

Earth's mantle composition revealed by mantle plumes

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$\frac{1}{2}$	The Composition of the Earth's Mantle Revealed by Mantle Plumes
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41 Abstract

42 Earth's mantle is integral to many processes that shape our planet, including convection, 43 crustal formation, crustal recycling, and global heat and volatile budgets. Still, many questions 44 remain unresolved about mantle composition and its influence on geodynamics today and 45 throughout geologic time. Because they originate at depths that can extend to the core-mantle 46 boundary, mantle plumes provide invaluable information about the composition of the deep 47 mantle. In this review, we discuss the effectiveness and challenges of using isotopic analyses of 48 plume-derived rocks to document the origin and composition of mantle heterogeneities, early-49 formed mantle reservoirs, crustal recycling processes, core-mantle interactions, and mantle 50 evolution. We discuss isotopic methods and improvements to existing isotopic systems to 51 characterize plume-derived ocean island basalts. Nevertheless, because mantle plumes vary in 52 many properties, including magmatic flux, temperature, tectonic environment, and compositions, 53 geochemical observations on plume-generated systems must be considered carefully before 54 making interpretations about Earth's interior. Consequently, plumes and their melts should be 55 evaluated along a spectrum that acknowledges and contextualizes their differences, particularly 56 mantle flux. Ultimately, the most important advancements in mantle geochemistry, architecture, 57 and dynamics will emerge from cross-disciplinary studies in diverse fields such as experimental 58 petrology, mineral physics, numerical geodynamics, seismology, and geochemistry.

60 Section 1 Introduction

61 The mantle plays a critical role in many of Earth's most dynamic systems. At 84% of 62 Earth's volume, the mantle is the source of mid-ocean ridge, convergent margin, and intraplate

volcanism, processes integral to forming and recycling oceanic and continental crust (White,

- 64 1985: Zindler and Hart, 1986; Hofmann, 1997; 2003; Labrosse et al., 2007; White, 2015). The
- 65 mantle also contributes to Earth's water and heat budgets via radioactive decay and
- 66 thermochemical convection. In the lower mantle (660-2890 km depth), seismic wave velocity
- 67 variations reflect differences in temperature and/or composition (Davies and Davies, 2009;
- 68 Tkalčić et al., 2015; Garnero, 2000; Koelemejier et al., 2016; Ritsema and Lekic, 2020),
- 69 suggesting that the lower mantle, or part of it, is a reservoir for compositionally distinct material,
- 70 including recycled and potentially ancient primitive components. Thus, understanding many
- 71 fundamental Earth processes relies on documenting the composition and spatial heterogeneity of
- 72 Earth's mantle today and its evolution throughout geologic time.
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74 At shallow mantle depths (<100 km) below spreading ridges, upwelling causes the upper mantle

- 75 to melt via adiabatic decompression. These processes generate mid-ocean ridge basalts (MORB),
- 76 which provide insight into the composition of the upper mantle (e.g., Gale et al., 2013 and
- references therein). By contrast, mantle plumes provide invaluable insight into the geochemistry
 of Earth's deeper interior and occur in all tectonic settings (Fig. 1a). They originate at different
- of Earth's deeper interior and occur in all tectonic settings (Fig. 1a). They originate at different depths, from shallow upwellings in the upper mantle (Duvernay et al., 2021) to deeply sourced
- depths, from shallow upwellings in the upper mantle (Duvernay et al., 2021) to deeply sourced
 plumes (Courtillot et al., 2003) that rise from near the core-mantle boundary (CMB) at ~2800
- 81 km. Above 1000 km (French and Romanowicz, 2015), mantle plumes form narrow, roughly
- 82 cylindrical pipes of anomalously hot mantle that upwell and partially melt to form ocean island
- basalts (OIBs) on oceanic plates. Mantle plume melting occurs at sublithospheric depths,
- 84 requiring a mantle source that is either hotter than the upper mantle, or enriched in rocks and/or
- 85 fluids that lower the solidus temperature. Thus, mantle plumes provide the heat and components
- 86 necessary for intraplate magmatism and to generate OIBs (Fig. 1b). Plume-generated oceanic

87 islands usually sample the mantle without chemical interference from the continental crust or

88 subcontinental lithospheric mantle, providing a unique geochemical window into the

composition of Earth's mantle and its evolution over time, including the sources of deeply rootedplumes.

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92 In this review, we discuss developments in the isotopic analysis of mantle plume-fed 93 ocean island basalts, an essential tool for documenting mantle heterogeneity (Fig. 1b). An NREE 94 review by Koppers et al. (2021) discusses progress in seismic imaging, mantle flow modelling, 95 plate tectonic reconstructions, and geochemical analyses of deep mantle plumes and their roles in 96 Earth processes. Our review, which complements that of Koppers et al. (2021), focuses on the 97 geochemistry and geodynamics of deep plumes that form well-studied oceanic islands (e.g., 98 Hawai'i, Réunion, Kerguelen, and Galápagos, among others). New perspectives on the 99 geochemical composition of the mantle have recently been developed from advancements in 100 analytical techniques and novel isotopic systems, allowing the resolution of smaller isotopic 101 variations in OIB samples. These new techniques and isotopic systems shed light on the 102 presence, source, and age of heterogeneities in the deep mantle. We present a comprehensive 103 perspective on enduring paradigms and new advances in mantle geochemistry, as well as insights 104 that the geochemistry of ocean island basalt provides toward understanding Earth's evolution. 105

106 Section 2 Fundamentals of Mantle Plumes

107 The strength of a plume's upwelling flux, its composition, and the duration of its activity 108 have been used to classify plumes (Courtillot et al., 2003; Jackson et al., 2018; Koppers et al., 109 2021; Fig. 1a). Primary plumes have a seismic velocity anomaly of at least -1.5% between 1,000 110 and 2,800 km depth (extending to the CMB), a linear and age-progressive volcanic chain, a large 111 igneous province (LIP) at the oldest end of the volcanic chain, a strong magmatic flux, and high 112 ³He/⁴He or other indications of compositions distinct from those of mid-ocean ridge basalts 113 (Courtillot et al., 2003; Montelli et al., 2006; Boschi et al., 2007; King and Adam, 2014; French 114 and Romanowicz, 2015).

115

Seismic tomography and geodynamical studies suggest that most OIB-generating
volcanoes are produced by plumes that originate along the edges of Large Low Shear Velocity
Provinces (LLSVP), commonly interpreted as thermochemical piles at the CMB (Burke and
Torsvik 2004; Thorne and Garnero, 2004; Torsvik et al., 2006; Burke et al., 2008; Doubrovine et

120 al., 2016; Garnero et al., 2016). Early geodynamical models explored ancient, accumulated

recycled crust as the LLSVP source (e.g., Christensen and Hofmann, 1994; Brandenburg et al.,

122 2008), whereas more recent models focus on the interplay between the recycled crust and a layer

123 of primordial iron-rich material with an excess density of about 1% (e.g., Li, et al. 2014;

Williams et al., 2015; Nakagawa and Tackley, 2014; Jones et al., 2021). Alternatively, dense and reduced mantle material may pool at the CMB, contributing to the formation of LLSVPs (Gu et

al., 2016). Laboratory experiments (Davaille, 1999; Limare et al., 2015) and numerical

simulations successfully reproduce the formation of large thermo-chemical plumes observed in

recent tomographic models (French and Romanowicz, 2014). In some models, both the LLSVP

and the ambient mantle supply material to plumes rising from the boundary between them

130 (Fourel et al., 2017).

131

132 Also detected at the core-mantle boundary, Ultra-Low Velocity Zones (ULVZs) are 133 characterized by strong S-wave (~30%) and P-wave velocity reduction (10%), best explained by 134 a ~10% density increase (Thorne and Garnero, 2004; McNamara, 2019 and references therein). 135 The ULVZs are discrete areas 10-40 km high that extend laterally for up to ~1000 km along the core-mantle boundary (Cottaar and Romanowicz, 2012). Models for the origin of ULVZs include 136 137 core-mantle reactions (Knittle and Jeanloz, 1989), the presence of dense silicate melt (Williams 138 and Garnero, 1996), relics of banded iron formations subducted 2-3 Ga ago (Dobson and 139 Brodholt, 2005), or zones of iron-enriched post-perovskite (Mao et al., 2006). Of importance to 140 mantle geochemistry is the possibility that ULVZs host geochemical signatures distinct from the 141 rest of the mantle, including some that may record early differentiation or diffusion across the 142 core-mantle boundary (e.g., Mundl-Petermeier et al., 2020; Yoshino et al., 2020). The high 143 density of ULVZs inhibits their convective stirring, and only the most vigorous plumes may 144 entrain thin tendrils of ULVZ material by viscous coupling (i.e., Williams et al., 2015). 145 146 Mineral physics research has explored ways that mantle heterogeneity can be expressed 147 through phase relations, density, and elastic moduli variations due to changes in bulk 148 composition (e.g., Lee et al., 2004; Ricolleau et al., 2010; Dorfman et al., 2013), water content 149 (e.g., Litasov and Ohtani, 2007; Zhou et al., 2022), and differences in redox state (e.g., Gu et al., 150 2016, Creasy et al., 2020). While accessory phases can vary in type and abundance, the dominant 151 phase in the lower mantle is bridgmanite, a Mg-silicate perovskite (Tschauner et al., 2014). The

strength of bridgmanite's structure may encourage the formation of narrow channels of

core-mantle boundary (Ballmer et al., 2017).

upwelling and downwelling, thereby stabilizing deep-rooted mantle upwellings from near the

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156 Geochemical research on mantle plumes reveals complex spatial variations in OIBs (Text 157 Box #1; Fig. 2). The best-studied example is Hawai'i, where the distinct isotopic compositions of 158 Loa- and Kea-trend volcanoes indicate a bilateral compositional asymmetry, or compositional 159 "stripes" in the plume (Abouchami et al., 2005). Specifically, the southwestern Loa chain 160 consists of more enriched material, and the northeastern Kea chain has more depleted signatures. 161 Weis et al. (2011) proposed that the Loa chain is sourced in the Pacific LLSVP and Kea lavas are supplied by the ambient lower mantle (Nobre-Silva et al., 2013a; Williamson et al., 2019), a 162 163 reflection of the plume's location along the northern boundary of the Pacific LLSVP. The 164 compositionally distinct materials from the LLSVP and the lower mantle only mix minimally 165 between the CMB and the surface, where they are expressed as distinct signatures in erupted 166 lavas (Kerr and Mériaux, 2004; Farnetani and Hofmann, 2009; Weis et al., 2011). Notably, 167 similar compositional patterns have been recognized in other LLSVP-sourced plumes, including the Samoan, Galápagos, Easter, and Marquesas Islands in the Pacific (Weis et al., 2011; Huang 168 169 et al., 2011; Chauvel et al., 2012; Payne et al., 2013; Harpp et al., 2014; Harpp and Weis, 2020), and, in the Atlantic at the western edge of the African LLSVP, Tristan and Gough (Rohde et al., 170 171 2013).

172

This new paradigm for plume origins (Weis et al., 2011) has led to additional nuances and proposals for plume models as well. In the Marquesas, the sizes of the heterogeneities appear to be smaller than in Hawai'i, potentially originating from within the plume itself instead of the LLSVP-lower mantle boundary (Chauvel et al., 2012). Harrison et al. (2017) suggest that rather than originating at the LLSVP-mantle interface, a drifting Hawaiian plume gets anchored on the

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- LLSVP, resulting in the entrainment of LLSVP material; this model helps explain the abrupt
 increase in plume flux along the chain after the bend. Finally, modelling results from Jones et al.
 (2017) propose that the compositional zonation in Hawai'i reflects a response to a major change
- 181 in absolute plate motion.
- 182 183

Buoyancy Flux of Plumes

184 The strength, or buoyancy flux, of a mantle plume influences the partial melting regime 185 of its corresponding oceanic island system (e.g., Schilling, 1991). Tholeiitic and alkalic basalts 186 are produced, respectively, by higher or lower degrees of partial melting. Thus, whether tholeiitic or alkalic basalts dominate an oceanic island provides insight into the buoyancy flux and the 187 188 mantle potential temperature of a plume system. For example, the Hawaiian chain represents a 189 rare occurrence of high-volume magmatism that produces tholeiitic basalts; other examples 190 include Réunion, Iceland, Galápagos, and Easter Islands (e.g., Sleep, 1990; King and Adam, 191 2014). These systems also have elevated buoyancy flux and/or mantle potential temperature 192 (Schilling, 1991; White et al., 1993; Kingsley et al., 1998; 2007; Jackson and Dasgupta, 2008; 193 Jackson et al., 2017). Iceland is distinct as the only oceanic island that follows a silica-saturated 194 tholeiitic evolution trend (Supplementary Fig. a; Gale et al., 2013). Alkalic lavas, formed from 195 lower degrees of partial melting, dominate some plumes with intermediate fluxes, such as the 196 Cook-Austral chain (Jackson et al., 2020b) and Society Islands (Duncan et al., 1986) (Fig. 1a). 197 Generally, however, most intraplate oceanic volcanoes produce dominantly alkalic melts (Haase 198 et al., 2019), suggesting that high-degree partial melting of some mantle plumes may be 199 uncommon, at least during the Cenozoic.

Furthermore, plume strength may be enhanced by proximity to an LLSVP, as proposed for Hawai'i (Harrison et al., 2017; Harrison and Weis, 2018). The volume of magma produced along the Hawaiian chain has increased over the last 45 Myr, in contrast to the trend predicted by mantle plume models (e.g., Wessel, 2016; Weis et al., 2020). Moreover, the highest-flux plumes, including Hawai'i, overlie "mega-ULVZ" structures at the CMB (Cottaar and Romanowicz, 2012), implying links between lower mantle structures, the strength of a plume, its temperature, and its melting conditions (Harrison et al., 2017).

207 208

Influence of Plate Motion and Plate Boundaries

209 A plume's compositional structure will be recorded by its volcanoes in different ways 210 depending on lithospheric thickness, proximity to a spreading ridge, plate motion vectors, and 211 the geometry of the compositional structure within the plume conduit itself. Lithospheric 212 thickness can influence the depth and degree of melting, spreading ridges can re-direct upper 213 mantle flow, and the direction of plate motion relative to the compositional cross-section of the 214 plume will dictate how plume compositions are expressed at the surface. As an example of the 215 latter case, since ~3-6 Ma at Hawai'i, both the LLSVP boundary and current Pacific plate motion 216 vector (Wessel and Kroenke, 2009) are oriented along similar NW-trending strikes, forming the 217 two parallel chains of compositionally distinct volcanoes (Weis et al., 2011; Farnetani et al., 218 2012). In the Galápagos, by contrast, the orientation of the LLSVP boundary is oblique to plate 219 motion, resulting in early erupted, enriched material from the LLSVP being buried beneath 220 younger, more depleted material from the ambient mantle (Harpp and Weis, 2020). In addition, 221 shifts in plate motion direction might shear mantle plume stems and generate ephemeral changes 222 in the spatial distribution of erupted, compositionally distinct material (e.g., Jones et al., 2017). 223

224 Plumes will interact with the adjacent spreading centers, causing plume material to be 225 incorporated into the return flow of the ridge and enhancing entrainment of depleted upper 226 mantle into plume-generated lavas as observed in the Azores, Galápagos, and Cretaceous 227 Hawaiian systems, among other near-ridge plumes (e.g., White et al., 1993; Harpp and White, 2001; Harrison et al., 2020). The near-zero lithospheric thickness of ridge-proximal plumes may 228 229 also increase plume melting and affect the magmatic architecture of ocean islands formed near

- 230 the ridge (e.g., Weis and Frey, 2002; Regelous et al., 2003; Harpp and Geist, 2018;). Near-ridge 231 plumes, including Iceland, Galápagos, Kerguelen, and Easter produce abundant tholeiitic lavas
- 232 that require higher degrees of partial melting than other mantle plumes (White et al., 1993;
- 233 Kingsley et al., 1998, 2007; Ito et al., 1996; Schilling, 1991; Weis and Frey, 2002). In plumes 234 near subduction zones, additional crustal flexure of the plate may generate melt and/or encourage
- 235 entrainment of upper mantle material, as proposed for Samoa (Konter and Jackson, 2012; 236 Jackson et al., 2014) and for volcanism that cannot be plume-related in the Emperor Seamounts 237 near the Aleutian Arc (e.g., Kerr et al., 2005).
- 238

239 **Section 3 Oceanic Island Volcanism**

240 Owing to the lack of interaction with continental material, ocean islands with deep plume 241 sources provide the most direct view and accurate representation of lower mantle composition 242 (e.g., Harrison et al., 2017; Weis et al., 2020). 243

244 **OIB: Geochemical Overview**

245 Oceanic island volcanoes feature a variety of volcanic rock types, including picro-basalts, 246 rhyolites, basanites, phonolites, and trachytes (Supplementary Fig. a). Nevertheless, the 247 dominant rock type is basalt. In this review, we focus on shield-stage basaltic magmas that form 248 lavas of tholeiitic or alkalic composition because they have experienced the least differentiation 249 and contamination en route to the surface. Another approach to studying mantle heterogeneity is 250 to analyze melt inclusions. Such studies (e.g., Saal et al., 2005; Stracke et al., 2019) detect 251 greater isotope heterogeneity than is observed in bulk analysis of erupted lavas. Melt inclusions sample geochemical variations on a much smaller scale (20-30 µm), capturing different aspects 252 of the magmatic system. They represent a "snapshot" of melt pockets prior to melt 253 254 amalgamation, magma mixing, and significant fractional crystallization than whole rock OIB 255 analyses. Melt inclusion analyses are challenging analytically and vulnerable to many processes 256 that disturb or distort their compositions post-entrapment, generating data with lower precision 257 because of their small size. This review focuses exclusively on isotopic analyses in rock samples 258 that integrate melts generated by many cubic kilometres of the mantle source (Rudge et al., 259 2013) (see Text Boxes 2 & 3).

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261 To some extent, the compositional diversity of ocean island basalts (especially compared 262 to the relative homogeneity of mid-ocean ridge basalts; Hofmann, 1997; Gale et al., 2013) 263 reflects the lower degrees of partial melting of OIBs compared to MORBs. That said, melting 264 systematics can only explain a small fraction of the observed variations (Hofmann, 1997; White, 265 2010). Characteristic features of major and trace element compositional variations in OIB 266 include enrichment in the light rare earth elements (REEs) compared to the primitive mantle (which refers to the composition of Earth's mantle soon after core formation), depletion in heavy 267 REEs relative to middle and light REEs, and near-constant ratios of the most incompatible 268 269 elements (left side of Supplementary Fig. b; Hofmann et al., 1986; Newsom et al., 1986;

Willbold and Stracke, 2006). Their rare earth element systematics suggest that most OIB melts
are generated primarily in the garnet stability field (>80 km depth), which reflects the higher
mantle temperatures of plumes (e.g., Gast, 1968). In contrast, most MORBs begin melting at
shallower levels where garnet is no longer stable, resulting in no significant middle to heavy
REE fractionation in the generated magmas.

275

276 In some cases, major element oxides and trace element concentrations correlate with the 277 dominant isotopic trends displayed by OIBs (Jackson and Dasgupta, 2008; Jackson et al., 2012), 278 which is notable because variations in major and trace elements are typically generated by 279 different processes (e.g., degree of melting, magmatic differentiation) than are variations in 280 isotopic compositions (e.g., compositional differences in time-integrated mantle sources). Thus, 281 correlations between major and trace elements and isotopic compositions in OIB may reflect 282 mixtures of compositionally-distinct sources melting to variable extents and/or the fact that the 283 compositionally distinct materials in the mantle differ in their major and trace element signatures 284 as well as their isotopic compositions (Rudge et al., 2013).

285

286 **OIB Isotopic Mantle End-members**

287 Radiogenic isotope ratios in ocean island lavas vary within a field constrained by a 288 minimum of four end-member isotopic compositions (HIMU, EM-I, EM-II, and DMM, Depleted 289 MORB Mantle; White, 1985; Zindler and Hart, 1986; Hart et al., 1992; Hofmann, 1997; Fig. 2a-290 d). Most ocean island chains define mixing arrays in bivariate isotope plots that extend between 291 one of the three end-member compositions and a single, focal area within the mantle isotopic 292 field in Sr-Nd-Pb(-Hf) isotopic space (Fig. 2 and Supplementary Figs. f-i; e.g., Zindler et al., 293 1982; White, 1985; Zindler and Hart, 1986; Hart et al., 1992; Stracke et al., 2005; White, 2015). 294 The focal area is proposed to be a fifth composition, variably named PREMA (PREvalent 295 MAntle; Zindler and Hart, 1986), FOZO (Focus Zone; Hart et al., 1992), C (Common 296 component; Hanan and Graham, 1996), or PHEM (Primitive HElium Mantle; Farley et al., 1992) 297 depending on the authors (Fig. 3 inset).

298

The five compositional end-members define the range of isotopic compositions in OIB, and thus in the mantle sampled by plumes. Except for PREMA, these end-members are chemically and isotopically distinct from each other and thought to come from separate chemical reservoirs in the mantle, resulting from processes that generate unique chemical signatures and evolve over time. Below, we consider the geochemical signatures of these mantle reservoirs (Supplementary Table 1), their origins, and the insights they provide into the composition and evolution of the mantle.

306

307 The HIMU Endmember

The HIMU mantle end-member is named for its high U/Pb (μ) source ratio (Zindler and Hart, 1986). The extreme U/Pb ratios required to generate HIMU Pb isotopic signatures (Fig. 2a) indicate that the original mantle source had high initial U/Pb (μ) and Th/Pb (ω) (Chauvel et al., 1992). The most commonly invoked mechanism to explain the removal of Pb required for the HIMU signature is dehydration of ancient, subducted oceanic crust, followed by storage in the

- 313 mantle for 1.5-2 billion years prior to incorporation into mantle plumes (Hofmann and White,
- 314 1982; White, 1985; Zindler and Hart, 1986; Chauvel et al., 1992, 1997; Stracke et al., 2005;
- 315 Kelley et al., 2005). Alternative explanations include contributions to the plume source of

316 carbonatitic silicate melts from recycled oceanic crust (Dasgupta et al., 2007; Jackson and

317 Dasgupta, 2008), ancient carbonate-metasomatized sub-continental lithospheric mantle (Weiss et

al., 2016; Homrighausen et al., 2018), and recycled Archean marine carbonates (Castillo, 2015).

319 Of the major mantle end-members sampled by plumes, HIMU has limited distribution, is the

least voluminous (Figs. 1 & 3), and is the dominant component in only a few small ocean islands

- 321 (Cook-Austral, St. Helena, Mangai, Tubuai, Rurutu).
- 322

323 The Enriched Mantle (EM-I and EM-II) End-members

324 On the basis of OIB isotopic systematics, Zindler and Hart (1986) identified two distinct 325 enriched mantle end-members (EM-I and EM-II). The EM-I end-member may originate from 326 recycling of delaminated subcontinental lithosphere and/or from subducted pelagic sediments or 327 Archean carbonates into the deep mantle (Hoffman and White, 1982; Weis et al., 1989; Chauvel 328 et al, 1992; Blichert-Toft et al., 1999; Eisele et al., 2002; Garapić et al., 2015; Delavault et al., 329 2016; Wang et al., 2018; Boyet et al., 2019; Cordier et al., 2021), but there is little consensus 330 about its origin. By contrast, the EM-II reservoir exhibits contributions from materials once present on continents (Zindler and Hart, 1986; Weaver, 1991; Chauvel et al., 1992; White and 331 332 Duncan, 1996; Jackson et al., 2007; Jackson and Dasgupta, 2008), although alternative models 333 have been proposed, including the incorporation of ancient metasomatized oceanic lithosphere 334 into the EM-II reservoir (Workman et al., 2004). The EM-I (Kerguelen, Heard, Pitcairn, Tristan-335 Gough, Hawai'i) and EM-II (Marguesas, Society, Samoan Islands) end-members dominate OIB-336 producing systems and are important contributors to the buoyancy flux of many plumes (Figs. 1 & 3).

337 & 338

339 The Prevalent Mantle (PREMA)

340 Most OIB isotopic arrays, especially major mantle plumes highlighted here, have one end 341 anchored at the center of the global isotopic OIB data field, the intermediate area defined as 342 PREMA (Zindler and Hart 1986). The PREMA reservoir represents the average ambient lower 343 mantle (Figs. 2 & 3 inset) and is compositionally distinct from the upper mantle. The high 344 ³He/⁴He ratios relative to MORB (Hanan and Graham, 1996) suggest that PREMA samples a 345 less degassed reservoir than other parts of the mantle (Class and Goldstein, 2005; Gonnermann 346 and Mukhopadhyay, 2009). PREMA may represent primitive mantle if that reservoir has non-347 chondritic Sm/Nd, Nb/U, and Ce/Pb (Nobre-Silva et al., 2013a; White, 2015, Hofmann et al., 348 2022). Alternatively, the PREMA reservoir could be a well-mixed combination of a less-349 processed, less-degassed mantle with recycled components (Zindler and Hart, 1986; Stracke et 350 al., 2006; Parai et al., 2019). Hawai'i, Iceland, and the Galápagos exhibit substantial PREMA 351 contributions (Nobre-Silva et al., 2013a; Harpp and Weis, 2020).

352

353 The Depleted Mantle Source in OIBs

The major and trace element characteristics of strongly depleted OIB lavas (Supplementary Figs. a-e) are consistent with a mantle source that has a long-term history of melt extraction and, therefore, depletion in the most incompatible trace elements (Salters and Stracke, 2004). The depleted component in OIBs, although easily masked by mixing with melts from enriched heterogeneities in the mantle source, has been shown to be a component of some Azores lavas, as evidenced by analysis of melt inclusions that record contributions from depleted melts prior to magma mixing and homogenization (Genske et al., 2019). Rare, depleted

361 signatures in Hawaiian lavas and xenoliths also support a depleted component in mantle plumes

(Frey et al., 2005; Bizimis et al., 2005; DeFelice et al., 2019). In Iceland, the Azores, and the
Galápagos, the depleted signature is attributed to their near-ridge settings, where higher degrees
of mantle melting occur under a thin lithosphere (e.g., White et al., 1976; Schilling et al., 1982;
Humphris et al., 1985; Hart et al., 1992; Moreira et al., 1999; Harpp and Weis, 2020).

366

367 Uncertainty persists regarding the origin of depleted mantle compositions in OIB (Hart et 368 al., 1992; Harrison et al., 2020; Stracke et al, 2022) and whether these compositions: 1) comprise 369 a large proportion of the lower mantle and, therefore, if either the DMM or an early-enriched 370 reservoir is a major matrix component in mantle plumes (Hofmann et al., 2022); 2) represent 371 melting of an entrained sheath of upper depleted mantle material; and/or 3) reflect large degrees 372 of melting of the plume source, as expected underneath thin lithosphere. In contrast to this 373 prevailing view of mantle components, a recent multi-variate statistical data analysis suggests 374 that the apparent overlap of MORB-OIB data trends in 2D isotope ratio diagrams does not 375 translate consistently to multi-dimensional isotope data space, leading to the proposal that 376 compositional variations displayed by MORB-OIB are controlled by smaller-scale, regional 377 domains, rather than a limited number of global-scale reservoirs (Stracke et al., 2022). Such 378 major differences in interpretation about the magnitude and dynamics of compositional 379 reservoirs highlights the need for a more nuanced understanding of these important parts of the 380 mantle and their roles in mantle plumes.

381

382 Section 4 Subduction and Mantle Heterogeneity

383 Early in the development of mantle plume theory, plumes were thought to be supplied 384 exclusively by the primitive lower mantle and depleted upper mantle (Allègre, 1982). Primarily 385 on the basis of geochemical data, the radical idea that the source of ocean island basalts might 386 contain ancient oceanic crust was proposed in the 1980s (Hofmann and White, 1982). This 387 hypothesis posits that oceanic plates are recycled via subduction into the lower mantle, where they are subsequently sampled by plumes; this cycle of downwelling and upwelling provided a 388 389 critical step forward for understanding mantle plumes and their role in the global plate tectonic 390 system. Geochemical evidence confirms the contribution of recycled oceanic crust to ocean 391 island mantle sources (White, 1985; Zindler and Hart, 1986; Chauvel et al., 1992, 1997; Stracke 392 et al., 2005; Kelley et al., 2005). Moreover, seismic data (Fukao and Obayashi, 2013) and 393 geodynamic models (Jones et al., 2021) document the transport of subducted plates to the lower 394 mantle.

395

396 The recycled oceanic crust consists of various materials, including basaltic crust and the 397 overlying sedimentary pile (Fig. 1b). Whereas basaltic crust has a chemical composition that is, 398 within an enrichment factor, not significantly different from its upper mantle source, the 399 composition of sedimentary material can be highly diverse. The average composition for global 400 subducting sediment (GLOSS; Plank and Langmuir, 1998) is similar to continental crust but 401 chemically distinct from the mantle or basaltic material; thus, even minuscule contributions of 402 sediment to the source of ocean island basalts can be detected using geochemical methods. Atmospheric and spallation-generated ¹⁰Be concentrations, lithium, boron, and iron isotope 403 404 compositions, as well as U-series disequilibrium studies have demonstrated that sediments 405 survive subduction processing to mantle depths (Morris et al., 2002; Turner et al., 2003; 406 Deschamps et al., 2010; Tang et al., 2014; Smith et al., 2021), confirming that their inclusion in

407 the mantle plume source is a viable model. Consequently, to understand mantle plumes and their

408 sources fully, it is essential to document the geochemical composition of the subducted oceanic 409 crust and the associated sediments transported into the lower mantle.

410

411 **Recycled Material in Ocean Island Basalts**

412 As sediment and oceanic crust are subducted into the mantle, they undergo distinct 413 compositional changes. Specifically, subducted material is dehydrated or melts and it loses a 414 large proportion of the fluid-mobile elements (e.g., Li, B, Cs), while retaining much of the more refractory elements (e.g., REE, HFSE; Porter and White, 2009; Ryan and Chauvel, 2014; Turner 415 416 and Langmuir, 2022), making it possible to identify and quantify the contributions of recycled 417 oceanic crust and sediment to mantle sources (e.g., Chauvel et al., 2008; Porter and White, 418 2009).

419

420 In particular, the presence of sediments in the OIB source has been posited to explain 421 some of the specific trace element characteristics of EM-I and EM-II basalts. The two canonical 422 ratios, Ce/Pb and Nb/U, have generally constant values in all mantle-derived magmas (25 ± 5 for 423 Ce/Pb and 47 ± 10 for Nb/U; Hofmann et al., 1986; Hofmann et al., 2022); in EM-I and EM-II 424 OIBs (Supplementary Fig. d), these ratios deviate from their universal mantle values toward 425 lower ones typical of continental crust (3.7 for Ce/Pb and 4.4 for Nb/U; Chauvel et al., 1992; White and Duncan, 1996; Rudnick and Gao, 2003; Jackson et al., 2007; Cordier et al., 2021), 426 427 providing some constraint on the origin of isotopic enrichment in the OIB source.

428

429 Radiogenic isotopes are even more effective than trace elements at detecting and 430 quantifying sedimentary material in OIB sources. For example, 6% sediment in the mantle 431 source shifts the Sr isotopic composition of Samoan basalts from 0.704 to elevated values 432 (~0.720) not measured in any other OIB (Jackson et al., 2007). Most EM-II basalts have 433 significantly less radiogenic Sr isotope ratios than those in Samoan lavas, corresponding to a 434 sediment contribution of <2% to their sources. Nevertheless, the community agrees that most 435 OIBs with radiogenic Sr coupled to unradiogenic Nd and Hf must originate from a source 436 containing some recycled sedimentary material (Stracke, 2012).

437

438 The most commonly invoked model to explain the combination of unradiogenic Sr 439 isotopic ratios with highly radiogenic Pb isotopic signatures, as documented in HIMU basalts 440 (Fig. 2d and Supplemental Fig. i), is the presence in the source of old (~2 Ga) oceanic crust that 441 lost some of its Pb during subduction. This interpretation is supported by the elevated Ce/Pb of 442 most HIMU basalts (typically >30; Cordier et al., 2021), which reflects the loss of Pb to 443 subduction fluids. Furthermore, the relationship between Nd and Hf isotope ratios in ocean 444 island basalts (Fig. 2c and Supplemental Fig. h) requires contributions from both recycled basalts 445 and sediments with ages ranging from Archean to present-day (Vervoort et al., 1999; Blichert-446 Toft et al., 1999; Chauvel et al., 2008).

447

448 Heavy noble gas (Ne, Ar, Kr, Xe) isotope ratios in mantle rocks are also sensitive tracers 449 of subducted material. Atmospheric heavy noble gases, which have distinctive elemental ratios 450 and isotopic compositions, are incorporated into the mantle through subduction (Holland and 451 Ballentine, 2006; Mukhopadhyay, 2012; Tucker et al., 2012; Parai et al., 2012; Péron et al.,

452 2021; Parai, 2022), though this "regassing" transport was likely inefficient prior to 2.5 Ga (Parai

453 and Mukhopadhyay, 2018; Péron and Moreira, 2018). Once corrected for shallow post-eruptive

- 454 atmospheric contamination, the Xe isotopic signatures of OIB mantle sources are dominated by
- 455 regassed atmospheric Xe (Parai et al., 2019). This is an unambiguous indication of surface-
- 456 derived material in the OIB mantle source, because the atmospheric Xe isotopic signature
- 457 reflects sources and processes distinct from mantle Xe (Caffee et al., 1999; Avice and Marty,
- 458 2020). Likewise, Kr isotopes in Iceland and Galápagos samples indicate strong regassing of
- 459 atmospheric Kr (Péron et al., 2021). Regassed atmospheric signatures are present even in
- 460 samples with high ${}^{3}\text{He}/{}^{4}\text{He}$ and primitive, solar-like Ne isotopes (Mukhopadhyay, 2012; Pető et
- 461 al., 2013; Péron et al., 2021).
- 462

463 The oceanic crust also carries distinctive signatures from the surface into the mantle. For 464 example, lithium (Li) is incorporated into oceanic crust during hydrothermal alteration and 465 serpentinization. Of the stable isotope systems commonly used in the geosciences, Li has the 466 largest relative mass difference between its two isotopes (⁶Li and ⁷Li). As such, low temperature, 467 aqueous processes result in extreme fractionation (Tomascak, 2004; Tang et al., 2014; Penniston-468 Dorland et al., 2017) and, consequently, Li isotopes are useful tracers of processes that involve 469 fluid mobilization, such as subduction (Fig. 4). During the subduction process, Li is transported 470 to the mantle wedge as oceanic slabs are dewatered and metamorphosed (Bouman et al., 2004; 471 Deschamps et al., 2010). Lithium isotopic values consistent with subduction alteration have been 472 measured in some OIBs from Hawai'i, Cook-Austral, St. Helena, and Azores (Chen and Frey, 473 2003; Vlastélic et al., 2009; Krienitz et al., 2012; Harrison et al., 2015), providing evidence for 474 the recycling of subduction-altered material into the OIB source. By contrast, MORBs exhibit a 475 relatively uniform Li isotopic composition (δ^7 Li = 3.5 ± 1.0‰; Marschall et al., 2017; Penniston-476 Dorland et al., 2017). There is also a measurable difference between Li isotopic compositions of 477 HIMU OIB (δ^7 Li = 2.5-8.5‰) and EM-I OIB (δ^7 Li = 0.5-4.5‰), which likely reflects the 478 diversity of subducted components that contribute to these mantle reservoirs (Krienitz et al., 479 2012; Harrison et al., 2015).

480

481 The type of subducted surface material present in OIB sources is best estimated using 482 isotopic systems with large natural fractionations. For example, stable isotopes of thallium (²⁰⁵Tl 483 and ²⁰³Tl) are fractionated up to 35 epsilon units, and exhibit large concentration contrasts between geochemical reservoirs (e.g., pelagic sediments: ε^{205} Tl and [Tl] up to +5 and 1000 ng/g 484 (Rehkämper et al., 2002); low-temperature altered oceanic crust: ϵ^{205} Tl and [Tl] as low as -15 485 and 5-50 ng/g (Nielsen et al., 2006a); mantle: ε^{205} Tl of -2 ± 0.5 and <1 ng/g Tl (Nielsen et al., 486 2017). Ocean island basalts exhibit a wide range of ε^{205} Tl values (-6.4 to +6.6; Brett et al., 2021). 487 488 Heavy ε^{205} Tl (up to +4) in Hawaiian tholeiites have been attributed to recycled subducted 489 sediment in the plume source (Nielsen et al., 2006b; Williamson et al., 2021), potentially sampled from the ambient mantle on the periphery of the Pacific LLSVP (Williamson et al., 490 2021). Conversely, light ε^{205} Tl (down to -10) in lavas from St. Helena may be traced to altered 491 492 oceanic crust in their source and in the HIMU mantle reservoir (Blusztajn et al., 2018). In some 493 cases, however, the Tl isotopic composition of OIB is ambiguous, requiring careful consideration 494 when interpreting results and using this isotopic system as a mantle tracer (Brett et al., 2021; 495 Williamson et al., 2021).

496

497 Finally, subducted material carries with it information about previous redox conditions at
498 Earth's surface. In specific circumstances, such as the extreme surface conditions during the
400 A data and a data

499 Archean prior to the Great Oxygenation Event at ~2.5-2.4 Ga (Farquhar et al., 2007), mass-

- 500 independent fractionation of stable isotopes such as sulfur (S) can occur. These signatures are
- 501 then incorporated into sedimentary materials and basalts at the surface. For example, negative S
- 502 isotopic anomalies have been detected in lavas from Mangaia (Cabral et al., 2013; Dottin III et
- al., 2020) and in basalts from Pitcairn (Delavault et al., 2016), which indicate that the HIMU
- 504 (Mangaia) and EM-I (Pitcairn) mantle sources include material that was present at Earth's
- 505 surface during the Archean, either in the form of Archean basaltic crust for Mangaia or Archean 506 sedimentary material for Pitcairn.
- 507

508 New isotopic tracers continue to be developed that enable the characterization of recycled 509 material in the OIB mantle source. For example, cerium (Ce) is redox-sensitive (Elderfield, 1988). Therefore, the measurement of the long-lived ¹³⁸La-¹³⁸Ce system may constrain the timing 510 511 of pelagic sediment recycling into the mantle because no Ce anomalies are expected in water 512 columns before the Great Oxygenation Event at ~2.5-2.4 Ga (Israel et al., 2020; Boyet et al., 513 2021). Collectively, a wide array of isotopic and trace element systems (see Text Box #2, Fig. 514 1b; Supplementary Figs. b-e) indicate that material previously at the surface of the Earth is 515 present in the source of OIBs. That said, all isotopic characteristics of OIB cannot be explained 516 only by recycling surficial material into the plume source; additional types of material must be present and the influence of several large-scale processes needs to be considered as well, 517 518 including the physical proximity of plumes to LLSVPs, the depth and source of plume

- 519 magmatism, and core-mantle interactions.
- 520

521 Section 5 Early-Formed Reservoirs

The OIB mantle source is a heterogeneous mixture of recycled surface materials, deep mantle material that separated early (>4.45 Ga) and experienced less degassing than the upper mantle, and potentially distinct remnant materials that formed early in Earth's history. Determining the age and the nature of early-formed materials is important for understanding the structure and dynamics of the lower mantle, especially given the spatial correlation of major mantle plumes with LLSVPs and ULVZs (e.g., Burke and Torsvik 2004; Torsvik et al., 2006; Doubrovine et al., 2016; Cottaar et al., 2022; see review by Hernlund and McNamara, 2015).

529

530 Tracing Early-Formed Reservoirs

531 Processes such as metal-silicate differentiation, magma ocean crystallization, and 532 degassing of volatiles during energetic accretionary impacts influenced the geochemistry of early 533 Earth's interior by fractionating groups of elements with different properties from each other. 534 Because these events operated only for relatively short periods close to 4.5 Ga, the best tools to 535 understand them and track their contributions to the OIB mantle are short-lived radionuclide systems, including ¹⁸²Hf-¹⁸²W, ¹⁴⁶Sm-¹⁴²Nd, ¹²⁹I-¹²⁹Xe, and ²⁴⁴Pu-¹³¹⁻¹³⁶Xe, with half-lives 536 537 between <10 Ma and ~100 Ma. Deviations in radiogenic products of some short-lived isotope systems (e.g., μ^{142} Nd and μ^{182} W) are small in OIBs (a few ppm), making their detection difficult 538 539 (Fig. 5; e.g., Touboul et al., 2012b; Horan et al., 2018; see Text Box #3). Volatile elements pose 540 additional challenges, owing to the loss of magmatic gas from samples and atmospheric 541 contamination during and after eruption. Nevertheless, progress has been made measuring μ^{142} Nd, μ^{182} W, and 129 Xe/ 130 Xe variations in OIBs, as well as interpreting the significance of 542 543 these anomalies for mantle history and dynamics.

544

545 Trace element abundances and ratios are also powerful tools for quantifying fractionation 546 processes in the early Earth. For example, mass balance calculations using (Nb, Ta)/U and 547 ¹⁴³Nd/¹⁴⁴Nd isotope ratios (Hofmann et al., 2022) demonstrate that continental crust and present-548 day depleted mantle could not have originated from the primitive mantle as previously thought 549 (e.g., Jacobsen and Wasserburg, 1979; O'Nions et al., 1979; DePaolo, 1980). The measurements of a radiogenic excess of 142 Nd (+7.9 ± 1.9 ppm) in the mantle relative to its building blocks 550 551 confirm this scenario (Frossard et al., 2022; Johnston et al., 2022). Therefore, the Earth's mantle 552 may be slightly depleted in incompatible elements and characterized by higher Sm/Nd than 553 chondrites. The Sm/Nd fractionation could be inherited from the accretion stage with the loss to 554 space of enriched crusts formed in planetesimals by collisional (Frossard et al., 2022), removing 555 the requirement for an early enriched reservoir to be preserved in the deep mantle (Boyet and 556 Carlson, 2005).

557

558 Many stable isotope ratios of major elements may preserve early-formed isotopic 559 signatures as well, because their values were not reset on a global scale (Text Box #2). Stable 560 isotope fractionation has been constrained through high pressure-temperature experiments that 561 simulate early differentiation events (e.g., Shahar et al., 2017) to predict the isotopic signatures 562 in the OIB mantle source, providing potent clues about the characteristics of early-formed 563 reservoirs. 564

565 Terrestrial Magma Ocean Relics

566 Small ¹⁴²Nd anomalies measured in a few OIB (-8 to +6 ppm; Fig. 5a) from Réunion 567 (Peters et al., 2018) and Samoa (Horan et al., 2018) suggest that early-formed reservoirs may be preserved in the deepest part of the mantle. Owing to the short half-life of ¹⁴⁶Sm (~103 Ma), the 568 variations measured in ¹⁴²Nd/¹⁴⁴Nd must reflect Sm/Nd fractionation that took place during the 569 570 first few hundred million years of Earth history. Because both Sm and Nd are strongly lithophile 571 rare earth elements and excluded from the metal phase during core-mantle differentiation (Faure 572 et al., 2021), early fractionation of Sm/Nd must have occurred exclusively via silicate 573 differentiation, providing evidence for crystallization of a terrestrial magma ocean. Most OIB are also characterized by negative ¹⁸²W anomalies (down to -25 ppm) (Mundl et al., 2017; Mundl-574 Petermeier et al., 2019; 2020; Peters et al., 2021), which may also represent the remnant of an 575 576 early terrestrial magma ocean (Fig. 5b). However, core-mantle interaction could also affect the 577 ¹⁸²W signal, making its interpretation ambiguous.

578

The short-lived ¹²⁹I-¹²⁹Xe system provides additional support for preservation of early-579 580 formed isotopic heterogeneity. Mantle Xe isotope compositions can be broken down 581 mathematically into component contributions from accretion (chondritic Xe), radioactive decay, 582 and atmospheric regassing (Caffee et al., 1999; Parai et al., 2019). Limited measurements of 583 mantle-derived samples (from OIBs, MORBs, back-arc basin basalts, volcanic gases, and 584 continental well gases) yield precise estimates of mantle source Xe compositions, corrected for 585 shallow atmospheric contamination (Moreira et al., 1998; Mukhopadhyay, 2012; Parai et al., 586 2012; Tucker et al., 2012; Peto et al., 2013; Parai and Mukhopadhyay, 2015; Caracausi et al., 2016; Peron and Moreira, 2018; Bekaert et al., 2019; Parai and Mukhopadhyay, 2021; Peron et 587 al., 2021). Ratios of ¹²⁹Xe/¹³⁰Xe (where ¹²⁹Xe is produced by decay of short-lived ¹²⁹I, and ¹³⁰Xe 588 589 is not radiogenic) from Iceland, (Mukhopadhyay, 2012), the Rochambeau Rift in Samoa (Peto et 590 al., 2013), and Galápagos (Péron et al., 2021) are low compared to the depleted mantle (Holland

and Ballentine, 2006; Tucker et al., 2012; Parai et al., 2012). Differential incorporation of
atmospheric Xe with low ¹²⁹Xe/¹³⁰Xe into the OIB mantle cannot account for the OIB
¹²⁹Xe/¹³⁰Xe signatures (Fig. 5d). Thus, a low I/Xe ratio must have been established in the OIB
mantle within the first ~100 Myr of Earth history, and its signature preserved despite ~4.45 Gyr
of convection (Mukhopadhyay, 2012). The low I/Xe may have come from inefficient degassing
of the deeper parts of the magma ocean, or low iodine abundances in the early-accreted
materials.

598

599 The paired I-Pu-Xe decay system provides additional insight into early magma ocean 600 history. Initially, catastrophic outgassing would have transported Xe out of the terrestrial magma ocean; after closure, products of ¹²⁹I decay and ²⁴⁴Pu fission would have been retained in the 601 silicate Earth. Because ¹²⁹I and ²⁴⁴Pu decay at different rates, the ¹²⁹Xe*/¹³⁶Xe_{Pu} ratio (where the 602 star indicates radiogenic ¹²⁹Xe from the decay of ¹²⁹I, and the subscript denotes ¹³⁶Xe from Pu-603 fission; Mukhopadhyay, 2012) can be used to calculate a "closure age" that marks the end of 604 605 open system magma ocean outgassing (Wetherill, 1975). The Iceland and Samoan Rochambeau Rift samples exhibit low 129 Xe*/ 136 Xe_{Pu} ratios compared to the MORB mantle. If the whole 606 mantle had an initially homogeneous I/Pu ratio, then low ¹²⁹Xe*/¹³⁶Xe_{Pu} ratios in OIBs would 607 608 indicate a late closure age for the OIB mantle relative to the MORB mantle, because less of the 609 shorter-lived ¹²⁹I would remain at the onset of Xe retention in the mantle. A more realistic 610 scenario may be that the mantle had an initially heterogeneous I/Pu, and regions of low I/Pu 611 reflected limited accretion of volatile-rich materials into the OIB mantle (Mukhopadhyay, 2012; 612 Caracausi et al., 2016; Parai et al., 2019). A relatively dry OIB mantle may have contributed to 613 inefficient mixing in both the terrestrial magma ocean and the solid mantle over Earth history 614 (Parai, 2022). Thus, the OIB I-Pu-Xe signature not only records heterogeneity in the early 615 mantle, but also provides insight into the mechanisms that preserve heterogeneities formed 616 during the early magma ocean.

617

618 The Effect of the Core on the OIB Source

619 Early core formation and its subsequent evolution likely play an important role 620 controlling radiogenic and stable isotope variations in OIBs. The Earth's metallic core physically 621 separated from the mantle during the first few tens of million years of Earth history (Kleine et 622 al., 2002, Yin et al., 2022; Walker, 2014), and probably trapped a significant proportion of the 623 lighter elements (e.g., ~ 10% of Si, O, S, C, N, and H; McDonough, 2016; Badro et al., 2015). 624 Incorporation of these light elements into the core may have changed the isotopic composition of 625 the mantle on a bulk scale (Shahar et al., 2016), however such fractionation would not generate 626 mantle heterogeneities if core formation occurred when the entire mantle and the entire core 627 were in equilibrium. For example, whole mantle-core equilibrium (Shahar et al., 2011) has been 628 proposed to explain the observation that the mantle is fractionated in silicon isotopes relative to 629 chondrites (Georg et al., 2007; Hin et al., 2017). In contrast, evidence from diamond inclusions 630 suggests that iron (Fe) isotopic heterogeneities exist in Earth's deep mantle. Cullinan-like, Large, 631 Inclusion-Poor, Pure, Irregular, and Resorbed (CLIPPIR) diamonds from Letseng, Lesotho, 632 which originate from depths of 360–750 km, exhibit heavy Fe isotopic signatures (δ^{56} Fe = 0.79– 633 0.90‰) that lie outside the near-0‰ range of known mantle compositions or expected reaction 634 products at depth (Smith et al., 2021). High pressure and temperature experiments suggest that 635 core formation on its own cannot account for such a large shift in Fe isotopic ratios (Elardo et al., 636 2019). Rather, these data provide evidence for the subduction of surface material characterized637 by light isotopic ratios into the lower mantle (Smith et al., 2021).

638

639 Owing to the lack of temporal control on stable isotope signatures, it is plausible that the 640 Fe stable isotope fractionation observed in the mantle reflects the cumulative effects of several 641 processes. These processes likely include both interactions between the core and the mantle as 642 well as the subtle but systematic heterogeneity in the convecting mantle caused by billions of 643 years of subduction. To identify and untangle all the possible fractionation mechanisms within 644 the mantle, more experiments need to be conducted in relevant pressure, temperature, and 645 compositional space.

646

647 Core-Mantle Interactions

648 Due to the extremely high temperatures at the CMB, mantle minerals in direct contact 649 with the liquid core may be in chemical equilibrium with that liquid. As the core cools and the 650 composition of the outer core changes because of ongoing crystallization of the inner core, some 651 elements may be diffusing across the core-mantle boundary as they are exsolved from the liquid 652 outer core. Thus, the composition of the core could be changing progressively, and mantle 653 heterogeneity may be increasing in response to the evolving core (Tronnes et al., 2019). 654 Experimental work by Hayden and Watson (2007) has shown that grain-boundary diffusion is an 655 efficient pathway for core-mantle interaction. In their experiments, siderophile elements diffused 656 through MgO at a rate high enough to transport those elements across geological length scales 657 (tens of kilometers) over 4.5 Ga.

658

659 Geochemical signatures of several highly siderophile elements suggest that the lower mantle was "polluted" with core material prior to being entrained into mantle plumes. The 660 661 resulting signatures include elevated Fe/Mn ratios, such as those in Hawaiian lavas (Humayun et 662 al., 2004), and radiogenic Os isotope enrichments detected in several mantle plumes on the world 663 (Brandon et al., 1998, 2003). Subsequent studies (e.g., Ravizza et al., 2001), however, raise 664 questions on these results. Despite further investigations (Brandon et al., 2003; 2005; Ireland et al., 2011), no other isotopic signature indicative of element transport across the core-mantle 665 boundary was identified until the development of high precision μ^{182} W measurements (Touboul 666 et al., 2012a; 2012b; Trinquier et al., 2016). Small negative anomalies in µ¹⁸²W (-25 ppm) have 667 been measured in OIBs (Fig. 5b; Mundl et al., 2017; Mundl-Petermeier et al., 2019; 2020; Peters 668 669 et al., 2021). In mantle-derived samples, the μ^{182} W shifts over time, from positive values in Hadean-Archean samples (4.3 to 2.7 Ga) to negative values in modern samples. This observation 670 671 suggests that the W signature in OIB may reflect a time-integrated core contribution of tungsten 672 to the mantle. The mechanism of interaction between the outer liquid core and the mantle 673 remains debated, but current work is focused on Si-Mg-Fe oxide exsolution (Rizo et al., 2019) 674 and diffusive exchange across the CMB between foundered oxidized, oceanic crust and the outer 675 core (Mundl-Petermeier et al., 2020; Yoshino et al., 2020).

676

677 Core-mantle interactions may also manifest in the I-Xe system. If iodine were more 678 strongly siderophile than Xe at core formation pressures and temperatures (Armytage et al.,

679 2013; Jackson et al., 2018), the core would have had elevated I/Xe and I/Pu compared to the

mantle. In this case, the core would supply high 129 Xe/ 130 Xe and 129 Xe*/ 136 Xe_{Pu} to the mantle.

However, OIBs sample a reservoir with low 129 Xe/ 130 Xe and 129 Xe/ 136 Xe_{Pu} compared to the rest

of the mantle. The core may have instead acted as a sink for lower mantle iodine during
accretion, with no subsequent transfer of radiogenic Xe back to the mantle over time (Jackson et al., 2018).

685

686 The core has been posited as a potential source of high ${}^{3}\text{He}/{}^{4}\text{He}$ in the OIB source (Porcelli and Halliday, 2001; Bouhifd et al., 2020; Roth et al., 2019; Olson and Sharp, 2022). 687 Negative μ^{182} W anomalies are broadly associated with elevated ³He/⁴He (Mundl et al., 2017; 688 689 Mundl-Petermeier et al., 2019; 2020; Peters et al., 2021; Jackson et al., 2020a) in some lavas 690 from Hawai'i, Samoa, Iceland, and the Galápagos, suggesting that core contributions could 691 supply both negative μ^{182} W and high ³He/⁴He to material in the lower mantle. In detail, however, the highest OIB ${}^{3}\text{He}/{}^{4}\text{He}$ ratios are associated with modest negative μ^{182} W, and the strongest 692 negative μ^{182} W anomalies are associated with only moderate 3 He/ 4 He. 693

694

695 Jackson et al. (2020a) suggested that recycled crust can mask He and W isotopic 696 signatures, proposing that He and W anomalies may only persist in mantle domains that are the 697 least affected by crustal recycling (consistent with the relationship between He isotopes and Th 698 enrichment; Class and Goldstein, 2005). Nevertheless, the most negative μ^{182} W anomalies found 699 to date are accompanied by strong indications of recycling in Kr and Xe isotopic compositions at 700 Fernandina Island, Galápagos (Péron et al., 2021). There is likewise a pronounced recycling 701 signature in the Kr and Xe isotopes at Iceland (Mukhopadhyay, 2012; Péron et al., 2021), where 702 some of the highest ³He/⁴He ratios have been detected. Additional measurements of W and noble 703 gases from samples that have also been thoroughly characterized for radiogenic isotopic 704 compositions are needed to resolve the relationship between core-hosted signatures and 705 contributions recycled versus primitive mantle domains.

706

707 Constraints on Lower Mantle Seismic Structures

Variations in the ¹⁸²Hf-¹⁸²W, I-Pu-Xe, and ¹⁴⁶Sm-¹⁴²Nd isotopic systems in OIBs require 708 709 that plumes sample early-formed reservoirs, likely from the deepest part of the mantle (Fig. 5). 710 Even though few lavas have been measured for all of these isotopic systems, the existing data 711 provide insight into the nature of early-formed mantle reservoirs. The ULVZs are speculated to be the source of the high ${}^{3}\text{He}/{}^{4}\text{He}$ and the most negative μ^{182} W in OIBs (e.g., Jackson et al., 712 2017; Mundl et al., 2017; Williams et al., 2019; Kim et al., 2019). If, core-mantle interaction 713 supplies high ${}^{3}\text{He}/{}^{4}\text{He}$ and the most negative μ^{182} W signatures (Rizo et al., 2019; Mundl-714 Petermeier et al., 2020; Peters et al., 2021), then the ULVZs may have formed via interactions 715 with the core. An alternative mechanism to explain variable μ^{182} W anomalies in OIB is early 716 silicate differentiation that modified the Hf/W ratios of mantle reservoirs, which subsequently 717 718 remained mostly isolated from the rest of the convecting mantle throughout Earth history (e.g., 719 Touboul et al., 2012a; Brown et al., 2014; Puchtel et al., 2016).

720

The LLSVPs, described as thermochemical piles, may represent relics of magma ocean crystallization after the Moon-forming giant impact (e.g., Labrosse et al., 2007; Lee et al., 2010 Ballmer et al., 2017; Gülcher et al., 2020). As noted above, variations in μ^{142} Nd measured in a few OIBs suggest that remnants of magma ocean crystallization may be preserved in the deep mantle (Peters et al., 2018). If the Moon-forming giant impact occurred ~4.4-4.35 Ga, as suggested by studies of both terrestrial and lunar samples (Morino et al., 2017; Borg et al., 2019; Lock et al., 2020), then the ¹⁸²Hf-¹⁸²W system was already extinct, which would leave the ¹⁸²W

16

isotope composition unchanged by the collision and explain the lack of correlation between

¹⁴²Nd/¹⁴⁴Nd and ¹⁸²W/¹⁸⁴W in OIB lavas (except for Réunion lavas; Peters et al., 2021).

Alternatively, LLSVPs may have formed from the accumulation of subducted material (e.g.,

731 Brandenburg and van Keken, 2007; Nakagawa et al., 2009) or from the sinking of dense, reduced

material (e.g., Gu et al., 2016; Creasy et al., 2020). Most likely, LLSVPs do not result from a

single process, but incorporate material from primordial and early events, ongoing convection,

and recycled subducted material (McNamara, 2019; Parai et al., 2019).

735

736 Section 6 Mantle Mixing and Convection

737 Linking the spatio-temporal geochemical variations of plume-derived lavas to the 738 heterogeneous structure of the deep mantle requires an understanding of the internal dynamics of 739 plumes which, in turn, depends on their rheology, composition, and excess temperature. In a 740 purely thermal plume, assuming a Newtonian rheology, the morphology is controlled by the 741 viscosity contrast between the hot plume and the colder ambient mantle. If the viscosity is 742 strongly temperature-dependent, the plume develops a mushroom-shape, with a large head and a 743 narrow tail (Richards et al., 1989). For a constant viscosity, the plume shape is finger-like (e.g., 744 Whitehead and Luther, 1975; Korenaga, 2005). Moreover, the internal flow across a purely 745 thermal plume depends on the viscosity contrast between the hot axial part of the conduit and its 746 colder periphery; the vertical velocity is maximum at the plume axis and decreases exponentially 747 with the square of the radial distance (e.g., Olson et al. 1993). Such a velocity profile generates 748 zones with high strain rates, where passive geochemical heterogeneities get stretched into filaments (Kerr and Mériaux, 2004, Farnetani and Hofmann, 2009).

749 750

751 The lower mantle, however, is likely to be compositionally heterogeneous, which raises 752 the question of how heterogeneous material entrained by a plume is deformed during upwelling 753 and how the plume morphology and flow across the conduit are modified by those 754 heterogeneities. Both laboratory experiments (e.g., Davaille 1999, Kumagai et al., 2008, Limare 755 et al., 2019) and numerical simulations (e.g., Christensen and Hofmann, 1994, Tackley, 1998, 756 Nakagawa and Tackley, 2014. Li et al., 2014, Gülcher et al., 2020, Jones et al., 2021) have 757 explored global convection and plume dynamics in a heterogeneous mantle. Compositional 758 heterogeneities are often simulated as intrinsically denser material (Gu et al., 2016), representing 759 either eclogitic recycled crust, which is denser than the surrounding pyrolitic mantle (e.g., Hirose 760 et al. 1999), or Fe-enriched, relatively primordial material (e.g., Deschamps et al., 2012, 761 Nakagawa and Tackley, 2014, Li et al., 2014). Rheological heterogeneities are often simulated as more viscous domains (e.g., Ballmer et al., 2017; Gülcher et al., 2020), either because of a silica 762 763 enrichment (e.g., Yamazaki et al., 2000, Ballmer et al., 2017), an increase in the mineral grain 764 size (Ammann et al., 2010), and/or a reduction of the water content (Hirth and Kohlstedt, 1996; 765 Karato, 2010; Parai, 2022). These studies indicate that variations in density and/or rheology 766 profoundly affect convective mixing efficiency by promoting the long-term preservation of deepseated heterogeneities. 767

768

Gülcher et al. (2021, Fig. 6) illustrates the results of numerical simulations of mantle plumes, featuring distinct lithological components: dense recycled basalt and the complementary depleted harzburgitic residue, a rheologically distinct bridgmanitic primordial material, and an ancient FeO-rich basal layer with the same physical properties as basalt. After 4.5 Ga of

convection, part of the recycled oceanic crust accumulates at depth and forms large piles, while

- the remainder is dispersed in the mantle, forming small streaks. The primordial material,
- intrinsically more viscous, partially survives as distinct "blobs", whereas a fraction of the ancient
- FeO-rich basal layer can be preserved by being incorporated into the denser basal piles.
- 777 Numerical simulations (Farnetani et al., 2018) focusing on mantle plumes carrying finite size
- 778 (30-40 km radius) rheological heterogeneities also indicate that intrinsically more viscous
- heterogeneities can resist stretching because they rotate during their ascent.
- 780

781 For thermo-chemical plumes, the subtle balance between positive thermal buoyancy and 782 negative compositional buoyancy induces oscillatory behavior (Davaille, 1999) and complex 783 internal dynamics, because some parts of the conduit may sink while others ascend (Kumagai et 784 al., 2008). Furthermore, the idea that isotopic zonation in the plume conduit preserves the large-785 scale zonation in the mantle source region may not be accurate for thermo-chemical plumes 786 because, under certain conditions, compositionally denser material rises preferentially at the 787 plume axis (Jones et al., 2016). However, if chemical heterogeneity is a passive component of 788 lower mantle structures (i.e., it has less effect on physical parameters such as density), and if 789 lower mantle structures differ mainly in their thermal properties, then isotopic zonation could 790 potentially be preserved in the plume conduit (Jones et al., 2016). Numerical simulations of 791 mantle plumes carrying finite size (30-40 km radius) rheological heterogeneities, 20-30 times 792 more viscous than the surrounding rocks, indicate that those heterogeneities do not stretch, but 793 instead simply rotate as they ascend (Farnetani et al., 2018). Viscous material that resists 794 stretching is more likely to preserve a distinct isotopic fingerprint.

795

796 Section 7 A New Paradigm for Mantle Plumes

797 The Hawaiian-Emperor chain has been used as the basis for many current paradigms 798 related to mantle plumes (Morgan, 1971). Data accumulated from ocean islands worldwide, 799 however, suggest that Hawai'i may be the exception for plume behavior, rather than the type-800 model. For example, the Hawaiian system has the highest buoyancy flux and mantle potential 801 temperature of any terrestrial plume (Fig. 1a; King and Adam, 2014; Putirka, 2008; Garcia et al., 802 2020), and younger segments of the Hawaiian chain record much higher melt flux than most 803 other plumes (e.g., Putirka, 2008; Garcia et al., 2015; Wessel, 2016). Furthermore, the 804 correlation between buoyancy flux, mantle potential temperature, and elevated ³He/⁴He supports 805 the inference that the Hawaiian plume results from dynamical processes rooted in the deep 806 mantle (Bao et al., 2022). Thus, the extent to which the Hawaiian plume can serve as the mantle 807 plume archetype should be questioned; its importance as an accessible and well-studied but 808 extreme example of intraplate volcanism, however, cannot be minimized.

809

810 Instead, OIBs may be evaluated more effectively using a range of variables, such as 811 plume strength and temperature, source mantle composition, and melting conditions. We propose 812 a mantle plume spectrum, based primarily on magma flux (King and Adam, 2014). The 813 Hawaiian-Emperor chain defines the mantle plume end-member with the strongest magma 814 production. Samoa, Iceland, and Galápagos are also classified close to the high-production end 815 of the spectrum; all have in common high ³He/⁴He ratios in some of their erupted lavas, elevated 816 buoyancy fluxes (Jackson et al., 2017), and the presence of slow velocity zones and an LLSVP at 817 their source (e.g., Williams et al., 2019). The other end of the spectrum is represented by weaker 818 plumes, with potentially shallower sources, which do not exhibit multiple mantle geochemical 819 components nor have mantle potential temperatures significantly hotter than MORBs. Examples

- 820 at this end of the spectrum include Ascension, Juan de Fuca/Cobb-Eickelberg, and Bowie-
- 821 Kodiak/Pratt-Welker, which have not been associated with a lower mantle seismic wave
- tomography anomaly that extends to the core-mantle boundary (i.e., French and Romanowicz,
- 823 2015), have isotopic compositions nearly indistinguishable from MORB (in part due to plume-
- ridge interaction, e.g., Bowie-Kodiak and Cobb-Eickelberg; Hegner and Tatsumoto, 1989;
- 825 Chadwick et al., 2014), and are among the coolest mantle plumes (Bao et al., 2022).
- 826

827 Between the strong Hawaiian-type plumes and the weak Ascension-type systems are 828 those that most closely emulate the classic model, such as Louisville, Kerguelen, Caroline, 829 Easter, Réunion, and Tristan. These plumes possess a voluminous head that formed a LIP, 830 followed by a plume tail and an age-progressive volcanic chain, and a buoyancy flux between 831 \sim 0.5-2 Mg s⁻¹ that wanes over time. The plume spectrum provides a reference framework for the 832 comparison of mantle plumes and plume chemistry, which will prevent inappropriate 833 comparisons between vastly dissimilar systems.

834

835 Section 8 Summary and Future Directions

836 Over the past couple of decades, the study of mantle plumes, their sources, and chemical 837 heterogeneity in the mantle has generated important hypotheses and ideas about many of Earth's 838 major processes, including convection, recycling, mantle residence times, and the nature of 839 interactions between various reservoirs throughout the Earth system. It is no coincidence that 840 advances in analytical geochemistry capabilities have paralleled the increasing sophistication of 841 mantle plume models. The improvement in precision, sensitivity, and resolving power of mass 842 spectrometers has opened new areas of the Periodic Table for analysis, including small isotopic 843 anomalies, short-lived isotopic systems, and small mass-dependent fractionations that reflect 844 early differentiation processes, recycling of subducted material into the mantle, and evidence for 845 material preserved from Earth's earliest history.

846

847 The focused development of novel geochemical systems provides insight into large-scale planetary processes and compositional evolution, offering a rich area for future discoveries. 848 Specifically, systems such as I-Pu-Xe, ¹⁸²W/¹⁸⁴W, and ¹⁴²Nd/¹⁴⁴Nd have the potential to resolve 849 850 interactions between the core and mantle, as well as examine the preservation and sampling of 851 early-formed reservoirs in the mantle. The capabilities required to analyze rare noble gases and 852 low-abundance W and Nd isotopes, however, exist in separate laboratories, necessitating 853 collaborative efforts to generate insight from different isotopic systems on the same set of 854 samples.

855

856 The improvement of analytical precision for the more commonly analyzed isotopic 857 systems (e.g., Nd, Pb, and Hf isotopes) is essential to continue advancing the characterization of 858 geochemical components in OIBs and examining differentiation processes throughout mantle 859 history. This objective includes targeting melt inclusions, where extreme compositions from 860 melted mantle heterogeneities may be captured prior to melt homogenization. Future work 861 should also focus on exploring correlations across elemental and isotopic data sets. A database of 862 high temperature and pressure isotopic fractionation factors will be essential to understand the 863 processes affecting different isotopic systems.

864

865 Some of the greatest insights in mantle geochemistry have come from targeted sampling 866 strategies, in which novel isotopic systems are applied to locations most likely to carry imprints 867 of specific processes. Such studies require effective collaborations among laboratories and 868 researchers, both for access to the advanced analytical techniques and to avoid analyzing sample 869 powders separated from their geologic contexts.

870

871 Collaborative studies between geophysicists, geochemists, and geodynamicists are key to 872 resolving important questions about how the transport of heterogeneities from Earth's mantle 873 reservoirs to the surface is controlled by partial melting, plume-lithosphere, and plume buoyancy 874 forces. Debate persists regarding how, during mantle transport, geochemical components are 875 entrained, mixed, stretched, stalled, melted, and ultimately expressed in erupted lavas. This 876 uncertainty propagates into the models that explain geochemical variations in erupted lavas, 877 which rely on the interpretation of spatial patterns and time-integrated signatures in those lavas. 878 A better understanding of mantle geodynamics, along with how lithology affects the melting and 879 mixing of magmas, is needed to provide better constraints for understanding the source, 880 evolution, and preservation of geochemical heterogeneities.

881

Finally, much is still unknown about the composition of seismically imaged mantle
heterogeneities, in both the shallow and deep mantle and how they relate to chemical
heterogeneities (e.g., Supplementary Fig. j, with a focus on the Pacific). The spatial differences

in OIB compositions, both between different plume systems and over time at individual plumes,

886 suggest systematic variations in mantle geochemical domains on many scales that are currently 887 poorly understood. Resolving uncertainties in mantle geodynamics and melt homogenization

poorly understood. Resolving uncertainties in manue geodynamics and melt homogenization processes will help determine whether these differences reflect distinct tectonic histories.

889 Clearly, much remains to be learned about mantle plumes and the composition of the Earth; the

890 greatest advances will likely emerge from cross-disciplinary studies in diverse fields such as

- 891 experimental petrology, mineral physics, numerical geodynamics, seismology, and
- 892 geochemistry.

893

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- 904

905 Author contributions

- 906 The authors contributed to all aspects of the article. DW shared the vision and all authors
- 907 contributed substantially to discussion of the content during various online meetings, as a group
- and for individual sections. All authors wrote the article. KH, LH, MB, and CC coordinated
- 909 sections. LH and NW compiled data and helped for figures. All authors reviewed and/or edited
- 910 the manuscript before submission.

911

912 Competing interests

- 913 The authors declare no competing interests.
- 914
- 915

916 Figures and captions

917 **Figure 1a: Plume buoyancy flux by location** (MilFil vol, Mg/s; King and Adam, 2014).

918 The MilFil volume method calculates the mean depth anomaly within a 500 km diameter circle 919 around a mantle plume, after filtering out small-scale features such as seamounts and islands.

- 920 The MilFil volume is a proxy for the bathymetric swell generated by the underlying mantle
- 921 plume, which is assumed to correlate with the magnitude of its flux. Circle diameters correspond
- to the magnitude of buoyancy flux. Colored circles: Plumes with geochemical data shown in
 figures 2-5. White circles: Mantle plume sites not included in subsequent geochemical figures in
- 924 this review. Grey circles: Mantle plumes that lack flux estimates. Basemap: Tomography slice
- 925 from the lowest mantle at 2800 km depth, extracted from the SEMUCB-WM1 model (French
- and Romanowicz, 2014), generated using the SubMachine online tool (Hosseini et al., 2018).
- 927 Red regions define the seismically slow Pacific and African-Atlantic Large Low Shear Velocity
- 928 Provinces (LLSVPs); blue regions are seismically faster parts of the lowermost mantle; velocity
- anomaly (dv/v) ranges from +2 to -2. Note the proximity of many mantle plumes relative to

930 LLSVPs and how buoyancy flux of mantle plumes varies by orders of magnitude globally.

931

932 Figure 1b: Schematic cross-section of the mantle illustrating major mantle structures and

- 933 locations of potential chemical reservoirs discussed in this review; the reservoirs are defined
- based on isotopic and trace element data from plume-generated OIB. Each reservoir is associated
- 935 with a text box listing the isotopic systems that are especially useful for their identification and
- 936 tracing (see text descriptions and Supplementary Table 2). Included are a heterogeneous LLSVP 937 (indicated by different shades of orange, including mantle plumes), ULVZs (red), and subducted
- (indicated by different shades of orange, including mantle plumes), ULVZs (red), and subducted
 oceanic lithosphere (blue) that entrains recycled surface materials (e.g., sediments, indicated in
- brown). The plume, LLSVP, and ULVZ morphologies (whose thickness has been exaggerated so
- 940 that it is visible at the scale of the diagram), are informed broadly by seismic studies (French &
- 941 Romanowicz 2015; Wamba et al., 2023) and geodynamic results (Farnetani & Samuel, 2005;
- 942 Davaille, 1999). The slab morphologies are guided roughly by seismic studies (Fukao &
- 943 Obayashi, 2013; Garnero & McNamara, 2008) and geodynamic results (Jones at al., 2021;
- 944 Nakagawa & Tackley, 2014). Of particular importance is the contribution of multiple mantle
- 945 reservoirs, including recycled material, to the sources of mantle plumes.
- 946

947 Figure 2: Radiogenic isotope compositions of a selection of major ocean islands. (a)

- 948 ${}^{206}Pb/{}^{204}Pb$ versus ${}^{208}Pb/{}^{204}Pb$; (b) ${}^{87}Sr/{}^{86}Sr$ versus ${}^{143}Nd/{}^{144}Nd$; (c) ${}^{143}Nd/{}^{144}Nd$ versus
- 949 176 Hf/¹⁷⁷Hf; (d) 206 Pb/ 204 Pb versus 87 Sr/ 86 Sr. Island chains are classified by their global end-
- 950 members which are indicated by the colour of their field in the legend (as in Fig. 1a). In all
- panels, the grey field outlines Indian, Atlantic, and Pacific MORB. Labels indicate the location
- of end-member compositions: DMM is the depleted MORB mantle; EM-I is enriched mantle I;
 EM-II is enriched mantle II; HIMU is high µ (U/Pb); and PREMA is PREvalent MAntle. Data
- were downloaded from the GeoRoc geochemistry database in October 2021 (further details on
- were downloaded from the Geokoc geochemistry database in October 2021 (further details on the dataset and references are available in the supplementary information). Data density (neurole
- the dataset and references are available in the supplementary information). Data density (panels

- a-d) is contoured and indicates that most oceanic island basalts have contributions from PREMAplus at least one additional end-member.
- 958

959 Figure 3: Contributions of major mantle reservoirs to global plume buoyancy flux. Flux 960 estimates (MiFil volumes; Mg/s) are from King and Adam (2014). Grey bars represent total 961 buoyancy flux for each end-member, black lines are median values, and the distribution around 962 the median for each mantle component is indicated by a coloured boxplot (color code as Fig. 1a). 963 Plumes groups: EM-I: Meteor, Fernando de Noronha, Tasmantid, Lord Howe, Marion, Tristan 964 da Cunha-Gough, Hawai'i-Emperor, Jan Mayen, Kerguelen, Pitcairn-Gambier, Rarotonga, 965 Discovery-Shona. EM-II: St. Paul-Amsterdam, Azores, Marquesas, Samoa, Tahiti-Society. 966 PREMA: Galápagos (also DM), Trindade-Martin, Crozet, Bouvet, Balleny, Ascension, 967 Comores, Reunion, Bowie-Kodiak (or Pratt-Welker; currently erupting DM), Caroline, Easter-968 Salas y Gomez, Juan de Fuca (also known as Cobb-Eickelberg and Patton-Murray; currently 969 erupting DM), Juan Fernandez, Louisville. HIMU: Vema, Bermuda, Cape Verde, Rurutu-Arago, 970 St. Helena, Great Meteor, Canary, Macdonald (currently erupting PREMA), Baja-Guadalupe 971 (also known as Fieberling), Socorro. DM (depleted mantle, not depleted MORB mantle 972 (DMM)): Iceland, Madeira, San Felix. Continental: Yellowstone, East Africa, Eifel, Darfur, 973 Afar (outlier in box plot), Tibesti, Cameroon, Hoggar, East Australia, Raton. EM-II and DM

- 974 groups have highest median fluxes; EM-I has largest total flux, dominated by Hawai'i-Emperor;
- 975 EM-I median flux is indistinguishable from PREMA and HIMU.
- 976 Mantle tetrahedron inset: Relationship between representative ocean island arrays and the five
- 977 main mantle end-member compositions of Zindler and Hart (1986) in three-dimensional isotopic
- 978 ratio space (⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ²⁰⁶Pb/²⁰⁴Pb; Hart et al., 1992).
- 979
- 980 **Figure 4: Lithium isotope compositions of ocean islands**. (a) δ^7 Li versus ²⁰⁶Pb/²⁰⁴Pb; (b)
- 981 Histogram of all current δ^7 Li measurements on OIB. Separate island chains are indicated by the
- 982 colour of their field in the legend, as in Fig. 1. In panel (a), the grey field includes data for
 983 Pacific, Atlantic, and Indian MORB. Labels indicate the location of end-member compositions,
- as in Fig. 2. OIB Lithium isotope data is from Chan et al., 2003; Kobayashi et al., 2004; Ryan
- and Kyle, 2004; Nishio et al., 2005; Chan et al., 2009; Vlastélic et al., 2009; Manga et al., 2011;
 Schusser et al., 2011; Krientiz et al., 2012, Genske et al., 2014; Harrison et al., 2015. MORB
- 987 data in panel (a) is from Elliott et al., 2006, Tomascek et al., 2008, and Marschall et al., 2017. All
- 988 Pb isotope values are normalized to the same standard values (SRM 981 value of 16.9405).
- 289 Lithium isotopes trace fluid mobilization processes such as subduction (Bouman et al., 2004;
- 990 Deschamps et al., 2010) and provide evidence for incorporation of recycled, subduction-altered
- 991 material into the OIB source.
- 992

Figure 5: Use of isotopic systems to detect early Earth reservoirs. Only major ocean island
 systems discussed in this manuscript are shown. (a) ¹⁴²Nd/¹⁴⁴Nd in parts per million (ppm)
 deviation from the terrestrial standard (JNdi-1, AMES, or vNd-b). Baffin Island samples are

- 996 included because they have the highest known ${}^{3}\text{He}/{}^{4}\text{He}$ ratios to date (up to 50 R_a; Stuart et al.,
- 2003). Error bars: 2SE (Standard Error; sample measured once) or 2SD (Standard Deviation;
- 998 samples measured several times), number of measurements indicated near symbol. External
- reproducibility (2SD) is estimated from repeated measurement of a standard reference material analyzed during the same analytical session as the samples, usually ~5 ppm (light grey, but
- 1001 Hyung and Jacobsen (2020) report a value of 1.1 ppm for 10 measurements of JNdi-1 (dark

- 1002 grey)). Symbols outlined in red are those for which authors consider the deviation significant
- 1003 compared to external reproducibility (Réunion: Peters et al., 2018; Samoa: Horan et al., 2018).
- 1004 Data from: Andreasen et al., 2008; Murphy et al., 2010; Jackson and Carlson, 2012; Burkhardt et
- 1005 al., 2016; Saji et al., 2016; de Leeuw et al., 2017; Garçon et al., 2018; Horan et al., 2018; Peters
- 1006 et al., 2018; Hyung and Jacobsen, 2020. (b) ¹⁸²W/¹⁸⁴W measured in OIB samples (ppm deviation
- 1007 relative to terrestrial standard, *Alfa Aesar*). Error bars: 2SE or 2SD for samples. External
- 1008 reproducibility is ~ 4-5 ppm; large deficits measured in OIB samples can be resolved clearly.
- 1009 Samples from Baffin Island are not included because ¹⁸²W results are controversial. The positive
- 1010 μ^{182} W measured by Rizo et al. (2016) could be an analytical artifact (Kruijer and Kleine, 2018).
- 1011 Data from: Mundl et al., 2017; Mundl-Petermeier et al., 2019; Rizo et al., 2019; Peters et al., 2021. Small acquisitions in automatical acquisitions from the state of th
- 2021. Small variations in extinct isotopic systems represent either potential contributions fromearly-formed material or core interaction with the plume source.
- 1014 (c) ¹²⁹Xe/¹³⁰Xe in mantle sources for Iceland (Mukhopadhyay, 2012), Samoa (Rochambeau Rift;
- 1015 Peto et al., 2013) and Galápagos (accumulated gas; Péron et al., 2021). Error bars are 1SD
- 1016 following convention in the noble gas literature. The depleted mantle source is 129 Xe/ 130 Xe = 7.8
- 1017 from MORBs and well gases (Moreira et al., 1998; Holland and Ballentine, 2006; Parai et al.,
- 1018 2012; Tucker et al., 2012); atmospheric 129 Xe/ 130 Xe = 6.496 (Basford et al., 1973), lower than
- 1019 OIB and MORB mantle sources. Noble gas systematics highlight the compositional differences
- 1020 between the MORB and OIB mantle sources.
- 1021 (d) Neither post-eruptive atmospheric contamination (illustrated by the arrays of step-crush data
- trending toward atmospheric values) nor incorporation of regassed atmospheric Xe into the
- mantle can explain the OIB data arrays in 129 Xe/ 130 Xe- 3 He/ 130 Xe space. The low 129 Xe/ 130 Xe in
- 1024 OIB mantle sources are thus interpreted to reflect a lower I/Xe ratio during the lifetime of 129 I
- 1025 compared to the upper mantle (Moreira et al., 1998; Parai and Mukhopadhyay, 2021).
- 1026

1027 Figure 6: Mantle convection simulations in two-dimensional spherical annulus geometry

- 1028 (Gülcher et al., 2021). Colors indicate distinct compositions: Basalt (blue, see also the
- 1029 composition triangle) ; Harzburgite (beige); a bridgmanitic primordial material (dark red),
- 1030 rheologically more viscous (by a factor $\lambda prim$), initially forming a layer of thickness Dprim. The
- 1031 model also features an ancient FeO-rich basal layer (magenta) with the same physical properties
- 1032 of basalt. The inset shows the age of material forming the basal piles. Models illustrate that the 1033 mantle is strongly heterogeneous after 4.5 Gyr of model time.
- 1034

1035 Supplementary information

1036 The online version contains supplementary material available at: 1037

1038 Supplementary Tables

- Supplementary Table 1: Geochemical characteristics of the major mantle end-members as
 defined by Zindler and Hart (1986), adjusted according to subsequent research as cited in the
 table.
- 1042
- 1043 **Supplementary Table 2**: Summary of isotopic systems typically used in mantle geochemistry.
- 1044 Systems are listed as either radiogenic or stable. Included are the measured ratios and commonly 1045 used notations as well as the sources or processes traced.
- 1046

1047 Data Compilation

- 1048 Figures 2, and Supplementary figures were constructed from a combined dataset of
- precompiled files for oceanic island groups from GeoRoc and several curated datasets (e.g., Weis
 et al., 2020; Harpp and Weis, 2020; Harrison et al., 2020). New data downloaded from the
- et al., 2020; Harpp and Weis, 2020; Harrison et al., 2020). New data downloaded from the
 GeoRoc geochemistry database was done in October 2021 and included data from Azores, Easter
- 1052 and Salas-y-Gomez Islands, Iceland, Kerguelen, and St Helena. GeoRoc data selection criteria
- 1053 started with geological setting (Ocean Island), selection of ocean island chain, type of material
- 1054 (whole rock), and type of rock (volcanic rock). This was combined with data downloaded from
- 1055 GeoRoc in July 2020 and 2021, some of which is presented in Harrison et al. (2020). This data 1056 included Samoa, Cook-Austral Islands, Pitcairn-Gambier, Easter, Galápagos, Society, and
- 1057 Mauritius (see their supplementary information for a full list of references). New Pitcairn and
- 1058 Society trace element concentration and isotope composition data from Cordier et al. (2021) was
- added to the GeoRoc compilation, along with data from the Galápagos from Harpp and Weis
- 1060 (2020). Hawaiian-Emperor data was taken from Weis et al. (2020). The total number of samples
- 1061 in the compiled dataset was 19,824. The format of each of these precompiled files was
- standardized and imported into R, a free open-source software for statistical computing for analysis and plotting. All datasets except those downloaded in October 2021 were renormalized
- 1064 to the same standard values to ensure comparability (i.e., Weis et al., 2020). For major element
- and isotope plots, no filters were used on the dataset to assess data quality, which varied between
- 1066 labs, instrumentation, methods, and detection limits over the past forty to fifty years (much of
- 1067 this metadata is not included in the GeoRoc database, or is inconsistently included and therefore 1068 difficult to apply across such a varied dataset). Most isotopic data is post-1990. For trace element
- plots, a filter of SiO₂ greater than 55 and total alkalis (Na₂O+K₂O) less than 8 was applied to
- 1070 remove highly silica-undersaturated samples or samples that were produced by anomalously low
- 1071 degrees of partial melting. This removes samples with heavily enriched incompatible trace
- element concentrations, which would skew the average results presented in the extended traceelement spider diagram.
- 1074

1075 Supplementary Figures

Major and trace element plots for a selection of major oceanic islands. DMM is the depleted MORB mantle; EM-I is enriched mantle I; EM-II is enriched mantle II; HIMU is high μ (U/Pb); and PREMA is PREvalent MAntle.

1079 **Figure (a):** Total alkalis (Na₂O+K₂O) versus SiO₂ for a selection of major oceanic islands. The

- 1080 dashed line is the tholeiitic-alkalic divide line from Macdonald and Katsura (1964). Because of
- 1082 clearly indicating that the vast majority of oceanic islands are basalts. The distribution frequency
- 1083 of the Na₂O+K₂O and SiO₂ data are shown along each axis on the right and top of the graph.
- 1084 **Figure (b): Average primitive mantle-normalized extended trace element compositions for** 1085 **a selection of maior ocean islands.** Averages were calculated for each oceanic island after
- 1085a selection of major ocean islands. Averages were calculated for each oceanic island after1086removing all samples with $SiO_2 > 55$ wt.% and total alkalis (Na_2O+K_2O) < 8 to ensure that</td>
- 1087 samples with elevated trace element concentrations caused by extremely low degrees of melting
- 1088 were not included in this compilation of average oceanic island compositions. Average trace
- 1089 element concentrations are normalized to primitive mantle values from McDonough and Sun
- 1090 (1995). Note the logarithmic scale. Details regarding data sources are provided in the
- 1091 supplementary information.

1092 Figure (c-e): Trace element ratio plots for a selection of major oceanic islands. Important

- 1093 trace element ratio plots are shown of all ocean island basalts together and separated into ocean
- 1094 island groups. Because of the large number of samples in the figure, the data have been
- 1095 contoured using a kernel density estimation, in the general plot and in the panels for each oceanic
- 1096 island group. The distribution frequency of the data is shown along each axis on the right and top
- 1097 of the graph of all ocean island data plot. The subscript "PM" indicates that each element
- 1098 concentration was normalized to the primitive mantle values of McDonough and Sun (1995).
- 1099 (c) (La/Sm)_{PM} versus Th/Ta (N = 3,021)
- 1100 (d) Nb/U versus Ce/Pb (N = 3,205)
- 1101 (e) (La/Sm)_{PM} versus Zr/Nb (N = 4,172).
- 1102 Data contours are representative of the specific mantle end-member for each plot and are
- 1103 coloured accordingly
- 1104

1105 Figure (f-i) Radiogenic isotope compositions of a selection of major oceanic islands. These

figures are the same as Fig. 2 with panels for each oceanic island group and one plot of all ocean

- 1107 islands plotted together. Kernel density estimation contours are drawn as in the trace element
- 1108 ratio supplementary figures.
- 1109

1110 Figure (j): Tomographic vertical cross-sections Bering Sea/NNW Pacific to southernmost

- 1111 **Pacific**. (a) Tomographic vertical cross-section from the Bering Sea/NNW Pacific Ocean to
- 1112 southernmost Pacific/Antarctic Ocean. Cross section captures the Hawai'i, Tahiti-Society, and
- 1113 Macdonald plumes, marked by magenta circles and labeled as (H), (T), and (M), respectively.
- 1114 Tomographic model from SEMUCB-WM1 (French and Romanowicz, 2014). After imagery 1115 rendered using the SubMachine online tool (Hosseini et al., 2018). Warm colors are velocity-
- slow regions, and blue velocity-fast of the shear velocity (Vs) variations in each model. (b)
- Global map view showing the location and extent of the tomographic cross-section slice (black
- 1118 line intersecting black, white, and green circles). Symbols and labels as in (a).
- 1119

1120 Text Box #1

1121 Mantle Plume and Large Igneous Province Fundamentals

1122

1123 Geodynamic models and analog experiments indicate that when plumes begin to rise through the

- 1124 mantle, upwelling material takes the form of a mushroom, with a large, semicircular head trailed
- 1125 by a narrow tail (Richards et al., 1989; Farnetani et al., 2002; Kerr and Mériaux, 2004; Lin and
- 1126 van Keken, 2006). Initial melt production is high, owing to the large volume of the plume head.
- 1127 When the plume head melts, it produces Large Igneous Provinces (LIPs) on land (e.g., Deccan,
- 1128 Siberian Traps), below sea level (e.g., Shatsky, Ontong-Java, Manihiki oceanic plateaus), or both
- 1129 (Kerguelen). This initial phase can last from one to several million years and requires
- 1130 involvement of significant volumes of mantle (Figure T1a). The LIP phase of plume activity is
- 1131 followed by a major reduction in melt production, which produces oceanic island basalts (OIBs)
- sourced from the plume tail; this phase often lasts 10s of millions of years (White and McKenzie,
- 1133 1989; Sleep, 1990; Campbell and Griffiths, 1990; White, 1993; Kumagai et al., 2008).
- 1134
- 1135 The sheer size of plume heads requires a large volume of material from the lower mantle. Indeed,
- 1136 mantle plumes are associated with low seismic velocities, reflecting the elevated temperature of
- ascending mantle material (Montelli et al., 2006; Putirka et al., 2007). Seismic studies of the

- lower mantle (e.g., Dziewonski and Woodhouse, 1987; Garnero, 2000; Masters et al., 2000;
- 1139 Garnero et al., 2007) have induced a profound shift in mantle plume models, which have evolved
- 1140 from the classical mushroom-shaped, thermal model toward more complex thermo-chemical
- 1141 structures. The internal dynamics of thermo-chemical plumes reflect the interplay between
- 1142 positive (thermal) and negative (compositional) buoyancy forces. Most often, the symmetrical
- 1143 geometry is lost (e.g., Tackley, 1998; Davaille, 1999, Farnetani and Samuel, 2005), since some
- 1144 parts of the plume conduit sink (Kumagai et al., 2008) while others ascend slowly.
- 1145
- 1146 The geochemical signatures of LIP phases reflect the complex relationship between
- 1147 compositional heterogeneity and the internal structures of mantle plumes. Components sampled
- 1148 by LIP melts include the plume material itself, upper mantle, and even lithospheric material, a
- signal often more strongly observed in LIPs emplaced on continents than in submarine settings.
- 1150 Geochemical contributions to LIPs can be identified using alteration-resistant, so-called
- 1151 "immobile elements," which include Th, Ti, Yb, and Nb. During mantle melting, these elements
- behave similarly and predictably, making them useful both as proxies for common mechanisms
- 1153 that affect mantle-derived melts and for different mantle and/or crustal components (e.g., Pearce
- et al., 2021). For example, elevated Th/Nb ratios in LIP melts reflect increased crustal
- 1155 contamination (Figure T1b). The TiO₂/Yb ratio increases with greater depth of melt generation
- 1156 (more melting in the garnet region of the mantle, >80 km); this ratio also gets larger as extent of
- 1157 partial melting decreases, a signature frequently observed in the OIB (plume tail) phase, when
- 1158 considerably less melt is being generated than during the LIP stage.
- 1159
- 1160 Case Study: The Kerguelen LIP
- 1161 The Kerguelen mantle plume produced a hybrid LIP, continental flood basalts in the early stages,
- an oceanic plateau (<85 Ma) and a plume trail (Frey et al., 2002). Kerguelen preserves signatures
- 1163 of multiple components whose origins span from the lower mantle to the crust, providing a
- 1164 valuable cross-section of the mantle reservoirs supplying the Kerguelen plume (Fig. T1b).
- 1165 Kerguelen melts plot dominantly within the oceanic field, overlapping other LIP fields and
- 1166 extending slightly into the transitional area between MORB-dominant and OIB-dominant LIP
- 1167 melts (Weis and Frey, 2002). A few older samples also overlap with the EM-OIB and
- 1168 lithospheric fields, the latter of which is interpreted as crustal contamination of LIP melts and 1169 commonly observed in continental settings (Pearce et al., 2021).
- 1170

1171 Figure T1a: Relative volumes of several Large Igneous Provinces (LIPs), shown as cross-

- 1172 sections of spheres scaled to estimates of the volume of partial melting (minimum and maximum
- diameters for 5 and 30% melting respectively) during their emplacement (modified from Coffin
- and Eldholm, 1994). NAIP = North Atlantic Igneous Province (continental), CRFB = Columbia
- 1175 River Flood Basalts (continental).
- 1176
- 1177 **Figure T1b: Discrimination diagram for Large Igneous Provinces** (modified from Pearce et
- 1178 al., 2021). Variations along the y-axis indicate level of crust contamination, while variations
- along the x-axis correspond to increasing depth of melting. SZLM = Subduction Zone-
- 1180 Lithospheric Mantle, EM = Enriched Mantle, OIB = Ocean Island Basalt, MORB = Mid-Ocean
- 1181 Ridge Basalt, and OPB = Ocean Plateau Basalt (equivalent to LIP). Red circles are Kerguelen
- samples (Doucet et al., 2005; Frey et al., 2002; Yang et al., 1998), with background fields also
- shown for Ontong-Java, Deccan, CRFB, and NAIP. Data sources same as in Pearce et al. (2021).

1184

1185 Text Box #2

1186 What is an isotope? Radiogenic versus Stable, Time Integration, and the Noble Gases

1187

1188 Isotopes of a chemical element have the same number of protons in their nucleus but differ in

- their number of neutrons. Consequently, they have the same atomic number and occupy the same 1189
- 1190 position on the Periodic Table but have different masses. Their relative abundances are measured
- 1191 by a mass spectrometer. Isotopes can be classified into broad categories on the basis of their
- 1192 stability (or lack thereof) and formation pathways. 1193

1194 **Radiogenic Isotopes**

1195 A radioactive isotope has an unstable atomic nucleus that emits radiation and is spontaneously 1196

- transformed into another isotope, the radiogenic product. The decay rate of a radioactive isotope 1197 is characterized by its half-life, which is the time for a given amount of the parent isotope to
- 1198 decay to half of its initial amount.
- 1199

1200 Time is the primary variable that generates the observed differences in radiogenic isotopic 1201 compositions in geologic settings. For example, geochronology uses two categories of

- 1202 radioactive isotopes—those with long half-lives (> 100 Myr) and those with a short half-lives (<100 Myr) relative to geological timescales. Isotopes with a long half-life (e.g., ⁸⁷Rb, ¹⁴⁷Sm) are 1203
- 1204 still decaying today and produce variations in the abundances of daughter products (in this

example, ⁸⁷Sr and ¹⁴³Nd, which are measured as ratios relative to a stable isotope of the same 1205

- element, ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd) that take millions to billions of years to develop. These 1206 1207 isotopic systems are used for geochronology and fingerprinting sources of materials. Conversely,
- 1208 radioactive isotopes with geologically short half-lives have now fully decayed and are extinct.
- 1209 Variations in the radiogenic isotope ratios produced by the decay of isotopes with short half-lives
- 1210 provide information about events that happened in the first few 100 million years, very early in
- 1211 Earth's history.
- 1212

1213 Neodymium provides a good example of the differences between short and long half-life isotope

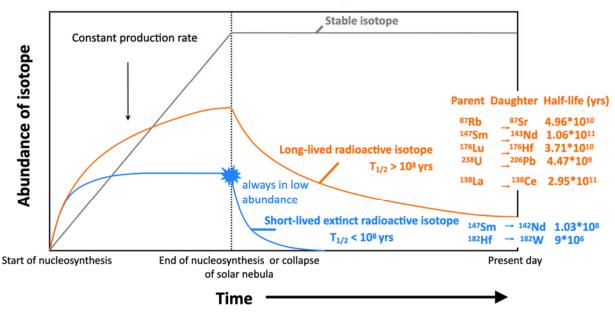
- systems. Neodymium has two radiogenic isotopes (¹⁴²Nd and ¹⁴³Nd) produced by the decay of 1214
- two radioactive isotopes of Sm (¹⁴⁶Sm and ¹⁴⁷Sm) with very different half-lives: 103 Myr and 1215
- 1216 106 Gyr. Therefore, the two isotopic systems display isotopic variations that reflect entirely
- different processes; the ¹⁴⁶Sm-¹⁴²Nd system tracks the presence of early Earth material and the 1217
- ¹⁴⁷Sm-¹⁴³Nd system documents long-term source changes. Whereas the ¹⁴⁷Sm-¹⁴³Nd system has 1218
- been analytically accessible since the 1980s, the variations in ¹⁴²Nd due to ¹⁴⁶Sm decay are so 1219 small that measuring ¹⁴²Nd/¹⁴⁴Nd is almost at the limit of the current analytical capabilities of
- 1220
- 1221 modern mass spectrometers, and only achievable since 2000.
- 1222
- 1223 Contrary to trace elements (i.e., elements that constitute less than 0.1 wt% of a rock or magma),
- 1224 radiogenic isotopic compositions are not affected by the degree of partial melting or the
- crystallization history of a melt. Radiogenic isotopic ratios (e.g., ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, 1225
- ²⁰⁶Pb/²⁰⁴Pb, ⁴He/³He or ¹⁷⁷Hf/¹⁷⁶Hf) of a basalt are therefore representative of the composition of 1226
- 1227 the material that melted to produce the basalt. Consequently, they provide time-integrated
- 1228 information about its origin. In contrast, variations of extinct radiogenic isotopic systems (e.g.,

1229 $^{142}Nd/^{144}Nd$, $^{182}W/^{184}W$, $^{129}Xe/^{130}Xe$) indicate the presence of material that differentiated from the rest of the mantle during accretion.

1232 Stable Isotopes

- 1233 <u>Stable isotopes</u> are those whose nucleus is stable, resulting in isotopic abundances that are
- 1234 invariant in time. Some of these isotopes, especially the light elements (H, Li, O, C, and N), can
- be fractionated by physical, biological and sometimes chemical processes, and are used to trace
- 1236 fractionation processes rather than the long-term evolution of the source of lavas. Examples
- 1237 include atmospheric weathering (O), groundwater interaction (H, O, C), sediment recycling (Li,
- 1238 Tl), and redox-changes (Fe).
- 1239

1231



Time Scales for Planetary Processes

1240

1241

1242 Noble Gases

1243 All noble gases (sometimes called rare gases) have radiogenic and stable isotopes. For a wide 1244 variety of radioactive systems (Table 2), parent-daughter fractionation by gas loss within the

- 1244 Variety of radioactive systems (Table 2), parent-daughter fractionation by gas loss within the 1245 lifetime of the radioactive isotope generates radiogenic noble gas isotope signatures over time.
- 1246

1247 The helium system provides a helpful example to illustrate important terms. In the helium

- 1248 system, ³He is **primordial**, because it is a stable, non-radiogenic isotope whose abundance was
- 1249 established during accretion; any primordial isotopes lost to the atmosphere are not replaced in
- 1250 Earth's noble gas budget. Primordial noble gas isotopes are no different from the stable, non-
- radiogenic normalizing isotopes used in other decay systems (*e.g.*, 204 Pb). Accordingly, recent noble gas studies report He isotope ratios as 4 He/ 3 He to be consistent with radiogenic isotope
- 1252 noble gas studies report he isotope ratios as he/ he to be consistent with radiogenic isotope 1253 convention. By contrast, ⁴He is continuously produced by radioactive decay of ²³⁵U, ²³⁸U, and
- ¹²⁵⁵²³²Th (among other radioactive isotopes; ⁴He is simply the alpha particle produced in these
- radioactive decay processes). Unradiogenic helium isotopic ratios reflect sampling of a reservoir
- 1256 that experienced less **degassing**, which is gas transport from the mantle to the atmosphere

- associated with mantle processing by partial melting and volcanism. A **less-degassed** mantle
- 1258 reservoir has relatively high ${}^{3}\text{He}/{}^{4}\text{He}$ (and therefore lower ${}^{4}\text{He}/{}^{3}\text{He}$) because it has retained more
- 1259 of its primordial He, and the impact of radiogenic ingrowth of ⁴He (through continuous alpha
- decay of radioactive U and Th) is muted compared to the rest of the mantle. A less-degassed
- 1261 reservoir is not necessarily primordial mantle. **Regassing** is the transport of atmospheric gases
- into the mantle via subducted slabs. Regassing of He is negligible as it is light enough to escapethe atmosphere. Atmospheric contamination during or after sample formation affects Ne, Ar, Kr
- and Xe isotopic compositions measured in all OIBs. This impact can be corrected to determine
- 1265 the **mantle source** composition and assess whether regassing has affected the mantle.
- 1266

1267 Text Box #3

1268 Analytical Precision in Determination of Radiogenic Isotopic Ratios

- 12691270 The measurement and the interpretation of isotopic variations measured in OIB require careful
- 1271 attention. For example, determinations of ${}^{142}Nd/{}^{144}Nd$ and ${}^{182}W/{}^{184}W$ ratios are mainly
- accomplished using thermal-ionization mass spectrometry (TIMS) techniques that allow high
- 1273 precision but also require considerable time and effort on the part of the analyst. Several studies
- indicate that analytical artifacts can produce small isotopic variations in TIMS measurements,which are linked to: 1) problematic mass-dependent fractionation correction when isotopic ratios
- do not follow the exponential law (Upadhyay et al., 2008); 2) inappropriate mass fractionation
- 1276 do not follow the exponential law (Opadhyay et al., 2008); 2) inappropriate mass fractionation 1277 correction when the rate of mass fractionation is too high for dynamic measurements (Roth et al.,
- 2014); 3) mixing of different sample reservoirs on the filaments (Upadhyay et al., 2008, Roth et al., 2014); 4) non-mass dependent isotopic variations (nuclear field shift) caused by the chemical
- separation protocol (Garçon et al., 2018; Kruijer and Kleine, 2018; Saji et al., 2016); and, just for
 the W system, 5) the need to improve the determination of O isotope composition for W isotope
 measurements done in oxide form by TIMS (Trinquier et al., 2016). Because deviations in the
- ¹²⁸³ ¹⁴²Nd/¹⁴⁴Nd and ¹⁸²W/¹⁸⁴W systems are small, they are expressed in μ -notation (deviation in parts per million relative to the average ratio measured in the terrestrial standard).
- 1285
- 1286 High precision isotopic ratio measurements have revealed small differences between the
- 1287 terrestrial standards commonly used in the different laboratories (e.g., variation of a few parts per
- 1288 million in ¹⁴²Nd/¹⁴⁴Nd ratios measured in LaJolla, JNdi-1, and AMES Nd standard) that were
- 1289 likely produced during the purification process (O'Neil et al., 2008; Saji et al., 2016). The
- 1290 development of a method based on a multi-mass-step acquisition scheme allows for all isotopic
- ratios of the element to be determined in dynamic mode, with subsequent application of qualitycontrol criteria (Garçon et al., 2018).
- 1293
- 1294 When publishing isotopic data, analytical uncertainty is reported as 2SD (standard deviation, 1295 calculated from repeated measurements of the same sample) or 2SE (standard error, where 2SE =
- 1296 $2SD/\sqrt{N}$, where N = number of measurements). The standard error corresponds to the internal
- 1297 error (based on counting statistics) when the sample is measured once. The scientific community
- has debated the significance of a deviation relative to its analytical precision extensively, without
- a clear resolution. Regardless of the choice of 2SD or 2SE, publications claiming high-precision
 isotopic measurements should thoroughly describe the analytical protocols used and all data
- 1300 isotopic measurements should thoroughly describe the analytical protocols used and all data 1301 associated with the measurement (interferences, mass bias, all measured ratios, and other
- 1302 phenomena that affect analytical results), as well as present the results for international, cross-

1303 calibrated reference standard materials. Rigorous analysis also includes performing an

- appropriate number of duplicate, replicate, and total blank measurements.
- 1305
- 1306 A key factor in achieving high-precision isotopic measurements of oceanic island basalts is
- 1307 ensuring that only the original, magmatic composition of the basalt are measured, which is
- achieved primarily through appropriate sample preparation procedures. For example, Rb-Sr, U-
- 1309 Pb, and stable Li isotopic systems are susceptible to perturbation from seawater alteration, and Tl
- isotopic measurements are sensitive to the presence of ferromanganese precipitation. Thesesecondary components must be removed by physical separation and cleaning followed by
- 1311 secondary components must be removed by physical separation and cleaning followed by1312 careful, systematic acid leaching procedures (Manhès et al., 1978; Dupré and Allègre, 1980;
- 1313 McDonough and Chauvel, 1991; Abouchami et al., 2000; Weis et al., 2006, 2007; Hanano et al.,
- 1314 2009; Nobre Silva et al., 2009, 2010; Williamson et al., 2021) to ensure that the measured data
- represent the original magmatic isotopic signatures representative of the magma sourcecomposition.
- 1317
- 1318 Finally, older OIB samples (> 7-10 Ma, depending on the isotopic system and analytical
- 1319 precision) must be age-corrected for in-situ decay since their eruption (e.g., Harrison et al., 2017;
- 1320 Harrison and Weis, 2018). This adjustment is especially important for samples where age
- 1321 correction will result in an isotopic ratio outside of the original analytical uncertainty, such as for
- 1322 Pb isotopic compositions in samples older than~15-20 Ma (Harrison et al., 2017). Age correction
- 1323 is completed using the decay equation and requires measurement of the elemental parent-
- daughter ratio of the unleached sample. For the U-Th-Pb system in particular, care must be takento estimate the primary U concentration in submarine OIB properly, as U is susceptible to
- 1325 to estimate the primary O concentration in submarine OIB property, as O is susceptible to
 1326 secondary alteration. For example, primary U can be estimated using the Th/U of unaltered
- 1327 samples (Nobre Silva et al., 2013b; Harrison et al., 2017).
- 1328

1329 Analytical Consistency and Comparability Between Labs

- 1330 A particularly problematic challenge in OIB studies (and in any study where the objective is to 1331 determine the source compositions of rocks) involves comparison of data generated in different
- 1332 analytical laboratories on the same samples. To compare isotopic compositions generated using
- 1333 different instruments and methods (e.g., TIMS, MC-ICP-MS) and in different laboratories,
- 1334 geochemists use a normalization scheme based on published values for standards and reference
- 1335 materials (e.g., Weis et al., 2011, 2020). For robust comparisons, it is essential to perform careful
- 1336 normalization to the same standard and reference values. Otherwise, the data are not comparable
- 1337 and spurious correlations may occur.
- 1338

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