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► **To cite this version:**

Dominique Weis, Karen S. Harpp, Lauren N. Harrison, Maud Boyet, Catherine Chauvel, et al.. Earth's mantle composition revealed by mantle plumes. *Nature Reviews Earth & Environment*, 2023, 4 (9), pp.604-625. 10.1038/s43017-023-00467-0 . hal-04285033

HAL Id: hal-04285033

<https://hal.science/hal-04285033>

Submitted on 16 Nov 2023

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The Composition of the Earth's Mantle Revealed by Mantle Plumes

Weis^{1*}, Dominique; Harpp², Karen; Harrison³, Lauren N.; Boyet⁴, Maud; Chauvel⁵, Catherine; Farnetani⁶, Cinzia G.; Finlayson⁷, Valérie A.; Lee⁸, Kanani K.M.; Parai⁹, Rita; Shahar¹⁰, Anat; Williamson¹¹, Nicole B.

* Corresponding author

1. Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia
2020-2207 Main Mall, Vancouver, BC, V6T-1Z4, Canada – dweis@mail.ubc.ca

2. Department of Earth and Environmental Sciences, Colgate University, Hamilton, NY 13346, USA -
kharp@colgate.edu

3. U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA -
lnharrison@usgs.gov

4. Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-
63000 Clermont-Ferrand, France - maud.boyet@uca.fr

5. Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, 1 rue Jussieu Paris
75005, France - chauvel@ipgp.fr

6. Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, 1 rue Jussieu Paris
75005, France - cinzia@ipgp.fr

7. Department of Geology, 8000 Regents Drive, University of Maryland, College Park, MD
20742, USA - vfinlays@umd.edu

8. Physics Department, U.S. Coast Guard Academy, 208 Smith Hall, 31 Mohegan Avenue
New London, CT 06320, USA - kanani.km.lee@uscga.edu

9. Department of Earth and Planetary Sciences, Washington University in St. Louis, 1 Brookings
Drive, Saint Louis, MO 63130, USA - parai@wustl.edu

10. Earth and Planets Laboratory, Carnegie Institution for Science, 5241 Broad Branch Rd.
N.W., Washington, DC 20015, USA - ashahar@carnegiescience.edu

11. Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia
2020-2207 Main Mall, Vancouver, BC, V6T-1Z4, Canada – nwilliam@eoas.ubc.ca

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.

59

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
63 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; Koelemeijer 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.

73

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
77 references therein). By contrast, mantle plumes provide invaluable insight into the geochemistry
78 of Earth's deeper interior and occur in all tectonic settings (Fig. 1a). They originate at different
79 depths, from shallow upwellings in the upper mantle (Duvernay et al., 2021) to deeply sourced
80 plumes (Courtilot 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
83 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
89 composition of Earth's mantle and its evolution over time, including the sources of deeply rooted
90 plumes.

91
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 **Section 2 Fundamentals of Mantle Plumes**

106
107 The strength of a plume's upwelling flux, its composition, and the duration of its activity
108 have been used to classify plumes ([Courtilot 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 $^3\text{He}/^4\text{He}$ or other indications of compositions distinct from those of mid-ocean ridge basalts
113 ([Courtilot et al., 2003](#); [Montelli et al., 2006](#); [Boschi et al., 2007](#); [King and Adam, 2014](#); [French](#)
114 [and Romanowicz, 2015](#)).

115
116 Seismic tomography and geodynamical studies suggest that most OIB-generating
117 volcanoes are produced by plumes that originate along the edges of Large Low Shear Velocity
118 Provinces (LLSVP), commonly interpreted as thermochemical piles at the CMB ([Burke and](#)
119 [Torsvik 2004](#); [Thorne and Garnero, 2004](#); [Torsvik et al., 2006](#); [Burke et al., 2008](#); [Dobrovine et](#)
120 [al., 2016](#); [Garnero et al., 2016](#)). Early geodynamical models explored ancient, accumulated
121 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](#);
124 [Williams et al., 2015](#); [Nakagawa and Tackley, 2014](#); [Jones et al., 2021](#)). Alternatively, dense and
125 reduced mantle material may pool at the CMB, contributing to the formation of LLSVPs ([Gu et](#)
126 [al., 2016](#)). Laboratory experiments ([Davaille, 1999](#); [Limare et al., 2015](#)) and numerical
127 simulations successfully reproduce the formation of large thermo-chemical plumes observed in
128 recent tomographic models ([French and Romanowicz, 2014](#)). In some models, both the LLSVP
129 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
136 core-mantle boundary (Cottaar and Romanowicz, 2012). Models for the origin of ULVZs include
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
152 strength of bridgmanite's structure may encourage the formation of narrow channels of
153 upwelling and downwelling, thereby stabilizing deep-rooted mantle upwellings from near the
154 core-mantle boundary (Ballmer et al., 2017).
155

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
162 supplied by the ambient lower mantle (Nobre-Silva et al., 2013a; Williamson et al., 2019), a
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
168 the Samoan, Galápagos, Easter, and Marquesas Islands in the Pacific (Weis et al., 2011; Huang
169 et al., 2011; Chauvel et al., 2012; Payne et al., 2013; Harpp et al., 2014; Harpp and Weis, 2020),
170 and, in the Atlantic at the western edge of the African LLSVP, Tristan and Gough (Rohde et al.,
171 2013).
172

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

178 LLSVP, resulting in the entrainment of LLSVP material; this model helps explain the abrupt
179 increase in plume flux along the chain after the bend. Finally, modelling results from Jones et al.
180 (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
187 or alkalic basalts dominate an oceanic island provides insight into the buoyancy flux and the
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.

200 Furthermore, plume strength may be enhanced by proximity to an LLSVP, as proposed
201 for Hawai‘i (Harrison et al., 2017; Harrison and Weis, 2018). The volume of magma produced
202 along the Hawaiian chain has increased over the last 45 Myr, in contrast to the trend predicted by
203 mantle plume models (e.g., Wessel, 2016; Weis et al., 2020). Moreover, the highest-flux plumes,
204 including Hawai‘i, overlie “mega-ULVZ” structures at the CMB (Cottaar and Romanowicz,
205 2012), implying links between lower mantle structures, the strength of a plume, its temperature,
206 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,](#)
228 [2001](#); [Harrison et al., 2020](#)). The near-zero lithospheric thickness of ridge-proximal plumes may
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
252 sample geochemical variations on a much smaller scale (20-30 μm), capturing different aspects
253 of the magmatic system. They represent a "snapshot" of melt pockets prior to melt
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).

260

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
267 (which refers to the composition of Earth's mantle soon after core formation), depletion in heavy
268 REEs relative to middle and light REEs, and near-constant ratios of the most incompatible
269 elements (left side of Supplementary Fig. b; [Hofmann et al., 1986](#); [Newsom et al., 1986](#);

270 Willbold and Stracke, 2006). Their rare earth element systematics suggest that most OIB melts
271 are generated primarily in the garnet stability field (>80 km depth), which reflects the higher
272 mantle temperatures of plumes (e.g., Gast, 1968). In contrast, most MORBs begin melting at
273 shallower levels where garnet is no longer stable, resulting in no significant middle to heavy
274 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

299 The five compositional end-members define the range of isotopic compositions in OIB,
300 and thus in the mantle sampled by plumes. Except for PREMA, these end-members are
301 chemically and isotopically distinct from each other and thought to come from separate chemical
302 reservoirs in the mantle, resulting from processes that generate unique chemical signatures and
303 evolve over time. Below, we consider the geochemical signatures of these mantle reservoirs
304 (Supplementary Table 1), their origins, and the insights they provide into the composition and
305 evolution of the mantle.
306

307 **The HIMU Endmember**

308 The HIMU mantle end-member is named for its high U/Pb (μ) source ratio (Zindler and
309 Hart, 1986). The extreme U/Pb ratios required to generate HIMU Pb isotopic signatures (Fig. 2a)
310 indicate that the original mantle source had high initial U/Pb (μ) and Th/Pb (ω) (Chauvel et al.,
311 1992). The most commonly invoked mechanism to explain the removal of Pb required for the
312 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
318 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
320 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
331 present on continents (Zindler and Hart, 1986; Weaver, 1991; Chauvel et al., 1992; White and
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 (Marquesas, Society, Samoan Islands) end-members dominate OIB-
336 producing systems and are important contributors to the buoyancy flux of many plumes (Figs. 1
337 & 3).

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 $^3\text{He}/^4\text{He}$ 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***

354 The major and trace element characteristics of strongly depleted OIB lavas
355 (Supplementary Figs. a-e) are consistent with a mantle source that has a long-term history of
356 melt extraction and, therefore, depletion in the most incompatible trace elements (Salters and
357 Stracke, 2004). The depleted component in OIBs, although easily masked by mixing with melts
358 from enriched heterogeneities in the mantle source, has been shown to be a component of some
359 Azores lavas, as evidenced by analysis of melt inclusions that record contributions from depleted
360 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

362 (Frey et al., 2005; Bizimis et al., 2005; DeFelice et al., 2019). In Iceland, the Azores, and the
363 Galápagos, the depleted signature is attributed to their near-ridge settings, where higher degrees
364 of mantle melting occur under a thin lithosphere (e.g., White et al., 1976; Schilling et al., 1982;
365 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
388 they are subsequently sampled by plumes; this cycle of downwelling and upwelling provided a
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.
403 Atmospheric and spallation-generated ^{10}Be concentrations, lithium, boron, and iron isotope
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
415 refractory elements (e.g., REE, HFSE; Porter and White, 2009; Ryan and Chauvel, 2014; Turner
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;
426 White and Duncan, 1996; Rudnick and Gao, 2003; Jackson et al., 2007; Cordier et al., 2021),
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 ($\delta^7\text{Li} = 3.5 \pm 1.0\text{‰}$; Marschall et al., 2017; Penniston-
476 Dorland et al., 2017). There is also a measurable difference between Li isotopic compositions of
477 HIMU OIB ($\delta^7\text{Li} = 2.5\text{-}8.5\text{‰}$) and EM-I OIB ($\delta^7\text{Li} = 0.5\text{-}4.5\text{‰}$), 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 (^{205}Tl
483 and ^{203}Tl) are fractionated up to 35 epsilon units, and exhibit large concentration contrasts
484 between geochemical reservoirs (e.g., pelagic sediments: $\epsilon^{205}\text{Tl}$ and [Tl] up to +5 and 1000 ng/g
485 (Rehkämper et al., 2002); low-temperature altered oceanic crust: $\epsilon^{205}\text{Tl}$ and [Tl] as low as -15
486 and 5-50 ng/g (Nielsen et al., 2006a); mantle: $\epsilon^{205}\text{Tl}$ of -2 ± 0.5 and <1 ng/g Tl (Nielsen et al.,
487 2017). Ocean island basalts exhibit a wide range of $\epsilon^{205}\text{Tl}$ values (-6.4 to +6.6; Brett et al., 2021).
488 Heavy $\epsilon^{205}\text{Tl}$ (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
490 sampled from the ambient mantle on the periphery of the Pacific LLSVP (Williamson et al.,
491 2021). Conversely, light $\epsilon^{205}\text{Tl}$ (down to -10) in lavas from St. Helena may be traced to altered
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
499 Archean prior to the Great Oxygenation Event at $\sim 2.5\text{-}2.4$ 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
503 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,
510 1988). Therefore, the measurement of the long-lived ^{138}La - ^{138}Ce system may constrain the timing
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
517 present and the influence of several large-scale processes needs to be considered as well,
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**

522 The OIB mantle source is a heterogeneous mixture of recycled surface materials, deep
523 mantle material that separated early (>4.45 Ga) and experienced less degassing than the upper
524 mantle, and potentially distinct remnant materials that formed early in Earth's history.
525 Determining the age and the nature of early-formed materials is important for understanding the
526 structure and dynamics of the lower mantle, especially given the spatial correlation of major
527 mantle plumes with LLSVPs and ULVZs (e.g., Burke and Torsvik 2004; Torsvik et al., 2006;
528 Dobrovine et al., 2016; Cottar 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
536 systems, including ^{182}Hf - ^{182}W , ^{146}Sm - ^{142}Nd , ^{129}I - ^{129}Xe , and ^{244}Pu - 131 - ^{136}Xe , with half-lives
537 between <10 Ma and ~ 100 Ma. Deviations in radiogenic products of some short-lived isotope
538 systems (e.g., $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$) are small in OIBs (a few ppm), making their detection difficult
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
542 $\mu^{142}\text{Nd}$, $\mu^{182}\text{W}$, and $^{129}\text{Xe}/^{130}\text{Xe}$ variations in OIBs, as well as interpreting the significance of
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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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
550 of a radiogenic excess of ^{142}Nd ($+7.9 \pm 1.9$ ppm) in the mantle relative to its building blocks
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 **Terrestrial Magma Ocean Relics**

566 Small ^{142}Nd 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
568 preserved in the deepest part of the mantle. Owing to the short half-life of ^{146}Sm (~103 Ma), the
569 variations measured in $^{142}\text{Nd}/^{144}\text{Nd}$ must reflect Sm/Nd fractionation that took place during the
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
574 also characterized by negative ^{182}W anomalies (down to -25 ppm) (Mundl et al., 2017; Mundl-
575 Petermeier et al., 2019; 2020; Peters et al., 2021), which may also represent the remnant of an
576 early terrestrial magma ocean (Fig. 5b). However, core-mantle interaction could also affect the
577 ^{182}W signal, making its interpretation ambiguous.

578
579 The short-lived ^{129}I - ^{129}Xe system provides additional support for preservation of early-
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.,
587 2016; Peron and Moreira, 2018; Bekaert et al., 2019; Parai and Mukhopadhyay, 2021; Peron et
588 al., 2021). Ratios of $^{129}\text{Xe}/^{130}\text{Xe}$ (where ^{129}Xe is produced by decay of short-lived ^{129}I , and ^{130}Xe
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

591 and Ballentine, 2006; Tucker et al., 2012; Parai et al., 2012). Differential incorporation of
592 atmospheric Xe with low $^{129}\text{Xe}/^{130}\text{Xe}$ into the OIB mantle cannot account for the OIB
593 $^{129}\text{Xe}/^{130}\text{Xe}$ signatures (Fig. 5d). Thus, a low I/Xe ratio must have been established in the OIB
594 mantle within the first ~ 100 Myr of Earth history, and its signature preserved despite ~ 4.45 Gyr
595 of convection (Mukhopadhyay, 2012). The low I/Xe may have come from inefficient degassing
596 of the deeper parts of the magma ocean, or low iodine abundances in the early-accreted
597 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
601 ocean; after closure, products of ^{129}I decay and ^{244}Pu fission would have been retained in the
602 silicate Earth. Because ^{129}I and ^{244}Pu decay at different rates, the $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}$ ratio (where the
603 star indicates radiogenic ^{129}Xe from the decay of ^{129}I , and the subscript denotes ^{136}Xe from Pu-
604 fission; Mukhopadhyay, 2012) can be used to calculate a “closure age” that marks the end of
605 open system magma ocean outgassing (Wetherill, 1975). The Iceland and Samoan Rochambeau
606 Rift samples exhibit low $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}$ ratios compared to the MORB mantle. If the whole
607 mantle had an initially homogeneous I/Pu ratio, then low $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}$ ratios in OIBs would
608 indicate a late closure age for the OIB mantle relative to the MORB mantle, because less of the
609 shorter-lived ^{129}I 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., $\sim 10\%$ 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 ($\delta^{56}\text{Fe} = 0.79\text{--}$
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 characterized
637 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
660 mantle was “polluted” with core material prior to being entrained into mantle plumes. The
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
665 al., 2011), no other isotopic signature indicative of element transport across the core-mantle
666 boundary was identified until the development of high precision $\mu^{182}\text{W}$ measurements (Touboul
667 et al., 2012a; 2012b; Trinquier et al., 2016). Small negative anomalies in $\mu^{182}\text{W}$ (-25 ppm) have
668 been measured in OIBs (Fig. 5b; Mundl et al., 2017; Mundl-Petermeier et al., 2019; 2020; Peters
669 et al., 2021). In mantle-derived samples, the $\mu^{182}\text{W}$ shifts over time, from positive values in
670 Hadean-Archean samples (4.3 to 2.7 Ga) to negative values in modern samples. This observation
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
680 mantle. In this case, the core would supply high $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}$ to the mantle.
681 However, OIBs sample a reservoir with low $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}$ compared to the rest

682 of the mantle. The core may have instead acted as a sink for lower mantle iodine during
683 accretion, with no subsequent transfer of radiogenic Xe back to the mantle over time (Jackson et
684 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
687 (Porcelli and Halliday, 2001; Bouhifd et al., 2020; Roth et al., 2019; Olson and Sharp, 2022).
688 Negative $\mu^{182}\text{W}$ anomalies are broadly associated with elevated $^3\text{He}/^4\text{He}$ (Mundl et al., 2017;
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 $\mu^{182}\text{W}$ and high $^3\text{He}/^4\text{He}$ to material in the lower mantle. In detail, however,
692 the highest OIB $^3\text{He}/^4\text{He}$ ratios are associated with modest negative $\mu^{182}\text{W}$, and the strongest
693 negative $\mu^{182}\text{W}$ anomalies are associated with only moderate $^3\text{He}/^4\text{He}$.

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 $\mu^{182}\text{W}$ 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 $^3\text{He}/^4\text{He}$ 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**

708 Variations in the ^{182}Hf - ^{182}W , I-Pu-Xe, and ^{146}Sm - ^{142}Nd isotopic systems in OIBs require
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
712 be the source of the high $^3\text{He}/^4\text{He}$ and the most negative $\mu^{182}\text{W}$ in OIBs (e.g., Jackson et al.,
713 2017; Mundl et al., 2017; Williams et al., 2019; Kim et al., 2019). If, core-mantle interaction
714 supplies high $^3\text{He}/^4\text{He}$ and the most negative $\mu^{182}\text{W}$ signatures (Rizo et al., 2019; Mundl-
715 Petermeier et al., 2020; Peters et al., 2021), then the ULVZs may have formed via interactions
716 with the core. An alternative mechanism to explain variable $\mu^{182}\text{W}$ anomalies in OIB is early
717 silicate differentiation that modified the Hf/W ratios of mantle reservoirs, which subsequently
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
721 The LLSVPs, described as thermochemical piles, may represent relics of magma ocean
722 crystallization after the Moon-forming giant impact (e.g., Labrosse et al., 2007; Lee et al., 2010
723 Ballmer et al., 2017; Gülcher et al., 2020). As noted above, variations in $\mu^{142}\text{Nd}$ measured in a
724 few OIBs suggest that remnants of magma ocean crystallization may be preserved in the deep
725 mantle (Peters et al., 2018). If the Moon-forming giant impact occurred ~ 4.4 - 4.35 Ga, as
726 suggested by studies of both terrestrial and lunar samples (Morino et al., 2017; Borg et al., 2019;
727 Lock et al., 2020), then the ^{182}Hf - ^{182}W system was already extinct, which would leave the ^{182}W

728 isotope composition unchanged by the collision and explain the lack of correlation between
729 $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{182}\text{W}/^{184}\text{W}$ in OIB lavas (except for Réunion lavas; Peters et al., 2021).
730 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
732 material (e.g., Gu et al., 2016; Creasy et al., 2020). Most likely, LLSVPs do not result from a
733 single process, but incorporate material from primordial and early events, ongoing convection,
734 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
749 filaments (Kerr and Mériaux, 2004, Farnetani and Hofmann, 2009).

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 pyrolytic 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
762 more viscous domains (e.g., Ballmer et al., 2017; Gülcher et al., 2020), either because of a silica
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 deep-
767 seated heterogeneities.

768

769 Gülcher et al. (2021, Fig. 6) illustrates the results of numerical simulations of mantle
770 plumes, featuring distinct lithological components: dense recycled basalt and the complementary
771 depleted harzburgitic residue, a rheologically distinct bridgmanitic primordial material, and an
772 ancient FeO-rich basal layer with the same physical properties as basalt. After 4.5 Ga of
773 convection, part of the recycled oceanic crust accumulates at depth and forms large piles, while

774 the remainder is dispersed in the mantle, forming small streaks. The primordial material,
775 intrinsically more viscous, partially survives as distinct "blobs", whereas a fraction of the ancient
776 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
779 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 $^3\text{He}/^4\text{He}$ 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 $^3\text{He}/^4\text{He}$ 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
822 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-
824 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 $\sim 0.5\text{-}2 \text{ Mg s}^{-1}$ 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
848 planetary processes and compositional evolution, offering a rich area for future discoveries.
849 Specifically, systems such as I-Pu-Xe, $^{182}\text{W}/^{184}\text{W}$, and $^{142}\text{Nd}/^{144}\text{Nd}$ have the potential to resolve
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

882 Finally, much is still unknown about the composition of seismically imaged mantle
883 heterogeneities, in both the shallow and deep mantle and how they relate to chemical
884 heterogeneities (e.g., Supplementary Fig. j, with a focus on the Pacific). The spatial differences
885 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
888 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

894 **Acknowledgements**

895 DW acknowledges support from the Natural Sciences and Engineering Research Council of
896 Canada through a Discovery Grant (From mantle geodynamics to environmental processes: a
897 geochemical perspective) and from UBC for the Killam Professorship. KH received support
898 from National Science Foundation grant RUI The Effect of a Mid-Ocean Ridge-Centered
899 Environment on a Zoned Mantle Plume and Associated Secondary Magmatism (NSF award
900 number 2018283). MB received funding from the European Research Council (ERC) under the
901 European Union's Horizon 2020 research and innovation program (Grant Agreement No.
902 682778). CC acknowledges support from ERC (Grant Agreement No. 833632 – Survival of
903 Hadean Remnants in a Dynamic mantle). RP was supported by NSF EAR 2145663.
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
908 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.

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Competing interests

The authors declare no competing interests.

Figures and captions

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

The MilFil volume method calculates the mean depth anomaly within a 500 km diameter circle around a mantle plume, after filtering out small-scale features such as seamounts and islands. The MilFil volume is a proxy for the bathymetric swell generated by the underlying mantle 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 this review. Grey circles: Mantle plumes that lack flux estimates. Basemap: Tomography slice 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). Red regions define the seismically slow Pacific and African-Atlantic Large Low Shear Velocity 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 LLSVPs and how buoyancy flux of mantle plumes varies by orders of magnitude globally.

Figure 1b: Schematic cross-section of the mantle illustrating major mantle structures and 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 with a text box listing the isotopic systems that are especially useful for their identification and tracing (see text descriptions and Supplementary Table 2). Included are a heterogeneous LLSVP (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 that it is visible at the scale of the diagram), are informed broadly by seismic studies (French & Romanowicz 2015; Wamba et al., 2023) and geodynamic results (Farnetani & Samuel, 2005; Davaille, 1999). The slab morphologies are guided roughly by seismic studies (Fukao & Obayashi, 2013; Garnero & McNamara, 2008) and geodynamic results (Jones et al., 2021; Nakagawa & Tackley, 2014). Of particular importance is the contribution of multiple mantle reservoirs, including recycled material, to the sources of mantle plumes.

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

$^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$; (b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$; (c) $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{176}\text{Hf}/^{177}\text{Hf}$; (d) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$. Island chains are classified by their global end-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 the dataset and references are available in the supplementary information). Data density (panels

956 a-d) is contoured and indicates that most oceanic island basalts have contributions from PREMA
957 plus 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 ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$; Hart et al., 1992).

979
980 **Figure 4: Lithium isotope compositions of ocean islands.** (a) $\delta^7\text{Li}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$; (b)
981 Histogram of all current $\delta^7\text{Li}$ 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,
984 as in Fig. 2. OIB Lithium isotope data is from Chan et al., 2003; Kobayashi et al., 2004; Ryan
985 and Kyle, 2004; Nishio et al., 2005; Chan et al., 2009; Vlastélic et al., 2009; Manga et al., 2011;
986 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, Tomasecek 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).
989 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
993 **Figure 5: Use of isotopic systems to detect early Earth reservoirs.** Only major ocean island
994 systems discussed in this manuscript are shown. (a) $^{142}\text{Nd}/^{144}\text{Nd}$ in parts per million (ppm)
995 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.,
997 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
999 reproducibility (2SD) is estimated from repeated measurement of a standard reference material
1000 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) $^{182}\text{W}/^{184}\text{W}$ measured in OIB samples (ppm deviation
1007 relative to terrestrial standard, *Alfa Aesar*). Error bars: 2SE or 2SD for samples. External
1008 reproducibility is $\sim 4\text{--}5$ ppm; large deficits measured in OIB samples can be resolved clearly.
1009 Samples from Baffin Island are not included because ^{182}W results are controversial. The positive
1010 $\mu^{182}\text{W}$ 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.,
1012 2021. Small variations in extinct isotopic systems represent either potential contributions from
1013 early-formed material or core interaction with the plume source.
1014 (c) $^{129}\text{Xe}/^{130}\text{Xe}$ 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 $^{129}\text{Xe}/^{130}\text{Xe} = 7.8$
1017 from MORBs and well gases (Moreira et al., 1998; Holland and Ballentine, 2006; Parai et al.,
1018 2012; Tucker et al., 2012); atmospheric $^{129}\text{Xe}/^{130}\text{Xe} = 6.496$ (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
1022 trending toward atmospheric values) nor incorporation of regassed atmospheric Xe into the
1023 mantle can explain the OIB data arrays in $^{129}\text{Xe}/^{130}\text{Xe}\text{--}^3\text{He}/^{130}\text{Xe}$ space. The low $^{129}\text{Xe}/^{130}\text{Xe}$ 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 λ_{prim}), initially forming a layer of thickness D_{prim} . 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 **Supplementary Tables**

1039 **Supplementary Table 1:** Geochemical characteristics of the major mantle end-members as
1040 defined by Zindler and Hart (1986), adjusted according to subsequent research as cited in the
1041 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
1049 precompiled files for oceanic island groups from GeoRoc and several curated datasets (e.g., [Weis](#)
1050 [et al., 2020](#); [Harpp and Weis, 2020](#); [Harrison et al., 2020](#)). New data downloaded from the
1051 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
1059 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
1062 standardized and imported into R, a free open-source software for statistical computing for
1063 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
1065 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
1069 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
1072 element concentrations, which would skew the average results presented in the extended trace
1073 element spider diagram.

1074

1075 **Supplementary Figures**

1076 **Major and trace element plots for a selection of major oceanic islands. DMM is the**
1077 **depleted MORB mantle; EM-I is enriched mantle I; EM-II is enriched mantle II; HIMU is**
1078 **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
1081 the large number of samples included in the figure (N = 19,691), the data have been contoured,
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 major ocean islands.** Averages were calculated for each oceanic island after
1086 removing all samples with SiO₂ > 55 wt.% and total alkalis (Na₂O+K₂O) < 8 to ensure that
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
1106 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-
1116 slow regions, and blue velocity-fast of the shear velocity (V_s) variations in each model. (b)
1117 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 **Text Box #1**

1120 **Mantle Plume and Large Igneous Province Fundamentals**

1121
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)
1132 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
1137 ascending mantle material ([Montelli et al., 2006](#); [Putirka et al., 2007](#)). Seismic studies of the

1138 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
1149 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
1152 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
1154 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,
1162 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
1173 diameters for 5 and 30% melting respectively) during their emplacement (modified from [Coffin
1174 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 al., 2021](#)).
1178 Variations along the y-axis indicate level of crust contamination, while variations
1179 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
1182 samples ([Doucet et al., 2005](#); [Frey et al., 2002](#); [Yang et al., 1998](#)), with background fields also
1183 shown for Ontong-Java, Deccan, CRFB, and NAIP. Data sources same as in [Pearce et al. \(2021\)](#).

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Text Box #2

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

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 position on the Periodic Table but have different masses. Their relative abundances are measured by a mass spectrometer. Isotopes can be classified into broad categories on the basis of their stability (or lack thereof) and formation pathways.

Radiogenic Isotopes

A radioactive isotope has an unstable atomic nucleus that emits radiation and is spontaneously transformed into another isotope, the radiogenic product. The decay rate of a radioactive isotope is characterized by its half-life, which is the time for a given amount of the parent isotope to decay to half of its initial amount.

Time is the primary variable that generates the observed differences in radiogenic isotopic compositions in geologic settings. For example, geochronology uses two categories of 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., ^{87}Rb , ^{147}Sm) are still decaying today and produce variations in the abundances of daughter products (in this example, ^{87}Sr and ^{143}Nd , which are measured as ratios relative to a stable isotope of the same element, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$) that take millions to billions of years to develop. These isotopic systems are used for geochronology and fingerprinting sources of materials. Conversely, radioactive isotopes with geologically short half-lives have now fully decayed and are extinct. Variations in the radiogenic isotope ratios produced by the decay of isotopes with short half-lives provide information about events that happened in the first few 100 million years, very early in Earth's history.

Neodymium provides a good example of the differences between short and long half-life isotope systems. Neodymium has two radiogenic isotopes (^{142}Nd and ^{143}Nd) produced by the decay of two radioactive isotopes of Sm (^{146}Sm and ^{147}Sm) with very different half-lives: 103 Myr and 106 Gyr. Therefore, the two isotopic systems display isotopic variations that reflect entirely different processes; the ^{146}Sm - ^{142}Nd system tracks the presence of early Earth material and the ^{147}Sm - ^{143}Nd system documents long-term source changes. Whereas the ^{147}Sm - ^{143}Nd system has been analytically accessible since the 1980s, the variations in ^{142}Nd due to ^{146}Sm decay are so small that measuring $^{142}\text{Nd}/^{144}\text{Nd}$ is almost at the limit of the current analytical capabilities of modern mass spectrometers, and only achievable since 2000.

Contrary to trace elements (i.e., elements that constitute less than 0.1 wt% of a rock or magma), radiogenic isotopic compositions are not affected by the degree of partial melting or the crystallization history of a melt. Radiogenic isotopic ratios (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^4\text{He}/^3\text{He}$ or $^{177}\text{Hf}/^{176}\text{Hf}$) of a basalt are therefore representative of the composition of the material that melted to produce the basalt. Consequently, they provide time-integrated information about its origin. In contrast, variations of extinct radiogenic isotopic systems (e.g.,

1229 $^{142}\text{Nd}/^{144}\text{Nd}$, $^{182}\text{W}/^{184}\text{W}$, $^{129}\text{Xe}/^{130}\text{Xe}$) indicate the presence of material that differentiated from
 1230 the rest of the mantle during accretion.

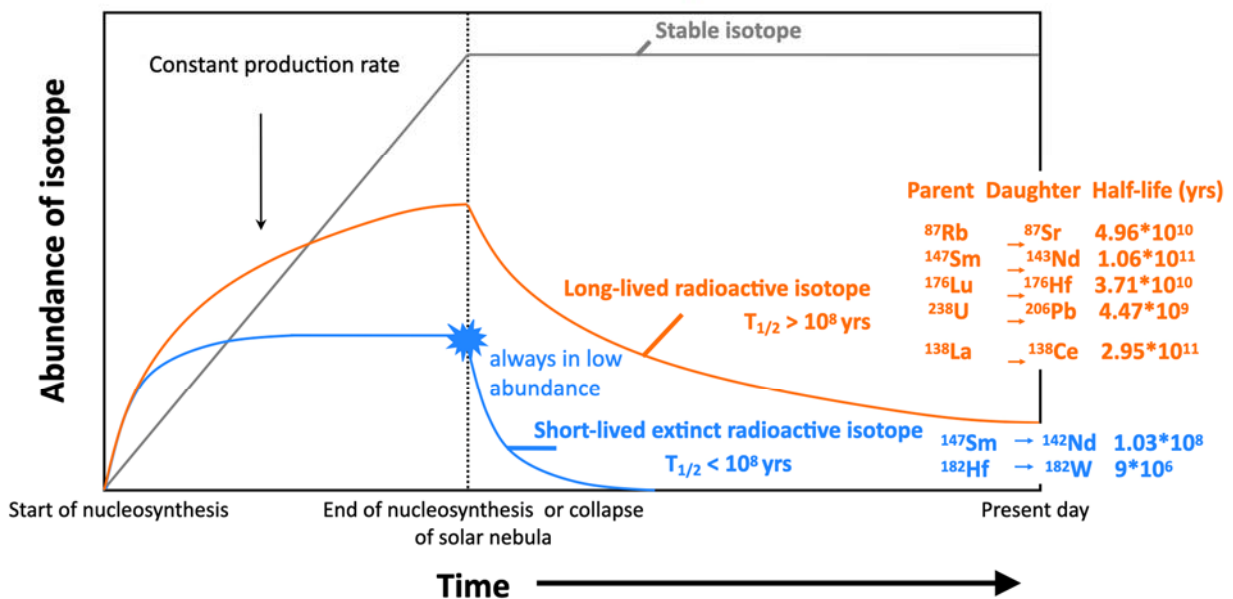
1231

1232 **Stable Isotopes**

1233 Stable isotopes 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
 1235 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

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
 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-
 1251 radiogenic normalizing isotopes used in other decay systems (e.g., ^{204}Pb). Accordingly, recent
 1252 noble gas studies report He isotope ratios as $^4\text{He}/^3\text{He}$ to be consistent with radiogenic isotope
 1253 convention. By contrast, ^4He is continuously produced by radioactive decay of ^{235}U , ^{238}U , and
 1254 ^{232}Th (among other radioactive isotopes; ^4He is simply the alpha particle produced in these
 1255 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

1257 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
1260 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
1262 into the mantle via subducted slabs. Regassing of He is negligible as it is light enough to escape
1263 the atmosphere. Atmospheric contamination during or after sample formation affects Ne, Ar, Kr
1264 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**

1269
1270 The measurement and the interpretation of isotopic variations measured in OIB require careful
1271 attention. For example, determinations of $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{182}\text{W}/^{184}\text{W}$ ratios are mainly
1272 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
1274 indicate that analytical artifacts can produce small isotopic variations in TIMS measurements,
1275 which are linked to: 1) problematic mass-dependent fractionation correction when isotopic ratios
1276 do not follow the exponential law (Upadhyay et al., 2008); 2) inappropriate mass fractionation
1277 correction when the rate of mass fractionation is too high for dynamic measurements (Roth et al.,
1278 2014); 3) mixing of different sample reservoirs on the filaments (Upadhyay et al., 2008, Roth et
1279 al., 2014); 4) non-mass dependent isotopic variations (nuclear field shift) caused by the chemical
1280 separation protocol (Garçon et al., 2018; Kruijer and Kleine, 2018; Saji et al., 2016); and, just for
1281 the W system, 5) the need to improve the determination of O isotope composition for W isotope
1282 measurements done in oxide form by TIMS (Trinquier et al., 2016). Because deviations in the
1283 $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{182}\text{W}/^{184}\text{W}$ systems are small, they are expressed in μ -notation (deviation in parts
1284 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 $^{142}\text{Nd}/^{144}\text{Nd}$ 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
1291 ratios of the element to be determined in dynamic mode, with subsequent application of quality-
1292 control 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 $2\text{SE} =$
1296 $2\text{SD}/\sqrt{N}$, 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
1298 has debated the significance of a deviation relative to its analytical precision extensively, without
1299 a clear resolution. Regardless of the choice of 2SD or 2SE, publications claiming high-precision
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
1304 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
1308 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
1310 isotopic measurements are sensitive to the presence of ferromanganese precipitation. These
1311 secondary components must be removed by physical separation and cleaning followed by
1312 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
1315 represent the original magmatic isotopic signatures representative of the magma source
1316 composition.

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-
1324 daughter ratio of the unleached sample. For the U-Th-Pb system in particular, care must be taken
1325 to estimate the primary U concentration in submarine OIB properly, as U 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 **Analytical Consistency and Comparability Between Labs**

1329 A particularly problematic challenge in OIB studies (and in any study where the objective is to
1330 determine the source compositions of rocks) involves comparison of data generated in different
1331 analytical laboratories on the same samples. To compare isotopic compositions generated using
1332 different instruments and methods (e.g., TIMS, MC-ICP-MS) and in different laboratories,
1333 geochemists use a normalization scheme based on published values for standards and reference
1334 materials (e.g., Weis et al., 2011, 2020). For robust comparisons, it is essential to perform careful
1335 normalization to the same standard and reference values. Otherwise, the data are not comparable
1336 and spurious correlations may occur.

1338

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