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1 **Dynamical Geochemistry: Mantle dynamics and its role in the formation of geochemical** 2 **heterogeneity**

3
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12 13 **Abstract**

14 Chemical geodynamics is a term coined nearly forty years ago to highlight the important link
15 between Earth's geochemical evolution and plate tectonics & mantle convection. Significant
16 progress in our understanding of this connection has taken place since then through advances
17 in the analytical precision of geochemical measurements; dramatically improved geophysical
18 imaging techniques; application of novel isotope systems; and great advances in computational
19 power. The latter especially has improved geodynamical models and data interpretation
20 techniques. We provide a review of these advances and their impact on chemical geodynamics,
21 or perhaps, dynamical geochemistry. To focus this review we will address primarily the role of
22 whole mantle convection and oceanic crust formation and recycling together with an update on
23 our understanding of noble gas systematics.

24 **Keywords**

25 Plate tectonics, mantle convection, geochemical evolution of Earth's crust and mantle

26 **Glossary and nomenclature**

27 MORB(s) – Mid-Oceanic Ridge Basalt(s)

28 OIB(s) – Ocean Island Basalt(s)

29 HW82 – Hofmann and White (1980, 1982)

30 EM1 – Enriched Mantle component 1

31 EM2 – Enriched Mantle component 2

32 HIMU – OIB component with high original $\mu=U/Pb$

33 LLSVPs – Large Low Shear Velocity Provinces

34 ULVZ – Ultra Low Velocity Zone

35 BSE – Bulk Silicate Earth

36 CHUR – CHondritic Uniform Reservoir

37

38

39 1. Introduction

40

41 Early observations of heterogeneity in lithophile isotopes measured in mid-oceanic ridge basalts
42 (MORBs) and ocean-island basalts (OIBs) led to the conceptual idea of a layered mantle
43 system. In this model, the upper mantle is depleted by prior extraction of the continental crust
44 and OIBs are explained by mixing between the depleted mantle and a lower mantle that has
45 been largely isolated from plate tectonics and mantle convection (e.g., DePaolo and
46 Wasserburg, 1976; O’Nions et al., 1979; Allègre et al., 1979). Noble gas systematics appeared
47 to provide strong support for such a layered system. For example, the $^3\text{He}/^4\text{He}$ measurements
48 in OIBs are wide-ranging whereas the ratio is relatively uniform in MORBs (e.g., Barfod et al.,
49 1999; Figure 1a). In addition, the fundamental observation that ~50% of ^{40}Ar that has been
50 produced from ^{40}K decay resides presently in the atmosphere and upper mantle concentrations
51 are low, was fully consistent with a lower mantle that is a largely undegassed reservoir (Hart et
52 al., 1979; Allègre et al., 1996).

53

54 Lithophile isotope ratios in OIBs and MORBs suggest mixing trends between various
55 components such as the two Enriched Mantle components (EM1 and EM2), HIMU (which is
56 formed from material that had high original $\mu=U/Pb$), and MORB. From some perspectives these
57 mixing trends seem to converge (Figure 1b) on a FOcal ZONE (FOZO; Hauri et al., 1994)
58 (alternatively called ‘C’ for Common component or PREMA for PREvalent MANTle; Zindler and
59 Hart, 1986; Hanan and Graham, 1996) which paradoxically has relatively high $^3\text{He}/^4\text{He}$ but
60 appears depleted in other regards (see discussion in van Keken et al., 2001). It should be noted
61 that the layered mantle hypothesis, in which the upper mantle is primarily composed of well
62 mixed MORB-source material with the lower mantle supplying the poorly mixed OIB
63 components, is at least somewhat contradicted by global observations of isotopic heterogeneity.
64 Lead isotope systematics, for example, show an OIB spread of data that is somewhat more
65 diverse, but largely overlaps with the MORB data (compare Figure 1c and 1d which are redrawn
66 on the same scale from Hofmann, 2014).

67

68 Hofmann and White (1980, 1982; hereafter called HW82) provided a striking counterview to the
69 layered convection hypothesis by suggesting that the long term formation of oceanic crust and
70 its recycling and sequestration in the deeper mantle could explain the observed isotopic
71 heterogeneity (Figure 2a). It is useful to quote the abstract of Hofmann and White (1982) in its
72 entirety:

73

74 *We propose the following model for the origin of “hot-spot” volcanism: Oceanic*
75 *crust is returned to the mantle during subduction. It is separated from the*
76 *surrounding peridotite, it sinks into the deeper mantle and accumulates at some*
77 *level of density compensation, possibly the core-mantle boundary. The*
78 *accumulated layer locally reaches thicknesses exceeding 100 km. Eventually, it*
79 *becomes unstable as a consequence of internal heating, and the resulting diapirs*
become the source plumes of ocean island basalts (OIB) and other hot-spot

80 *volcanism. This mechanism may trigger upper mantle convection as suggested*
81 *by Morgan [1]. Our model provides possible explanations for (1) the high trace*
82 *element concentrations of OIB, (2) the seemingly contradictory isotopic evidence*
83 *for both enrichment and depletion of magmaphile elements in OIB sources, (3)*
84 *the phenomenon of apparent mantle isochrons in oceanic basalts, and (4) the*
85 *apparently episodic nature of continental igneous activity. The model can be*
86 *tested further, as more knowledge accumulates about the actual bulk*
87 *composition of the oceanic crust, including its alteration products and sediment*
88 *cover.*

89
90 In this review we have two main goals. The first is to address how the HW82 hypothesis has
91 been tested and expanded upon by geochemical, geophysical, and geodynamical studies. The
92 second is to provide an update on our understanding of noble gas systematics and how they
93 constrain the evolution of the Earth's interior.

94
95 This review chapter is not intended to capture all advances in “chemical geodynamics” (Zindler
96 and Hart, 1984) that have been made since the publication of HW82. Rather, it will provide an
97 exploration of how well main hypothesis in HW82 has stood the test of time amidst new
98 geochemical techniques & observations and abundant geophysical evidence for heterogeneity
99 in the lowermost mantle. Previous reviews that further explored chemical geodynamics in a
100 broader sense are provided by van Keken et al. (2002), G.F. Davies (2011), and Tackley
101 (2015). Basic descriptions of mixing processes that lead to the formation and destruction of
102 geochemical heterogeneities are in Kellogg (1992), van Keken et al. (2003), and van Keken
103 (2013). A review linking mantle mixing with possible seismic observations is in Stixrude and
104 Lithgow-Bertelloni (2012). Updated overviews of the geochemical observations in MORBs and
105 OIBs are in Stracke et al. (2005), Hofmann (2014), Hanyu and Chen (2021) and Weis et al.
106 (2023). Finally, overviews of the nature of LLSVPs and their geophysical relationships to
107 oceanic crust recycling are provided by McNamara (2019) and M. Li (2021).

109 2. Geophysical implications of long-term oceanic crust recycling.

110 2.1 Recycling of oceanic lithosphere and the formation of LLSVPs

111 We will take the viewpoint that plate tectonics has been in operation for most of Earth's history.
112 The long-term formation of chemically heterogeneous oceanic lithosphere at mid-oceanic ridges
113 and its recycling at subduction zones may provide a natural explanation of the formation of the
114 Large Low Shear Velocity Provinces (LLSVPs) that are seen at the base of the Earth's mantle.
115 A simple calculation adds quantitative support to this hypothesis. Reymer and Schubert (1984)
116 suggest 675 km³/km/Myr of oceanic crust is being subducted. With a total length of 37,000 km
117 of destructive plate margins and an age of 4.5 Gyr for the Earth we find that 1.1×10¹¹ km³ of
118 crust has been recycled. This is 13% of the volume of the mantle. The total volume of the

¹ Morgan W.J., 1971. Convection plumes in the lower mantle. Nature 342, 42-43.

119 LLSVPs has recently been estimated to be about 8% of that of the mantle (Cottaar and Lekic,
120 2016). Since the LLSVPs are not composed of pure oceanic crust but of a mixture of oceanic
121 crust, harzburgite, and ambient mantle there appears to be a more than sufficient amount of
122 oceanic crust has been recycled to allow for gradual but steady re-entrainment of oceanic crust
123 from the piles. A corollary of this back-of-the-envelope computation is that with an average melt
124 fraction of 10-20% the oceanic crust production estimate suggests between 65–130% of the
125 mantle has been processed at a mid-oceanic ridge. Since parts of the mantle will be processed
126 more than once, it seems very unlikely that the whole mantle will have lost its primitive signal by
127 surface melting.

128
129 A first convincing dynamical model that shows the formation of LLSVP-like structures due to
130 recycling of oceanic lithosphere with dense crust was provided by Christensen and Hofmann
131 (1994; Figure 2d). Computational limitations at the time restricted their models to lower
132 convective vigor than present day's but a scaling argument allowed them to extrapolate their
133 results to realistic convective vigor. This enabled them to determine that the accumulated
134 oceanic crust imparted a chemical signature on the model that is similar to that observed in Nd-
135 Pb and Pb-Pb data with a pseudo-isochron of 2.1 Gyr. Brandenburg and van Keken (2007)
136 confirmed these models and were able to use Earth-like convective vigor that led to similar
137 findings. Significant other work that shows the possibility of long-term oceanic lithosphere
138 recycling causing LLSVPs is provided in G.F. Davies (2002), Brandenburg et al. (2008; Figure
139 2b), Nakagawa et al. (2012; Figure 2c), Mulyukova et al. (2015), Huang et al. (2020), Jones et
140 al. (2021; Figure 2e), M. Li and McNamara (2022), and Panton et al. (2023).

143 2.2 Seismological observations

144 2.2.1 Tomography

145
146 Indications for large scale compositional heterogeneity in the deep mantle are seen in the
147 earliest tomographic models that used low-order spherical harmonics (e.g., Dziewonski et al.,
148 1977; Dziewonski, 1984; Woodhouse and Dziewonski, 1989). Significant improvements in
149 seismic tomography have allowed convincing imaging of two nearly anti-podal LLSVPs which
150 are dominant in all modern tomographic models (see reviews in Garnero et al., 2016, and
151 Cottaar and Lekic, 2016). A common interpretation of these regions is that they are both warmer
152 and denser than ambient mantle, forming long-lived thermochemical piles that are formed either
153 from primordial heterogeneity that has not been fully entrained by mantle convection, subducted
154 oceanic lithosphere, where the eclogitic nature of the oceanic crust causes the high density, or a
155 combination thereof. Mantle convection modeling lends support to such an interpretation where
156 continuous thermochemical piles are kept in shape by surrounding downwellings (see
157 discussion in Garnero et al., 2016). An interesting contrasting interpretation from the full
158 waveform modeling based tomographic model SEMUCB-WM1 (French and Romanowicz, 2014)
159 is that the features that make up the LLSVPs appear to be clusters of thermochemical plumes,
160 rather than continuous piles (Davaille and Romanowicz, 2020). Of course, the chemically

161 distinct material in this interpretation could remain composed of recycled oceanic lithosphere
162 with denser oceanic crust.

163 Seismic tomography approaches can be combined or augmented with other geophysical
164 constraints to confirm the high density of the LLSVPs. For example, Ishii and Tromp (1999)
165 showed by incorporating free-air gravity measurements that the density is higher in the regions
166 of lower P- and S-wave velocity, suggesting a thermochemical origin for the LLSVPs. Employing
167 the sensitivity of Earth's diurnal tides to the density distribution in the mantle, Lau et al. (2017)
168 showed that the LLSVPs have an average density contrast with the ambient mantle of 0.5-0.8%.

169 It has become possible to use sensitivity kernels developed for some tomographic
170 models, such as S20RTS (Ritsema et al., 1999) and S40RTS (Ritsema et al., 2011), to explicitly
171 test whether a certain dynamical model, after mapping temperature and composition to seismic
172 velocities, can reproduce the features seen in the tomographic models. An early example is in
173 Bull et al. (2009) who argued that thermochemical piles fit the observed characteristics better
174 than plume clusters. A counterpoint was provided by Schubert et al. (2009) and D.R. Davies et
175 al. (2012) who argued for a purely thermal origin of the LLSVPs. Recently, Jones et al. (2020)
176 showed that the long-term oceanic crust recycling as in the models of Brandenburg et al. (2008)
177 could reasonably explain the imaged velocity contrast and extent of the two LLSVPs in S40RTS
178 if the density contrast between oceanic crust and ambient mantle was 3.8% or higher. Similarly,
179 the spectral content of the filtered geodynamical models appears similar to that in S40RTS for
180 higher density contrasts, but not when the density contrast between oceanic crust and mantle is
181 low (see Figure 5 in Jones et al., 2020). Since the thermochemical piles in these models are
182 mixtures of oceanic crust, depleted mantle, and ambient mantle, the density contrast between
183 crust and mantle should not be taken to be representative of the density contrast between
184 LLSVP and ambient mantle – clearly this contrast will be significantly lower.

185 2.2.2 Scattering

186 High-frequency waveform analysis allows for the determination of compositional heterogeneity
187 in the deep mantle at much higher resolution than what seismic tomography can provide (see
188 review in Kaneshima, 2016). Scattered wave energy in the lower mantle generally is interpreted
189 as being caused by subducted oceanic crust. For example, Kaneshima and Helffrich (2009)
190 observed clusters of scatterers below Pacific subduction zones at depths of 1100–1800 km that
191 could be explained by seismically distinct basalt layers in folds with spacing of 100–200 km,
192 which is similar to what we expect for coherent slabs in the early stages of folding. Other recent
193 evidence from scattering for the presence of coherent oceanic crust in the lower mantle below
194 subduction zones is provided by, e.g., He and Zheng (2018), Zhang et al. (2020), and Ritsema
195 et al. (2020).

196 Haugland et al. (2018) provided a direct test whether long-term recycled oceanic
197 lithosphere characterized by a denser basalt component could explain PKIKP precursors that
198 are related to scattering of PKP waves by heterogeneity in the deep mantle. They used the
199 models of Brandenburg et al. (2008) to predict P-wave velocity perturbation and modeled
200 seismic wave propagation using the axisymmetric waveform modeling method AxiSEM (Nissen-
201 Meyer et al., 2014). They showed that models where the oceanic crust had the same density as
202 the surrounding mantle could not explain the PKIKP precursors but that models where the
203 oceanic crust had an excess density could. They only investigated the latter in a model where

204 the oceanic crust had an excess density with respect to that of the depleted harzburgitic
205 component of 7%. This translates to an excess density of the crust with respect to 'normal'
206 peridotitic mantle of 4.3% (see discussion in Jones et al., 2020). Frost et al. (2017, 2018) also
207 studied scattering of PKP waves and showed that scattering intensity increased in the
208 lowermost 1000 km of the mantle and that the scattering intensity was correlated with regions of
209 low seismic velocity with some stronger scattering near the edges of the LLSVPs, which they
210 explained with a model where oceanic crust accumulates on the sides of piles of pre-existing
211 heterogeneity. Hiemer and Thomas (2022) observed scattering at the bottom 200–400 km of the
212 mantle below the mid-Atlantic and determined from comparison with synthetic models that the
213 scatterers had a correlation length of 10 km and velocity contrast of 5% which could be caused
214 by subducted oceanic crust, although their work could not distinguish this from other potential
215 features in D" such as Ultra Low Velocity Zones (ULVZs) with an iron-rich post-perovskite
216 component (see Ma and Thomas, 2020 and references therein) or melt pockets (Hedlin and
217 Shearer, 2000). Kaneshima (2023) demonstrated the presence of scatterers in the transition
218 zone and lower mantle below the Samoan hotspot that is interpreted as caused by basaltic
219 materials entrained in the Samoan plume rising from the Pacific LLSVP.
220

221 2.3 Entrainment of dense lower mantle piles by plumes

222
223 The HW82 hypothesis relies on the return of the matured oceanic crust to the Earth's surface,
224 which requires either slow entrainment by large scale mantle convection or direct entrainment in
225 mantle plumes rising from the LLSVPs. Since plumes are generally associated with the
226 transport of heat and geochemical heterogeneity from the deep Earth, the latter mechanism
227 may be the most direct and efficient, but this also requires that thermal plumes are capable of
228 entraining the dense material. Significant work in the last two decades has studied the
229 interaction of a dense layer at the base of the mantle with thermal plumes rising from it. This has
230 demonstrated that plumes are strongly modified from the classical mantle plume shapes seen in
231 early, and inspiring, laboratory experiments (e.g., Griffiths and Campbell, 1990). Farnetani and
232 Samuel (2005) suggested we should abandon the thermal plume paradigm in favor of seeing
233 plumes as complex geometrical entities. Lin and van Keken (2005; 2006a; 2006b) showed that
234 the interaction between thermal and (negative) compositional buoyancy leads to time-
235 dependent effects in axisymmetric spherical plumes that could explain temporal variations in
236 ocean island chain volcanism but also that plumes might stall at depth due to an effective
237 neutral buoyancy, a mechanism also demonstrated by Samuel and Bercovici (2006). Dannberg
238 and Sobolev (2015) showed how the effect of entrainment of eclogite could cause large plumes
239 that would not cause significant uplift, possibly explaining the formation of large igneous
240 provinces, a mechanism demonstrated earlier by Lin and van Keken (2006b).

241 The numerical studies above are complemented by laboratory studies. While perhaps
242 not every Earth-like scenario can be simulated in a laboratory, these models certainly have the
243 advantage that they, by their very nature, accurately satisfy the governing principles of
244 conservation of mass, momentum, and energy. These same principles form the basis of partial
245 differential equations that are solved using approximate methods in numerical studies. Figure 3a
246 shows the now classic example of rising thermochemical plumes from Kumagai et al. (2008).

247 The orange layer has a higher density and temperature is indicated by the lighter contour lines
248 (that are formed by crystals in the fluid that turn opaque over a narrow temperature range). The
249 relative density contrast between the dense layer and the thermal effect is indicated by the
250 buoyancy number B which increases from left to right in Figure 3a. The buoyancy number is the
251 ratio of the estimated chemical buoyancy divided by the estimated thermal buoyancy, that is,
252 $B = \Delta\rho / (\rho \alpha \Delta T)$ where $\Delta\rho$ is the compositional density contrast, ρ is the density of the ambient
253 fluid, α is the thermal expansivity, and ΔT is the temperature contrast across the bottom
254 boundary layer. This provides a clear demonstration that the plumes rise easily with a
255 compositional component at low $B < 0.3$, that plumes can stagnate at intermediate B (0.3–0.9),
256 and that plumes rise again as thermal plumes leaving the dense layer behind at high $B > 1$.
257 Given that the estimated chemical excess density from seismological observations and from
258 numerical experiments is $\sim 1\%$, it follows (with the reasonable values $\alpha = 2 \times 10^{-5}/\text{K}$ and
259 $\Delta T = 1500 \text{ K}$) that $B \sim 0.33$, suggest plume entrainment of the dense material is moderately
260 efficient.

261
262 Some detailed comparisons between laboratory and numerical experiments exist that give us
263 confidence that these approaches provide quantitative information about thermochemical
264 plumes rising through the Earth's mantle. Early comparisons between laboratory and numerical
265 experiments of thermal plumes showed good general agreement if the right laboratory
266 conditions were taken into account (van Keken, 1997). A detailed study comparing thermal
267 plumes with finite element methods using an axisymmetric cylinder geometry was provided by
268 Vatteville et al. (2009) showing excellent agreement in the evolution of the temperature and
269 velocity fields. Figure 3b shows one example that is similar to the first frame in Figure 3a. Minor
270 differences in the detailed temporal evolution that were left unexplained were resolved by
271 modeling of the plumes in the actual 3D Cartesian box geometry of the laboratory experiment
272 (D.R. Davies et al., 2011) showing that accurate implementation of the boundary conditions in
273 Stokes flow remains important. To our knowledge there are no such detailed comparisons
274 available for thermochemical plume simulations, but a comparison between the existing models
275 of Kumagai et al. (2008) and Lin and van Keken (2006b) provides at least good quantitative
276 agreement (compare Figure 3 frames c1 and c2 with frames of the Kumagai experiments that
277 are obtained at similar buoyancy number as those in the numerical experiments.)

278

279 3. Geochemical consequences: the lithophile element/isotope perspective

280

281 When Hofmann and White suggested in 1982 that recycled oceanic crust played a crucial role in
282 the origin of plume generated magmas, their main argument was that ocean island basalts are
283 rich in very incompatible elements and such enrichments cannot be produced by melting of a
284 normal peridotite source. Indeed, to reproduce the light rare earth content of OIB requires very
285 small and in some cases impossibly small degrees of melting (Gast, 1968) if the source is
286 assumed to be the same as that of mid-oceanic ridge basalts. At that time, the number of
287 radiogenic isotopic data for OIB was very small and most of them had values intermediate
288 between a depleted mantle, MORB source, and a non-differentiated reservoir often called

289 CHUR (CHondritic Uniform Reservoir) or BSE (Bulk Solid Earth). However, few ocean islands
290 had Sr and Nd isotopes that required the presence in their source of material more enriched
291 than BSE, an observation that weakened the generally accepted model of mixed MORB source
292 (upper mantle) and BSE source (lower mantle) for plume magmatism, and provided support for
293 HW82.

294

295 The evidence for the presence of recycled oceanic material in the mantle has now grown
296 drastically and is not necessarily limited to the source of ocean island basalts. This includes
297 evidence from the major and trace element concentrations, evidence from the radiogenic
298 isotopes but also evidence from traditional and non-traditional stable isotopes.

299

300 From a major and minor elements point of view, several authors (for example, Hauri, 1996;
301 Hirschmann and Stolper, 1996; Kogiso et al., 1997) demonstrated early on that the presence of
302 recycled oceanic crust could explain the main geochemical and petrological features of intra-
303 plate volcanism but also that of mid-oceanic ridges. However, a big step forward happened
304 when Sobolev et al. (2005) highlighted that the high nickel and silica contents of Hawaiian lavas
305 could not result from simple melting of a peridotite source. Instead, they suggested that in a
306 rising plume a recycled oceanic crust present as eclogite reacts with the surrounding peridotite
307 to produce a pyroxenite that in turn melts when approaching the lithosphere under Hawaii. In
308 the case of Hawaii, the proportion of recycled crust in the plume source was estimated at about
309 20% but in other cases, the proportion of recycled crust can be much lower. For example, it is
310 estimated to be ~10% for Iceland (Sobolev et al., 2007) and ~5% for Gambier in the Pitcairn
311 chain (Delavault et al., 2015). While such interpretation is generally well accepted by the
312 community, alternative views have also been provided (see, for example, Herzberg et al., 2014,
313 or Weiss et al., 2016).

314

315 The clearest geochemical indices of the presence of recycled oceanic crust (which generally
316 includes a sedimentary cover) comes from the radiogenic isotopes because sediments have
317 both isotopic compositions and trace element contents that differ drastically from those of the
318 mantle. Indeed, the presence of few percent of sediment in the source of an OIB has a
319 significant effect on the isotopic composition of the lavas. The best example was published by
320 M.G. Jackson et al. (2007; Figure 4a). They demonstrated that the presence of 6% sediment in
321 the mantle source of some Samoa lavas shifted their Sr isotopic composition from 0.704 to
322 extreme values (~0.720) not measured in any other OIB. However, most EM2 basalts have
323 significantly lower radiogenic Sr isotope ratios than those detected in Samoan lavas, but their Sr
324 isotopic composition still requires a sediment contribution up to 2%. Altogether, the community
325 agrees that most OIBs with radiogenic Sr coupled to unradiogenic Nd and Hf must come from a
326 source containing some recycled sedimentary material (for a review see Stracke, 2012). Other
327 evidence for the presence of recycled sediments comes from the relationship between Nd and
328 Hf isotopes in ocean islands (see figure 4c and Chauvel et al., 2008) because mixing recycled
329 basaltic crust and depleted mantle creates an array that is not consistent with the known OIB
330 array. A small but significant proportion of sediment is required to reproduce the OIB mantle
331 array (Figure 4b).

332

333 Evidence for the presence of recycled basaltic crust without sediment is only found in the so-
334 called HIMU ocean islands (Figure 4b). Their very radiogenic Pb isotopes require a large
335 increase of their U/Pb and Th/Pb ratios about 2 Gyr ago, an increase that is most easily
336 explained by the loss of Pb during dehydration of the basaltic crust in the mantle wedge of
337 subduction zones. Basaltic crust recycled more recently than 2 Gyr ago is more difficult to
338 identify from a radiogenic isotopes point of view because there is not enough time for the
339 change in parent-daughter ratio to have an impact on the daughter isotopic ratio (Figure 4b).
340 The consequence is that any recycled basaltic crust younger than 1.5 Gyr ago has Pb isotopic
341 ratios that are subdued and difficult to identify and the presence of significant amounts of such
342 material in the mantle cannot be pinned down from a radiogenic isotope perspective.

343
344 From a trace elements point of view, evidence for the presence of recycled crust in the source
345 of mantle magmas includes of course the enrichment in incompatible trace elements of OIB,
346 enrichment impossible to produce by simple melting of the mantle. Other evidence is more
347 subtle and highlights the involvement of sedimentary material associated to the subducted
348 basaltic crust and present in the material recycled in the mantle. The clearest cases are the
349 deviation from mantle values of ratios of cerium to lead (Ce/Pb) and niobium to uranium (Nb/U).
350 Indeed, Hofmann et al. (1986) demonstrated that MORB and OIB shared constant Ce/Pb (25 ± 5)
351 and Nb/U (47 ± 10) but these 'canonical' values are very different from both BSE (Ce/Pb=9 and
352 Nb/U=30) and Continental Crust (Ce/Pb=4 and Nb/U=10). Such constancy implies that Ce and
353 Pb on one hand, and Nb and U on the other, have similar incompatibilities during mantle
354 melting. Any deviation from the canonical values requires that material with an exotic origin is
355 present in the source of the volcanics. If OIB volcanics have a Ce/Pb and/or Nb/U ratio lower
356 than the canonical values, it potentially suggests that continental material contributes to the
357 source of the lavas. Qualitatively, material with a primitive mantle origin would also lower the
358 two ratios but mass balance calculations show that the proportion of BSE required to modify
359 Ce/Pb or Nb/U is much larger than if the material is of crustal origin. Few OIBs have lower than
360 average Ce/Pb and Nb/U and those include several islands in the Polynesian archipelagos
361 (Society: White and Duncan, 1996 and Cordier et al., 2021; Marquesas: Chauvel et al. 2012;
362 Pitcairn-Gambier: Cordier et al., 2021) but also islands in the Samoa chain (M.G. Jackson et al.,
363 2007). Among mid-oceanic ridge basalts, the Central Indian ridge also stands as an exception
364 with its slightly lower than average canonical ratios (Rehkämper and Hofmann, 1997)
365 suggesting the presence of poorly mixed recycled sediments in that part of the upper mantle. At
366 the other end of the spectrum are found few islands with higher than average ratios. We can cite
367 here St. Helena in the South Atlantic, several islands along the Austral and Pitcairn chains, and
368 lavas from the Canaries.

369
370 Traditional and non-traditional stable isotopes also prove useful in tracing in plume sources the
371 presence of material that once was at the surface of the Earth. The most convincing evidence
372 comes from sulfur isotopic analyses of some ocean islands. Indeed, prior to the Great Oxidation
373 Event 2.4 Gyr ago, the atmosphere was not as oxygen rich as today and material formed at the
374 surface of the Earth had sulfur isotopic compositions that deviated from a mass fractionation line
375 (Farquhar et al., 2007). Cabral et al. (2013) found that such mass-independent fractionation
376 occurred in sulfides present in lavas from Mangaia island. Delavault et al. (2016) reported even

377 larger anomalies in samples from Pitcairn seamounts (Figure 5). The presence of such
378 anomalies in present-day volcanics requires the existence in their source of material that not
379 only was present at the surface of the Earth at some stage but also that this material is older
380 than 2.4 Gyr ago.

381
382 Other potential indices of the presence of surface material in the source of OIB can be found in
383 the isotopic compositions of lithium or thallium, two elements that are significantly fractionated in
384 low temperature environments (see, e.g., Penniston-Dorland et al., 2017, Rehkämper et al.,
385 2002 and Nielsen et al., 2017) but not in mantle conditions. For example, lithium isotopic
386 heterogeneities have been reported for islands such as Hawaii, Rurutu, St. Helena, and the
387 Azores (Chan and Frey, 2003; Vlastélic et al., 2009; Krienitz et al., 2012; L.N. Harrison et al.
388 2015) and large and significant variations of thallium isotopes have been reported by several
389 groups (Blusztajn et al., 2018; Brett et al., 2021; Williamson et al., 2021). Finally, elements such
390 as magnesium or calcium are not diagnostic because the isotopic variability is small among OIB
391 but the fact that their isotopic ratios are not constant suggests that heterogeneities produced at
392 the Earth's surface might be integrated in their source deep in the mantle (see Teng, 2017, and
393 review by Soderman et al., 2022).

394

395 4. Geochemical consequences: noble gases and volatiles

396 4.1 Foundational context

397
398 The inert, or noble, gases have provided an observational cornerstone in our determination of
399 the geochemical origins and geodynamic evolution of the Earth's silicate mantle (see reviews
400 by, e.g., Porcelli and Ballentine, 2002; Ozima and Podosek, 2002; Moreira, 2013; Péron et al.,
401 2018; Mukhopadhyay and Parai, 2019). Noble gases in the Earth's mantle can be grouped into
402 four types: i) those trapped during the Earth's accretion; ii) those formed by the decay of extinct
403 radionuclides (^{244}Pu , ^{129}I) in the early history of the Earth; iii) gases generated by the decay and
404 interaction from extant radionuclides over Earth history (e.g. U, Th, K); and iv) atmospheric
405 noble gases recycled into the mantle. Each has a distinct and resolvable isotopic signature
406 within the 23 stable isotopes that form the noble gas system. The varying proportions of these
407 different noble gas components found in different mantle samples and their geological and
408 tectonic contexts provide a unique insight into the dynamics of the mantle that have preserved
409 these volatile records and variably mixed them over Earth history.

410
411 The ground breaking recognition of a primordial ^3He signature in volcanic gases and seawater
412 (Mamyrin et al., 1969; Clarke et al., 1969) identified this as a volatile gas that was incorporated
413 into the Earth during its accretion. Since helium is lost by Jeans' escape (Jeans, 1925), the
414 Earth's atmosphere has a distinct $^3\text{He}/^4\text{He}$ isotopic composition ($1.4 \times 10^{-6} = 'R_a'$) and low
415 concentration (5.4 ppm) compared to other volatiles. This results in both low contamination of
416 helium in mantle samples by seawater or atmosphere exposure during eruption or degassing,

417 and negligible recycling back into the mantle; simplifying its interpretation as a 'primordial' gas
418 trapped during the accretion of Earth.

419
420 Primordial ^3He together with ^4He that is generated by the decay of U and Th means that the
421 $^3\text{He}/^4\text{He}$ isotopic composition of the mantle evolves as a function of time through the evolution of
422 $^3\text{He}/(\text{U}+\text{Th})$ and convective mixing. Mantle $^3\text{He}/^4\text{He}$ and its variance provides an unprecedented
423 insight into the interaction of the chemical reservoirs in the Earth's mantle. Indeed, the
424 observation that plumes forming oceanic islands sample a portion of the mantle with a higher
425 $^3\text{He}/^4\text{He}$ than the mantle supplying mid-oceanic ridges demands long-lived chemical
426 heterogeneity within the mantle system (Kurz et al., 1982; Allègre et al., 1987)

427
428 With mantle-derived helium readily resolved in ocean water, gas residence and the distribution
429 of ^3He in the oceans provide an estimate of the present day helium (^3He and ^4He) degassing
430 flux (1060 mol ^3He per year; Lupton & Craig, 1975; Farley et al., 1995). Combined with the
431 ocean crust formation rate (20 km³/yr) and average partial melting forming the crust (10%) the
432 ^3He flux in turn provided an estimate of the upper mantle ^3He concentration (1.18×10^9 atoms
433 ^3He per gram); at the time, arguably the most robust estimate of the concentration of any mantle
434 volatile (Kellogg and Wasserburg, 1990). Identification of the ratio of ^3He to other volatiles (such
435 as the heavier noble gases, carbon, water, and nitrogen) in mantle samples thus provides a
436 primary reference for determining their concentration, origin, and evolution in the mantle (Craig
437 and Lupton, 1976; Kurz et al., 1982; Allègre et al., 1983; 1987; Marty and Jambon, 1987; Javoy
438 and Pineau, 1991; Trull et al., 1993; Marty, 1995).

439
440 Unlike ^4He , ^{40}Ar accumulates in the atmosphere. Because it is generated by β^+ decay of ^{40}K it
441 provided an early insight into the volume of the mantle that must have been degassed and was
442 identified as a direct measure of mantle convection dynamics (Hart et al., 1979). Refinement of
443 the BSE K content led to an estimate of mantle degassing efficiency of circa 50% (Allègre et al.,
444 1996). This agrees with the outgassing efficiency derived using the excess radiogenic ^{136}Xe
445 observed in the atmosphere, resulting from ^{144}Pu and U decay (circa 40% degassing; Porcelli
446 and Ballentine 2002). Since U and Pu are refractory lithophile elements these are independent
447 of concerns about the BSE estimate for the more volatile K (Lassiter, 2004).

448
449 It follows that the ^{40}Ar generated by the BSE K must be the sum of that in the mantle and
450 atmosphere. The concentration of ^{40}Ar in the mantle, calculated from the ^3He and $^3\text{He}/^{40}\text{Ar}^*$
451 (where $^{40}\text{Ar}^*$ is the ^{40}Ar in excess of that from atmospheric contributions), is low and does not
452 fulfil this simple mass balance if this concentration is extrapolated to the whole silicate mantle.
453 This provides the basis for conceptual models requiring an unsampled region of the mantle to
454 contain significantly higher concentrations of ^{40}Ar to make up the difference. This region or
455 domain is often equated with the source of high $^3\text{He}/^4\text{He}$ seen in OIBs (Kurz et al., 1982; Allègre
456 et al., 1996). Further key observations that provide the foundations on which, together, the
457 structure and dynamics of the Earth's mantle start to be defined include the observed mantle
458 heat flow. While consistent with the whole mantle U+Th, this is higher than the concomitant flux
459 of ^4He accounted for by the U+Th in the upper mantle (depths less than 660 km) alone. This led
460 to the proposal that the 660 km boundary layer in the Earth's mantle provided a barrier through

461 which heat but not He could efficiently escape (O’Nions and Oxburgh, 1983). In contrast, the
462 calculated concentration of ^3He relative to U+Th in the mantle underlying mid ocean ridges if the
463 system were a simple closed ‘box’ (Jochum et al., 1983) predicts a more radiogenic helium
464 $^3\text{He}/^4\text{He}$ signature ($2.6 R_a$) than that observed ($8 R_a$). This difference between model and
465 observation required a helium flux from deeper in the mantle system (below 660 km) to buffer
466 the $^3\text{He}/^4\text{He}$ of the upper mantle (Allègre et al., 1983; 1987). Such a flux is compatible with the
467 ‘heat-helium paradox’ only if the flux from the deep to shallow mantle is high in ^3He and low in
468 ^4He – which is consistent with the observed high $^3\text{He}/^4\text{He}$ in OIB (Figure 1a).

469
470 Models that assume the flux of gas from the different reservoirs has reached steady state were
471 first built to account for He (Kellogg and Wasserburg, 1990), He, Ne, and Ar (O’Nions and
472 Tolstikhin, 1994) and then all noble gases (Porcelli and Wasserburg, 1995a; 1995b), with the
473 latter notably identifying recycling of heavy noble gases back into the mantle necessary for the
474 Xe mass balance. These papers were foundational in showing that the abundance and isotopic
475 composition of the noble gases in the upper mantle (above 660 km) and atmosphere could be
476 broadly described by the same layered mantle construct used to account for the radioelement
477 isotopic evolution of the mantle and crust (e.g., DePaolo and Wasserburg, 1976; O’Nions et al.,
478 1979; Allègre et al., 1979). The noble gas models nevertheless also placed firm constraints on
479 the dynamics between the upper and lower mantle (limited mass exchange), the noble gas
480 abundance and isotopic composition of the lower mantle (higher noble gas concentrations and
481 more primitive and therefore higher $^3\text{He}/^4\text{He}$ and lower $^{40}\text{Ar}/^{36}\text{Ar}$ when compared with the upper
482 mantle) and relationship between the lower mantle and upper mantle volatiles (the deep mantle
483 gas fluxes to the upper mantle). With new observations from seismic tomography, dynamical
484 modeling, and deep mantle geochemistry these layered mantle constructs are no longer tenable
485 but the requirement to account for the same observational foundations remains.

486
487 The dynamical models of Brandenburg et al. (2008) point to a resolution of the missing Ar
488 problem. Even while these models have Earth-like convective vigor as measured by plate
489 velocities and surface heat flow, they outgas only ~70% of ^3He and only ~50% of radiogenically
490 produced ^{40}Ar . This suggests that Ar is not really ‘missing’; it is still contained in the Earth due to
491 the relative inefficiency of mantle outgassing. These results were confirmed by Tucker et al.
492 (2022) who also showed that subducted atmosphere derived Ar could reasonably reproduce
493 mantle $^{40}\text{Ar}/^{36}\text{Ar}$.

494
495

496 4.2 Distribution and Character of Noble Gases in the MORB-Source Mantle

497
498 The small variance in MORB $^3\text{He}/^4\text{He}$ ($7.94\pm 0.99 R_a$; Moreira, 2013) relative to that in OIB
499 remains a defining difference between these two mantle domains, with data from earlier studies
500 summarised in Barfod et al. (1999; see Figure 1a), Graham (2002), and Moreira (2013). There
501 are significant departures from this range in ridge segments associated with plume components.
502 These include the Reykjanes ridge in the North Atlantic (Hilton et al., 2000); the Shona and
503 Discovery anomalies in the South Atlantic (Moreira et al., 1995); and the Saint Paul-Amsterdam

504 plateau on the Southeast Indian Ridge (Graham et al., 2014). Correlation with radiogenic
505 tracers, such as Sr, and ridge depth can be used to argue for ridge-entrained plume
506 components (Moreira, 2013). A detailed study of 150 samples from 1500 km of the Southeast
507 Indian ridge (Graham et al., 2014) shows $^3\text{He}/^4\text{He}$ that varies from 7.5 to 10.2 R_a with spectral
508 analysis identifying wavelength power at 1000, 100, and 30 km. That $^3\text{He}/^4\text{He}$ varies on this
509 length scale with axial depth is interpreted to be due to coupling between regional variations in
510 mantle temperature, melt production, and $^3\text{He}/^4\text{He}$ controlled by folding and stretching of
511 heterogeneities during regional (1000 km) and mesoscale (100 km) mantle flow, with the 30 km
512 length scale likely imposed by the partial melting process.

513
514 A significant insight into mantle dynamics has been provided by developments in understanding
515 neon provenance in different mantle sources. Samples from the mantle with a $^{20}\text{Ne}/^{22}\text{Ne}$ isotopic
516 component higher than air ($^{20}\text{Ne}/^{22}\text{Ne}=9.80$) were first unambiguously identified in gas rich
517 MORB and OIB (Sarda et al., 1988) and Zaire cubic diamonds (Ozima and Zashu, 1988). Later
518 work (Honda et al., 1991; 1993; Hiyagon et al., 1992; Poreda and Farley, 1992; Ballentine,
519 1997; D. Harrison et al., 1999; Caffee et al., 1999) confirmed the conclusion of Ozima and
520 Zashu (1988) that this was a Solar-like isotopic signature, in both the deep and shallow mantle.
521 Determination of whether this represented a trapped implanted Solar wind component in
522 accretionary material (Ne-B ~ 12.5 ; Black, 1971; 1972a; 1972b; Moreira, 2013; Moreira and
523 Charnoz, 2016; Péron et al., 2017) or a Solar Nebula value ($^{20}\text{Ne}/^{22}\text{Ne} = 13.36 \pm 0.09$; Heber et
524 al., 2012) has been crucial in defining the basis for interpreting the origin of inert gases in the
525 mantle and identification of the processes that have variably preserved and altered their isotopic
526 and element composition in the Earth's mantle (Porcelli and Ballentine, 2002; Moreira, 2013;
527 Mukhopadhyay and Parai, 2019).

528
529 The source $^{20}\text{Ne}/^{22}\text{Ne}$ value in mantle-derived samples is obscured by sample interaction with
530 air and seawater on eruption. High precision data from gas rich MORB 'popping rocks' showed
531 an air-mantle mixing line, with $^{20}\text{Ne}/^{22}\text{Ne}$ plotted against $^{21}\text{Ne}/^{22}\text{Ne}$, appearing to stop at
532 $^{20}\text{Ne}/^{22}\text{Ne} \sim 12.5$ (Moreira et al., 1998; see also Figure 6). Early evaluation of the plume-source
533 mantle suggested a similar (Trieloff et al., 2000), but equally ambiguous value (D. Harrison et
534 al., 1999; Ballentine et al., 2001). Mantle-derived carbon dioxide natural gases have provided a
535 useful sample resource. Bravo Dome is a magmatic carbon dioxide gas field in Harding County,
536 New Mexico. The natural addition of a crustal radiogenic 'spike' to the magmatic gases provided
537 an unambiguous assessment of the upper mantle $^{20}\text{Ne}/^{22}\text{Ne}$ (12.49 ± 0.04) corroborating the
538 limit found in MORB (Ballentine et al., 2005; Ballentine and Holland 2008; Holland and
539 Ballentine, 2006). In contrast, $^{20}\text{Ne}/^{22}\text{Ne}$ values plume samples have subsequently been found
540 higher than the shallow mantle (MORB-source) limit (D. Harrison et al., 1999; Yokochi and
541 Marty 2004; Mukhopadhyay, 2012).

542
543 The convergence of the isotopic composition of Ar, Kr and Xe in well gases (Ballentine et al.,
544 2005; Ballentine and Holland 2008; Holland and Ballentine, 2006; Holland et al., 2009) with
545 those in gas rich Atlantic MORB (Moreira et al., 1998; Parai et al., 2019) indicates that the
546 magmatic fluids in continental gases are similarly sourced. Residual gases in basalt glasses can
547 undergo extensive elemental fractionation during magma outgassing. Continental magmatic

548 gases could represent the complementary, but also elementally fractionated, component. In
549 addition, the convergence of the elemental composition of well gases with gas-rich MORB also
550 shows that significant elemental fractionation has not occurred. This means that this sample
551 resource can be used to determine the relative elemental abundance of noble gases in the
552 mantle – confident that we have excluded eruptive processing or crustal contributions
553 (Ballentine and Holland, 2008; Holland and Ballentine, 2006).

554
555 In addition to information about the accretionary source(s) and early-Earth environment, the
556 heavy noble gases Ar, Kr, and Xe show an overprint in the mantle component (distinct from the
557 eruptive addition of air) that has an elemental and isotopic composition identical to that of
558 dissolved air in seawater/marine pore fluids. This overprint accounts for all of the well gas
559 mantle ^{36}Ar and 80% of the ^{130}Xe , isotopes little affected by radiogenic sources in the mantle
560 and is interpreted as a clear signature of volatile element recycling into the mantle (Holland and
561 Ballentine 2006; Sumino et al., 2010; Kobayashi et al., 2017). This is in contrast to earlier work
562 which viewed subduction as an efficient barrier to volatile subduction (Staudacher and Allègre,
563 1988).

564
565 Noble gases have a high solubility in amphibole and ring-structure bearing minerals (C.R.M.
566 Jackson et al., 2013; 2015), providing a transport mechanism in cold subduction zones (Smye
567 et al., 2017). Observational evidence for the unfractionated subduction of a seawater or marine
568 pore fluid signature has been preserved in hydrated mineral inclusions that have been exhumed
569 from >100 km depth from multiple subduction zones (Sumino et al., 2010; Kobayashi et al.,
570 2017). Subduction plays a central role in transport of seawater noble gas signatures into the
571 mantle (Holland and Ballentine 2006; Ballentine and Holland, 2008; Sumino et al., 2010;
572 Kendrick et al., 2011; 2013; Chavrit et al., 2016; Kobayashi et al., 2017; Smye et al., 2017), with
573 Xe isotope systematics being used to show that 80–90% of the Xe in both the MORB and OIB-
574 source mantle is recycled atmosphere-derived Xe (Parai and Mukhopadhyay, 2015; Tucker et
575 al., 2012).

576
577 The broader impact of seawater noble gas subduction can be seen in samples from the
578 Southwest Indian Ridge (Parai et al., 2012). This study is one of the first systematic applications
579 of Ne isotopes to correct for eruption related air-contamination. Fourteen samples from across
580 1100 km of ridge show correlations between $\text{CO}_2/{}^3\text{He}$ and Ne, Ar and Xe isotopic compositions
581 as a function of longitude. The total amplitude in the resolved mantle $^{40}\text{Ar}/^{36}\text{Ar}$ is between
582 12,000 to 50,000. Using ${}^3\text{He}/{}^4\text{He}$ to minimise any plume influence, significant heterogeneity in
583 Ar and Xe isotopes remains. This is a variance in isotopic character that is likely controlled by
584 heterogenous recycling or mixing of volatiles into the ridge mantle source which, similar to the
585 ${}^3\text{He}/{}^4\text{He}$ length scale variance (Graham et al., 2014), provides an observational constraint for
586 mantle mixing models.

587

588

589 4.3 Distribution and Character of Noble Gases in the Mantle

590

591 The resolved MORB-source Ne isotopic composition ($^{20}\text{Ne}/^{22}\text{Ne}\sim 12.5$) is indistinguishable from
592 that of Solar wind irradiated meteoritic accretionary material (Black, 1972a; 1972b; Ballentine et
593 al., 2005; Moreira, 2013; Péron et al., 2017; 2018). This source interpretation is consistent with
594 identification of an upper mantle chondritic signature in both the Kr and Xe isotopic
595 compositions (Holland et al., 2009; Caracausi et al., 2016). In contrast, the $^{20}\text{Ne}/^{22}\text{Ne}$ of plumes
596 or plume-influenced MORBs show maximum $^{20}\text{Ne}/^{22}\text{Ne}$ values higher than MORB (Sarda et al.,
597 2000; Yokochi and Marty 2004; Mukhopadhyay, 2012; Péron et al., 2016). These have been
598 interpreted as a possible Solar Nebula gas signal preserved in the deep mantle (Solar
599 $^{20}\text{Ne}/^{22}\text{Ne}=13.36 \pm 0.09$; Heber et al., 2012) which may represent a discrete volatile component
600 in the OIB mantle (Mukhopadhyay, 2012; Parai et al., 2019; Parai and Mukhopadhyay, 2021).
601 Xenon isotopes from Iceland (Mukhopadhyay, 2012) provide evidence that the OIB-source
602 mantle preserves a long-lived geochemical record, consistent with preservation of a Solar
603 Nebula Ne signal. The xenon isotope ratios generated by the extinct radionuclides ^{129}I and
604 ^{244}Pu , and therefore signals generated within the first circa 100 Myr, show that the OIB-source
605 had I/Pu ratios lower than that recorded in the MORB-source mantle. This signal has also been
606 used to argue for the preservation of an early volatile poor (low I/Pu; dry) accretionary stage in
607 the deep mantle (Mukhopadhyay, 2012; Mukhopadhyay and Parai, 2019; Parai and
608 Mukhopadhyay, 2021). The $^3\text{He}/^{22}\text{Ne}$ elemental ratio in OIB is also similar to Solar Nebula
609 values and distinct from the $\sim 3\times$ higher value observed in MORB. The difference has been
610 attributed to magma ocean-atmosphere equilibration and punctuated degassing & early
611 atmosphere loss (Honda and Macdougall, 1998; Coltice et al., 2011; Moreira, 2013; Tucker and
612 Mukhopadhyay, 2014). It is important to note that while both MORB and OIB show evidence for
613 having recycled noble gases in common, there are multiple lines of evidence now that show
614 they preserve a different history of planetary volatile accretion, radiogenic ingrowth, and mixing
615 within the mantle. This record is incompatible with models requiring the OIB-source mantle to
616 provide the volatile source, or flux, for the MORB-source mantle.

617

618 Our conceptual understanding that underpins much of the modeling has focussed on a potential
619 deep source for the excess ^3He , and related heavier accretionary noble gases. This is needed
620 to balance the observed $^3\text{He}/^4\text{He}$ in MORB with the inferred concentration of ^3He and radiogenic
621 ingrowth from U+Th, now within a whole mantle convection setting (e.g., Porcelli and Elliott,
622 2008). The core has received considerable attention since it is large, formed early and has been
623 isolated from the mantle for most of Earth history. While the earliest work suggested that helium
624 would not partition into the forming core (Matsuda et al., 1993), updated silicate/metal
625 partitioning conditions brought this back into consideration (Porcelli and Halliday 2001; Bouhifd
626 et al., 2013). Most recently ab-initio thermodynamics have been used to derive the partition
627 coefficients of noble gases between liquid iron and silicate melt at core-forming and silicate
628 equilibration conditions (from 3500 K at 50 GPa to 4200 K at 135 GPa; Y. Li et al., 2022). While
629 able to predict a concentration of helium in the core that could sustain the ^3He in the silicate
630 mantle, this study found the partition coefficients for Ne to be three orders of magnitude lower

631 than He. This predicts $^3\text{He}/^{22}\text{Ne}$ in the core to be three orders of magnitude higher than that
632 observed in plume derived melts, which have near Solar Nebula values, and suggests that a
633 core-source able to simply account for both ^3He as well as related accretionary noble gases is
634 unlikely.

635

636 A source for the high ^3He concentrations and associated heavy noble gases in a stable silicate
637 reservoir within the deep mantle have also been proposed. These have in part been inspired by
638 heterogeneities at the core-mantle boundary that are seismically observed (LLSVPs and
639 ULVZs) and appear to be related to plumes (French and Romanowicz, 2015; Williams et al.,
640 2019; Heyn et al., 2020) and their likely connection to recycled oceanic crust (Hofmann and
641 White, 1982; Christensen and Hofmann, 1994; Kendall and Silver, 1996; Coltice and Ricard,
642 1999; Sobolev et al., 2000; Tolstikhin et al., 2006; Thompson et al., 2019; Gréaux et al., 2019;
643 M.G. Jackson et al., 2021). This link is strengthened by geodynamical models that show that
644 early oceanic crust subduction can sequester ^3He and other primordial components in ancient
645 LLSVP precursors (Jones et al., 2021). While not always explicit in the publications that explore
646 the ^3He origins, accretionary models can be divided into those that would produce a Solar wind
647 irradiated signature in both deep silicate reservoir and MORB-source mantle – and those that
648 would preserve a Solar Nebula signature in the deep silicate reservoir (OIB-source) but would
649 need the residual mantle to be overprinted with a Solar wind irradiated signature that evolves to
650 source MORB.

651

652 The subduction of early and dry oceanic crust (to facilitate volatile subduction efficiency)
653 containing a high load of Solar wind irradiated carbonaceous chondritic dust would result in
654 adding a Solar wind irradiated noble gas signature to the mantle, concentrating this signature at
655 the core-mantle boundary (Tolstikhin and Hofmann, 2005). Continuous subduction of
656 cosmogenic material over Earth history (Allègre et al., 1993; Anderson 1993) does not simply
657 account for Solar-like noble gas concentrations in the mantle (Stuart, 1994). In contrast,
658 subduction does provide a mechanism for the occurrence of marine pore fluid signatures in both
659 MORB and OIB (Holland and Ballentine, 2006; Mukhopadhyay, 2012). Also, ingassing of
660 nebular gas from a gravitationally accreted early atmosphere into a magma ocean (Mizuno et
661 al., 1980; Harper and Jacobsen 1996; Porcelli et al., 2001; Yokochi and Marty, 2004;
662 Mukhopadhyay, 2012; Tucker and Mukhopadhyay, 2014) would add a Solar Nebula signature
663 into the mantle. Incomplete degassing of the deeper mantle and isolation at depth early in Earth
664 history (Wen et al., 2001), or foundering of dense undegassed melts (Lee et al., 2010) to form
665 D'' both provide a mechanism that could account for the Solar Nebula signal seen in some
666 OIBs.

667

668 Mechanisms not associated with the deep seismic features that can produce $^3\text{He}/^4\text{He}$
669 heterogeneity more broadly dispersed in the mantle may involve high viscosity regions in the
670 mantle which are predicted to escape efficient mixing (Manga, 1996; Merveilleux du Vignaux
671 and Fleitout, 2001; Manga, 2010; Ballmer et al., 2017). This consistent with statistical analysis
672 of radiogenic isotope systems that original identified a common component (the aforementioned
673 PREMA, FOZO, or 'C') categorising this as stochastically distributed small-scale isotopic
674 heterogeneities (Stracke et al., 2022).

675
676 The redetermination of the reference chondritic halogen (Cl, Br and I) concentrations has been
677 made possible by the application of neutron irradiation noble gas mass spectrometry (NI-
678 NGMS), an analytical technique successfully employed for decades in Ar-Ar geochronology and
679 related systems (Burgess et al., 2002; 2009; Ruzié-Hamilton et al., 2016). Contrary to previous
680 bulk sample analysis, this enabled mg quantities of sample to be picked from the least altered
681 and contaminated portions of the meteorite samples (Clay et al., 2017). Prior studies provided
682 significantly higher halogen concentrations in chondrites and required exceptional accretionary
683 processes to account for them (e.g., Dreibus et al., 1979; Lodders, 2003). Authors still contend
684 that the bulk analysis of chondrite samples produces a more representative analysis (Lodders
685 and Fegley, 2023) but rely on speculation where they cite ‘...suspect analytical problems’ with
686 NI-NGMS. Speculation and suspicion notwithstanding, the Clay et al. (2017) results provide for
687 a monotonous behavior of the halogens during accretion, depleted in the Bulk Silicate Earth in
688 proportion to their condensation temperature, similar to other lithophile elements. In contrast to
689 their BSE abundance, 80 to 90% of the BSE halogens are concentrated in the oceans and
690 continental crust (Burgess et al., 2002), cannot have been emplaced by accretion after core
691 formation (too low concentration in chondrites), and are likely to have been efficiently extracted
692 from the accreting Earth in water-containing melts since they are highly hydrophilic. This is
693 consistent with other evidence for a volatile or water-rich main accretionary phase (Clay et al.,
694 2017).

695
696 Extra-terrestrial and magmatic are susceptible to acquiring an overprint from the high halogen
697 concentrations found at Earth’s surface. The processes controlling an overprint of magmatic
698 signatures were investigated in detail by Broadley et al. (2017) to develop protocols that
699 minimised this analytical complexity. This widened the samples available to study and
700 contributed to showing significant recycling of the terrestrial surface halogens to the
701 subcontinental lithospheric mantle (Sumino et al., 2010; Broadley et al., 2016; Kobayashi et al.,
702 2019). Indeed, sudden release of subducted and accumulated lithospheric mantle halogens at
703 the end of the Permian, during the Siberian Flood Basalt eruptions, may have significantly
704 contributed to the surface environmental degradation that resulted in one of the largest
705 extinctions in our planetary record (Broadley et al., 2018). Consideration of how surface
706 halogens are added to the oceanic crust shows them to be dominantly mineral bound with Cl
707 concentrations in hydrated oceanic crust at concentrations where subduction is readily able to
708 account for the Cl in the MORB source mantle (Barnes and Sharp, 2006; John et al., 2011;
709 Kendrick et al., 2011; 2013; 2017; Beaudoin et al., 2022), pointing to a significant overprint of
710 surface halogens over any accretionary signals in mantle halogens today. The subduction
711 process preserves the relative abundance of the different halogens, enriching them compared
712 with non-mineral bound volatile species such as the noble gases in both the MORB-source
713 shallow mantle (Kobayashi et al., 2017; 2019; Bekaert et al., 2021) and Hawaiian plume source
714 (Broadley et al., 2019).

715 Discussion and Conclusions

716 In the review above we have tried to highlight areas of progress in our understanding of the
717 evolution of Earth’s crust and mantle with a particular emphasis on oceanic crust recycling,

718 constraints from noble gas systematics, and use of novel geochemical systems. Of course, new
719 research also unearths new conflicts, contradictions, and areas where we clearly lack an
720 understanding of how the Earth's mantle evolved. We end this chapter by highlighting a few
721 important areas where we still lack sufficient understanding.

722

723 1. Why are HIMU OIBs so rare if they represent recycled oceanic crust over Earth history
724 (Chauvel et al., 1992; Stracke et al., 2005)? Indeed, if formation and subduction of
725 oceanic crust occurred over most of Earth history, large quantities of oceanic crust
726 should have been reinjected into the mantle (see section 2.1). The rarity of HIMU OIBs
727 might be explained by the necessary combination of two factors: an old age (> 1.5 Ga)
728 and the complete absence of a sedimentary layer that would immediately hide the
729 geochemical characteristics of pure oceanic crust (see Chauvel et al., 1992 or Shimoda
730 and Kogiso, 2019). If oceanic crust is recycled for less than about 500 Ma, it would not
731 have time to develop the radiogenic Pb isotopic compositions that characterise HIMU
732 OIB but it could potentially be traced using trace element characteristics such as
733 elevated Ce/Pb or Nb/La ratios. The geochemical community has maybe not paid
734 enough attention to the message carried by trace elements and too much to the
735 fingerprints given by isotopic systems.

736

737 2. Using trace elements and Nd isotopes mass balance calculations, Hofmann et al. (2022)
738 demonstrated that the chemical budget between present-day mantle (as sampled by
739 both MORB and OIB) and continental crust requires that they both originate from a
740 'residual mantle' formed early on. The enriched reservoir complementary to this 'residual
741 mantle' is either totally hidden and never sampled by volcanism or it has been lost to
742 space. Further work combining geochemistry and geodynamics is required to try to
743 understand where it may have been preserved and whether it could be contained in the
744 LLSVPs (e.g., Jones et al., 2021). Alternatively, maybe it is sampled by kimberlites as
745 suggested by Woodhead et al. (2019). Further geochemical studies on kimberlites, that
746 also suggest that PREMA is preserved in the LLSVPs (Guiliani et al., 2021) might help
747 provide an answer.

748

749 3. The negative correlation between He and W isotopic compositions as observed by
750 Mundl et al. (2017) and Mundl-Petermeier et al. (2019; 2020) among OIBs raises
751 puzzling questions for its origin. Indeed, with helium being a noble gas and tungsten a
752 siderophile element, no simple melting or fractionation process can explain such
753 correlation. Mundl-Petermeier et al. (2020) suggest that mixing of three distinct
754 reservoirs could account for the observed correlation. They locate one of these
755 reservoirs in the general convective mantle. The other two are the LLSVPs and ULVZs
756 at the core-mantle boundary that are assumed to be isolated for billions of years from
757 the rest of the mantle. If pristine Hadean material were to be stored in the deep Earth it
758 should potentially also be recognizable in terms of ^{142}Nd isotopic compositions.
759 However, it is not the case since at this stage since all analysed OIBs except maybe for
760 one (Peters et al., 2018) do not show any significant deviation from the ^{142}Nd BSE value.
761 Alternative explanations remain to be found. For example, very recently, Peters et al.

(2023) suggested that interaction between metal and silicate occurring at low pressures during core formation could potentially account for a reservoir with very negative tungsten isotopic composition but it remains that one cannot completely eliminate the possibility that the He-W correlation might be fortuitous with helium and tungsten tracing independent sources that only mix when melting proceeds. Constraints from dynamical modeling on this question can be found in Ferrick and Korenaga (2023).

4. It has become clear that multiple sources and accretionary processes deliver noble gases and related volatiles to the mantle together with a mechanism or mechanisms that variably preserve their distinct signatures in the OIB and MORB-source mantle. In the broadest sense we need to build a mantle that preserves and traps Solar Nebula gases, exemplified by ^3He , in the OIB-source, with the conjunction of stabilised silicate material at the core mantle boundary providing a preservation mechanism for this component in the mantle. While this component provides its high $^3\text{He}/^4\text{He}$, Nebular $^{20}\text{Ne}/^{22}\text{Ne}$ and $^3\text{He}/^{22}\text{Ne}$, this does not and cannot significantly contribute to the mantle that supplies MORB (Mukhopadhyay, 2012). Delivery of a Solar wind irradiated Ne component together with chondritic Kr and Xe must overprint any Solar Nebula residue. There is still considerable infall of accreting material after the magma ocean phase of planetary formation and the opportunity for dry subduction of Solar wind irradiated chondritic material – but the need for a ^3He source or flux remains, unless we have the concentration of ^3He in the MORB-mantle wrong (Ballentine et al., 2002).
5. We have taken here the viewpoint that oceanic lithosphere with dense crust is the prime source for deep mantle heterogeneity. We have ignored here the potential interaction of the oceanic lithosphere with the mantle transition zone that is between the 410 km and 660 km seismological discontinuities. In particular the endothermic nature of the 660 km discontinuity has been used to argue for the potential of slabs to slow down or stagnate in the transition zone (Christensen, 1996) as is observed for example in the western Pacific (Fukao et al., 2006). In addition, while it has long been argued that subducted oceanic crust is denser than ambient upper mantle (e.g., Ringwood, 1967) it is less dense at the top of the lower mantle (Irifune and Ringwood, 1993) which could allow for further accumulation of oceanic crust. Trapping of the oceanic crust at this depth could occur as it is subducted into the lower mantle helped by rheological contrasts (e.g., van Keken et al., 1996) or due to separation of stagnant slab segments (e.g., Feng et al., 2021). It could also occur over time as the subducted oceanic crust is entrained by upwellings and then retained below the 660 km discontinuity (van Summeren et al., 2009; Nakagawa et al., 2012; Yan et al., 2020). It also has been argued that slabs stagnate a little deeper in the lower mantle (Ballmer et al., 2015) potentially leading to further reduction in the efficiency of oceanic crust subduction. Seismic observations provide direct evidence for heterogeneity in the mantle transition zone (Goes et al., 2022; Yu et al., 2023) that suggests the transition zone modulates convection. Since the seismic observations are best explained by a mechanical mixture of basalt and refractory peridotite (Goes et al., 2022), it is unlikely that the transition zone completely blocks descent of the oceanic lithosphere to the deep mantle, as the transition zone

806 (with a volume of 10% of the Earth's mantle) would become completely filled by oceanic
807 crust if subduction only proceeds to the base of the transition zone. The slower mixing
808 predicted by these observations may help explain why the models presented in
809 Brandenburg et al. (2018), that while providing reasonable global overlap with
810 observations of HIMU, EM1, and the MORB-source, effectively predict an upside down
811 mantle with a depleted lower mantle and enriched upper mantle (Tucker et al., 2020).

812
813 Aside from future progress in the individual scientific approach we expect that significant
814 progress can be made by interdisciplinary research that specifically combines geochemical and
815 geophysical observations with geodynamical modeling that incorporate experimental and
816 theoretical constraints on the constitution of Earth's mantle, which would form an expansion of
817 the work presented by, for example, van Keken and Ballentine (1998, 1999), Xie and Tackley
818 (2004a; 2004b) and Brandenburg et al. (2008).

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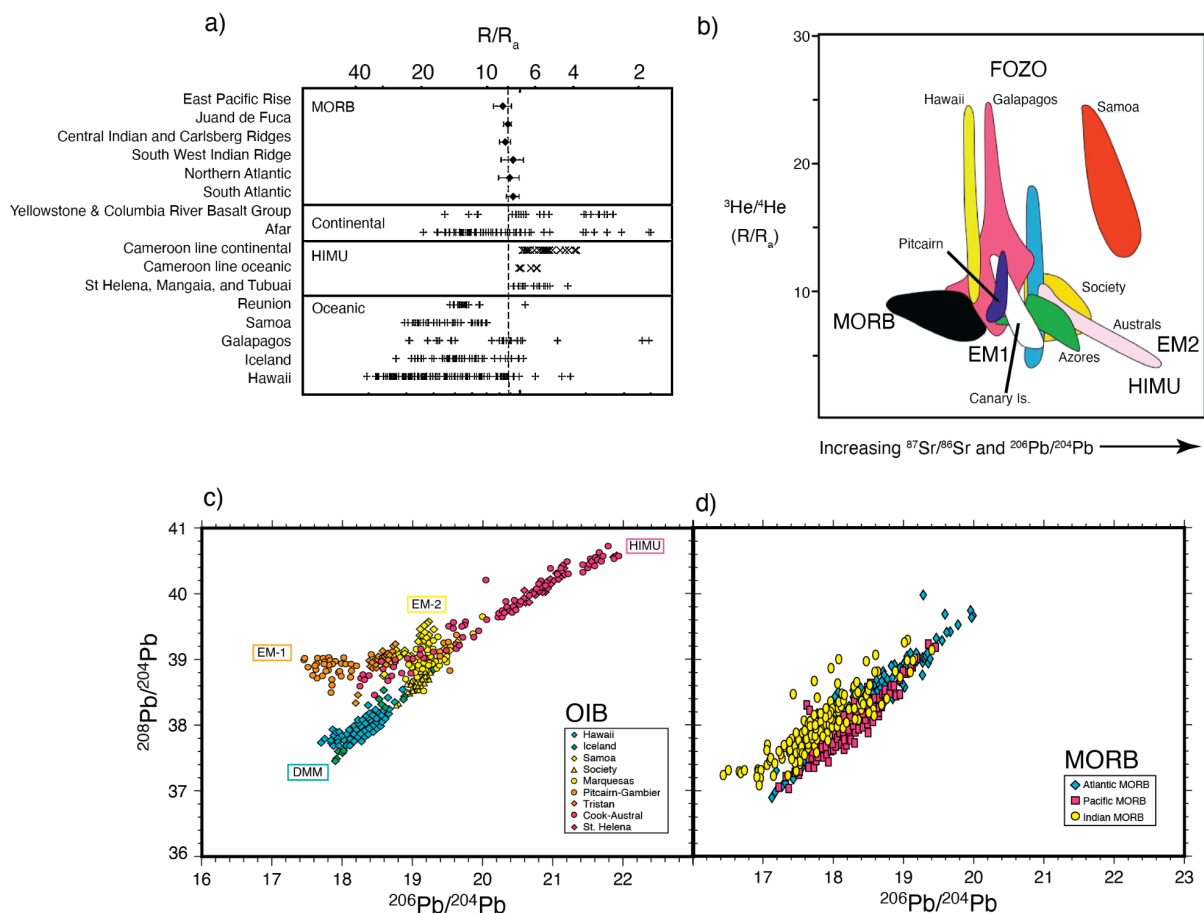
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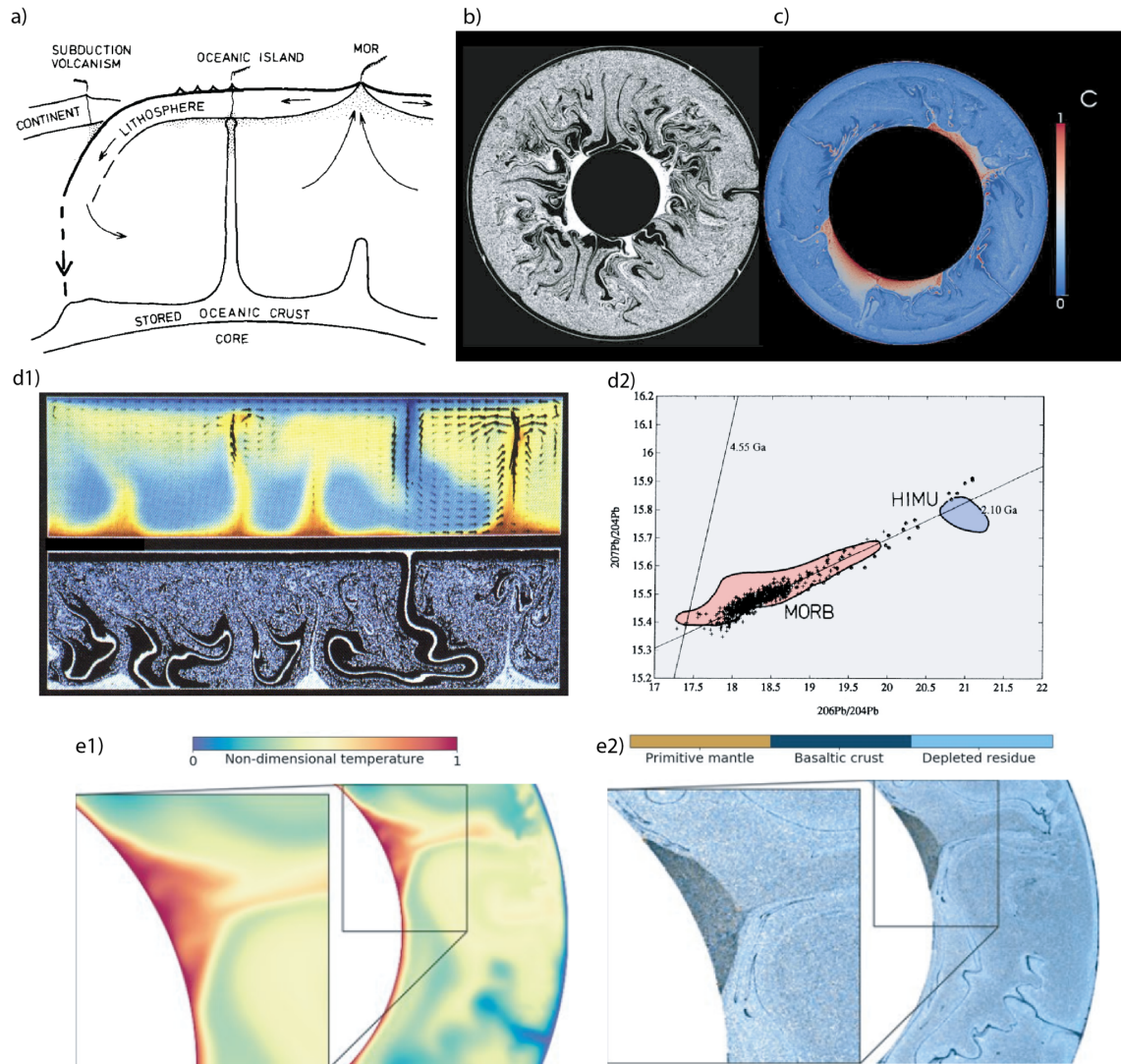
838 Figures

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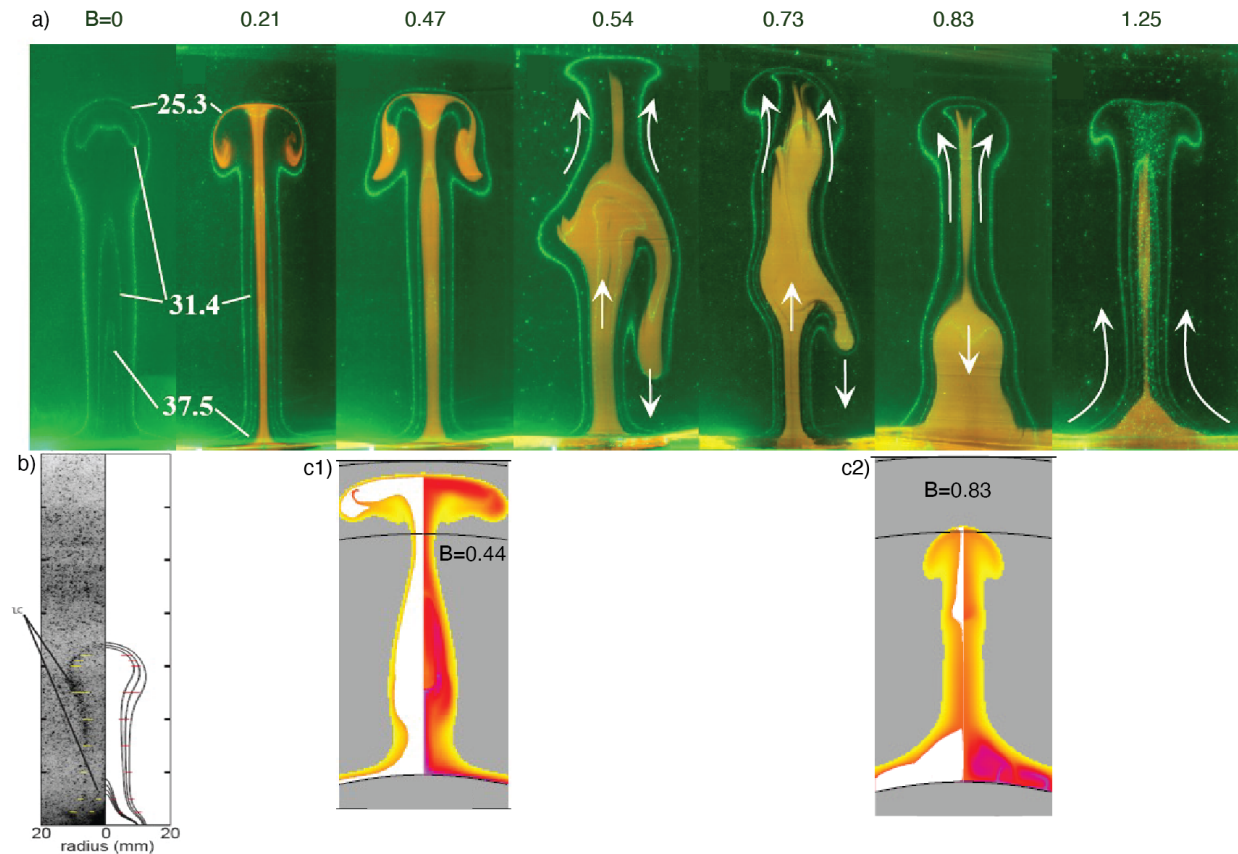
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842 Figure 1. a) Redrawn from Barfod et al. (1999): helium isotopic ratios suggest a dramatic more
843 homogeneous upper mantle (assuming MORBs sample this) than the lower mantle (assuming
844 OIBs sample this); $R = ^3\text{He}/^4\text{He}$, $R_a = R$ of the present day atmosphere. b) Redrawn from van
845 Keken et al. (2002): Data envelopes for various hotspots suggest mixing lines between MORB,
846 EM1, EM2, HIMU, and FOZO endmembers; c) Redrawn from Hofmann (2014): heterogeneity
847 shown in Pb-Pb isotopes in OIBs with apparent mixing lines between endmembers. d) Redrawn
848 from Hofmann (2014) on the same scale as panel c for MORB. While the spread of isotopic
849 ratios in MORBs is somewhat less than that in OIBs the MORB source is clearly not nearly as
850 homogeneous as is suggested from the helium isotopic ratios (panel a).



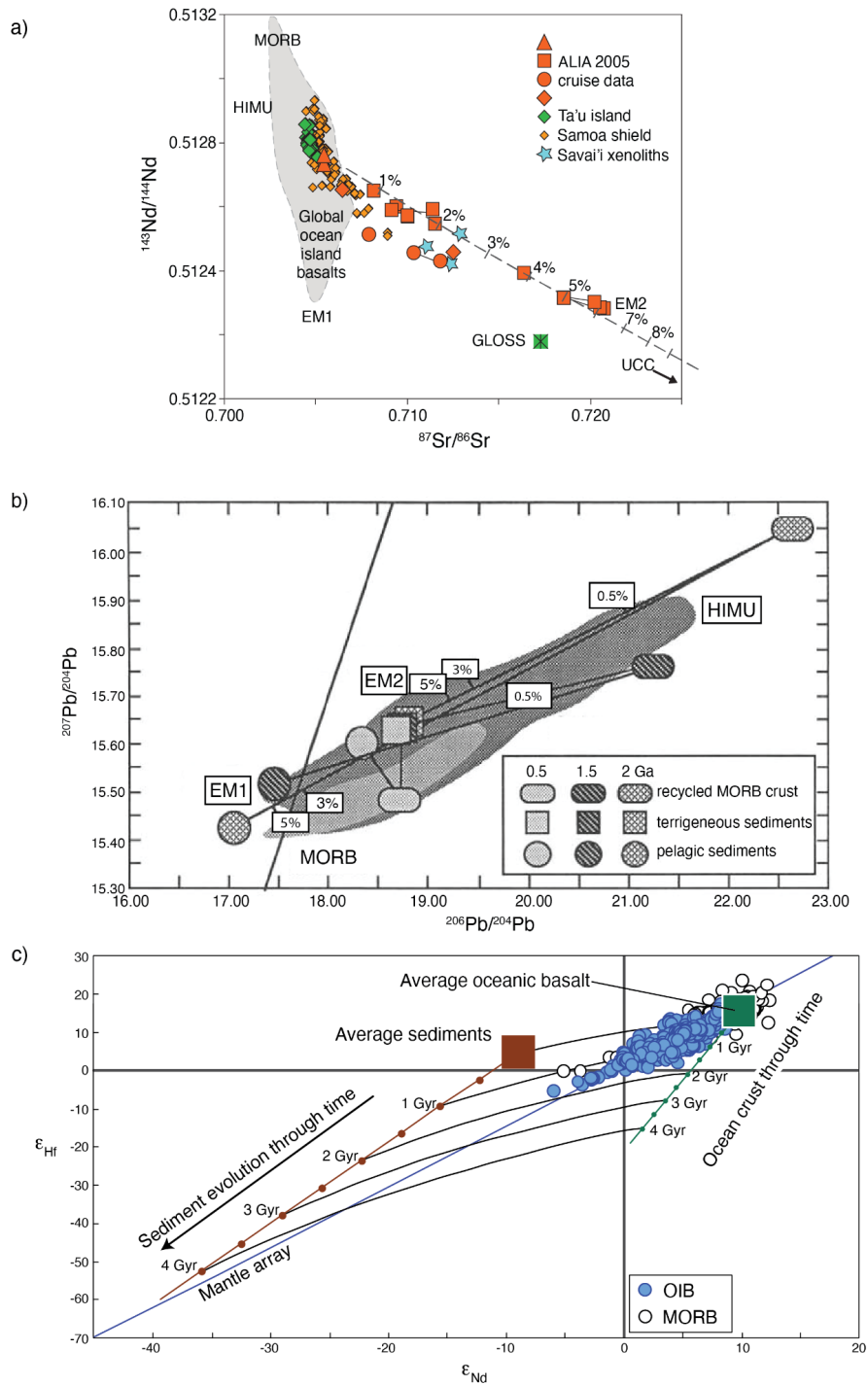
851
 852 Figure 2. a) Cartoon from HW82 providing the suggestion for the importance of oceanic
 853 lithosphere recycling and storage of oceanic crust at the base of the mantle for OIB chemistry.
 854 b) From Brandenburg et al. (2008). Eclogite tracers are shown in white indicate the
 855 concentration of oceanic crust at the base of the mantle (model with basalt excess density of
 856 3.6% with respect to ambient mantle); c) From Nakagawa et al. (2012). Model computed with
 857 self-consistent material properties showing accumulation of oceanic crust in dense piles
 858 (indicated by high C) at the base of the mantle and, to some extent, at the base of the transition
 859 zone. d1+d2) from Christensen and Hofmann (1994). d1: Ocean crust segregation and recycling
 860 modeled with kinematic plates; top frame shows nondimensional temperature and lower frame
 861 shows eclogite component in white. d2: Pb-Pb isotopes derived from the model reproducing
 862 approximately the MORB and HIMU fields (but see argument about transit time scaling in the
 863 paper). e1+e2) from Jones et al. (2021). e1: temperature showing high temperature in the
 864 thermochemical pile with convective motions. e2: tracers showing accumulation of oceanic crust
 865 at the base of the mantle. In this application it is suggested that the thermochemical piles can
 866 trap primitive mantle potentially providing a natural explanation for the preservation of ancient
 867 heterogeneity.

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870 Figure 3. Examples of entrainment of a dense layer by thermochemical plumes. a) From
 871 Kumagai et al. (2008). Laboratory plumes starting from a heater entrain a denser orange layer.
 872 The green color is from the laser sheet that illuminates the near-cylindrical plume. Contour lines
 873 labeled in the first two frames on the left indicate temperatures in the fluid, a technique made
 874 possible by the use of crystals that are opaque under a narrow temperature range. From left to
 875 right the density of the orange fluid increases leading to increasing less efficient entrainment by
 876 the thermal plume. B is the non-dimensional buoyancy number that indicates the ratio of
 877 compositional to thermal buoyancy. b) From Vatteville et al. (2009): comparison of a starting
 878 plume between a similar laboratory set up as that in a) but without dense layer. On the left the
 879 opaqueness indicates the ranges where the temperature is between a certain interval.
 880 Horizontal lines indicate the same temperature ranges from laser diffraction. On the right is the
 881 numerical simulation of this experimental setup showing excellent agreement. c) Numerical
 882 simulations from Lin and van Keken (2006b) with colors indicate temperature. The white layer is
 883 dense material with a buoyancy number indicated. Comparison with the results in frame a)
 884 suggest similar dynamics is suggested between laboratory and numerical experiments, showing
 885 the complementarity of these two approaches.

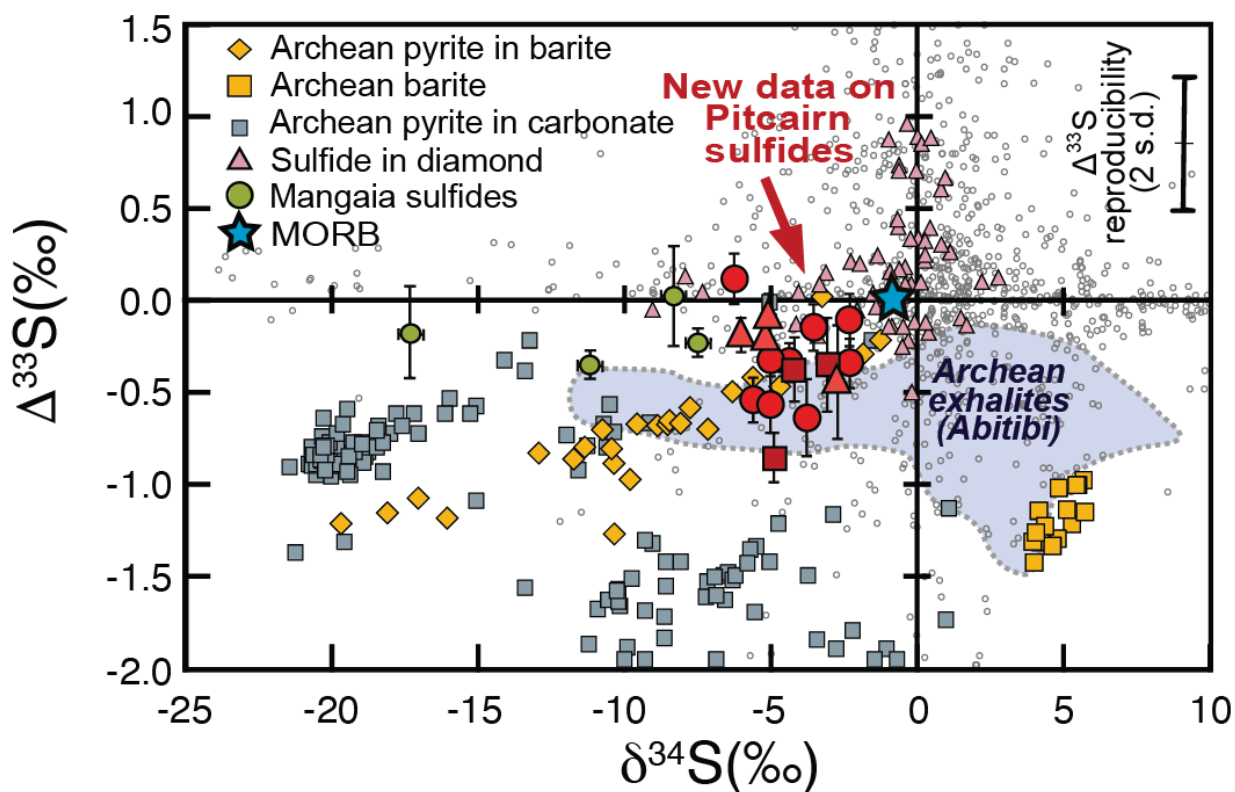


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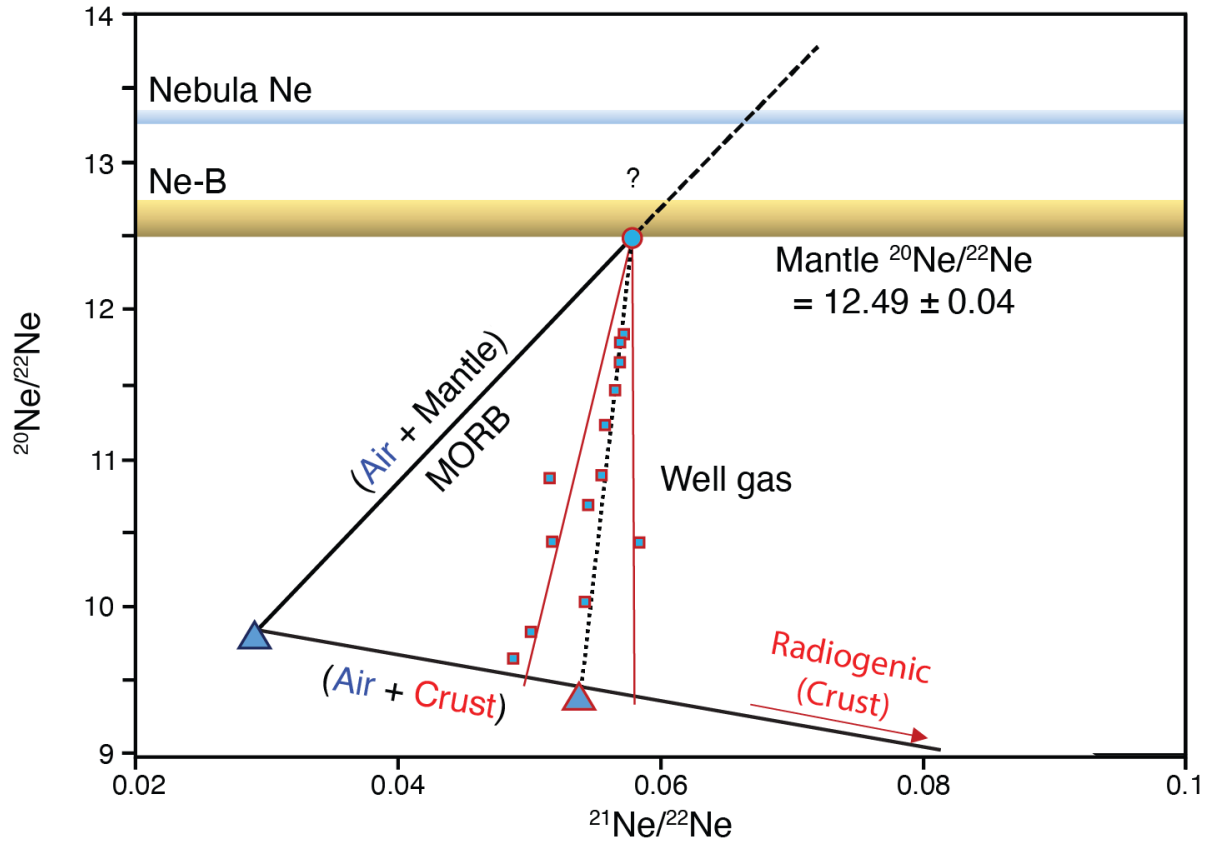
888 Figure 4. Specific recycling of oceanic crust and associated sediments and how it can be traced
 889 using radiogenic isotopic systems. a) In 2007, M.G. Jackson et al. reported extremely
 890 radiogenic Sr isotopes for a basaltic sample collected along the Samoan archipelago in the
 891 Pacific. These extreme values resemble what is known on continental crust or in oceanic
 892 sedimentary material (GLOSS). Such high Sr isotopic compositions can only be explained by
 893 the recycling of crustal material in the Earth's mantle. b) the range of Pb isotopic compositions

894 of ocean island basalts (dark grey field) and MORB (light grey field) can be reproduced by the
 895 involvement of recycled basaltic crust and associated sediments with varying ages (Chauvel et
 896 al., 1992); HIMU compositions lie next to pure oceanic crust recycled more than 1.5 Ga ago,
 897 while EM1 and EM2 compositions correspond respectively to old pelagic and terrigenous
 898 sediments; c) the Hf-Nd mantle array requires the involvement of both recycled oceanic crust
 899 and oceanic sediments in the source of OIB and MORB (Chauvel et al., 2008).
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 902 Figure 5: Sulphur isotopes diagram modified from Delavault et al. (2016) showing the existence
 903 of mass-independent fractionation anomalies ($\Delta^{33}\text{S}$ different from 0) in sulfides from Mangaia
 904 island (Cabral et al., 2013) and Pitcairn seamounts (Delavault et al., 2016).
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Figure 6. The three isotopes of neon provide a clear view on the origin of Ne in the Earth's upper mantle. Air is ubiquitous in all samples measured. Early work was not able to unambiguously distinguish the mantle source composition and resolve between Ne isotopic compositions related to a Solar wind irradiated accretionary source (Ne-B) vs Solar Nebula gases with a higher $^{20}\text{Ne}/^{22}\text{Ne}$ ratio which require fundamentally different processes to be operating in the planetary accretion of volatile elements. Ancient groundwater in the continental crust contains dissolved air with a crustal radiogenic component. When magmatic gases in the continental contact this fluid it generates a unique mixing line in the neon system. The intersection or triangulation of this mixing line with the MORB-air mixing line unambiguously determines the mantle source Ne isotope composition. The mantle Ne isotopic value determined is indistinguishable from Solar wind irradiated accretionary material (Ne-B)(Ballentine et al., 2005; 2008; Holland and Ballentine, 2006).

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