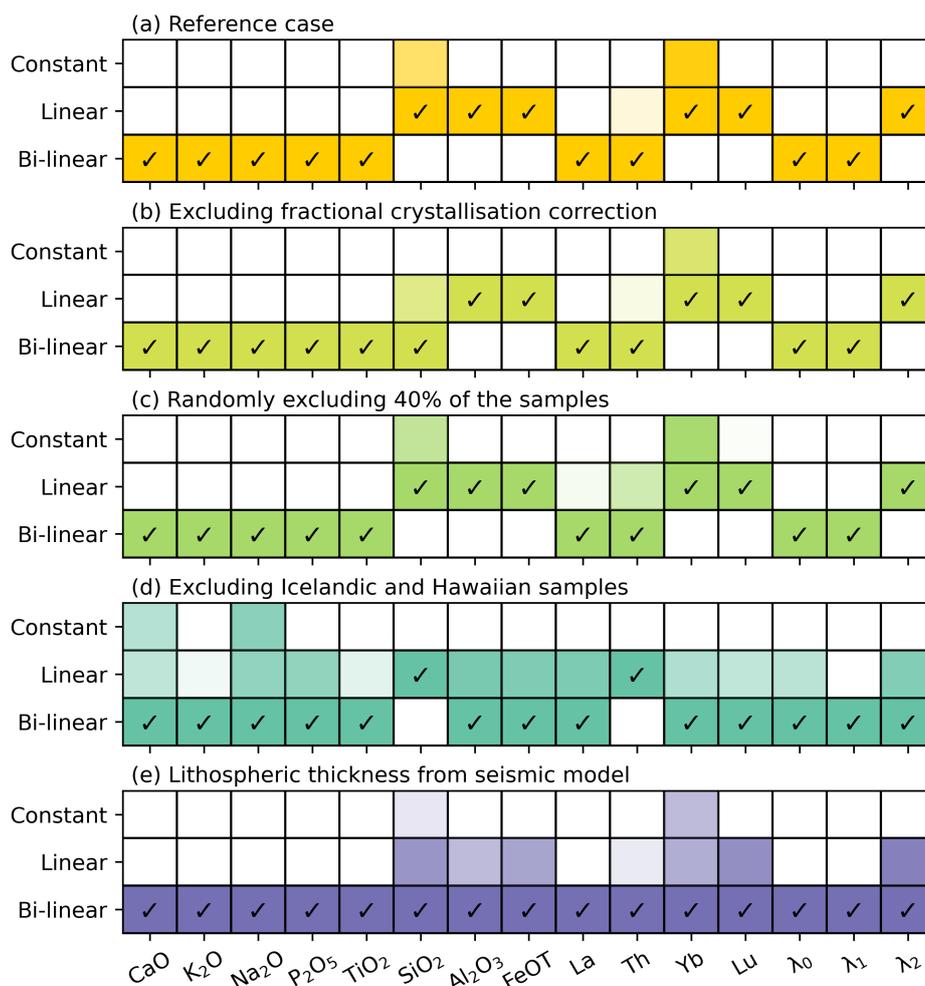


Figure 13. (a) Optimal model type for each geochemical parameter under our reference setup (filtered OIB samples from all localities corrected for fractional crystallisation, with lithospheric thicknesses from basin-specific plate-cooling models; as in Figure 7). (b) Same as the reference setup except data are not corrected for fractional crystallisation. (c) Same as the reference setup except 40 % of the data are randomly removed. (d) Same as the reference setup except Icelandic and Hawaiian samples were excluded. (e) Same as the reference setup albeit with lithospheric thickness taken from the model based on seismic tomography.

779 spheric thickness remains unchanged for all major and minor elements, and REE shape
 780 parameters (Figure 13b). In most cases, the preference for either linear or bi-linear
 781 models also remains unchanged, the exception being SiO₂, for which the non-corrected data
 782 shows a preference for a bi-linear model. This behaviour is a direct consequence of imposing the
 783 SiO₂ > 43 wt.% filtering criteria: for the non-fractionation corrected data, this results in a
 784 hard cut-off of all data below this value and preferentially increases preferred model values in
 785 thicker lithosphere, whereas following fractionation correction, the kink is smoothed out and
 786 SiO₂ linearly decreases with increasing lithospheric thickness (Supplementary Figures S7 and S8).
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4.5.2 Data Subsets

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The possibility of bias from specific samples was tested by removing some data to see if the observed trends remain - so-called bootstrapping. We randomly removed 20% and 40% of all OIB samples while keeping all other variables consistent. In most of these tests, the preferred model and the trend for each of the geochemical parameters did not change (Figure 13c). Exceptions occurred when the preferred model was close to the edge of a threshold before removing some samples. Nonetheless, our overall interpretation remains valid, and the observed geochemical trends are not strongly affected by sampling bias.

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4.5.3 Heavily Sampled Localities

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Hawaii and Iceland are heavily sampled in comparison to other localities in our OIB database, yielding high-density data clusters that may potentially introduce bias into the results. Nevertheless, we find that excluding these sites does not generally alter evidence in favour of the lid effect. For all geochemical parameters, there is still strong preference for either a linear or bi-linear model over a constant one. The two exceptions occur for Ca and Na, where the evidence with respect a constant model is still greater than 2 but less than 20 (Figure 13d).

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With regards to preference for a bi-linear versus linear fit, removal of these localities has more of an influence on results. For geochemical parameters where all sites are optimally fitted by bi-linear models, excluding Iceland and Hawaii can either increase or reduce values of $\log_{10} E_2 - \log_{10} E_1$, depending on the parameter (Supplementary Figure S4a and e). In general, more parameters transition to preferring a bi-linear model (e.g., Al_2O_3 , FeOT, Yb, Lu and λ_2), with Si maintaining preference for a linear model and only Th switching from a bi-linear to linear model. This indicates that evidence in favour of bi-linear trends is not attributable to potential sampling bias from Hawaii and Iceland.

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Nevertheless, it is interesting to note that excluding Icelandic and Hawaiian samples has an impact on the slope of the trend in thick lithosphere (beyond the kink depth of ~ 55 km). For incompatible elements Th, La, TiO_2 and P_2O_5 , the slope after the kink increases (Supplementary Figure S9), which is also the case for λ_0 and λ_1 (Supplementary Figure S10), albeit still at a lower rate than would be expected from theoretical arguments for melting at constant potential temperature and composition. For Na_2O and K_2O , it reduces the rate of concentration decrease with increasing lithospheric thickness (Supplementary Figure S9). All of these differences can likely be attributed to the concentrations of incompatible elements in Hawaiian basalts being lower than those of other OIBs on lithosphere of similar thickness. As noted in Section 2.4, Hawaiian basalts are dominated by tholeiites, whereas all other OIBs on thick lithosphere have alkali basalt affinities. Tholeiites are produced by higher degrees of partial melting (e.g., Yoder Jr & Tilley, 1962) and concentrations of incompatible elements are therefore expected to be diluted, which is consistent with the Hawaiian plume being hotter and stronger than other plumes beneath thick lithosphere (e.g., Hoggard, Parnell-Turner, & White, 2020). Hawaiian OIBs may also originate from a source that is more depleted in highly incompatible elements if, as suggested by Hofmann and Jochum (1996) and Pietruszka et al. (2013), it contains a significant amount of recycled oceanic gabbro. Regardless of the exact nature of the Hawaiian plume, its distinctive characteristics, coupled with the large number of samples available, can influence the slope of geochemical trends in thick lithosphere but does not refute evidence for the lid effect.

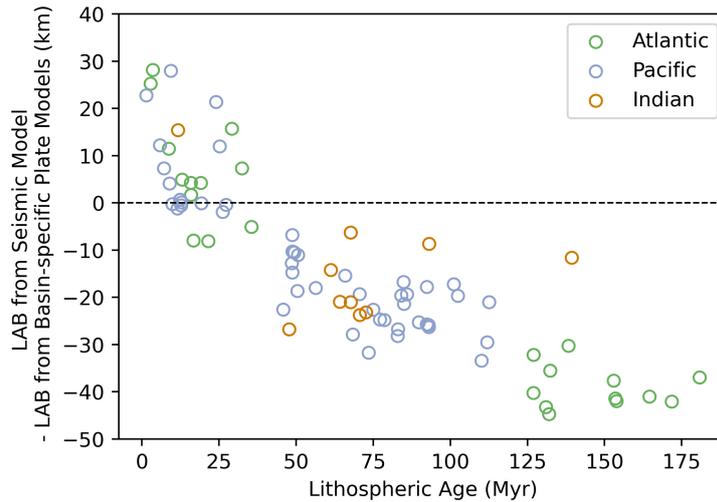


Figure 14. Difference between local lithospheric thickness beneath each island from the seismic model and that predicted by the basin-specific plate models, as a function of lithospheric age at time of OIB eruption. Localities in the Atlantic, Pacific and Indian Oceans are represented by green, blue and red circles, respectively.

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4.5.4 *Alternative Estimates of Lithospheric Thickness*

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As introduced in Section 2.2, a limitation of theoretical cooling models is that they cannot capture local deviations in lithospheric thickness away from the average value for ocean floor of a given age (e.g., D. R. Davies et al., 2019). By comparing expected values with local estimates obtained from seismological constraints, we demonstrate that there are systematic differences between the two at the sites of OIBs in our database (Figure 14). For ocean islands on lithosphere younger than ~ 30 Ma, such as at Easter Island or the Azores, seismically inferred estimates of local lithospheric thickness systematically exceed expectations from plate-cooling models. This offset is likely artificial, being a consequence of surface wave tomography having limited resolution at depths shallower than ~ 75 km and therefore smearing shallow velocity structure into greater depths in regions of thin lithosphere (see Section 2.2). For older lithosphere on the other hand, seismically inferred estimates of present-day lithospheric thickness beneath each ocean island are consistently thinner than expectations from plate models. In contrast to the artifacts in regions of thin lithosphere, this observation is likely real and probably reflects destabilisation and thinning of the lithosphere by the underlying mantle plume (e.g., G. F. Davies, 1994; Dumoulin et al., 2001). As a consequence of these two effects, the majority of lithospheric thickness estimates beneath OIBs from the seismic model fall in the 40–100 km range, which is slightly narrower than the associated range of 30–120 km from plate-cooling models.

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When switching to estimates of lithospheric thickness inferred from the seismic model, we find that all geochemical trends are best fitted by bi-linear models, including those that display linear trends when using lithospheric thickness from basin-specific plate models (Supplementary Figure S4f). In particular, there is a moderate preference ($5 < \log_{10} E_2 - \log_{10} E_1 < 10$) for bi-linear models in the cases of Al_2O_3 , FeO and Yb, as well as a slight preference ($2 < \log_{10} E_2 - \log_{10} E_1 < 5$) in the cases of SiO_2 , Lu, and λ_2 . Nevertheless, constant models still perform poorly (Figure 13e), and our dataset displays robust evidence for existence of the lid effect.

4.6 Processes Contributing to Observed Geochemical Trends

In our reference setup, bi-linear trends generally fall into two categories: (i) the highly incompatible elements (Th, K, La, P, Ti, Na), in which concentrations are entirely controlled by melt fraction and therefore indicate that F remains approximately constant at lithospheric thicknesses greater than that of the kink; and (ii) for CaO and parameters describing REE patterns (λ_0 and λ_1), where the depth of the kink is being determined by the combined effects of changing melt fraction interacting with the spinel-garnet phase transition. For the latter, the role of this phase change is to maintain HREE concentrations with increasing lithospheric thickness, while allowing the concentration of the LREE to continue to increase as F reduces.

It is important to note that the kinks in our bi-linear trends may not, in reality, reflect sharp change points, but rather a gradual transition in the trend as a function of increasing lithospheric thickness. While our findings show that the kink is generally identified at a depth of 50–60 km (Supplementary Figure S3), since these trends are sensitive to both variations in F and the spinel-garnet phase transition, it is incorrect to infer the phase transition depth directly from the kink depth. This point is further emphasised by the fact that we observe garnet signatures in some OIBs that are generated beneath thin lithosphere (e.g., through trends of Yb, Lu, λ_2), which can be attributed to the memory effect of high-pressure melts from the garnet stability field incompletely mixing with lower pressure melts from the spinel stability field.

Our resulting inferences of melt fraction as a function of lithospheric thickness (Figure 12a) suggest that, beyond a certain lithospheric thickness, F becomes approximately constant. This behaviour is unexpected since, based on the lid effect and theoretical models of plate cooling, we would expect lithosphere to continue to thicken and, all other aspects being equal, cause a continuous reduction in F . One potential explanation for this behaviour could be progressive thinning of overlying lithosphere by upwelling plume material. Small-scale convection above mantle plumes is known to be more prevalent beneath thicker lithosphere (e.g., Dumoulin et al., 2001; van Hunen et al., 2003; Ballmer et al., 2011; Le Voci et al., 2014; D. R. Davies et al., 2016; Duvernay et al., 2021), making it more likely that the base of older lithosphere would become unstable upon plume impingement. This argument is supported by our observation in Section 4.5.4 and Figure 14 that seismically inferred estimates of lithospheric thickness are consistently thinner than those predicted by plate-cooling models in older lithosphere. Accordingly, beyond the ~ 55 km kink depth, lithospheric thickness above mantle plumes is unlikely to increase at a rate consistent with cooling model expectations, thereby reducing the rate of the expected reduction in melt fraction. A further contributing factor is that, since the solidus temperature increases with pressure (Figure 12b), weaker plumes with lower excess temperatures may fail to cross the solidus and generate melt beneath thick lithosphere. This effect would be compounded by the fact that weaker plumes generate smaller melt volumes that are more likely to get trapped at depth and not erupt onto the seafloor. We refer to this behaviour as the ‘temperature effect’ and have investigated two lines of independent evidence that might support it.

First, we have explored potential relationships between lithospheric thickness and the potential temperature of OIB sources as estimated from geochemical or geophysical arguments (e.g., Putirka, 2008; P. Ball et al., 2021; Bao et al., 2022, Supplementary Figure S11). No clear patterns have emerged (although such estimates are known to be uncertain; e.g., Herzberg et al., 2007; Bao et al., 2022). Secondly, we have compared lithospheric thickness to recent analyses of plume buoyancy flux from Hoggard, Parnell-Turner, and White (2020). Here, we find that magmatic plumes beneath thicker lithosphere generally have higher buoyancy fluxes, potentially indicative of higher excess temperatures (Figure 15). This observation is consistent with the suggestion that, beyond the kink depth, melt fractions are approximately constant due to preferential sampling of progressively

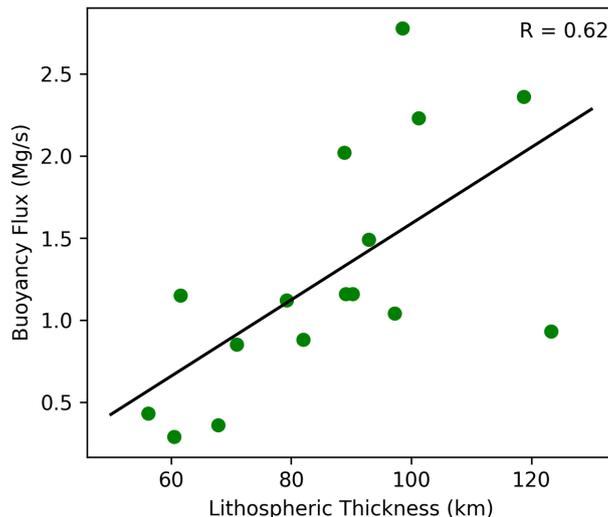


Figure 15. Relationship between buoyancy flux of magmatic plumes from Hoggard, Parnell-Turner, and White (2020) and lithospheric thickness estimated from the basin-specific plate models (for values greater than the kink depth of ~ 55 km).

915 hotter plumes from regions of thicker lithosphere (i.e., the rate of decrease in F is at least
916 partially offset by the increase in plume temperature).

917 Taken together, local variations in lithospheric thickness away from average expecta-
918 tions from theoretical cooling models, sampling biases associated with progressively
919 hotter plumes in regions of thicker lithosphere, and source region heterogeneities, are all
920 plausible contributors to observed incompatible element trends.

921 4.7 Limited Evidence for Melt Re-equilibration at Base of Lithosphere

922 Both Iceland and Hawaii have a large number of samples and exhibit a wide spread
923 of compositions (e.g. Figure 16). Previous studies have attributed these ranges to vari-
924 ations in the fertility of the mantle source (e.g., Humphreys & Niu, 2009; Niu et al., 2011;
925 Jones et al., 2017). Furthermore, Niu (2021) have also suggested that none of this spread
926 can be attributed to differences in the initial melting pressure (i.e. there is no memory
927 effect), since OIB melts re-equilibrate with the surrounding mantle during their ascent
928 to the surface. Melting in an ascending mantle plume is expected to occur over a depth
929 range of several tens of kilometres. If such re-equilibration reactions do occur, however,
930 we would expect major element concentrations buffered by olivine and pyroxene to be
931 strongly homogenised, while highly incompatible trace elements (e.g., Th, K and La) that
932 have $D' < 0.01$ in both the garnet and spinel stability fields should retain their origi-
933 nal spread.

934 Our analyses have found no evidence to support such a process for re-equilibration
935 of plume-derived melts: in other words, we find robust evidence for preservation of geo-
936 chemical signatures across a range of depths in erupted melt products (i.e., the mem-
937 ory effect). OIBs from Hawaii and Iceland, for example, show a negative correlation be-
938 tween SiO_2 and FeOT (Figure 16a–b), which can be attributed to melts generated at a
939 range of different pressures and has previously been suggested to occur in many OIBs
940 (e.g., Scarrow & Cox, 1995). In the case of Iceland, most of the data cluster at ~ 46.5
941 wt.% SiO_2 , but some samples extend towards ~ 42 wt.% SiO_2 . The high SiO_2 samples
942 could relate to melts generated at low pressure, while samples with lower SiO_2 are gen-

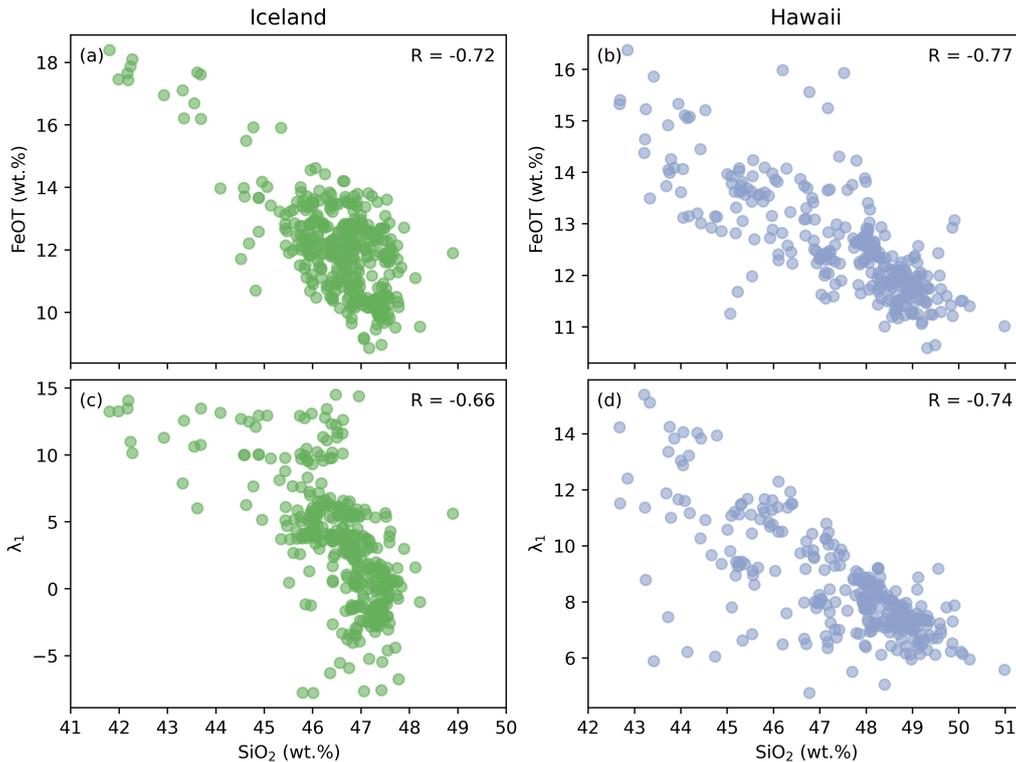


Figure 16. Co-variation of pressure-sensitive geochemical parameters for OIB samples located at Iceland and Hawaii. (a) FeOT as a function of SiO₂ for Icelandic samples, following application of filtering and corrections for fractional crystallisation. (b) Same for Hawaiian samples. (c–d) Same for λ₁ values as a function of SiO₂.

943 erated by smaller degrees of melting at higher pressure. There is also a cluster of sam-
 944 ples at the high SiO₂ end of the Hawaiian array, albeit at 48.5 wt.% SiO₂, with the data
 945 more evenly spread across the array. As with Iceland, we suggest that the low-SiO₂, high-
 946 FeOT basalts at Hawaii are produced by melts separating from the mantle at depth (i.e.
 947 far below the lithospheric lid) and that they have subsequently erupted without under-
 948 going re-equilibration during their ascent.

949 Importantly, whilst variations in FeOT at a given SiO₂ can potentially be explained
 950 by mantle source heterogeneity, the correlation between SiO₂ and λ₁ provides convinc-
 951 ing support for melting across a range of pressures without complete homogenisation and
 952 mixing (Figure 16c–d). Melt re-equilibration would be expected to bound major element
 953 concentrations within a limited range, but have little impact on incompatible trace ele-
 954 ment concentrations. Accordingly, following re-equilibration, limited correlation would
 955 be expected between major and trace elements, which is not borne out by our observa-
 956 tions.

957 5 Conclusions

958 Our study yields insights into the role of lithospheric thickness variations in influ-
 959 encing the geochemical characteristics of OIBs. Our results support existence of the lid
 960 effect, in which lithospheric thickness limits the lowest melting pressure of upwelling man-
 961 tle plumes and has an important influence on OIB geochemistry. Our statistical anal-

962 yses suggest that REE patterns, and major and trace element concentrations, are influ-
 963 enced by lithospheric thickness, with some geochemical parameters best fitted by linear
 964 trends and others by bi-linear trends with a kink at thicknesses of 50–60 km. Although
 965 other factors such as source heterogeneity, melts separating from the mantle at various
 966 depths below the lid, and bias from heavily sampled localities are expected to influence
 967 OIB geochemical trends, the observed trends remain overall consistent with expectations
 968 from the lid effect.

969 Such trends can be explained by a combination of pressure-driven changes in melt
 970 fraction and mineral assemblage, especially the spinel-garnet transition. The behavior
 971 of highly incompatible elements suggests that the melt fraction decreases rapidly with
 972 increasing lithospheric thickness until thicknesses reach ~ 55 km, but subsequently de-
 973 creases at a significantly lower rate with increasing thicknesses. This behaviour is incon-
 974 sistent with theoretical expectations based solely on the lid effect and suggests that: (i)
 975 plumes impinging beneath thicker lithosphere may be more effective at thinning the over-
 976 lying lid, thereby modulating changes in melt fraction; and (ii) only melts from plumes
 977 with higher potential temperatures can penetrate thick lithosphere and reach the seafloor,
 978 consistent with solidus temperatures increasing with pressure and evidence that mag-
 979 matic plumes under thicker lithosphere have higher buoyancy fluxes.

980 The depth of the spinel-garnet transition zone cannot be directly identified from
 981 the trends observed herein. Nonetheless, the signature of this phase transition is evident
 982 in observed trends for Yb, Lu, and λ_2 . These trends require that a signature of melt pro-
 983 duced within the garnet zone is carried by many OIBs originating beneath thin litho-
 984 sphere, indicative of a memory effect within plume-derived melts. This interpretation
 985 is further supported by geochemical trends from different samples generated in the same
 986 plume: it is therefore likely that some OIB melts, generated at varying pressures, can
 987 ascend to the surface separately without re-equilibrating at the base of the lithosphere.

988 Taken together, our results have implications for magma generation, migration and
 989 mixing beneath OIBs, which will be vital for connecting these intricate processes to the
 990 larger-scale dynamics of upwelling mantle plumes. Our study provides quantitative con-
 991 straints on the relationship between modern OIB geochemistry and lithospheric thick-
 992 ness, which will underpin future efforts to invert the geochemical composition of volcanic
 993 lavas for the temperature and pressure of their mantle source (e.g., Klöcking et al., 2020;
 994 P. W. Ball et al., 2021), including those preserved from earlier periods of Earth’s his-
 995 tory, revealing changes in lithospheric thickness through space and time. Such point-wise
 996 constraints are also required by a new class of data-driven geodynamical simulation that
 997 aim to recover the spatial and temporal evolution of the mantle and its impact at the
 998 surface (e.g., Ghelichkhan et al., 2023; Bunge et al., 2023).

999 **Open Research**

1000 The unfiltered dataset of geochemical analyses for OIBs was extracted from the open-
 1001 source GeoRoc database (<https://georoc.eu>) in February, 2023. The dataset, which in-
 1002 cludes OIB geochemistry, lithospheric thickness, Python scripts for Bayes factor anal-
 1003 ysis and two-phase melting, and other information, is achieved at Zenodo (Jiang, 2024).
 1004 Figures have been prepared using Matplotlib (Hunter, 2007).

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