Earth's mantle composition revealed by mantle plumes

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Abstract

Mantle plumes can originate at depths near the core—mantle boundary (~2,800 km). As such, they provide invaluable information about the composition of the deep mantle, and insight into convection, crustal formation, crustal recycling, global heat and volatile budgets. In this Review, we discuss the effectiveness and challenges of using isotopic analyses of plume-generated rocks to infer mantle composition and its influence on geodynamics. Isotopic analyses of plumederived ocean island basalts, including radiogenic (Sr, Nd, Pb, Hf, W, noble gas) and stable isotopes, permit determination of mantle plume composition and its influence on geodynamics, giving insight into the composition of mantle heterogeneities, the nature and timing of earlyformed mantle reservoirs, crustal recycling processes, core-mantle interactions, and mantle evolution. Nevertheless, the magmatic flux, temperature, tectonic environment, and compositions of mantle plumes can vary. Consequently, plumes and their melts should be evaluated along a spectrum that acknowledges their different properties, particularly mantle flux, before making interpretations about Earth's interior. Future work should focus on documenting correlations across elemental and isotopic data sets on the same sample powder, refining isotopic fractionation factors, and coordinating targeting sampling strategies, to provide insight into specific mantle and plume processes. This work requires collaboration across geochemical laboratories, as well as among geochemists, mineral physicists, seismologists, and geodynamicists.

[H1] Introduction

The mantle has an important role in many of Earth's most dynamic systems. Comprising 84% of the Earth's volume, the mantle is integral to the formation of mid-ocean ridges, convergent margins, and intraplate volcanism, which, in turn drive the formation and recycling of oceanic and continental crust (White, 1985; Zindler and Hart, 1986; Hofmann, 1997; 2003; Labrosse et al., 2007; White, 2015). The mantle also contributes to Earth's water and heat budgets through radioactive decay and thermochemical convection. Seismic wave velocity variations reflect differences in temperature and/or composition in the lower mantle (660–2,890 km deep) (Davies and Davies, 2009; Tkalčić et al., 2015; Garnero, 2000; Koelemejier et al., 2016; Ritsema and Lekic, 2020), suggesting that the lower mantle, or part of it, is a reservoir for compositionally distinct material, including recycled and potentially ancient primitive components. Thus, understanding many fundamental Earth processes relies on documenting the composition and spatial heterogeneity of Earth's mantle today and its evolution throughout geological time.

At shallow mantle depths (<100 km), upwelling causes the upper mantle to melt through adiabatic decompression, leading to the generation of mid-ocean ridge basalts (MORB), an important source of information about the composition of the upper mantle (Gale et al., 2013). By contrast, mantle plumes occur in all tectonic settings (**Fig. 1a**), originating at different depths, from shallow mantle upwellings (<<660 km) (Duvernay et al., 2021) to deep sources at the coremantle boundary (CMB, ~2800 km) (Courtillot et al., 2003). Consequently, mantle plumes provide invaluable insight into the geochemistry of Earth's deep interior.

Once plumes rise above 1,000 km (French and Romanowicz, 2015), they form narrow, roughly cylindrical pipes of anomalously hot mantle that upwell and melt partially to form ocean island basalts (OIBs) on oceanic plates. Mantle plume melting occurs at sublithospheric depths,

requiring a mantle source that is either hotter than the upper mantle, or enriched in rocks and/or fluids that lower the solidus temperature. Thus, mantle plumes provide the heat and fertile mantle components necessary for intraplate magmatism and to generate OIBs (**Fig. 1b**). Plumegenerated oceanic islands usually sample the mantle without chemical interference from the continental crust or subcontinental lithospheric mantle, providing a geochemical window into the composition of Earth's mantle and its evolution over time, including the sources of deeply rooted plumes.

Previous articles have discussed progress in seismic imaging, mantle flow modelling, plate tectonic reconstructions, and geochemical analyses of deep mantle plumes and their roles in Earth processes (Koppers et al., 2021). This Review focuses on the geochemistry and geodynamics of deep plumes that form well-studied oceanic islands (such as, Hawai'i, Réunion, Kerguelen, and Galápagos, among others). Advances in analytical techniques and isotopic systems are enabling the resolution and quantification of small isotopic variations in OIB samples. These techniques and isotopic systems are providing new perspectives on the presence, source, and age of heterogeneities in the deep mantle.

In this Review, we discuss developments in the isotopic analysis of mantle plume-fed OIBs, and their effectiveness as an essential tool for documenting mantle heterogeneity (**Fig. 1b**). We describe the fundamentals of mantle plumes, including their origin, physical and dynamical behavior, and their compositional variations, with an emphasis on contributions from distinct mantle reservoirs. We illustrate the utility of different isotopic systems and recent advances in their analysis for documenting the contributions made by subduction and crustal recycling to the plume source, identifying early-formed reservoirs in Earth's mantle and their role in Earth evolution, and quantifying the extent of mixing of mantle reservoirs and convection. Lastly, we explore the importance of buoyancy flux for understanding plumes, as well as the need for coordinated, interdisciplinary approaches in future mantle plume research.

[H1] Fundamentals of mantle plumes

The strength of upwelling flux, the composition, and the duration of magmatic activity have been used to classify mantle plumes (Courtillot et al., 2003; Jackson et al., 2018; Koppers et al., 2021; **Fig. 1a, Box 1**). Primary plumes come from between 1,000 and 2,800 km depth (extending to the CMB) and are defined as having a seismic velocity anomaly of at least –1.5%, a linear and age-progressive volcanic chain, a large igneous province (LIP) at the oldest end of the volcanic chain, a strong magmatic flux, and high ³He/⁴He or other indications of compositions distinct from those of MORBs (Courtillot et al., 2003; Montelli et al., 2006; Boschi et al., 2007; King and Adam, 2014; French and Romanowicz, 2015). Primary plumes are the focus of this Review, and in this section we discuss their origin, flux and the influence of plate tectonics.

[H2] Plumes origins and physical characteristics

Most OIB-generating volcanoes are produced by plumes that originate along the edges of Large Low Shear Velocity Provinces (LLSVP), commonly interpreted as thermochemical piles at the CMB (Burke and Torsvik 2004; Thorne and Garnero, 2004; Torsvik et al., 2006; Burke et al., 2008; Doubrovine et al., 2016; Garnero et al., 2016). Early geodynamical models explored whether ancient, accumulated recycled crust could be in the source of the LLSVP (Christensen

and Hofmann, 1994; Brandenburg et al., 2008), whereas models developed since the early 2010s focus on the interplay between the recycled crust and a layer of primordial iron-rich material with an excess density of about 1% (Li, et al. 2014; Williams et al., 2015; Nakagawa and Tackley, 2014; Jones et al., 2021). Alternatively, dense and reduced mantle material could pool at the CMB, contributing to the formation of LLSVPs (Gu et al., 2016). Laboratory experiments (Davaille, 1999; Limare et al., 2015) and numerical simulations can reproduce the formation of large thermo-chemical plumes observed in tomographic models (French and Romanowicz, 2014). In some models, both the LLSVP and the ambient mantle supply material to plumes rising from the boundary between them (Fourel et al., 2017).

Also detected at the CMB, Ultra-Low Velocity Zones (ULVZs) are characterized by strong reductions in S-wave (~30%) and P-wave (10%) velocities, which are best explained by a ~10% density increase in the material (Thorne and Garnero, 2004; McNamara, 2019). The ULVZs are 10–40 km high regions that extend laterally for up to ~1,000 km along the CMB (Cottaar and Romanowicz, 2012). Models for the origin of ULVZs consider the effects of coremantle reactions (Knittle and Jeanloz, 1989), as well as the presence of dense silicate melt (Williams and Garnero, 1996), relics of banded iron formations subducted 2–3 Ga ago (Dobson and Brodholt, 2005), or zones of iron-enriched post-perovskite (Mao et al., 2006). It is possible that ULVZs could host geochemical signatures distinct from the rest of the mantle, including records of early differentiation or diffusion across the CMB (Mundl-Petermeier et al., 2020; Yoshino et al., 2020). The high density of ULVZs inhibits their convective stirring, and only the most vigorous plumes can entrain thin tendrils of ULVZ material by viscous coupling (Williams et al., 2015).

Mineral physics research has explored ways in which mantle heterogeneity can affect phase relations, density, and elastic moduli through changes in bulk composition (Lee et al., 2004; Ricolleau et al., 2010; Dorfman et al., 2013), water content (Litasov and Ohtani, 2007; Zhou et al., 2022), and redox state (Gu et al., 2016, Creasy et al., 2020). Although accessory phases can vary in type and abundance, the dominant phase in the lower mantle is bridgmanite, a Mg-silicate perovskite (Tschauner et al., 2014). The strength of bridgmanite's structure could encourage the formation of narrow channels of upwelling and downwelling, thereby stabilizing deep-rooted mantle upwellings from near the CMB (Ballmer et al., 2017).

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

This proposed plume origin (Weis et al., 2011) has led to additional nuances and suggestions for plume models. In the Marquesas, the sizes of compositional heterogeneities in the plume are much smaller than in Hawai'i and are generated from much lower degree of partial melting plumelets that originate from a large dome structure in the mantle, under Polynesia (Chauvel et al., 2012). Rather than originating at the LLSVP—lower mantle interface, a drifting Hawaiian plume has become anchored on the LLSVP, resulting in the entrainment of LLSVP material after that event (Harrison et al. 2017). This model would explain the abrupt increase in plume flux along the Hawaiian chain after the bend in its path. The compositional zonation in Hawai'i could also reflect a major change in absolute plate motion (Jones et al. 2017).

[H2] Buoyancy flux of plumes

The strength, or buoyancy flux, of a mantle plume influences the partial melting regime of its corresponding oceanic island system (Schilling, 1991). Tholeitic and alkalic basalts are produced by higher or lower degrees of partial melting, respectively. Thus, whether tholeiitic or alkalic basalts dominate an oceanic island provides insight into the buoyancy flux and the mantle potential temperature of a plume system. For example, the Hawaiian chain represents a rare occurrence of high-volume magmatism that produces tholeiitic basalts over 85 Myr. Other examples include Réunion, Iceland, Galápagos, and Easter Islands (Sleep, 1990; King and Adam, 2014), systems that also have elevated buoyancy flux and/or mantle potential temperature (Schilling, 1991; White et al., 1993; Kingsley et al., 1998; 2007; Jackson and Dasgupta, 2008; Jackson et al., 2017). Iceland is the only oceanic island that follows a silica-saturated tholeiitic evolution trend (Supplementary Fig. 1; Gale et al., 2013). Alkalic lavas, formed from lower degrees of partial melting, dominate some plumes with intermediate fluxes, such as the Cook-Austral chain (Jackson et al., 2020b) and Society Islands (Duncan et al., 1986) (Fig. 1a). Generally, however, most intraplate oceanic volcanoes produce dominantly alkalic melts (Haase et al., 2019), suggesting that a high degree of partial melting might be uncommon in some mantle plumes, at least during the Cenozoic.

Furthermore, plume strength could be increased by proximity to an LLSVP, as proposed for Hawai'i (Harrison et al., 2017; Harrison and Weis, 2018). The volume of magma produced along the Hawaiian chain has increased by almost an order of magnitude over the last 45 Myr, which contrasts with the predicted decrease through time according to mantle plume models (Richards et al., 1989; Wessel, 2016; Weis et al., 2020). Moreover, the highest-flux plumes, including Hawai'i, overlie mega-ULVZ structures at the CMB (Cottaar and Romanowicz, 2012), implying that lower mantle structures, the strength of a plume, its temperature, and its melting conditions could all be linked (Harrison et al., 2017).

[H2] Influence of plate motion and plate boundaries

The compositional structure of a plume is recorded by its volcanoes in different ways depending on the lithospheric thickness, proximity to a spreading ridge, plate motion vectors, and the geometry of the compositional structure within the plume conduit itself. Lithospheric thickness can influence the depth and degree of melting, spreading ridges can re-direct upper mantle flow, and the direction of plate motion relative to the compositional cross-section of the plume determines how plume compositions are expressed at the surface. For example, since ~3–6 Ma at Hawai'i, both the LLSVP boundary and current Pacific plate motion vector (Wessel and Kroenke, 2009) have been oriented along NW-trending strikes, which yields two parallel chains of compositionally distinct volcanoes (Weis et al., 2011; Farnetani et al., 2012). By contrast, in

the Galápagos, the orientation of the LLSVP boundary is oblique to plate motion, resulting in early erupted, enriched material from the LLSVP being buried beneath younger, more depleted material from the ambient mantle (Harpp and Weis, 2020). Additionally, shifts in plate motion direction could shear mantle plume stems and generate ephemeral changes in the spatial distribution of erupted, compositionally distinct material (Jones et al., 2017).

When plumes interact with adjacent spreading centers, plume material can be incorporated into the return flow of the ridge, which increases the entrainment of depleted upper mantle into plume-generated lavas as observed in the Azores, Galápagos, and Cretaceous-age Hawaiian eruptions, among other near-ridge plumes (White et al., 1993; Harpp and White, 2001; Harrison et al., 2020). The near-zero lithospheric thickness of ridge-proximal plumes could also increase plume melting and affect the magmatic architecture of ocean islands formed near the ridge (Weis and Frey, 2002; Regelous et al., 2003; Harpp and Geist, 2018). Near-ridge plumes, including Iceland, Galápagos, Kerguelen, and Easter produce abundant tholeitic lavas that require higher degrees of partial melting than other mantle plumes (White et al., 1993; Kingsley et al., 1998, 2007; Ito et al., 1996; Schilling, 1991; Weis and Frey, 2002). In plumes near subduction zones, additional crustal flexure of the plate could generate melt and/or encourage the entrainment of upper mantle material, as proposed for Samoa (Konter and Jackson, 2012; Jackson et al., 2014) and for volcanism that cannot be plume-related in the Emperor Seamounts near the Aleutian Arc (Kerr et al., 2005).

[H1] Oceanic island volcanism

Owing to the lack of interactions with continental material, ocean islands with deep plume sources provide the most direct view and best representation of lower mantle compositions (Harrison et al., 2017; Weis et al., 2020).

[H2] A geochemical overview of OIBs

Oceanic island volcanoes feature a variety of volcanic rock types, including picro-basalts, rhyolites, basanites, phonolites, and trachytes (Supplementary Fig.1). Nevertheless, the dominant rock type is basalt. This Review focuses on shield-stage basaltic magmas that form lavas with tholeiitic or alkalic compositions because they have experienced the least differentiation and contamination en route to the surface. Another approach to studying mantle heterogeneity is to analyze melt inclusions, which enables the detection of smaller isotope heterogeneities than is possible with bulk analysis of erupted lavas (Saal et al., 2005; Stracke et al., 2019). Melt inclusions sample geochemical variations on the scale of 20–30 µm, capturing different aspects of the magmatic system than either whole-rock or mineral phase analysis. They represent a snapshot of melt pockets that existed prior to melt amalgamation, magma mixing, and substantial fractional crystallization. Melt inclusion analyses are analytically challenging and vulnerable to many processes that disturb or distort the composition of the post-entrapment melts, generating data less representative than whole rock or mineral-phase analysis because of inclusions' small size. Therefore, this Review focuses exclusively on isotopic analyses of rock samples that integrate the composition of melts generated by large mantle volumes (many km³) (Rudge et al., 2013) (Box 2).

The compositional diversity of OIBs (especially compared with the relative homogeneity of MORBs; Hofmann, 1997; Gale et al., 2013) reflects the lower degree of partial melting of OIBs compared to MORBs. However, melting systematics can only explain a small fraction of the observed compositional variations (Hofmann, 1997; White, 2010). Characteristic features of

major and trace element compositional variations in OIBs include the enrichment of light rare earth elements (REEs) compared with the primitive mantle (which refers to the composition of Earth's mantle soon after core formation), depletion in heavy REEs relative to middle and light REEs, and near-constant ratios of the most incompatible elements (**left side of Supplementary Fig 2**; Hofmann et al., 1986; Newsom et al., 1986; Willbold and Stracke, 2006; incompatible elements are those whose charge or ionic radius is too large to substitute into mantle minerals; some of the most incompatible elements in mantle lithologies include Ce, Nb, Zr, U, Th, Ta, La, Sm, Pb). The REE patterns of OIBs suggest that most OIB melts are generated primarily in the garnet stability field (>80 km depth) (Gast, 1968), which reflects the higher (100-200°C) mantle temperatures of plumes (Putirka et al., 2007). In contrast, most MORBs begin melting at shallower levels where garnet is no longer stable (<80 km), inducing no substantial middle to heavy REE fractionation in the generated magmas.

In some cases, the concentrations of major element oxides and trace elements correlate with the dominant isotopic trends displayed by OIBs (Jackson and Dasgupta, 2008; Jackson et al., 2012). Variations in major and trace elements are typically generated by different processes (such as the degree of melting and magmatic differentiation) from those that produce variations in isotopic compositions (for example, compositional differences in time-integrated mantle sources). Thus, correlations between major and trace element concentrations and isotopic compositions in OIB might reflect mixtures of compositionally distinct sources melting to variable extents and/or the fact that the compositionally distinct materials in the mantle differ in their major and trace element signatures as well as their isotopic compositions (Rudge et al., 2013).

[H2] OIB isotopic mantle end-members

Radiogenic isotope ratios in ocean island lavas vary within a field constrained by a minimum of four end-member isotopic compositions (HIMU, high U/Pb ratio (μ); EM-I, enriched mantle I; EM-II, enriched mantle II; and DMM, Depleted MORB Mantle White, 1985; Zindler and Hart, 1986; Hart et al., 1992; Hofmann, 1997; **Fig. 2**). Most ocean island chains define mixing arrays in bivariate isotope plots that extend between one of the three end-member compositions and a single, focal area within the mantle field in Sr–Nd–Pb(–Hf) isotopic space (**Fig. 2 and Supplementary Figs. 6–9**; Zindler et al., 1982; White, 1985; Zindler and Hart, 1986; Hart et al., 1992; Stracke et al., 2005; White, 2015). The focal area is proposed to be a fifth composition, known variably as PREMA (PREvalent MAntle; Zindler and Hart, 1986), FOZO (Focus Zone; Hart et al., 1992), C (Common component; Hanan and Graham, 1996), or PHEM (Primitive HElium Mantle; Farley et al., 1992) (**Fig. 3a,b**).

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

[H3] The HIMU endmember

The HIMU mantle end-member is named for its high U/Pb (commonly referred as μ) source ratio (Zindler and Hart, 1986). The extreme U/Pb ratios required to generate HIMU Pb isotopic signatures (**Fig. 2a**) indicate that the original mantle source had high initial U/Pb (μ) and Th/Pb (ω) (Chauvel et al., 1992). The mechanism that is most often used to explain the removal of Pb required for the HIMU signature to occur is the dehydration of ancient, subducted oceanic crust, which is then stored in the mantle for 1.5–2 billion years before being incorporated into mantle plumes (Hofmann and White, 1982; White, 1985; Zindler and Hart, 1986; Chauvel et al., 1992, 1997; Stracke et al., 2005; Kelley et al., 2005). Alternative explanations include the addition to the plume source of carbonatitic silicate melts from recycled oceanic crust (Dasgupta et al., 2007; Jackson and Dasgupta, 2008), ancient carbonate-metasomatized sub-continental lithospheric mantle (Weiss et al., 2016; Homrighausen et al., 2018), or recycled Archean marine carbonates (Castillo, 2015). Of the major mantle end-members sampled by plumes, HIMU has limited distribution, is the least voluminous (**Figs. 1 & 3a,b**), and is the dominant component in only a few small ocean islands mostly in the Pacific ocean (such as, Cook–Austral, St. Helena, Mangai, Tubuai, Rurutu).

[H3] Enriched mantle end-members

On the basis of OIB isotopic systematics, two distinct enriched mantle end-members (EM-I and EM-II) can be identified (Zindler and Hart 1986). There is little consensus on the origin of the EM-I end-member (Eisele et al., 2002; Cordier et al., 2021), however hypotheses include the subduction and recycling of various near-surficial and surficial materials (Hoffman and White, 1982; Chauvel et al., 1992), including delaminated subcontinental lithosphere (Boyet et al., 2019), depleted MORB material (Weis et al., 1989) and/or pelagic sediments (Blichert-Toft et al., 1999) or Archean carbonates (Garapić et al., 2015; Delavault et al., 2016; Wang et al., 2018), which are incorporated into the deep mantle. By contrast, the EM-II reservoir exhibits contributions from continental crust materials (Zindler and Hart, 1986; Weaver, 1991; Chauvel et al., 1992; White and Duncan, 1996; Jackson et al., 2007; Jackson and Dasgupta, 2008), although alternative models have been proposed, including the incorporation of ancient metasomatized oceanic lithosphere into the EM-II reservoir (Workman et al., 2004). The EM-I (Kerguelen, Heard, Pitcairn, Tristan–Gough, Hawai'i) and EM-II (Marquesas, Society, Samoan Islands) end-members dominate OIB-producing systems and are important contributors to the buoyancy flux of many plumes (Figs. 1 & 3a,b).

[H3] The prevalent mantle

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

[H3] The depleted mantle source in OIBs

The major and trace element characteristics of strongly depleted OIB lavas (Supplementary Figs. 1–5) are consistent with a mantle source that has a multimillion-year long history of melt extraction and is therefore depleted in the most incompatible trace elements (Salters and Stracke, 2004). Although the depleted component in OIBs is easily masked by mixing with melts from enriched heterogeneities in the mantle source, analysis of melt inclusions that record contributions from depleted melts prior to magma mixing and homogenization show that it is a component of some Azores lavas (Genske et al., 2019). Rare, depleted signatures in Hawaiian lavas and xenoliths also support a depleted component in mantle plumes (Frey et al., 2005; Bizimis et al., 2005; DeFelice et al., 2019). In Iceland, the Azores, and the Galápagos, the depleted signature is attributed to their near-ridge settings, where higher degrees of mantle melting occur under a thin lithosphere (White et al., 1976; Schilling et al., 1982; Humphris et al., 1985; Hart et al., 1992; Moreira et al., 1999; Harpp and Weis, 2020).

Uncertainty persists regarding the origin of depleted mantle compositions in OIB (Hart et al., 1992; Harrison et al., 2020; Stracke et al, 2022), leading to several potential hypotheses. First, these compositions could comprise a large proportion of the lower mantle meaning that the DMM or an early-enriched reservoir could be a major matrix component in mantle plumes (Hofmann et al., 2022). Second, they could represent the melting of an entrained sheath of depleted upper mantle material. Last, they could reflect large degrees of melting of the plume source, as expected underneath thin lithosphere. In contrast, multi-variate statistical data analysis suggests that the apparent overlap of MORB–OIB data trends in 2D isotope ratio diagrams does not translate consistently to multi-dimensional isotope data space (Stracke et al., 2022). Therefore, the compositional variations displayed by MORB–OIB could be controlled by smaller-scale, regional domains, rather than a limited number of global-scale reservoirs (Stracke et al., 2022). Such differences in the interpreted magnitude and dynamics of compositional reservoirs highlights the need for a more nuanced understanding of these important parts of the mantle and their roles in mantle plumes.

[H1] Subduction and mantle heterogeneity

Early in the development of mantle plume theory, plumes were thought to be supplied exclusively by the primitive lower mantle and depleted upper mantle (Allègre, 1982). On the basis of geochemical data, the idea that the source of OIBs might contain ancient oceanic crust was proposed in the 1980s (Hofmann and White, 1982). This hypothesis posits that oceanic plates are recycled via subduction into the lower mantle, where they are subsequently sampled by plumes; this proposed cycle of downwelling and upwelling provided an important step forward in understanding mantle plumes and their role in the global plate tectonic system. Geochemical evidence acquired since the hypothesis was proposed has confirmed that recycled oceanic crust contributes to ocean island mantle sources (White, 1985; Zindler and Hart, 1986; Chauvel et al., 1992, 1997; Stracke et al., 2005; Kelley et al., 2005). Consistent with the recycling model, seismic data (Fukao and Obayashi, 2013) and geodynamic models (Jones et al., 2021) document the transport of subducted plates to the lower mantle.

[H2] Recycled material in OIBs

The recycled oceanic crust consists of various materials, including basaltic crust and the overlying sedimentary pile (**Fig. 1b**). Although basaltic crust has a chemical composition that is, within an enrichment factor, not substantially different from that of the upper mantle source, the composition of sedimentary material can be highly diverse. The average composition of global subducting sediment (GLOSS; Plank and Langmuir, 1998) is similar to that of continental crust but is chemically distinct from the mantle or basaltic material. Thus, even minuscule contributions of sediment to the source of OIBs can be detected using geochemical methods. Atmospheric and spallation-generated ¹⁰Be concentrations, Li, B, and Fe isotope compositions, as well as U-series disequilibrium measurements demonstrate that sediments survive subduction processing to mantle depths (Morris et al., 2002; Turner et al., 2003; Deschamps et al., 2010; Tang et al., 2014; Smith et al., 2021), confirming that the inclusion of recycled sediments in the mantle plume source is a viable model to account for some of the heterogeneities. Consequently, to understand mantle plumes and their sources fully, it is essential to document the geochemical composition of the subducted oceanic crust and the associated sediments that are transported into the lower mantle.

As sediment and oceanic crust are subducted into the mantle, they undergo distinct compositional changes. Specifically, subducted material is dehydrated or melts and it loses a large proportion of the fluid-mobile elements (such as, Li, B and Cs), while retaining refractory elements such as REE and high field strength elements (Porter and White, 2009; Ryan and Chauvel, 2014; Turner and Langmuir, 2022). These changes enable the identification and quantification of the contributions of recycled oceanic crust and sediment to mantle sources (Chauvel et al., 2008; Porter and White, 2009).

The presence of sediments in the OIB source could explain some of the specific trace element characteristics of EM-I and EM-II basalts. The two canonical ratios, Ce/Pb and Nb/U, generally have constant values in all mantle-derived magmas (25 ± 5 for Ce/Pb and 47 ± 10 for Nb/U; Hofmann et al., 1986; Hofmann et al., 2022). In EM-I and EM-II OIBs (**Supplementary Fig. 4**), these ratios deviate from their universal mantle values towards lower values typical of continental crust (3.7 for Ce/Pb and 4.4 for Nb/U; Chauvel et al., 1992; White and Duncan, 1996; Rudnick and Gao, 2003; Jackson et al., 2007; Cordier et al., 2021), providing some constraints on the origin of isotopic enrichment in the OIB source.

[H2] Characterization of recycled material in the mantle

Radiogenic isotopes are more effective than trace elements for detecting and quantifying sedimentary material in OIB sources. For example, 6% sediment in the mantle source shifts the Sr isotopic composition of Samoan basalts from 0.704 to ~0.720; such high values have not been measured in any other OIB to date (Jackson et al., 2007). Most EM-II basalts have much less radiogenic Sr isotopic ratios than Samoan lavas, corresponding to a sediment contribution of <2% in their sources. Nevertheless, most OIBs with radiogenic Sr coupled to unradiogenic Nd and Hf must originate from a source that contains some recycled sedimentary material (Stracke, 2012).

The most common model used to explain the coupling of unradiogenic Sr isotopic ratios with highly radiogenic Pb isotopic signatures observed in HIMU basalts (**Fig. 2d and Supplementary Fig. 9**) is the presence of old (~2 Ga) oceanic crust in the source that has lost some of its Pb during subduction. This interpretation is supported by the elevated Ce/Pb of most HIMU basalts (typically >30; Cordier et al., 2021), which reflects the loss of Pb to subduction

fluids. Furthermore, the relationship between the Nd and Hf isotopic ratios in OIBs (**Fig. 2c and Supplementary Fig. 8**) requires that mantle plume sources include contributions from recycled basalts and sediments with ages ranging from Archean to present-day (Vervoort et al., 1999; Blichert-Toft et al., 1999; Chauvel et al., 2008).

Heavy noble gas (Ne, Ar, Kr, Xe) isotopic ratios in mantle rocks are also sensitive tracers of subducted material. Atmospheric heavy noble gases, which have distinctive elemental ratios and isotopic compositions, are incorporated into the mantle through subduction (Holland and Ballentine, 2006; Mukhopadhyay, 2012; Tucker et al., 2012; Parai et al., 2012; Péron et al., 2021; Parai, 2022); however, this regassing transport is likely to have been inefficient prior to 2.5 Ga (Parai and Mukhopadhyay, 2018; Péron and Moreira, 2018). Once they have been corrected to account for shallow post-eruptive atmospheric contamination, the Xe isotopic signatures of OIB mantle sources are dominated by regassed atmospheric Xe (Parai et al., 2019). This observation clearly shows that there is surface-derived material in the OIB mantle source because the atmospheric Xe isotopic signature reflects sources and processes that are distinct from mantle Xe (Caffee et al., 1999; Avice and Marty, 2020). Likewise, Kr isotopes in Iceland and Galápagos samples indicate strong regassing of atmospheric Kr (Péron et al., 2021). Regassed atmospheric signatures are present even in samples with high ³He/⁴He and primitive, solar-like Ne isotopes (Mukhopadhyay, 2012; Pető et al., 2013; Péron et al., 2021).

The oceanic crust also carries distinctive signatures from the surface into the mantle. For example, Li is incorporated into oceanic crust during hydrothermal alteration and serpentinization. Of the stable isotope systems commonly used in the geosciences, Li has the largest relative mass difference between its two isotopes (⁶Li and ⁷Li). As such, low temperature, aqueous processes result in extreme fractionation (Tomascak, 2004; Tang et al., 2014; Penniston-Dorland et al., 2017) and, consequently, Li isotopes can trace processes that involve fluid mobilization, such as subduction (Fig. 2 e,f). During the subduction process, Li is transported to the mantle wedge as oceanic slabs are dewatered and metamorphosed (Bouman et al., 2004; Deschamps et al., 2010). Variations in Li isotopic values ($\delta^7 \text{Li} > 4$; Li isotopes are measured as the ratio of ⁷Li to ⁶Li, which is normalized to the ratio of a NIST Li carbonate standard; that value is then scaled up by a factor of 1000 to yield the δ^7 Li value) consistent with subduction alteration have been measured in some OIBs from Hawai'i, Cook-Austral, St. Helena, and Azores (Chen and Frey, 2003; Vlastélic et al., 2009; Krienitz et al., 2012; Harrison et al., 2015), providing evidence for the recycling of subduction-altered material into the OIB source. By contrast, MORBs exhibit a relatively uniform Li isotopic composition ($\delta^7 \text{Li} = 3.5 \pm 1.0\%$; Marschall et al., 2017; Penniston-Dorland et al., 2017). There is also a measurable difference between the Li isotopic compositions of HIMU OIB ($\delta^7 \text{Li} = 2.5 - 8.5\%$) and EM-I OIB $(\delta^7 \text{Li} = 0.5-4.5\%)$, which reflects the diversity of subducted components that contribute to these mantle reservoirs (Krienitz et al., 2012; Harrison et al., 2015).

Isotopic systems with large natural fractionations can provide good estimates of the type of subducted surface material present in OIB sources. For example, stable isotopes of thallium (205 Tl and 203 Tl) are fractionated up to 35 epsilon units (ε^{205} Tl is the deviation in parts per ten thousand of 205 Tl/ 203 Tl relative to a reference value), and exhibit large concentration contrasts between geochemical reservoirs. Pelagic sediments have ε^{205} Tl and Tl concentrations [Tl] up to +5 and 1000 ng g⁻¹, respectively (Rehkämper et al., 2002); low-temperature altered oceanic crust has ε^{205} Tl and [Tl] as low as -15 and 5–50 ng g⁻¹, respectively (Nielsen et al., 2006a); and for the mantle ε^{205} Tl = -2 ± 0.5 and [Tl] <1 ng g⁻¹ (Nielsen et al., 2017). OIBs exhibit a wide range of ε^{205} Tl values (-6.4 to +6.6; Brett et al., 2021). Elevated ε^{205} Tl (up to +4) in Hawaiian tholeiites

have been attributed to recycled subducted sediment in the plume source (Nielsen et al., 2006b; Williamson et al., 2021), potentially sampled from the ambient mantle on the periphery of the Pacific LLSVP (Williamson et al., 2021). Conversely, low ε^{205} Tl (down to -10) in lavas from St. Helena can be attributed to altered oceanic crust in their source and in the HIMU mantle reservoir (Blusztajn et al., 2018). In some cases, however, the Tl isotopic composition of OIB is ambiguous, requiring careful consideration when interpreting results and using this isotopic system as a mantle tracer (Brett et al., 2021; Williamson et al., 2021).

Subducted material also carries information about previous redox conditions at Earth's surface. In specific circumstances, such as the extreme surface conditions during the Archean prior to the great oxygenation event at ~2.5–2.4 Ga (Farquhar et al., 2007), mass-independent fractionation of stable isotopes such as S can occur creating isotopic anomalies. These signatures are then incorporated into sedimentary materials, and basalts at the surface. For example, negative S isotopic anomalies have been detected in lavas from Mangaia (Cabral et al., 2013; Dottin III et al., 2020) and in basalts from Pitcairn (Delavault et al., 2016). These observations indicate that the HIMU (Mangaia) and EM-I (Pitcairn) mantle sources include material that was present at Earth's surface during the Archean, either in the form of Archean basaltic crust for Mangaia or Archean sedimentary material for Pitcairn.

Isotopic tracers that enable the characterization of recycled material in the OIB mantle source continue to be developed. For example, Ce is redox-sensitive (Elderfield, 1988). Therefore, measurements of the long-lived ¹³⁸La-¹³⁸Ce system can constrain the timing of pelagic sediment recycling into the mantle because no Ce anomalies are expected in water columns before the great oxygenation event at ~2.5–2.4 Ga (Israel et al., 2020; Boyet et al., 2021). Collectively, many isotopic and trace element systems (Box 2, Fig. 1b and Supplementary Figs. 2–5) indicate that material that was previously at the surface of the Earth is present in the source of OIBs. However, not all isotopic characteristics of OIB can be explained by recycling surficial material into the plume source alone. Additional types of material must be present and the influence of several large-scale processes must also be considered, including the physical proximity of plumes to LLSVPs, the depth and source of plume magmatism, and core—mantle interactions.

[H1] Early-formed reservoirs

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

[H2] Tracing early-formed reservoirs

Processes such as metal—silicate differentiation, magma ocean crystallization, and degassing of volatiles during energetic accretionary impacts influenced the geochemistry of the interior of the early Earth by fractionating groups of elements with different properties from each other. Because these events only occurred for relatively short periods close to 4.5 Ga, the best tools to understand them and track their contributions to the OIB mantle are short-lived radionuclide systems, such as ¹⁸²Hf-¹⁸²W, ¹⁴⁶Sm-¹⁴²Nd, ¹²⁹I-¹²⁹Xe, and ²⁴⁴Pu-¹³¹⁻¹³⁶Xe, with

half-lives between <10 Ma and ~100 Ma. Variations in the radiogenic products of some short-lived isotope systems are small in (such as $\mu^{142}Nd$ ~15 and $\mu^{182}W$ ~30 ppm, where the notation indicates deviations in parts per million relative to the terrestrial reference), making them difficult to detect (**Fig. 4**, Touboul et al., 2012b; Horan et al., 2018; **Box 3**). Volatile elements pose additional challenges, owing to the loss of magmatic gas from samples and atmospheric contamination during and after eruption. Nevertheless, progress has been made measuring $\mu^{142}Nd$, $\mu^{182}W$, and $\mu^{129}Xe/\mu^{130}Xe$ variations in OIBs, as well as interpreting the importance of these anomalies for mantle history and dynamics.

Trace element abundances and their ratios are also powerful tools for quantifying fractionation processes in the early Earth. For example, mass balance calculations using (Nb, Ta)/U and 143 Nd/ 144 Nd isotope ratios (Hofmann et al., 2022) demonstrate that continental crust and present-day depleted mantle could not have originated from the primitive mantle as previously thought (Jacobsen and Wasserburg, 1979; O'Nions et al., 1979; DePaolo, 1980). This conclusion is supported by the delicate measurement of a radiogenic excess of 142 Nd (+7.9 ± 1.9 ppm) in the mantle relative to its building blocks (Frossard et al., 2022; Johnston et al., 2022). Therefore, the Earth's mantle could be slightly depleted in incompatible elements and characterized by higher Sm/Nd than chondrites. The Sm/Nd fractionation could be inherited from the accretion stage when Earth's protocrust, enriched in incompatible elements and formed in planetesimals, was lost to space during collisional events (Frossard et al., 2022), removing the need for an early enriched reservoir to have been preserved in the deep mantle (Boyet and Carlson, 2005).

Many stable isotope ratios of major elements can also preserve early-formed isotopic signatures because their values were not reset on a global scale (**Box 2**). Stable isotope fractionation has been constrained through high pressure—temperature experiments that simulate early differentiation events (Shahar et al., 2017) to predict the isotopic signatures in mantle sources, and determine stable isotope fractionation factors that enable distinguishing potential stable isotopic heterogeneities of early-formed reservoirs.

[H2] Terrestrial magma ocean relics

Small ¹⁴²Nd anomalies measured in some OIBs (–8 to +6 ppm; **Fig. 4a**) from Réunion (Peters et al., 2018) and Samoa (Horan et al., 2018) suggest that early-formed reservoirs might be preserved in the deepest part of the mantle. Owing to the short half-life of ¹⁴⁶Sm (~103 Ma), the variations measured in ¹⁴²Nd/¹⁴⁴Nd must reflect the Sm/Nd fractionation that took place during the first few hundred million years of Earth's history. Both Sm and Nd are lithophile REEs and were excluded from the metal phase during core–mantle differentiation (Faure et al., 2021); therefore, early fractionation of Sm/Nd must have occurred exclusively through silicate differentiation, providing evidence for the crystallization of a terrestrial magma ocean. Most OIBs are also characterized by negative ¹⁸²W anomalies (μ¹⁸²W down to –25 ppm) (Mundl et al., 2017; Mundl-Petermeier et al., 2019; Peters et al., 2021), which could also represent the remnant of an early terrestrial magma ocean (**Fig. 4b**). However, core–mantle interactions could affect the ¹⁸²W signal, making it difficult to interpret (Rizo et al., 2019; Mundl-Petermeier et al., 2020).

The short-lived ¹²⁹I–¹²⁹Xe system provides additional support for the preservation of early-formed isotopic heterogeneity (measured as ¹²⁹Xe/¹³⁰Xe; ¹²⁹Xe is produced by the decay of short-lived ¹²⁹I, and ¹³⁰Xe is not radiogenic). Mantle Xe isotope compositions can be broken down into component contributions from accretion (chondritic Xe), radioactive decay, and atmospheric regassing (Caffee et al., 1999; Parai et al., 2019). Limited measurements of mantle-

derived samples from OIBs and MORBs (Moreira et al., 1998; Mukhopadhyay, 2012; Parai et al., 2012; Tucker et al., 2012; Parai and Mukhopadhyay, 2015; Peron and Moreira, 2018; Parai and Mukhopadhyay, 2021; Peron et al., 2021), as well as back-arc basin basalts (Peto et al., 2013), volcanic and continental well gases (Caracausi et al., 2016; Bekaert et al., 2019) yield precise estimates of mantle source Xe compositions, corrected for shallow atmospheric contamination. Ratios of ¹²⁹Xe/¹³⁰Xe from Iceland, (Mukhopadhyay, 2012), the Rochambeau Rift sampling Samoa (Peto et al., 2013), and Galápagos (Péron et al., 2021) are low compared to those of the depleted mantle (Holland and Ballentine, 2006; Tucker et al., 2012; Parai et al., 2012). Differential incorporation of atmospheric Xe with low ¹²⁹Xe/¹³⁰Xe into the OIB mantle cannot account for these OIB ¹²⁹Xe/¹³⁰Xe signatures (Fig. 4c,d). Thus, a low I/Xe ratio must have been established in the OIB mantle within the first ~100 Myr of Earth's history, and its signature preserved despite ~4.45 Gyr of convection (Mukhopadhyay, 2012). The low I/Xe ratio could reflect inefficient degassing of the deeper parts of the magma ocean, or low I abundances in the early-accreted materials.

The paired I–Pu–Xe decay system provides additional insight into early magma ocean history. Initially, catastrophic outgassing would have transported Xe out of the terrestrial magma ocean. After closure the products of ¹²⁹I decay and ²⁴⁴Pu fission would have been retained in the silicate Earth. Because ¹²⁹I and ²⁴⁴Pu decay at different rates, the ¹²⁹Xe*/¹³⁶Xe_{Pu} ratio (where the star indicates radiogenic ¹²⁹Xe produced by ¹²⁹I decay, and the subscript denotes ¹³⁶Xe from Pufission; Mukhopadhyay, 2012) can be used to calculate a closure age that marks the end of open system magma ocean outgassing (Wetherill, 1975). The Iceland and Samoan Rochambeau Rift samples exhibit low ¹²⁹Xe*/¹³⁶Xe_{Pu} ratios compared to the MORB mantle. If the whole mantle had an initially homogeneous I/Pu ratio, then low ¹²⁹Xe*/¹³⁶Xe_{Pu} ratios in OIBs would indicate a late closure age for the OIB mantle relative to the MORB mantle, because less of the shorterlived ¹²⁹I would remain at the onset of Xe retention in the mantle. A more realistic scenario might be that the mantle had an initially heterogeneous I/Pu, and regions of low I/Pu reflect the limited accretion of volatile-rich materials into the OIB mantle (Mukhopadhyay, 2012; Caracausi et al., 2016; Parai et al., 2019). A relatively dry OIB mantle could have contributed to inefficient mixing in both the terrestrial magma ocean and the solid mantle throughout Earth history (Parai, 2022). Thus, the OIB I-Pu-Xe signature not only records the heterogeneity of the early mantle, but also provides insight into the mechanisms that preserve heterogeneities formed during the early magma ocean stage.

[H2] The effect of the core on the OIB source

Early core formation and its subsequent evolution have likely had an important role in controlling radiogenic and stable isotope variations in OIBs. The Earth's metallic core physically separated from the mantle during the first few tens of million years of Earth's history (Kleine et al., 2002, Yin et al., 2022; Walker, 2014), trapping a substantial proportion of light elements (~10% of Si, O, S, C, N, and H; McDonough, 2016; Badro et al., 2015). The incorporation of these light elements into the core could have changed the isotopic composition of the mantle on a bulk scale (Shahar et al., 2016); however, such fractionation would not generate mantle heterogeneities if the core formed when the entire mantle and core were in equilibrium. For example, whole mantle—core equilibrium (Shahar et al., 2011) has been proposed to explain the fractionation of the mantle in silicon isotopes relative to chondrites (Georg et al., 2007; Hin et al., 2017). In contrast, evidence from diamond inclusions suggests that Fe isotopic heterogeneities exist in Earth's deep mantle. Cullinan-like, Large, Inclusion-Poor, Pure,

Irregular, and Resorbed (CLIPPIR) diamonds from Letseng, Lesotho, which originate from depths of 360–750 km, exhibit heavy Fe isotopic signatures (δ^{56} Fe = 0.79–0.90‰) that lie outside the near-0‰ range of known mantle compositions or expected reaction products that occur at these depths (Smith et al., 2021). High pressure and temperature experiments suggest that core formation on its own cannot account for such a large shift in Fe isotopic ratios (Elardo et al., 2019). Rather, these data provide evidence for the subduction of surface material characterized by light isotopic ratios into the lower mantle (Smith et al., 2021).

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

[H3] Core–mantle interactions

The extremely high temperatures at the CMB can cause mantle minerals that are in direct contact with the liquid core to be in chemical equilibrium with that liquid. As the core cools and the composition of the outer core changes because of the ongoing crystallization of the inner core, some elements might diffuse across the CMB as they are exsolved from the liquid outer core. Thus, the composition of the core could be changing progressively, increasing mantle heterogeneity as the core evolves core (Tronnes et al., 2019). Grain-diffusion experiments found that siderophile elements diffuse through MgO at a high enough rate to transport those elements across geological length scales (tens of kilometers) over 4.5 Ga, demonstrating that grain-boundary diffusion is an efficient pathway for core—mantle interactions (Hayden and Watson 2007).

Geochemical signatures of several highly siderophile elements suggest that the lower mantle was polluted with core material prior to being entrained into mantle plumes. The resulting signatures include elevated Fe/Mn ratios, such as those in Hawaiian lavas (Humayun et al., 2004), and radiogenic Os isotope enrichments detected in several mantle plumes (Brandon et al., 1998, 2003). Despite further investigations (Brandon et al., 2003; 2005; Ireland et al., 2011), no other isotopic signature indicative of element transport across the CMB was identified until high precision µ¹⁸²W measurements could be performed (Touboul et al., 2012a; 2012b; Trinquier et al., 2016). Small negative anomalies in μ^{182} W (-25 ppm) have been measured in OIBs (**Fig. 4b**; Mundl et al., 2017; Mundl-Petermeier et al., 2019; Rizo et al., 2019; Peters et al., 2021). In mantle-derived samples, μ^{182} W shifts from positive values in Hadean–Archean samples (4.3–2.7) Ga) to negative values in modern samples. This observation suggests that the W signature in OIBs could reflect a time-integrated core contribution of W to the mantle. The mechanism of the interaction between the outer liquid core and the mantle remains uncertain, but current work is focused on the exsolution of Si-Mg-Fe oxide (Rizo et al., 2019) and diffusive exchange across the CMB between foundered oxidized, oceanic crust and the outer core (Mundl-Petermeier et al., 2020; Yoshino et al., 2020).

Core—mantle interactions could also manifest in the I–Xe system. If iodine were more strongly siderophile than Xe at core formation pressures and temperatures (Armytage et al., 2013; Jackson et al., 2018), the core would have had elevated I/Xe and I/Pu compared to the mantle. In this case, the core would supply high ¹²⁹Xe/¹³⁰Xe and ¹²⁹Xe*/¹³⁶Xe_{Pu} to the mantle. However, OIBs sample a reservoir with low ¹²⁹Xe/¹³⁰Xe and ¹²⁹Xe*/¹³⁶Xe_{Pu} relative to the rest of

the mantle suggesting that the core might have acted as a sink for lower mantle I during accretion, with no subsequent transfer of radiogenic Xe back to the mantle over time (Jackson et al., 2018).

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

One proposal to explain the relationship between He and W isotopes in OIB is that their anomalies only persist in mantle domains least affected by crustal recycling, because recycled crust contributions overwhelm He and W isotopic signatures from core material (Jackson et al. 2020a). This hypothesis is consistent with Th enrichment observed in OIB samples with low ³He/⁴He, as recycled crust has high Th abundances, which decays radioactively producing ⁴He (Class and Goldstein, 2005). Nevertheless, the most negative μ^{182} W anomalies measured to date are accompanied by strong indications of recycling in Kr and Xe isotopic compositions at Fernandina Island, Galápagos (Péron et al., 2021). Similarly, there is a pronounced recycling signature in the Kr and Xe isotopes in Iceland (Mukhopadhyay, 2012; Péron et al., 2021), where some of the highest ³He/⁴He ratios have been detected. Additional measurements of W and noble gases from samples with thoroughly characterized radiogenic isotopic compositions are needed to resolve the relationship between core-hosted signatures, the contribution from recycled crustal material, and primitive mantle domains.

[H2] Constraints on lower mantle seismic structures

Variations in the 182 Hf $^{-182}$ W, I $^{-182}$ W, I $^{-182}$ W, I $^{-182}$ Nd isotopic systems in OIBs require that plumes sample early-formed reservoirs, likely from the deepest part of the mantle (**Fig. 4**). Although few lavas have been measured for all of these isotopic systems, the existing data provide insight into the nature of early-formed mantle reservoirs. The ULVZs are speculated to be the source of the high 3 He $^{/4}$ He and the most negative μ^{182} W in OIBs (Jackson et al., 2017; Mundl et al., 2017; Williams et al., 2019; Kim et al., 2019). If core–mantle interactions supply high 3 He $^{/4}$ He and the most negative μ^{182} W signatures (Rizo et al., 2019; Mundl-Petermeier et al., 2020; Peters et al., 2021), then the ULVZs might have formed through interactions with the core. An alternative mechanism to explain variable μ^{182} W anomalies in OIBs is early silicate differentiation that modified the Hf/W ratios of mantle reservoirs, which subsequently remained largely isolated from the rest of the convecting mantle (Touboul et al., 2012a; Brown et al., 2014; Puchtel et al., 2016).

The LLSVPs, described as thermochemical piles, might contain relics of magma ocean crystallization that occurred after the Moon-forming giant impact (Labrosse et al., 2007; Lee et al., 2010 Ballmer et al., 2017; Gülcher et al., 2020). Variations in μ^{142} Nd measured in some OIBs suggest that remnants of magma ocean crystallization could be preserved in the deep mantle (Peters et al., 2018). If the Moon-forming giant impact occurred ~4.4–4.35 Ga, as suggested by both terrestrial and lunar samples (Morino et al., 2017; Borg et al., 2019; Lock et al., 2020), then the 182 Hf- 182 W system was already extinct. Therefore, the mantle 182 W isotope composition would be unchanged by the collision, explaining the lack of correlation between 142 Nd/ 144 Nd and

¹⁸²W/¹⁸⁴W in OIB lavas (except for Réunion lavas; Peters et al., 2021). Alternatively, LLSVPs might have formed from the accumulation of subducted material (Brandenburg and van Keken, 2007; Nakagawa et al., 2009) or from the sinking of dense, reduced material (Gu et al., 2016; Creasy et al., 2020). It is likely that LLSVPs do not result from a single process, but incorporate material from primordial and early events, ongoing convection, and recycled subducted material (McNamara, 2019; Parai et al., 2019).

[H1] Mantle mixing and convection

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

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

Numerical simulations of mantle plumes (**Fig. 5**) suggest that after 4.5 Ga of convection, part of the recycled oceanic crust accumulates along the core-mantle boundary and forms large piles, while the remainder is dispersed in the mantle as small streaks (Gülcher et al. 2021). The primordial material, which is intrinsically more viscous than the surrounding mantle, partially survives as distinct blobs, and a fraction of the ancient FeO-rich basal layer can be preserved by incorporation into the denser basal piles. Numerical simulations (Farnetani et al., 2018) of mantle plumes carrying finite size (30–40 km radius) rheological heterogeneities that are 20–30 times more viscous than the surrounding rocks indicate that these heterogeneities can resist stretching

because they rotate during their ascent through the mantle. Such material could preserve and transport a distinct isotopic fingerprint from the deep mantle to the surface in mantle plumes.

For thermo-chemical plumes, the subtle balance between positive thermal buoyancy and negative compositional buoyancy induces oscillatory behavior (Davaille, 1999) and complex internal dynamics, because some parts of the conduit might sink whereas other parts ascend (Kumagai et al., 2008). Furthermore, the idea that isotopic zonation in the plume conduit preserves large-scale zonation in the mantle source region might not be accurate for thermo-chemical plumes because, under certain conditions, compositionally denser material rises preferentially at the plume axis (Jones et al., 2016). However, if chemical heterogeneity is a passive component of lower mantle structures (that is, if it has little effect on physical parameters such as density), and if lower mantle structures differ from each other mainly in their thermal properties, then isotopic zonation could potentially be preserved in the plume conduit (Jones et al., 2016).

[H1] Importance of mantle flux

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

Instead, OIBs can be effectively evaluated using a range of variables, such as plume strength and temperature, source mantle composition, and melting conditions. These variables can be assessed across a mantle plume spectrum, based primarily on magma flux (King and Adam, 2014). The Hawaiian–Emperor chain defines the mantle plume end-member with the strongest magma production. Samoa, Iceland, and Galápagos are also classified close to the highproduction end of the spectrum. They all have high ³He/⁴He ratios in some of their erupted lavas, elevated buoyancy fluxes (Jackson et al., 2017), and slow velocity zones and an LLSVP at their source (Williams et al., 2019). The other end of the spectrum is represented by weaker plumes, with potentially shallower sources, which do not exhibit multiple mantle geochemical components nor have mantle potential temperatures substantially hotter than MORBs. Examples at this end of the spectrum include Ascension, Cobb-Eickelberg seamounts on the Juan de Fuca ridge, and the Bowie-Kodiak (also called Pratt-Welker) seamount chain, which have not been associated with a lower mantle seismic wave tomography anomaly that extends to the CMB (French and Romanowicz, 2015). They also have isotopic compositions that are nearly indistinguishable from MORBs in part owing to plume-ridge interactions (such as Bowie-Kodiak and Cobb-Eickelberg (Hegner and Tatsumoto, 1989; Chadwick et al., 2014)), and are among the coolest mantle plumes (Bao et al., 2022).

Between the strong Hawaiian-type plumes and the weak Ascension-type systems are those that most closely emulate the classic model, such as Louisville, Kerguelen, Caroline,

Easter, Réunion, and Tristan. These plumes possess a voluminous head that formed a LIP, a plume tail that formed an age-progressive volcanic chain, and a buoyancy flux between $\sim 0.5-2$ Mg s⁻¹ that wanes over time. This flux-based plume spectrum provides a systematic reference framework for comparing mantle plumes and plume chemistry, which will prevent inappropriate comparisons between vastly dissimilar systems.

[H1] Summary and future perspectives

The study of mantle plumes, their sources, and chemical heterogeneity in the mantle has generated important hypotheses and ideas about major mantle processes such as convection, recycling of crustal materials, and mantle residence times, as well as the nature of interactions between various reservoirs throughout the Earth system. It is no coincidence that advances in analytical geochemistry capabilities have occurred alongside the increasing sophistication of mantle plume models. The improvement in precision, sensitivity, and resolving power of mass spectrometers has opened areas of the Periodic Table for analysis, including small isotopic anomalies, short-lived isotopic systems, and small mass-dependent fractionations that reflect early differentiation processes, recycling of subducted material into the mantle, and evidence for material preserved from Earth's earliest history.

The focused development of new isotopic and elemental analysis methods provides insight into large-scale planetary processes and compositional evolution, offering opportunities for future discoveries. Specifically, systems such as I–Pu–Xe, ¹⁸²W/¹⁸⁴W, and ¹⁴²Nd/¹⁴⁴Nd have the potential to resolve core—mantle interactions, and to document the preservation and sampling of early-formed reservoirs in the mantle. However, laboratories rarely have the capabilities to analyze both rare noble gases and low-abundance W and Nd isotopes, necessitating collaborative efforts to generate insights from different isotopic systems on the same set of samples.

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

Some of the greatest insights in mantle geochemistry have come from targeted sampling strategies, in which isotopic systems are applied to locations that are likely to carry imprints of specific processes. Again, such studies require collaborations between laboratories and researchers, both for access to the advanced analytical techniques and to avoid analyzing sample powders in isolation from their geological contexts.

Collaborations between geophysicists, geochemists, and geodynamicists are key to resolving important questions about how the transport of heterogeneities from Earth's mantle reservoirs to the surface is controlled by partial melting, plume-lithosphere interactions, and plume buoyancy forces. Debate persists regarding how geochemical components are entrained, mixed, stretched, stalled, and melted during mantle transport and ultimately expressed in erupted lavas. This uncertainty propagates into the models that explain geochemical variations in erupted lavas, which rely on the interpretation of spatial patterns and time-integrated signatures in those lavas. A better understanding of mantle geodynamics, along with how lithology affects the

melting and mixing of magmas, is needed to provide better constraints for understanding the source, evolution, and preservation of geochemical heterogeneities in the mantle.

Finally, much is still unknown about the composition of seismically imaged mantle heterogeneities, in both the shallow and deep mantle and how they relate to chemical heterogeneities (**Supplementary Fig. 10**). The spatial differences in OIB compositions, both between different plume systems and over time at individual plumes, suggest that there are systematic variations in mantle geochemical domains on many scales that are currently poorly understood. Resolving uncertainties in mantle geodynamics and melt homogenization processes will help to determine whether these differences reflect distinct tectonic histories. Clearly, much remains to be learned about mantle plumes and the composition of the Earth. It is likely that the greatest advances will emerge from cross-disciplinary studies in diverse fields such as experimental petrology, mineral physics, numerical geodynamics, seismology, and geochemistry.

References

- Abouchami, W., Galer, S.J.G. & Hofmann, A.W. High precision lead isotope systematics of lavas from the Hawaiian Scientific Drilling Project. *Chem. Geol.* **169**, 187–209 (2000).
- Abouchami, W., Hofmann, A.W., Galer, S.J.G., Frey, F.A., Eisele, J. & Feigenson, M. Lead isotopes reveal bilateral asymmetry and vertical continuity in the Hawaiian mantle plume. *Nature* **434**, 851-856 (2005).
- Allègre, C.J. Chemical geodynamics. *Tectonophysics* 81, 109-132 (1982).
- Ammann, M.W., Brodholt, J.P., Wookey, J. & Dobson, D.P. First-principles constraints on diffusion in lower-mantle minerals and a weak D" layer. *Nature* **465**, 462–465 (2010).
- Andreasen R., Sharma M., Subbarao K.V., Viladkar, S.G. Where on Earth is the enriched Hadean reservoir? *Earth Planet. Sci. Lett.* **266**,14–28 (2008).
- Armytage, R.M.G., Jephcoat, A.P., Bouhifd, M.A. & Porcelli, D. Metal-silicate partitioning of iodine at high pressures and temperatures: Implications for the Earth's core and (129)*Xe budgets. *Earth Planet. Sci. Lett.* **373**, 140-149 (2013).
- Avice, G. & Marty, B. Perspectives on atmospheric evolution from noble gas and nitrogen isotopes on Earth, Mars & Venus. *Space Sci. Rev.* **216**, 1-18 (2020).
- Badro, J., Brodholt, J.P., Pieta, H., Siebert, J. & Ryerso, F.J. Core formation and core composition from coupled geochemical and geophysical constraints. *Proc. Natl. Acad. Sci. USA* **112**, 12310–12314 (2015).
- Ballmer, M.D., Houser, C., Hernlund, J.W., Wentzcovitch, R.M. & Hirose, K. Persistence of strong silica-enriched domains in the Earth's lower mantle. *Nature Geosci.* **10**, 236–241. (2017).
- Bao, X., Lithgow-Bertelloni, C.R., Jackson, M.G. & Romanowicz, B. On the relative temperatures of Earth's volcanic hotspots and mid-ocean ridges. *Science* **375**, 57-61. (2022).
- Basford, J.R., Dragon, J.C., Pepin, R.O., Coscio Jr., M.R., Murthy, V.R. Krypton and xenon in lunar fines. Proceedings of the Lunar Science Conference. *Geochim. Cosmochim. Acta* Suppl. 4, 1915–1955 (1973).
- Bekaert, D.V., Broadley, M.W., Caracausi, A. & Marty, B. Novel insights into the degassing history of Earth's mantle from high precision noble gas analysis of magmatic gas. *Earth Planet. Sci. Lett.* **525**, 115766 (2019).

- Bizimis, M., Sen, G., Salters, V.J.M. & Keshav, S. Hf-Nd-Sr isotope systematics of garnet pyroxenites from Salt Lake Crater, Oahu, Hawaii: evidence for a depleted component in Hawaiian volcanism. *Geochim. Cosmochim. Acta* **69** (10), 2629–2646 (2005).
- Blichert-Toft, J., Frey, F.A. & Albarède, F. Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts. *Science* **285**, 879-882 (1999).
- Blusztajn J., Nielsen S. G., Marschall H. R., Shu Y., Ostrander C. M. & Hanyu T. Thallium isotope systematics in volcanic rocks from St Helena constraints on the origin of the HIMU reservoir. *Chem. Geol.* **476**, 292–301. (2018).
- Borg, L. E. et al. Isotopic evidence for a young lunar magma ocean. *Earth Planet Sc Lett* **523**, 115706 (2019).
- Boschi, L., Becker, T.W. & Steinberger, S. Mantle plumes: Dynamic models and seismic images. *Geochem. Geophys. Geosystems* **8(10)**, Q10006 (2007).
- Bouhifd, M.A., Jephcoat, A.P., Porcelli, D., Kelley, S.P. & Marty, B. Potential of Earth's core as a reservoir for noble gases: Case for helium and neon. *Geochem. Perspect. Lett.* **15**, 15-18 (2020).
- Bouman, C., Elliott, T. & Vroon, P.Z. Lithium inputs to subduction zones. *Chem. Geol.* **212**, 59-79 (2004).
- Boyet, M. & Carlson, R. W. ¹⁴²Nd evidence for early (> 4.53 Ga) global differentiation of the silicate Earth. *Science* **309**, 576–581 (2005).
- Boyet, M., Doucelance, R., Israel, C., Bonnand, P., Auclair, D., Suchorski, K. & Bosq, C. New constraints on the origin of the EM-1 component revealed by the measurement of the La-Ce isotope systematics in Gough Island lavas. *Geochem. Geophys. Geosystems* **20**(5), 2484-2498 (2019).
- Boyet, M., Garcon, M., Arndt, N., Carlson, R.W. & Konc, Z. Residual liquid from deep magma ocean crystallization in the source of komatiites from the ICDP drill core in the Barberton Greenstone Belt. *Geochim. Cosmochim. Acta* **304**, 141-159 (2021).
- Brandenburg, J.P. & van Keken, P.E. Deep storage of oceanic crust in a vigorously convecting mantle. *J. Geophys. Res. Solid Earth* **112 (B6)**, B06403 (2007).
- Brandenburg, J.P., Hauri, E.H., van Keken, P.E. & Ballentine, C.J. A multiple-system study of the geochemical evolution of the mantle with force-balanced plates and thermochemical effects. *Earth Planet. Sci. Lett.* **276**, 1-13 (2008).
- Brandon, A.D., Walker, R.J., Morgan, J.W., Norman, M.D. & Prichard, H.M. Coupled 186Os and 187Os evidence for core-mantle interaction. *Science* **280**, 1570–1573 (1998)
- Brandon, A.D., Walker, R.J., Puchtel, I.S., Becker, H., Humayun, M. & Revillon, S. Os-186-Os-187 systematics of Gorgona Island komatiites: implications for early growth of the inner core. *Earth Planet. Sci. Lett.* **206**, 411-426 (2003).
- Brandon, A.D., Humayun, M., Puchtel, I.S., Leya, I. & Zolensky, M. Osmium isotope evidence for an s-process carrier in primitive chondrites. *Science* **309**, 1233-1236 (2005).
- Brett, A., Prytulak, J., Rehkämper, M., Hammond, S.J., Chauvel, C., Stracke, A. & Willbold, M. Thallium elemental and isotopic systematics in ocean island lavas. *Geochim. Cosmochim. Acta* **301**, 187-210 (2021).
- Brown, S. M., Tanton, L. T. E. & Walker, R. J. Effects of magma ocean crystallization and overturn on the development of 142Nd and 182W isotopic heterogeneities in the primordial mantle. *Earth Planet. Sci. Lett.* **408**, 319–330 (2014).

- Burkhardt, C., Borg, L.E., Brennecka, G.A., Shollenberger, Q.R., Dauphas, N., Kleine, T., 2016. A nucleosynthetic origin for the Earth's anomalous ¹⁴²Nd composition. *Nature* **537**, 394–398 (2016).
- Burke, K. & Torsvik, T. H. Derivation of Large Igneous Provinces of the past 200 million years from long-term heterogeneities in the deep mantle. *Earth Planet. Sci. Lett.* **227**, 531-538 (2004).
- Burke, K., Steinberger, B., Torsvik, T.H. & Smethurst, M.A. Plume generation zones at the margins of large low shear velocity provinces on the core mantle boundary. *Earth Planet. Sci. Lett.* **265**, 49-60 (2008).
- Cabral, R.A., Jackson, M.G., Rose-Koga, E.F., Koga, K.T. Koga, Whitehouse, M.J. et al. Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust. *Nature* **496**, 90-493 (2013).
- Caffee, M.W., Hudson, G.B., Velsko, C., Huss, G.R., Alexander, Jr. E.C. & Chivas, A.R. Primordial noble gases from Earth's mantle: Identification of a primitive volatile component. *Science* **285**, 2115-2118 (1999).
- Campbell, I.H. & Griffiths, R.W. Implications of mantle plume structure for the evolution of flood basalts. *Earth Planet. Sci. Lett.* **99**, 79-93 (1990).
- Caracausi, A., Avice, G., Burnard, P.G., Furi, E. & Marty, B. Chondritic xenon in the Earth's mantle. *Nature* **533**, 82-85 (2016).
- Castillo, P.R. The recycling of marine carbonates and sources of HIMU and FOZO ocean island basalts. *Lithos* **216–217**, 254-263 (2015).
- Chadwick, J., Keller, R., Kamenov, G., Yogodzinski, G. & Lupton, J. The Cobb hot spot: HIMU-DMM mixing and melting controlled by a progressively thinning lithospheric lid. *Geochem. Geophys. Geosystems* **15**, 3107–3122 (2014).
- Chan, L.-H. & Frey, F.A. Lithium isotope geochemistry of the Hawaiian plume: Results from the Hawaii Scientific Drilling Project and Koolau Volcano. *Geochem. Geophys. Geosystems* **4(3)**, 8707 (2003).
- Chan, L., Lassiter, J.C., Hauri, E.H., Hart, S.R. & Blusztajn, J. Lithium isotope systematics of lavas from the Cook-Austral Islands: Constraints on the origin of HIMU mantle. *Earth Planet. Sci. Lett.* **277**, 433-442 (2009).
- Chauvel, C., Hofmann, A.W. & Vidal, P. HIMU EM the French-Polynesian connection. *Earth Planet. Sci. Lett.* **110**, 99–119 (1992).
- Chauvel, C., McDonough, W., Guille, G., Maury, R. & Duncan, R. Contrasting old and young volcanism in Rurutu Island, Austral chain. *Chem. Geol.* **139**, 125-143 (1997).
- Chauvel, C., Lewin, E., Carpentier, M., Arndt, N.T. & Marini, J.-C. Role of recycled oceanic basalt and sediment in generating the Hf-Nd mantle array. *Nature Geosci.* **1(1)**: 64-67 (2008).
- Chauvel, C., Maury, R.C., Blais, S., Lewin, E., Guillou, H., Guille, G., Rossi, P. & Gutscher, M.-A. The size of plume heterogeneities constrained by Marquesas isotopic stripes. *Geochem. Geophys. Geosystems* **13(1)**, (2012).
- Christensen, U. R. & Hofmann, A. W. Segregation of subducted oceanic crust in the convecting mantle, *J. Geophys. Res. Solid Earth* **99**, 19867-19884 (1994).
- Class, C. & Goldstein, S.L. Evolution of helium isotopes in the Earth's mantle. *Nature* **436**, 1107-1112 (2005).
- Coffin, M. & Eldholm, O. Large igneous provinces: crustal structure, dimensions, and external consequences. *Rev. Geophys.* **32**, 1–36 (1994).

- Cordier, C., Delavault, H. & Chauvel, C. Geochemistry of the Society and Pitcairn-Gambier mantle plumes: What they share and do not share. *Geochim. Cosmochim. Acta* **306** 362-384 (2021).
- Cottaar, S. & Romanowicz, B. An unsually large ULVZ at the base of the mantle near Hawaii. *Earth Planet. Sci. Lett.* **355**, 213–222 (2012).
- Cottaar, S., Martin, C., Li, Z. & Parai, R. The root to the Galápagos mantle plume on the coremantle boundary. *Seismica* 1, (2022).
- Courtillot, V., Davaille, A., Besse, J. & Stock, J. Three distinct types of hotspots in the Earth's mantle. *Earth Planet. Sci. Lett.* **205**, 295-308 (2003).
- Creasy, N., Girard, J., Eckert, J.O. & Lee, K.K.M. The role of redox on Bridgmanite crystal chemistry and calcium speciation in the lower mantle. *J. Geophys. Res. Solid Earth* **125(10)**, 2020JB020783 2020).
- Dannenberg, J. & Sobolev, S. V. Low-buoyancy thermochemical plumes resolve controversy of classical mantle plume concept. *Nature Comm.* **6**, 6960 (2015).
- Dasgupta, R., Hirschmann, M. M., & Smith, N. D. Partial melting experiments of peridotite+ CO2 at 3 GPa and genesis of alkalic ocean island basalts. *J. Petrol.* **48(11)**, 2093-2124 (2007).
- Davaille, A. Simultaneous generation of hotspots and superswells by convection in a heterogeneous planetary mantle. *Nature* **402**, 756–760 (1999).
- Davies, D.R. & Davies, J.J. Thermally-driven mantle plumes reconcile multiple hot-spot observations. *Earth Planet. Sci. Lett.* **278**, 50-54 (2009).
- DeFelice, C., Mallick, S., Saal, A.E. & Huang, S. An isotopically depleted lower mantle component is intrinsic to the Hawaiian mantle plume. *Nature Geosci.* **12**, 487–492 (2019.
- Delavault, H., Chauvel, C., Thomassot, E., Devey, C.W. & Dazas, B. Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. *Proc. Natl. Acad. Sci. U.S.A.* **113(46)**: 12952-12956 (2016).
- de Leeuw, G.A.M., Ellam, R.M., Stuart, F.M. & Carlson, R.W. Nd-142/Nd-144 inferences on the nature and origin of the source of high He-3/He-4 magmas. *Earth Planet. Sci. Lett.* **472**, 62-68 (2017).
- DePaolo, D.J. Crustal growth and mantle evolution: inferences from models of element transport and Nd and Sr isotopes. *Geochim. Cosmochim. Acta* **44**, 1185–1196 (1980).
- DePaolo D. J. and Weis D. Hotspot Volcanoes and Large Igneous Provinces, in Continental Scientific Drilling: A Decade of Progress, and Challenges for the Future, Editors: U. Harms, C. Koeberl & M.D. Zoback, Springer, p. 259-288 (2007).
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M. & Hattori, K. In situ characterization of serpentinites from forearc mantle wedges: Timing of serpentinization and behavior of fluid-mobile elements in subduction zones. *Chem. Geol.* **269**, 262-277 (2010).
- Deschamps, F., Cobden, L. & Tackley, P.J. The primitive nature of large low shear-wave velocity provinces. *Earth Planet. Sci. Lett.* **349-350**, 198-208 (2012).
- Dobson, D.P. & Brodholt, J.P. Subducted banded iron formations as a source of ultralow-velocity zones at the core-mantle boundary. *Nature* **434**, 371–374 (2005).
- Dorfman, S. M., Meng, Y., Prakapenka, V. B., & Duffy, T. S. Effects of Fe-enrichment on the equation of state and stability of (Mg,Fe)SiO3 perovskite. *Earth Planet. Sci. Lett.* **361**, 249–257 (2013).

- Dottin III, J.W., Labidi, J., Jackson, M.G., Woodhead, J. & Farquhar, J. Isotopic evidence for multiple recycled sulfur reservoirs in the Mangaia mantle plume. *Geochem. Geophys. Geosystems* **21(10)**, e2020GC009081 (2020).
- Doubrovine P.V., Steinberger, B. & Torsvik, T.H. A failure to reject: Testing the correlation between large igneous provinces and deep mantle structures with EDF statistics. *Geochem. Geophys. Geosystems* 17, 1130-1163 (2016).
- Doucet, S., Scoates, J., Weis, D. & Giret, A. Constraining the components of the Kerguelen mantle plume: A Hf-Pb-Sr-Nd isotopic study of picrites and high-MgO basalts from the Kerguelen Archipelago. *Geochem. Geophys. Geosystems* **6**, Q04007 (2005).
- Duncan, R.A., McCulloch, M.T., Barsczus, H.G. & Nelson, D.R. Plume versus lithospheric sources for melts at Ua Pou, Marquesas Islands. *Nature* **322**, 534–538 (1986).
- Duvernay, T., Davies, D.R., Mathews, C.R., Gibson, A. H. & Kramer, S.C. Linking Intraplate Volcanism to Lithospheric Structure and Asthenospheric Flow. *Geochem Geophys Geosystems* **22**, *e2021GC009953* (2021).
- Dupré, B. & Allègre, C. J. Pb–Sr–Nd isotopic correlation and the chemistry of the North Atlantic mantle. *Nature* **286**, 17–22 (1980).
- Dziewonski, A.M. & Woodhouse, J.H. Global images of the Earth's interior. *Science* **236**, 37–48 (1987).
- Elderfield, H. The oceanic chemistry of the rare-earth elements. *Philos. Trans. R. Soc. London. Series A* **325**(1583), 105-126 (1988).
- Eisele, J., Sharma, M., Galer, S.J.G., Blichert-Toft, J., Devey, C.W. & Hofmann, A.W. The role of sediment recycling in EM-1 inferred from Os, Pb, Hf, Nd, Sr isotope and trace element systematics of the Pitcairn hotspot. *Earth Planet. Sci. Lett.* **196**, 197-212 (2002).
- Elardo, S.M., Shahar, A., Mock, T.D. & Sio, C.K. The effect of core composition on iron isotope fractionation between planetary cores and mantles. *Earth Planet Sc Lett* **513**, 124–134 (2019).
- Elliott, T., Thomas, A., Jeffcoate, A. & Niu, Y. Lithium isotope evidence for subduction-enriched mantle in the source of mid-ocean-ridge basalts. *Nature*, **443**, 565-568 (2006).
- Farley K.A., Natland J.H. & Craig H. Binary mixing of enriched and undegassed (primitive?) mantle components (He, Sr, Nd, Pb) in Samoan lavas. *Earth Planet. Sci. Lett.* **111**, 183–199 (1992).
- Farnetani, C.G., Legras, B. & Tackley, P.J. Mixing and deformation in mantle plumes. *Earth Planet. Sci. Lett.* **196(1)** 1-15 (2002).
- Farnetani, C.G. & Samuel, H. Beyond the thermal plume paradigm. *Geophys. Res. Lett.* **32**, L07311 (2005).
- Farnetani, C.G. & Hofmann, A.W. Dynamics and internal structure of a lower mantle plume conduit. *Earth Planet. Sci. Lett.* **282**, 314-322 (2009).
- Farnetani, C.G., Hofmann, A.W. & Class, C. How double volcanic chains sample geochemical anomalies from the lowermost mantle. *Earth Planet. Sci. Lett.* **359–360**, 240–247 (2012).
- Farnetani, C.G., Hofmann, A.W., Duvernay T. & Limare A. Dynamics of rheological heterogeneities in mantle plumes. *Earth Planet. Sci. Lett.* **499**, 74–82 (2018).
- Farquhar, J., Peters, M., Johnston, D.T., Strauss, H., Masterson, A., Wiechert, U. & Kaufman, A.J. Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry. *Nature* **449(7163)** 706-709 (2007).

- Faure P., Boyet M., Bouhifd M.A., Manthilake G., Hammouda T. and Devidal J.-L.. Determination of the refractory enrichment factor of the bulk silicate Earth from metal-silicate experiments on Rare Earth Elements. *Earth Planet. Sci. Lett.*, **554**, 116644 (2021).
- Fourel, L., Limare, A., Jaupart, C., Surducan, E., Farnetani, C.G., Kaminski, E.C., Neamtu, C. & Surducan, V. The Earth's mantle in a microwave oven: thermal convection driven by a heterogeneous distribution of heat sources, *Exp. Fluids*, 58:90 (2017).
- French, S.W. & Romanowicz, B. Whole-mantle radially anisotropic shear velocity structure from spectral-element waveform tomography. *Geophys. J. Int.* **199**, 1303–1327 (2014).
- French, S.W. & Romanowicz, B. Broad plumes rooted at the base of the Earth's mantle beneath major hotspots. *Nature* **525**, 95-99 (2015).
- Frey, F.A., Weis, D., Borisova, A. & Xu, G. Involvement of continental crust in the formation of the Cretaceous Kerguelen Plateau: New perspectives from ODP Leg 120 sites. *J. Petrol.* **43**, 1207–1239 (2002).
- Frey, F.A., Huang, S., Blichert-Toft, J., Regelous, M. & Boyet, M. Origin of depleted components in basalt related to the Hawaiian hot spot: evidence from isotopic and incompatible element ratios. *Geochem. Geophys. Geosystems* 6, Q02L07 (2005).
- Frossard, P., Israel, C., Bouvier, A. & Boyet, M. Earth's composition was modified by collisional erosion. *Science* **377**, 1529–1532 (2022).
- Fukao, Y. & Obayashi, M. Subducted slabs stagnant above, penetrating through, and trapped below the 660 km discontinuity, *J. Geophys. Res. Solid Earth* **118**, **11**, 5920-5938 (2013).
- Gale, A., Dalton, C.A., Langmuir, C.H., Su, Y. & Schilling, J.G. The mean composition of ocean ridge basalts. *Geochem. Geophys. Geosystems* **14**, 489-518 (2013).
- Garapić, G., Jackson, M.G., Hauri, E.H., Hart, S.R., Farley, K.A., Blusztajn, J.S. & Woodhead, J.D. A radiogenic isotopic (He-Sr-Nd-Pb-Os) study of lavas from the Pitcairn hotspot: Implications for the origin of EM-1 (enriched mantle 1). *Lithos* **228**, 1-11 (2015).
- Garcia MO., Smith JR., Tree JP., Weis D., Harrison L., Jicha BR. Petrology, geochemistry, and ages of lavas from Northwest Hawaiian Ridge volcanoes, in Neal, C.R., Sager, W.W., Sano, T., and Erba, E., eds., The Origin, Evolution, and Environmental Impact of Oceanic Large Igneous Provinces. *Spec. Pap. Geol. Soc. Am.* **511**, p. 1–25, (01) (2015).
- Garcia, M.O., Tree, J.P., Wessel, P. & Smith, J. R. Pūhāhonu: Earth's biggest and hottest shield volcano. *Earth Planet. Sci. Lett.* **542**, 116296 (2020).
- Garcon, M., Boyet, M., Carlson, R.W., Horan, M.F., Auclair, D. & Mock, T.D. Factors influencing the precision and accuracy of Nd isotope measurements by thermal ionization mass spectrometry. *Chem. Geol.* **476**, 493-514 (2018).
- Garnero, E.J. Heterogeneity of the lowermost mantle, *Ann. Rev. Earth Planet. Sci.* **28**, 509-537 (2000).
- Garnero, E., Lay, T. & McNamara, A. Implications of lower mantle structural heterogeneity for existence and nature of whole mantle plumes. *Spec. Pap. Geol. Soc. Am.* **430**, Plates, Plumes, and Planetary Processes 79–101 (2007).
- Garnero, E.J. & McNamara, A. Structure and dynamics of Earth's lower mantle. *Science* **320**, 626-628 (2008).
- Garnero, E.J., McNamara, A.K. & Shim, S.H. Continent-sized anomalous zones with low seismic velocity at the base of the Earth's mantle. *Nature Geosci.* **9**, 481-489 (2016).
- Gast, P.W. Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochim. Cosmochim. Acta* **32**: 1057-1086 (1968).

- Georg, R.B., Reynolds, B.C., West, A.J., Burton, K.W. & Halliday, A.N. Silicon isotope variations accompanying basalt weathering in Iceland. *Earth Planet. Sci. Lett.* **261**, 476-490 (2007).
- Genske, F.S., Turner, S.P., Beier, C., Chu, M.-F., Tonarini, S., Pearson, N.J. & Haas, K.M. Lithium and boron isotope systematics in lavas from the Azores islands reveal crustal assimilation. *Chem. Geol.* **373**, 27-36 (2014).
- Genske, F., Stracke, A., Berndt, J. & Klemme, S. Process-related isotope variability in oceanic basalts revealed by high-precision Sr isotope ratios in olivine-hosted melt inclusions. *Chem. Geol.* **524**, 1–10 (2019).
- Gonnermann, H.M., & Mukhopadhyay, S. Preserving noble gases in a convecting mantle. *Nature*, 459(7246), 560-563 (2009). Graham, D. W. Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: Characterization of mantle source reservoirs. *Rev. Mineral. Geochem.* 47(1), 247-317 (2002).
- Gu, T., Li, M., McCammon, C., Lee, K.K.M., Redox-induced lower mantle density contrast and effect on mantle structure and primitive oxygen. *Nature Geosci* .9, 723–727 (2016).
- Gülcher, A.J.P., Gebhardt, D.J., Ballmer, M.D. & Tackley, P.J. Variable dynamic styles of primordial heterogeneity preservation in the Earth's lower mantle, *Earth Planet. Sci. Lett.* **536**, 116160 (2020).
- Gülcher, A.J.P., Ballmer, M.D., & Tackley, P.J. Coupled dynamics and evolution of primordial and recycled heterogeneity in Earth's lower mantle. *Solid Earth* **12**, 2087–2107 (2021).
- Haase, K.M., Beier, C. & Kemner, F. A comparison of the magmatic evolution of Pacific intraplate volcanoes: constraints on melting in mantle plumes. *Front. Earth Sci.* **6**, 242 doi: 10.3389/feart.2018.00242 (2019).
- Hanan, B.B. & Graham, D.W. Lead and helium isotope evidence from oceanic basalts for a common deep source of mantle plumes. *Science* **272** 991-995 (1996).
- Hanano, D., Scoates, J.S. & Weis, D. Alteration mineralogy and the effect of acid-leaching on the Pb-isotope systematics of ocean-island basalts. *Am. Min.* **94**, 17–26 (2009).
- Harpp, K.S. & White, W.M. Tracing a mantle plume: Isotopic and trace element variations of Galapagos seamounts. *Geochem. Geophys. Geosystems* **2** (2001).
- Harpp, K.S., Hall, P.S. & Jackson, M.G. Galápagos and Easter: A tale of two hotspots. In:
 Harpp, K.S., Mittelstaedt, E., d'Ozouville, Noémi, Graham, D.W. (Eds.), The Galápagos:
 A natural laboratory for the earth sciences. *Geophys. Monog. Series* 204, American Geophysical Union, 27-40 (2014).
- Harpp, K.S. & Geist, D.J. The Evolution of Galapagos Volcanoes: An Alternative Perspective. *Frontiers in Earth Science* **6**, 50 (2018).
- Harpp K. & Weis D. Insights into the origins and compositions of mantle plumes: A comparison of Galapagos and Hawai'i. *Geochem. Geophys. Geosystems* **21**, e2019GC008887. (2020).
- Harrison, L.N., Weis, D., Hanano, D. & Barnes, E. Lithium isotopic signature of Hawaiian basalts. In: Carey, R., Cayol, V., Poland, P., Weis, D. (Eds.), Hawaiian volcanoes: From source to surface. *Geophys. Monog. Ser.* **208**, American Geophysical Union, 74-104 (2015).
- Harrison, L., Weis, D. & Garcia, M.O. The link between Hawaiian mantle plume composition, magmatic flux, and deep mantle geodynamics. *Earth Planet. Sci. Lett.* **463**, 298-309, (2017).

- Harrison, L.N. & Weis, D. The size and emergence of geochemical heterogeneities in the Hawaiian mantle plume constrained by Sr-Nd-Hf isotopic variation over ~47 million years. *Geochem. Geophys. Geosystems* **19** 2823-2842(2018).
- Harrison, L.N., Weis, D. & Garcia, M.O. The Multiple Depleted Mantle Components in the Hawaiian-Emperor Chain. *Chem. Geol.* **532**, 1-22 (2020).
- Hart, S.R., Hauri, E. H., Oschmann, L. A. & Whitehead J. A. Mantle plumes and entrainment: isotopic evidence. *Science* **256**, 517–520 (1992).
- Hayden, L.A. & Watson, E.B. A diffusion mechanism for core-mantle interaction. *Nature* **450**, 709-711 (2007).
- Hegner, E. & Tatsumoto, M. Pb, Sr, and Nd isotopes in seamount basalts from the Juan de Fuca Ridge and Kodiak-Bowie Seamount chain northeast Pacific. *J. Geophys. Res. Solid Earth* **94(B12)** 17839-17846 (1989).
- Hernlund, J. W. & McNamara, A.K. The Core-Mantle boundary region. *Treatise on Geophysics*, 2nd edition, 7, 461-519 (2015).
- Hirose, K., Fei, Y., Ma, Y. & Mao, H-K. The fate of subducted basaltic crust in the Earth's lower mantle. *Nature* **397**, 53-56 (1999).
- Hin, R.C., Coath, C.D., Carter, P.J., Nimmo, F., Lai, Y.-G., Pogge von Strandmann, P.A.E., Willbold, M., Leinhardt, Z.M., Walter, M.J., Elliott, T. Magnesium isotope evidence that accretional vapour loss shapes planetary compositions. *Nature* **549**, 511–515 (2017).
- Hirth, G. & Kohlstedt, D.L. Water in the oceanic upper mantle: implications for rheology, melt extraction and the evolution of the lithosphere. *Earth Planet. Sci. Lett.* **144**, 93–108 (1996).
- Hofmann, A.W. & White, W.M. Mantle plumes from ancient oceanic-crust. *Earth Planet. Sci. Lett.* **57**, 421–436 (1982).
- Hofmann, A.W., Jochum, K., Seufert, M. & White, W.M. Nb and Pb in oceanic basalts new constraints on mantle evolution. *Earth Planet. Sci. Lett.* **79**, 33–45 (1986).
- Hofmann, A.W. Mantle geochemistry: the message from oceanic volcanism. *Nature* **385**, 219-229 (1997).
- Hofmann, A.W. Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements. In: Carlson, R. (Ed.), *Treatise on Geochemistry* (first ed.) **2**, 61-102 (2003).
- Hofmann, A. W., Class, C. & Goldstein, S. L. Size and Composition of the MORB+OIB Mantle Reservoir. *Geochem. Geophys. Geosystems* **23**, e2022GC010339. (2022).
- Holland, G. & Ballentine, C. J. Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* **441**, 186-191, (2006).
- Homrighausen, S., Hoernle, K., Hauff, F., Geldmacher, J., Wartho, J. A., van den Bogaard, P. & Garbe-Schönberg, D. Global distribution of the HIMU end member: Formation through Archean plume-lid tectonics. *Earth-Science reviews* **182**, 85-101 (2018).
- Horan, M., Carlson, R.W., Walker, R.J., Jackson, M., Garcon, M. & Norman, M. Tracking Hadean processes in modern basalts with 142-Neodymium. *Earth Planet. Sci. Lett.* **484**, 184–191 (2018).
- Hosseini, K., Matthews, K. J., Sigloch, K., Shephard, G. E., Domeier, M., & Tsekhmistrenko, M. SubMachine: Web-based tools forexploring seismic tomography and other models of Earth's deep interior. *Geochem. Geophys. Geosystems* **19**, 1464–1483. (2018).
- Hyung, E. & Jacobsen, S. B. The ¹⁴²Nd/¹⁴⁴Nd variations in mantle-derived rocks provide constraints on the stirring rate of the mantle from the Hadean to the present. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 14738–14744 (2020).

- Huang, S., Hall, P.S. & Jackson, M.G. Geochemical zoning of volcanic chains associated with Pacific hotspots. *Nature Geosci.* **4(12)**, 874-878 (2011).
- Humayun, M., Qui, L. & Norman, M.D. Geochemical evidence for excess iron in the mantle beneath Hawaii. *Science* **306**, 91-94 (2004).
- Humphris, S.E., Thompson, G., Schilling, J.-G. & Kingsley, R.H. Petrological and geochemical variations along the Mid-Atlantic Ridge between 46°S and 32°S: Influence of the Tristan da Cunha mantle plume. *Geochim. Cosmochim. Acta* 49, 1445-1464 (1985).
- Hyung, E. & Jacobsen, S. B. The ¹⁴²Nd/¹⁴⁴Nd variations in mantle-derived rocks provide constraints on the stirring rate of the mantle from the Hadean to the present. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 14738–14744 (2020).
- Ireland, T.J., Walker, R.J., & Brandon, A.D., ¹⁸⁶Os-¹⁸⁷Os systematics of Hawaiian picrites revisited: New insights into Os isotopic variations in ocean island basalts. *Geochim. Cosmochim. Acta* **75**, 4456-4475 (2011).
- Israel, C., Boyet, M., Doucelance, R., Bonnand, P., Frossard, P., Auclair, D. & Bouvier, A. Formation of the Ce-Nd mantle array: Crustal extraction vs. recycling by subduction. *Earth Planet. Sci. Lett. 530*, 115941 (2020).
- Ito, G., Lin, J. & Gable, C.W. Dynamics of mantle flow and melting at a ridge-centered hotspot: Iceland and the Mid-Atlantic Ridge. *Earth Planet. Sci. Lett.* **144** 53-74 (1996).
- Jackson, M.G., Kurz, M.D., Hart, S.R. & Workman, R.K. New Samoan lavas from Ofu Island reveal a hemispherically heterogeneous high He-3/He-4 mantle. *Earth Planet. Sci. Lett.* **264**, 360-374 (2007).
- Jackson, M.G. & Dasgupta, R. Compositions of HIMU, EM1, and EM2 from global trends between radiogenic isotopes and major elements in ocean island basalts. *Earth Planet. Sci. Lett.* **276**, 175-186 (2008).
- Jackson, M.G., Weis, D. & Huang, S. Major element variations in Hawaiian shield lavas: Source features and perspectives from global ocean island basalt (OIB) systematics. *Geochem. Geophys. Geosystems* **13**, 919 Q09009, (2012).
- Jackson, M.G. & Carlson, R.W. Homogeneous superchondritic 142Nd/144Nd in the mid-ocean ridge basalt and ocean island basalt mantle. *Geochem. Geophys. Geosystems* **13**,1–10 (2012).
- Jackson, M.G., Hart, S.R., Konter, J.G., Kurz, M.D., Blusztajn, J. & Farley, K.A. Helium and lead isotopes reveal the geochemical geometry of the Samoan plume. *Nature* **514**, 355–358 (2014).
- Jackson, M.G., Konter, J.G. & Becker, T.W. Primordial helium entrained by the hottest mantle plumes. *Nature* **542**, 340-343 (2017).
- Jackson, M.G., Becker, T.W. & Konter, J.G. Geochemistry and distribution of recycled domains in the mantle inferred from Nd and Pb isotopes in oceanic hot spots: Implications for storage in the large low shear wave velocity provinces. *Geochem. Geophys. Geosystems* 19(9), 3496-3519 (2018).
- Jackson, M.G., Blichert-Toft, J., Halldórsson, S.A., Mundl-Petermeier, A., Bizimis, M., Kurz, M.D., Price, A.A., Hardardóttir, S., Willhite, L.N., Breddam, K., Becker, T.W. & Rischer, R.A. Ancient helium and tungsten isotopic signatures preserved in mantle domains least modified by crustal recycling. *Proc. Natl. Acad. Sci. U.S.A.* 117, 30993-31001 (2020a).
- Jackson, M.G., Halldórsson, S.A., Price, A., Kurz, M.D., Konter, J.G., Koppers, A.A.P. & Day, J.M.D. Contrasting old and young volcanism from Aitutaki, Cook Islands: Implications for a hotspot origin. *J. Petrol.* **61(3)**, egaa037 (2020b).

- Jacobsen, S.B. & Wasserburg, G. J. The mean age of mantle and crustal reservoirs. *J. Geophys. Res. Solid Earth* **84**, 7411–7427 (1979).
- Johnston, S., Brandon, A., McLeod, C. Rankenburg, K., Becker, H. & Copeland, P. Nd isotope variation between the Earth–Moon system and enstatite chondrites. *Nature* **611**, 501-506 (2022).
- Jones, T.D., Davies D.R., Campbell I.H., Wilson C.R. & Kramer S.C. Do mantle plumes preserve the heterogeneous structure of their deep-mantle source? *Earth Planet. Sci. Lett.* **434**, 10–17 (2016).
- Jones, T.D., Davies, D.R., Campbell, I.H., Iaffaldano, G., Yaxley, G., Kramer, S.C. & Wilson, C.R. The concurrent emergence and causes of double volcanic hotspot tracks on the Pacific plate. *Nature*, **545**, 472-476 (2017).
- Jones, T. D., Sime, N. & van Keken, P. E. Burying Earth's primitive mantle in the slab graveyard. *Geochem. Geophys. Geosystems* **22**, e2020GC009396 (2021).
- Karato, S. Rheology of the deep upper mantle and its implications for the preservation of the continental roots: a review. *Tectonophysics* **481**, 82–98 (2010).
- Kelley, K.A., Plank, T., Farr, L., Ludden, J., & Staudigel, H. Subduction cycling of U, Th, and Pb. *Earth Planet. Sci. Lett.* **234**(3-4), 369-383 (2005).
- Kerr, R. & Mériaux, C. Structure and dynamics of sheared mantle plumes. *Geochem. Geophys. Geosystems* **5**, 12 (2004).
- Kerr, B.C., Scholl, D.W. & Klemperer, S.L. Seismic stratigraphy of Detroit Seamount, Hawaiian-Emperor Seamount chain: Post-hot-spot shield-building volcanism and deposition of the Meiji drift. *Geochem. Geophys. Geosystems* 6 (7), Q07L10 (2005).
- Kim, Y. et al. Structural Transitions in MgSiO3 Glasses and Melts at the Core-Mantle Boundary Observed via Inelastic X-ray Scattering. *Geophys. Res. Lett.* **46**, 13756–13764 (2019).
- King, S.D. & Adam, C. Hotspot swells revisited. Phys. Earth. Planet. Int. 235, 66-83 (2014).
- Kingsley, R.H. & Schilling, J.-G. Plume-ridge interaction in the Easter-Gr y Gomez seamount chain Easter Microplate system: Pb isotope evidence. *J. Geophys. Res.* **103**, 24,159 24,177 (1998).
- Kingsley, R.H., Blichert-Toft, J., Fontignie, D. & Schilling, J.-G. Hafnium, neodymium, and strontium isotope and parent-daughter element systematics in basalts from the plume-ridge interaction system of the Salas y Gomez Seamount Chain and Easter Microplate. *Geochem. Geophys. Geosyst.* **8**, Q04005 (2007).
- Kleine, T., Münker, C., Mezger, K. & Palme, H. Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* **418**, 952–955. (2002).
- Knittle, E. & Jeanloz, R. Melting curve of (Mg,Fe)SiO3 perovskite to 96 GPa: Evidence for a structural transition in lower mantle melts, *Geophys. Res. Lett.* **16**, 421-424 (1989).
- Kobayashi, K., Tanaka, R., Moriguti, T., Shimizu, K. & Nakamura, E. Lithium, boron, and lead isotope systematics of glass inclusions in olivines from Hawaiian lavas: evidence for recycled components in the Hawaiian plume. *Chem. Geol.* **212**, 143-161 (2004).
- Koelemeijer P., Ritsema J., Deuss A., van Heijst H.-J. SP12RTS: a degree-12 model of shear-and compressional-wave velocity for Earth's mantle. *Geophys. J. Int.* **204**, 1024-103 (2016).
- Konter, J.G. & Jackson, M.G. Large volumes of rejuvenated volcanism in Samoa: Evidence supporting tectonic influence on late-stage volcanism. *Geochem. Geophys. Geosystems* **13(1)**, Q0AM04 (2012).

- Koppers, A.A.P., Becker, T.W., Jackson, M.G., Konrad, K., Muller, R.D., Romanowicz, B., Steinberger, B. & Whittaker, J.M. Mantle plumes and their role in Earth processes. *Nature Reviews Earth & Environment* 2, 382–401 (2021).
- Korenaga, J. Firm mantle plumes and the nature of the core-mantle boundary region. *Earth Planet. Sci. Lett.* **232**, 29–37 (2005).
- Krienitz, M.S., Garbe-Schonberg, C.D., Romer, R.L., Meixner, A., Haase, K.M. & Stroncik, N.A. Lithium isotope variations in ocean island basalts implications for the development of mantle heterogeneities. *J. Petrol.* **53**, 2333–2347 (2012).
- Kruijer, T.S. & Kleine, T. No W-182 excess in the Ontong Java Plateau source. *Chem. Geol.* **485**, 24-31 (2018).
- Kumagai, I., Davaille, A., Kurita, K. & Stutzmann, E. Mantle plumes: Thin, fat, successful, or failing? Constraints to explain hot spot volcanism through time and space. *Geophys. Res. Lett.* **35**, L16301 (2008).
- Labrosse, S., Hernlund, J.W. & Coltice, N. A crystallizing dense magma ocean at the base of the Earth's mantle. *Nature* **450**, 866-869 (2007).
- Lee, C.T.A., Luffi, P., Hoink, T., Li, J., Dasgupta, R., Hernlund, J. Upside-down differentiation and generation of a 'primordial' lower mantle. *Nature* **463**, 930-933 (2010).
- Lee, K.K.M., O'Neill, B., Panero, W.R., Shim, S.H., Benedetti, L.R., Jeanloz, R. Equations of state of the high-pressure phases of a natural peridotite and implications for the Earth's lower mantle. *Earth Planet. Sci. Lett.* **223**, 3–4, 381-393, (2004).
- Li, M., McNamara, A.K. & Garnero, E.J. Chemical complexity of hotspots caused by cycling oceanic crust through mantle reservoirs. *Nature Geosci.* 7, 366-370 (2014).
- Limare, A., Jaupart, C., Kaminski, E., Fourel, L. & Farnetani C.G. Convection in an internally heated stratified heterogeneous reservoir. *J. Fluid Mech.* **870**, 67–105 (2019).
- Lin, S.C. & van Keken, P.E. Dynamics of thermochemical plumes: 2. Complexity of plume structures and its implications for mapping mantle plumes. *Geochem. Geophys. Geosystems* **7(3)**, Q03003. (2006).
- Litasov, K.D., & Ohtani, E. Effect of water on the phase relations in Earth's mantle and deep water cycle, *in* Ohtani, E., ed., Advances in High-Pressure Mineralogy: *Spec. Pap. Geol. Soc. Am.* **421**, p. 115–156, (2007).
- Lock, S.J., Bermingham, K.R., Parai, R. & Boyet, M. Geochemical Constraints on the Origin of the Moon and Preservation of Ancient Terrestrial Heterogeneities. *Space Sci. Rev.* **216**, 109 (2020).
- Manhès, G., Minster, J.-F. & Allègre, C.J. Comparative uranium-thorium-lead and rubidium-strontium study of the Saint Sèverin amphoterite: consequences for early solar system chronology. *Earth Planet Sc Lett* **39**, 14–24 (1978).
- Manga, T., Wiechert, U., Stuart, F.M., Halliday, A.N. & Harrison, D. Combined Li-He isotopes on Iceland and Jan Mayen basalts and constraints on the nature of the North Atlantic mantle. *Geochem. Cosmochim. Acta* **75**, 922-936 (2011).
- Mao, W.L., Mao, H-K., Sturhahn, W., Zhao, J., Prakapenka, V.B., Meng, Y., Shu, J., Fei, Y., Russell J., Hemley R.J. Iron-Rich Post-Perovskite and the Origin of Ultralow-Velocity Zones, *Science*, **312**, 564-565 (2006).
- Marschall, H.R., Wanless, V.D., Shimizu, N., Pogge von Strandmann, P.A.E., Elliott, T. & Monteleone, B.D. The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle. *Geochim. Cosmochim. Acta* **207**, 102-138 (2017).

- Masters, G., Laske, G., Bolton, H. & Dziewonski, A. The relative behavior of shear velocity, bulk sound speed, and compressional velocity in the mantle: Implications for chemical and thermal structure. *Geophys. Monogr. Ser.* **117**, 63–87 (2000).
- McDonough, W.F. & Chauvel, C. Sample Contamination Explains the Pb Isotopic Composition of Some Rurutu Island and Sasha Seamount Basalts. *Earth Planet. Sci. Lett.* **105**, 397–404 (1991).
- McDonough, W.F. The Composition of the Lower Mantle and Core. *Deep Earth: Physics and Chemistry of the Lower Mantle and Core, Geophysical Monograph* **217**. 145-159. Edited by H. Terasaki and R.A. Fischer. AGU, John Wiley & Sons, Inc (2016).
- McNamara, A.K. A review of large low shear velocity provinces and ultra-low velocity zones. *Tectonophysics* **760**, 199–220 (2019).
- Montelli, R., Nolet, G., Dahlen, F.A. & Masters, G. A catalog of deep mantle plumes: New results from finite frequency tomography. *Geochem. Geophys. Geosystems* **7(11)**, Q11007 (2006).
- Morgan, W. Convection plumes in the lower mantle. *Nature* **230**, 42–43 (1971).
- Moreira, M., Kunz, J. & Allègre, C. Rare gas systematics in popping rock: Isotopic and elemental compositions in the upper mantle. *Science* **279**, **5354** 1178-1181 (1998).
- Moreira, M., Doucelance, R., Kurz, M.D., Dupré, B. & Allègre, C.J. Helium and lead isotope geochemistry of the Azores Archipelago. *Earth Planet. Sci. Lett.* **169**, 189-205 (1999).
- Morino, P., Caro, G., Reisberg, L. & Schumacher, A. Chemical stratification in the post-magma ocean Earth inferred from coupled 146,147Sm–142,143Nd systematics in ultramafic rocks of the Saglek block (3.25–3.9 Ga; northern Labrador, Canada). *Earth Planet. Sci. Lett.* **463**, 136–150 (2017).
- Morris, J., Valentine, R. & Harrison, T. 10Be imaging of sediment accretion and subduction along the northeast Japan and Costa Rica convergent margins. *Geology* **30(1)**, 59-62 (2002).
- Mukhopadhyay, S. Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. *Nature* **486**, 101-104, (2012).
- Mundl, A., Touboul, M., Jackson, M.G., Day, J.M.D., Kurz, M.D., Lekic, V., Helz, R.T. & Walker, R.J. Tungsten-182 heterogeneity in modern ocean island basalts. *Science*, **356**, 66-69 (2017).
- Mundl-Petermeier, A., Walker, R.J., Jackson, M.G., Blichert-Toft, J., Kurz, M.D. & Halldorsson, S.A. Temporal evolution of primordial tungsten-182 and He-3/He-4 signatures in the Iceland mantle plume. *Chem. Geol.* **525**, 245-259 (2019).
- Mundl-Petermeier, A., Walker, R.J., Fischer, R.A., Lekic, V., Jackson, M.G. & Kurz, M.D. Anomalous 182W in high 3He/4He ocean island basalts: Fingerprints of Earth's core? *Geochim. Cosmochim. Acta* 71, 194–211 (2020).
- Murphy, DT., Brandon, A.D., Debaille, V., Burgess, R. & Ballentine, C. In search of a hidden long-term isolated sub-chondritic ¹⁴²Nd/¹⁴⁴Nd reservoir in the deep mantle: Implications for the Nd isotope systematics of the Earth. *Geochim. Cosmochim. Acta* **74**, 738–750 (2010)
- Nakagawa, T., Tackley, P.J., Deschamps, F. & Connolly, J.A.D. Incorporating self-consistently calculated mineral physics into thermochemical mantle convection simulations in a 3-D spherical shell and its influence on seismic anomalies in Earth's mantle. *Geochem. Geophys. Geosystems* **10**, Q03004 (2009).

- Nakagawa, T. & Tackley, P.J. Influence of combined primordial layering and recycled MORB on the coupled thermal evolution of Earth's mantle and core. *Geochem. Geophys. Geosystems* **15**, 619–633 (2014).
- Newsom, H.E., White, W.M., Jochum, K.P. & Hofmann, A.W. Siderophile and chalcophile element abundances in oceanic basalts, Pb isotope evolution and growth of the Earth's core. *Earth Planet. Sci. Lett.* **80**, 299-313 (1986).
- Nielsen, S.G., Rehkämper, M., Teagle, D.A., Butterfield, D.A., Alt, J.C. & Halliday, A.N. Hydrothermal fluid fluxes calculated from the isotopic mass balance of thallium in the ocean crust. *Earth Planet. Sci. Lett.* **251(1)**, 120-133 (2006a).
- Nielsen, S.G., Rehkämper, M., Norman, M.D., Halliday, A.N. & Harrison, D. Thallium isotopic evidence for ferromanganese sediments in the mantle source of Hawaiian basalts. *Nature* **439**, 314-317 (2006b).
- Nielsen, S.G., Rehkämper, M. & Prytulak, J. Investigation and application of thallium isotope fractionation. *Rev. Mineral. Geochem.* **82(1)**, 759-798 (2017).
- Nishio, Y., Nakai, S., Yamamoto, J., Sumino, H., Matsumoto, T., Prikhod'ko, V. & Arai, S. Lithium isotopic systematics of the mantle-derived ultramafic xenoliths: implications for EM1 origin. *Earth Planet. Sci. Lett.* **217**, 245-261 (2004).
- Nobre Silva I., Weis D., Barling J., Scoates J.S. Basalt leaching systematics and consequences for Pb isotopic compositions by MC-ICP-MS. *Geochem. Geophys. Geosystems* **10**, Q08012, (2009).
- Nobre Silva I.G., Weis D., Scoates J.S. Effects of acid leaching on the Sr-Nd-Hf isotopic compositions of ocean island basalts. *Geochem. Geophys. Geosystems* **11**, Q09011, (2010).
- Nobre Silva I., Weis D., Scoates J. Isotopic systematics of the early Mauna Kea shield phase and insight into the deep mantle beneath the Pacific Ocean. *Geochem. Geophys. Geosystems* **14**, 659-676, (2013a).
- Nobre-Silva, I.G., Weis, D., Scoates, J.S. & Barling, J. The Ninetyeast Ridge and its Relation to the Kerguelen, Amsterdam and St. Paul Hotspots in the Indian Ocean. *J. Petrol.* **54**, 1177–1210 (2013b).
- Olson, P., Schubert, G. & Anderson C. Structure of axisymmetric mantle plumes. *J. Geophys. Res.* **98**, 6829-6844 (1993).
- Olson, P.L. & Sharp, Z.D. Primordial helium-3 exchange between Earth's core and mantle. *Geochem. Geophys. Geosystems* **23**, e2021GC009985 (2022).
- O'Neil, J., Carlson, R.W., Francis, D. & Stevenson, R.K. Neodymium-142 evidence for hadean mafic crust. *Science* **321**, 1828-1831 (2008).
- O'Nions, R.K., Evensen, N.M. & Hamilton, P.J. Geochemical modeling of mantle differentiation and crustal growth. *J. Geophys. Res. Solid Earth* **84**, 6091–6101 (1979).
- Parai, R., Mukhopadhyay, S. & Standish, J.J. Heterogeneous upper mantle Ne, Ar and Xe isotopic compositions and a possible Dupal noble gas signature recorded in basalts from the Southwest Indian Ridge. *Earth Planet. Sci. Lett.* **359**, 227-239, (2012).
- Parai, R. & Mukhopadhyay, S. The evolution of MORB and plume mantle volatile budgets: Constraints from fission Xe isotopes in Southwest Indian Ridge basalts. *Geochem. Geophys. Geosystems* **16**, 719-735 (2015).
- Parai, R. & Mukhopadhyay, S. Xenon isotopic constraints on the history of volatile recycling into the mantle. *Nature* **560**, 223-227 (2018).

- Parai, R., Mukhopadhyay, S., Tucker, J.M. & Pető, M.K. The emerging portrait of an ancient, heterogeneous and continuously evolving mantle plume source. *Lithos* **346-347**, 105153, 105153 (2019).
- Parai, R. & Mukhopadhyay, S. Heavy noble gas signatures of the North Atlantic Popping Rock 2 Pi D43: Implications for mantle noble gas heterogeneity. *Geochim. Cosmochim. Acta* **294**, 89-105 (2021).
- Parai, R. A dry ancient plume mantle from noble gas isotopes. *Proc. Natl. Acad. Sci. U.S.A.* **119**(29), (2022).
- Payne, J.A., Jackson, M.G. & Hall, P.S. Parallel volcano trends and geochemical asymmetry of the Society hotspot track. *Geology* **41(1)**, 19-22 (2013).
- Pearce, J.A., Ernst, R.E., Peate, D.W. & Rogers, C. LIP printing: Use of immobile element proxies to characterize Large Igneous Provinces in the geologic record. *Lithos* **392-393**, 106068 (2021).
- Penniston-Dorland, S., Liu, X.-M. & Rudnick, R.L. Lithium isotope geochemistry. *Rev. Mineral. Geochem.* **82**, 165-217 (2017).
- Péron, S. & Moreira, M. Onset of volatile recycling into the mantle determined by xenon anomalies. *Geochem. Perspect. Lett.* **9**, 21-25 (2018).
- Péron, S., Mukhopadhyay, S., Kurz, M.D. & Graham, D.W. Deep-mantle krypton reveals Earth's early accretion of carbonaceous matter. *Nature* **600**, 462-467 (2021).
- Peters, B.J., Carlson, R.W., Day, J.M.D. & Horan, M.F. Hadean silicate differentiation preserved by anomalous Nd-142/Nd-144 ratios in the Reunion hotspot source. *Nature* **555**, 89-93 (2018).
- Peters, B.J., Mundl-Petermeier, A., Carlson, R.W., Walker, R.J. & Day, J.M.D. Combined Lithophile-Siderophile Isotopic Constraints on Hadean Processes Preserved in Ocean Island Basalt Sources. *Geochem. Geophys. Geosystems* 22, e2020GC009479 (2021).
- Pető, M. K., Mukhopadhyay, S. & Kelley, K. A. Heterogeneities from the first 100 million years recorded in deep mantle noble gases from the Northern Lau Back-arc Basin. *Earth Planet. Sci. Lett.* **369**, 13-23, (2013).
- Plank, T. & Langmuir, C.H. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* **145** 325-394 (1998).
- Porcelli, D. & Halliday, A. The core as a possible source of mantle helium. *Earth Planet. Sci. Lett.* **192**, 45–56 (2001).
- Porter, K.A. & White, W.M. Deep mantle subduction flux. *Geochem. Geophys. Geosystems* **10(12)** Q12016 (2009).
- Puchtel, I.S., Blichert-Toft, J., Touboul, M., Horan, M.F. & Walker, R.J. The coupled W-182-Nd-142 record of early terrestrial mantle differentiation. *Geochem. Geophys. Geosystems* 17, 2168-2193 (2016).
- Putirka, K.D., Perfit, M., Ryerson, F.J. & Jackson, M.G. Ambient and excess mantle temperatures, olivine thermometry, and active vs. passive upwelling. *Chem. Geol.* **241**, 177-206 (2007).
- Putirka, K. Excess temperatures at ocean islands: Implications for mantle layering and convection. *Geology* **36**, 283-286 (2008).
- Regelous, M., Hofmann, A.W., Abouchami, W. & Galer, S.J.G. Geochemistry of lavas from the Emperor Seamounts, and the geochemical evolution of Hawaiian magmatism from 85 to 42 Ma. *J. Petrol.* **44**, 113-140 (2003).

- Rehkämper, M., Frank, M., Hein, J. R., Porcelli, D., Halliday, A., Ingri, J. & Liebetrau, V. Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits. *Earth Planet. Sci. Lett.* **197(1)**, 65-81 (2002).
- Richards, M.A., Duncan, R.A. & Courtillot, V.E. Flood basalts and hotspot tracks: Plume heads and tails, *Science* **246**, 103-107, (1989).
- Ricolleau, A., Perrillat, J.-P., Fiquet, G., Daniel, I., Matas, J., Addad, A., Menguy, N., Cardon, H., Mezouar, M., & Guignot, N. Phase relations and equation of state of a natural MORB: Implications for the density profile of subducted oceanic crust in the Earth's lower mantle. *J. Geophys. Res.* **115**, B08202. (2010).
- Ritsema, J. & Lekic, V. Heterogeneity of seismic wave velocity in Earth's mantle. *Ann. Rev. Earth Planet. Sci.* **48**, 377-401 (2020).
- Rizo, H., Walker, R.J., Carlson, R. W., Horan, M.F., Mukhopadhyay, S., Manthos, V., Francis, D. & Jackson, M.G. Preservation of Earth-forming events in the tungsten isotopic composition of modern flood basalts. *Science* **352**, 809–812 (2016).
- Rizo, H., Andrault, D., Bennett, N.R., Humayun, M., Brandon, A., Vlastélic, I., et al. ¹⁸²W evidence for core-mantle interaction in the source of mantle plumes. *Geochem. Perspect. Lett.* **11**, 6–11. (2019).
- Rohde, J., Hoernle, K., Hauff, F., Werner, R., O'Connor, J., Class, C., Garbe-Schönberg, D. & Jokat, W. 70 Ma chemical zonation of the Tristan-Gough hotspot track. *Geology* **41(3)**, 335–338 (2013).
- Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Rudge, J.F., Guitreau, M. Blichert-Toft, J. Combined Sm-147, Sm-146-Nd-143, Nd-142 constraints on the longevity and residence time of early terrestrial crust. *Geochem. Geophys. Geosystems* **15(6)**, 2329-2345 (2014).
- Roth, A.S.G., Liebske, C., Maden, C., Burton, K.W., Schonbachler, M. & Busemann, H. The primordial He budget of the Earth set by percolative core formation in planetesimals. *Geochem. Perspect. Lett* **9**, 26–31 (2019).
- Rudge, J.F., Maclennan, J. & Stracke, A. The geochemical consequences of mixing melts from a heterogeneous mantle. *Geochim. Cosmochim. Acta*, **114**, 112-143 (2013).
- Rudnick, R.L. & Gao, S. Composition of the Continental Crust. In: Treatise on Geochemistry Editors-in-Chief: Heinrich, D.H., Karl, K.T. (Eds.), Pergamon, Oxford, pp. 1-64 (2003).
- Ryan, J.G. & Kyle, P.R. Lithium abundance and lithium isotope variaitons in mantle sources: insights from intraplate volcanic rocks from Ross Island and Marie Byrd Land (Antarctica) and other oceanic islands. *Chem. Geol.* **212**, 125-142 (2004).
- Ryan, J.G. & Chauvel, C., The Subduction-Zone Filter and the Impact of Recycled Materials on the Evolution of the Mantle. In: *Treatise on Geochemistry* (Second Edition) Holland, H.D., Turekian, K.K. (Eds.), Elsevier, Oxford, pp. 479-508 (2014).
- Saal, A.E., Hart, S.R., Shimizu, N., Hauri, E.H. & Layne, G.D. Pb isotopic variability in melt inclusions from the EMI–EMII–HIMU mantle end-members and the role of the oceanic lithosphere. *Earth Planet Sc Lett.* **240**, 605–620 (2005).
- Saji N.K., Wielandt D., Paton C., Bizzaro M. Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS. *J. Anal. At.Spectrom.* **31**, 1490-1504 (2016).
- Saji, N.S., Larsen, K., Wielandt, D., Schiller, M., Costa, M.M., Whitehouse, M.J., Rosing, M.T. & Bizzarro, M. Hadean geodynamics inferred from time-varying in the early Earth rock record ¹⁴²Nd/¹⁴⁴Nd in the early Earth rock record. *Geochem. Perspect. Lett.* **7**,43–48 (2018).

- Salters, V.J.M. & Stracke, A. Composition of the depleted mantle. *Geochem. Geophys. Geosystems* 5, Q0500 (2004).
- Schilling, J.G., Kingsley, R.H., & Devine, J.D. Galápagos hot spot-spreading center system: 1. Spatial petrological and geochemical variations (83oW–101oW). *J. Geophys. Res. Solid Earth*, **87(B7)**, 5593-5610 (1982).
- Schilling, J-G. Fluxes and excess temperatures of mantle plumes inferred from their interaction with migrating mid-ocean ridges. *Nature* **352**, 397–403 (1991).
- Schuessler, J.A., Schoenberg, R. & Sigmarsson, O. Iron and lithium isotope systematics of the Heckla volcano, Iceland Evidence for Fe isotope fractionation during magma differentiation. *Chem. Geol.* **258**, 78-91 (2009).
- Shahar, A., Hillgren, VJ., Young, E.D., Fei, Y., Macris, C.A., Deng L. High-temperature Si isotope fractionation between iron metal and silicate. *Geochim. Cosmochim. Acta* **75** (23), 7688-7697 (2011).
- Shahar, A., Schauble, E.A., Caracas, R., Gleason, A.E., Reagan, M.M., Xiao, Y., Shu, J. & Mao, W. Pressure-dependent isotopic composition of iron alloys. *Science* **352**, 580-582 (2016).
- Shahar, A., Elardo, S.M. & Macris, C.A. Equilibrium Fractionation of Non-Traditional Stable Isotopes: An Experimental Approach, *Rev. Min. Geoch.*, **82**, 65-84 (2017).
- Sleep, N.H. Hotspots and mantle plumes: Some phenomenology. *J. Geophys. Res. Solid Earth* **95**, 6715-6736 (1990).
- Smith, E. M., Ni, P., Shirey, S. B., Richardson, S. H., Wang, W. & Shahar, A. Heavy iron in large gem diamonds traces deep subduction of serpentinized ocean floor. *Sci. Adv.* **7(14)**, eabe9773 (2021).
- Stracke, A., Hofmann, A.W. & Hart, S.R. FOZO, HIMU, and the rest of the mantle zoo. *Geochem. Geophys. Geosystems* **6(5)**, Q05007 (2005).
- Stracke, A., Bourdon, B. & McKenzie, D. Melt extraction in the Earth's mantle: Constraints from U-Th-Pa-Ra studies in oceanic basalts. *Earth Planet. Sci. Lett.* **244**, 97-112 (2006).
- Stracke, A. Earth's heterogeneous mantle: A product of convection-driven interaction between crust and mantle. *Chem. Geol.* **330–331(0)** 274-299 (2012).
- Stracke, A., Genske, F., Berndt, J. & Koornneef, J.M. Ubiquitous ultra-depleted domains in Earth's mantle. *Nature Geosci.* **12**, 851–855 (2019).
- Stracke, A., Willig, M., Genske, F., Béguelin, P. & Todd, E. Chemical Geodynamics Insights From a Machine Learning Approach. *Geochem. Geophys. Geosystems* **23**, e2022GC010606 (2022).
- Stuart, F.M., Lass-Evans, S., Fitton, J.G. & Ellam, R.M. High He-3/He-4 ratios in picritic basalts from Baffin Island and the role of a mixed reservoir in mantle plumes. *Nature* **424**, 57-59 (2003).
- Tackley, P.J. Three-dimensional simulations of mantle convection with a thermo-chemical basal boundary layer: D"?, in The Core-Mantle Boundary Region, *Geophys. Monogr. Ser.*, **28**, edited by M. Gurnis et al., pp. 231 253, AGU, Washington, D. C. (1998).
- Tang, M., Rudnick, R.L. & Chauvel, C. Sedimentary input to the source of Lesser Antilles lavas: A Li perspective. *Geochim. Cosmochim. Acta* **144**, 43-58 (2014).
- Thorne, M.S. & Garnero, E.J. Inferences on ultralow-velocity zone structure from a global analysis of SPdKS waves. *J. Geophys. Res. Solid Earth* **109** B08301 (2004).
- Tkalčić, H., Young, M., Muir, J. B., Davies, D.R. & Mattesini, M. Strong, multi-scale heterogeneity in Earth's lowermost mantle. *Sci. Rep.* **5**, 18416, (2015).

- Tomascak, P.B. Developments in the understanding and application of lithium isotopes in the earth and planetary sciences. *Rev. Mineral. Geochem.* **55(1)**, 153-195 (2004).
- Tomascak, P.B., Langmuir, C.H., le Roux, P.J. & Shirey, S.B. Lithium isotopes in global midocean ridge basalts. *Geochim. Cosmochim. Acta*, **72**, 1626-1637 (2008).
- Torsvik, T.H., Smethurst, M. A., Burke, K. & Steinberger, B. Large igneous provinces generated from the margins of the large low-velocity provinces in the deep mantle. *Geoph. J. Int.* **167**, 1447-1460 (2006).
- Touboul, M., Puchtel, I.S. & Walker, R.J. W-182 evidence for long-term preservation of early mantle differentiation products. *Science* **335**, 1065-1069 (2012a).
- Touboul, M. & Walker, R. J. High precision tungsten isotope measurement by thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **309**, 109–117 (2012b).
- Trinquier A., Touboul M., Walker R.J. High-Precision Tungsten Isotopic Analysis by Multicollection Negative Thermal Ionization Mass Spectrometry Based on Simultaneous Measurement of W and 18O/16O Isotope Ratios for Accurate Fractionation Correction. *Anal. Chem.* **88**, 1542-1546 (2016).
- Tronnes, R.G., Baron, M.A., Eigenmann, K.R., Guren, M.G., Heyn, B.H., Loken, A. & Mohn, C.E. Core formation, mantle differentiation, and core-mantle interaction within Earth and terrestrial planets. *Tectonophysics* **760**, 165-198 (2019).
- Tschauner, O., Ma, C., Beckett, J.R., Prescher, C., Prakapenka, V.B., & Rossman, G.R. Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite. *Science*, **346**(6213), 1100–1102. (2014).
- Tucker, J. M., Mukhopadhyay, S. & Schilling, J.-G. The heavy noble gas composition of the depleted MORB mantle (DMM) and its implications for the preservation of heterogeneities in the mantle. *Earth Planet. Sci. Lett.* **355–356**, 244–254 (2012).
- Turner, S., Bourdon, B. & Gill, J. Insights into magma genesis at convergent margins from Useries isotopes. *Rev. Mineral. Geochem.* **52**, 255-315 (2003).
- Turner, S.J. & Langmuir, C.H. Sediment and ocean crust both melt at subduction zones. *Earth Planet. Sc. Lett.* **584**, 117424 (2022).
- Upadhyay D., Scherer E.E., Mezger K. Fractionation and mixing of Nd isotopes during thermal ionization mass spectrometry: implications for high precision ¹⁴²Nd/¹⁴⁴Nd analyses. *J. Anal. At. Spec.* **23**, 561-568 (2008).
- Vervoort, J.D., Patchett, P.J., Blichert-Toft, J. & Albarède, F. Relationships between Lu-Hf and Sm-Nd isotopic systems in the global sedimentary system. *Earth Planet. Sci. Lett* **168**,79-99 (1999).
- Vlastélic, I., Koga, K., Chauvel, C., Jaques, G. & Télouk, P. Survival of lithium isotopic heterogeneities in the mantle supported by HIMU-lavas from Rurutu Island, Austral Chain. *Earth Planet. Sci. Lett.* **286(3-4)**, 456-466 (2009).
- Walker, R.J. Siderophile element constraints on the origin of the Moon. *Phil. Trans. Roy. Soc. A. London*, **372**, 20130258 (2014).
- Wamba, M.D., Montagner, J.-P. & Romanowicz, B. Imaging deep-mantle plumbing beneath La Réunion and Comores hot spots: Vertical plume conduits and horizontal ponding zones. *Sci Adv* **9**, eade3723 (2023).
- Wang, X.-J. et al. Recycled ancient ghost carbonate in the Pitcairn mantle plume. *Proc. National Acad. Sci.* **115**, 8682–8687 (2018).
- Weaver, B.L. The origin of ocean island basalt end-member compositions: trace element and isotopic constraints. *Earth Planet. Sci. Lett.* **104**, 381-397 (1991).

- Weis, D., Bassias, Y., Gautier, I. & Mennessier, J.-P. Kerguelen Plateau (South Indian Ocean): Isotopic study of MD48 dredge basalts: Kerguelen type signature. *Geochim. Cosmochim. Acta* 53, 2125-2131 (1989).
- Weis, D. & Frey, F.A. Submarine basalts of the Northern Kerguelen Plateau: Interaction between the Kerguelen plume and the Southeast Indian Ridge revealed at ODP Site 1140. *J. Petrol.* **43**, 1287-1309 (2002).
- Weis, D., Kieffer, B., Maerschalk, C., Barling, J., De Jong, J., Williams, G.A., Hanano, D., Pretorius, W., Mattielli, N., Scoates, J.S., Goolaerts, A., Friedman, R.M., Mahoney, J.B. High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. *Geochem. Geophys. Geosystems* 7, Q08006 (2006).
- Weis, D., Kieffer, B., Hanano, D., Nobre Silva, I., Barling, J., Pretorius, W., Maerschalk, C., Mattielli, N. Hf isotope compositions of U.S. Geological Survey reference materials. *Geochem. Geophys. Geosystems* **8(6)**, Q06006 (2007).
- Weis, D., Garcia, M.O., Rhodes, J.M., Jellinek, M. & Scoates, J.S. Role of the deep mantle in generating the compositional asymmetry of the Hawaiian mantle plume. *Nature Geosci.* **4**, 831–838 (2011).
- Weis D., Harrison L., McMillan R. & Williamson N.W.B. Fine-scale structure of Earth's deep mantle resolved through statistical analysis of Hawaiian basalt geochemistry. *Geochem. Geophys. Geosystems* **21**, e2020GC009292. (2020).
- Weiss, Y., Class, C., Goldstein, S.L. & Hanyu, T. Key new pieces of the HIMU puzzle from olivines and diamond inclusions. *Nature* **537**, 666-670 (2016).
- Wessel, P., & Kroenke, L.W. Observations of geometry and ages constrain relative motion of Hawaii and Louisville plumes. *Earth Planet. Sci. Lett.* **284**(3-4), 467-472 (2009).
- Wessel, P. Regional–residual separation of bathymetry and revised estimates of Hawaii plume flux. *Geophys. Jour. Int.* **204**, 932–947 (2016).
- Wetherill, G. W. Radiometric Chronology of the Early Solar System. *Ann. Rev. Nucl. Sci.* **25**, 283–328 (1975).
- White, R.S. & McKenzie, D.P. Volcanism at rifts. Sci. Am. 261(1), 62-71 (1989).
- White, R.S. Melt production rates in mantle plumes. *Phil. Trans. Roy. Soc. London* **342**, 137-153 (1993).
- White, W.M., Schilling, J.-G. & Hart, S.R. Evidence for the Azores mantle plume from strontium isotope geochemistry of the Central North Atlantic. *Nature* **263**, 659–663 (1976).
- White, W.M. Sources of oceanic basalts: Radiogenic isotopic evidence. *Geology* **13**, 115-118 (1985).
- White, W.M., McBirney, A.R., & Duncan, R.A. Petrology and geochemistry of the Galápagos Islands: Portrait of a pathological mantle plume. *J. Geophys. Res. Solid Earth* **98**(B11), 19533-19563 (1993).
- White, W.M. & Duncan, R.A. Geochemistry and geochronology of the Society Islands: New evidence for deep mantle recycling. In: Basu, A. & Hart, S. (Ed.), *Earth Processes reading the isotopic code*. American Geophysical Union, Washington, pp. 183-206 (1996).
- White, W.M. Oceanic island basalts and mantle plumes: the geochemical perspective. *Ann. Rev. Earth Planet. Sci.* **38**, 133-160 (2010).
- White, W.M. Probing the Earth's deep interior through geochemistry. *Geochem. Perspect.* **4(2)**, 95-251 (2015).
- Whitehead, J.A. & Luther, D.S. Dynamics of laboratory diapir and plume models. *J. Geophys. Res. Solid Earth* **80**, 705–717 (1975).

- Willbold, M. & Stracke, A. Trace element composition of mantle end-members: Implications for recycling of oceanic and upper and lower continental crust. *Geochem. Geophys. Geosystems* 7, Q04004 (2006).
- Williams, C.D., Li, M., McNamara, A.K., Garnero, E.J. & van Soest, M.C. Episodic entrainment of deep primordial mantle material into ocean island basalts. *Nature Comm.* **6**, 1-7 (2015).
- Williams, C.D., Mukhopadhyaya, S., Rudolph, M.L. & Romanowitcz, B. Primitive helium is sourced from seismically slow regions in the lowermost mantle. *Geochem. Geophys. Geosystems* **20**, 4130-4145 (2019).
- Williams, Q. & Garnero, E.J. Seismic evidence for partial melt at the base of Earth's mantle. *Science* **273**, 1528–1530 (1996).
- Williamson N.M.B., Weis D., Scoates J.S., Pelletier H. & Garcia M.O. Tracking the geochemical transition between the Kea-Dominated Northwest Hawaiian Ridge and the bilateral Loa-Kea Trends of the Hawaiian Islands. *Geochem. Geophys. Geosystems* **20**, 4354-4369 (2019).
- Williamson, N.M.B., Weis, D. & Prytulak, J. Thallium isotopic compositions in Hawaiian lavas: Evidence for recycled materials on the Kea side of the Hawaiian mantle plume. *Geochem. Geophys. Geosystems* **22(9)** e2021GC009765, (2021).
- Workman, R.K., Hart, S.R., Jackson, M., Regelous, M., Farley, K.A., Blusztajn, J., Kurz, M. & Staudigel, H. Recycled metasomatized lithosphere as the origin of the enriched mantle II (EM2) end-member: Evidence from the Samoan volcanic chain. *Geochem. Geophys. Geosystems* 5, Q04008 (2004).
- Workman, R. & Hart, S. Major and trace element composition of the depleted MORB mantle (DMM). *Earth Planet. Sci. Lett.* **231**, 53–72 (2005).
- Yamazaki, D., Kato, T., Yurimoto, H., Ohtani, E. & Toriumi, M. Silicon self-diffusion in MgSiO3 perovskite at 25 GPa. *Phys. Earth Planet. Inter.* **119**, 299–309 (2000).
- Yang, H., Frey, F.A., Weis, D., Giret, A. Pyle, D. Michon, G. Petrogenesis of the flood basalts forming the northern Kerguelen Archipelago: Implications for the Kerguelen Plume. *J. Petrol.* **39**, 711–748 (1998).
- Yin, Y., Zhang, Q., Zhang, Y., Zhai, S. & Liu, Y. Electrical and thermal conductivity of Earth's core and its thermal evolution—A review. *Acta Geochimica* **41**, 665–688 (2022).
- Yoshino, T., Makino, Y., Suzuki, T., & Hirata, T. Grain boundary diffusion of W in lower mantle phase with implications for iso-topic heterogeneity in oceanic island basalts by core-mantle interactions. *Earth Planet. Sci. Lett.* 530, 115887. (2020).
- Zhou, W-Yi, Hao, M., Zhang, J.S., Chen, B., Wang, R., & Schmandt, B. Constraining composition and temperature variations in the mantle transition zone. *Nature Commun.* 13, 101038 (2022).
- Zindler, A., Jagoutz, E. & Goldstein, S. Nd, Sr and Pb isotopic systematics in a three-component mantle: a new perspective. *Nature* **298**, 519-523 (1982).
- Zindler, A. & Hart, S. Chemical geodynamics. Ann. Rev. Earth Planet. Sci. 14, 493-571 (1986).

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Author contributions

All authors contributed to all aspects of the article. DW shared the vision and all authors contributed substantially to discussion of the content during various online meetings, as a group and for individual sections. All authors wrote the article. KH, MB, and CC coordinated sections. LH, VAF and NBW compiled data and helped for figures. All authors reviewed and/or edited the manuscript.

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Competing interests

The authors declare no competing interests.

Data Availability

Figures 2 a-f, and Supplementary figures were constructed from a combined dataset of precompiled files for oceanic island groups from GeoRoc and several curated datasets (Weis et al., 2020; Harpp and Weis, 2020; Harrison et al., 2020). New data were downloaded from the GeoRoc geochemistry database in October 2021 and included data from Azores, Easter and Salas y Gomez Islands, Iceland, Kerguelen, and St Helena. Primary GeoRoc data selection criteria were geological setting (Ocean Island), selection of ocean island chain, type of material (whole rock), and type of rock (volcanic rock). GeoRoc data from the initial search were combined with additional data downloaded from GeoRoc in July 2020 and 2021, some of which is presented in ref. (Harrison et al. (2020)). These data included Samoa, Cook-Austral Islands, Pitcairn-Gambier, Easter, Galápagos, Society, and Mauritius (see their supplementary information for a full list of references). New Pitcairn and Society trace element concentration and isotope composition data from ref. (Cordier et al. (2021)) were added to the GeoRoc compilation, along with data from the Galápagos from ref.(Harpp and Weis (2020)). Hawaiian-Emperor data were taken from ref. (Weis et al. (2020)). The total number of samples in the compiled dataset is 19,824 and most isotopic data is post-1990. The format of each of these precompiled files was standardized and imported into R, a free open-source statistical computing application for analysis and plotting. All datasets except those downloaded in October 2021 were renormalized to the same standard values to ensure comparability (Weis et al., 2020). For major element and isotope plots, no filters were used on the dataset to assess data quality, which varied between labs, instrumentation, methods, and detection limits over the past forty to fifty years (much of this metadata is not included in the GeoRoc database, or is inconsistently included and therefore

difficult to apply across such a varied dataset). For trace element plots, a filter of SiO₂ greater than 55 wt.% and total alkalis (Na₂O+K₂O) less than 8 wt.% was applied to remove highly silica-undersaturated samples or lavas that were produced by anomalously low degrees of partial melting. This filter removes samples with heavily enriched incompatible trace element concentrations, which would skew the average results presented in the extended trace element spider diagram.

Figure captions

Figure 1: Mantle plume locations and buoyancy flux compared to major mantle structures and locations of potential chemical reservoirs. a | A map of the velocity anomaly ($\delta Vs/Vs$) on a tomography slice from the lowest mantle at 2,800 km depth, extracted from the SEMUCB-WM1 model (French and Romanowicz, 2014), generated using the SubMachine online tool (Hosseini et al., 2018). Red, warmer, regions indicate the seismically slow Pacific and African-Atlantic Large Low Shear Velocity Provinces (LLSVPs); blue, cooler, indicate regions that are seismically faster parts of the lowermost mantle. The mean depth anomaly within a 500 km diameter circle around a mantle plume was calculated with the MiFil volume method, after filtering out small-scale features such as seamounts and islands (King and Adam, 2014). The MiFil 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. The circle diameters correspond to the magnitude of buoyancy flux defined by the key on the right of the figure. The colored circles correspond to plumes with geochemical data shown in Figures 2–5 and Supplementary Figures 1-9. The white circles indicate mantle plume sites not included in subsequent figures. The grey circles indicate mantle plumes without flux estimates. Note the geographic proximity of mantle plumes to LLSVPs and how mantle plume buoyancy flux varies globally by orders of magnitude. **b** | Schematic cross-section of the mantle illustrating major mantle structures and locations of potential chemical reservoirs, including a heterogeneous LLSVP (indicated by different shades of orange, including mantle plumes), Ultra-Low Velocity Zones (ULVZs) (red), and subducted oceanic lithosphere (blue) that transports recycled surface materials into the mantle (such as sediments shown in brown). The reservoirs are defined by isotopic and trace element data from plume-generated ocean island basalt. Mantle mineral assemblages are shown from shallower to deeper mantle depths and consist of olivine (Ol), pyroxene (Py), garnet (Gt), ringwoodite (Ri), bridgmanite (Bm), and ferropericlase (Fp). The insets associated with each reservoir list the isotopic systems that are used to identify and trace the reservoir and the processes (Supplementary Table 2) and the processes that can be examined using these isotopic systems on material associated with each reservoir. The morphologies of the plumes, LLSVPs, and ULVZs (whose thickness has been exaggerated to be visible at the scale of the diagram), are informed broadly by seismic studies (French and Romanowicz, 2015; Wamba et al., 2023) and geodynamic results (Farnetani and Samuel, 2005; Davaille, 1999). The slab morphologies are guided roughly by seismic studies (Fukao and Obayashi, 2013; Garnero and McNamara, 2008) and geodynamic results (Jones at al., 2021; Nakagawa and Tackley, 2014). Mantle plume compositions reflect contributions from multiple mantle reservoirs, including recycled crustal material. EM-I: enriched mantle I; EM-II: enriched mantle II; HIMU: high μ (U/Pb).

Figure 2: Radiogenic and Li isotope compositions of a selection of major ocean islands. a \mid $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$; **b** \mid $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$; **c** \mid $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{176}\text{Hf}/^{177}\text{Hf}$; **d** \mid $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$. Island chains are classified by their global end-members, which

are indicated by their colour. In all panels, the grey field outlines Indian, Atlantic, and Pacific mid-ocean ridge basalts (MORB). The location of end-member compositions are indicated: DMM, depleted MORB mantle; EM-I enriched mantle I; EM-II, enriched mantle II; HIMU, high μ (U/Pb); PREMA, PREvalent MAntle. $e \mid \delta^7 Li$ versus $^{206} Pb/^{204} Pb$, the grey field includes data for Pacific, Atlantic, and Indian mid-ocean ridge basalts (MORB) (Elliott et al., 2006, Tomascek et al., 2008, and Marschall et al., 2017). $f \mid$ Histogram of $\delta^7 Li$ measurements of ocean island basalt (OIB) (Chan et al., 2003; Kobayashi et al., 2004; Ryan and Kyle, 2004; Nishio et al., 2005; Chan et al., 2009; Vlastélic et al., 2009; Manga et al., 2011; Schusser et al., 2011; Krientiz et al., 2012, Genske et al., 2014; Harrison et al., 2015). All Pb isotope values are normalized to the same standard values (SRM 981 value of $^{206} Pb/^{204} Pb$ =16.9405). The lines outside the plots are histograms of data distribution. These plots illustrate the compositional distribution of the major mantle endmembers sampled by OIBs, and highlight the important observation that most oceanic island basalts have contributions from PREMA and at least one additional end-member.

Figure 3: Representations of major mantle reservoir contributions to global plume buoyancy flux and to mantle plumes in 2-D space. a | An estimate of the total buoyancy flux for each end-member (grey bars), the black thick lines indicate the median values, and the colored box plot indicates the distribution around the median for each mantle component (King and Adam 2014). n is the number of plume locations included in the flux calculations for each group. The color circles indicate four outliers, such as mantle plumes with buoyancy flux substantially higher than the rest of the plumes in their respective group. The plumes groups are enriched mantle I (EM-I): Meteor, Fernando de Noronha, Tasmantid, Lord Howe, Marion, Tristan da Cunha-Gough, Hawai'i-Emperor, Jan Mayen, Kerguelen, Pitcairn-Gambier, Rarotonga, Discovery-Shona; enriched mantle II (EM-II): St. Paul-Amsterdam, Azores, Marquesas, Samoa, Tahiti-Society; PREvalent MAntle (PREMA): Galápagos (also depleted mantle, DM), Trindade-Martin, Crozet, Bouvet, Balleny, Ascension, Comores, Reunion, Bowie-Kodiak (or Pratt-Welker; currently erupting DM), Caroline, Easter-Salas y Gomez, Juan de Fuca (also known as Cobb-Eickelberg and Patton-Murray; currently erupting DM), Juan Fernandez, Louisville; high μ (U/Pb) (HIMU): Vema, Bermuda, Cape Verde, Rurutu–Arago, St. Helena, Great Meteor, Canary, Macdonald (currently erupting PREMA), Baja-Guadalupe (also known as Fieberling), Socorro; DM: Iceland, Madeira, San Felix; continental: Yellowstone, East Africa, Eifel, Darfur, Afar, Tibesti, Cameroon, Hoggar, East Australia, Raton. EM-II and DM groups have highest median fluxes; EM-I has the largest total flux, dominated by Hawai'i–Emperor; EM-I median flux is indistinguishable from PREMA and HIMU. **b** | The relationship between representative ocean island arrays and the five main mantle end-member compositions (Zindler and Hart 1986) in three-dimensional isotopic ratio space (87Sr/86Sr, 143Nd/144Nd, 206Pb/204Pb) (Hart et al., 1992). The horizontal line between DM and HIMU corresponds to FOZO, the focal zone. Of the major mantle endmembers, Enriched Mantle (EM-I and -II) contributes most to mantle plume flux on a global scale, whereas HIMU is the smallest source of material, regardless of the parameter used to represent plume flux.

Figure 4: Isotopic systems used to detect early Earth reservoirs. a $\mid \mu^{142} Nd$, that is $^{142}Nd/^{144}Nd$ in parts per million (ppm) deviation from the terrestrial standard (JNdi-1, AMES, or vNd-b) measured in ocean island basalt samples (Andreasen et al., 2008; Murphy et al., 2010; Jackson and Carlson, 2012; Burkhardt et al., 2016; Saji et al., 2016; de Leeuw et al., 2017; Garçon et al., 2018; Horan et al., 2018; Peters et al., 2018; Hyung and Jacobsen, 2020). Baffin

Island samples are included because they have the highest ³He/⁴He ratios measured to date (Stuart et al., 2003). The error bars indicate 2SE (standard error when the sample was measured once) or 2SD (standard deviation when samples were measured several times), the number of measurements is indicated near the symbol. External reproducibility (2SD) is estimated by repeatedly measuring a standard reference material during the same analytical session as the samples (light grey, ~5 ppm; dark grey, 1.1 ppm based on 10 measurements of JNdi-1 (Hyung and Jacobsen 2020)). Red outlines indicate values with a SD that is significant compared to external reproducibility (Réunion (Peters et al., 2018); Samoa (Horan et al., 2018)). b | As in a but for μ^{182} W (μ^{182} W is 182 W/ 184 W measured in OIB samples and reported in parts per million deviation relative to terrestrial standard, (Alfa Aesar)) (Mundl et al., 2017; Mundl-Petermeier et al., 2019; Rizo et al., 2019; Peters et al., 2021). External reproducibility is ~4–5 ppm; large deficits measured in OIB samples can be resolved clearly. Samples from Baffin Island are not included because ¹⁸²W results are controversial; the positive µ¹⁸²W could be an analytical artifact (Rizo et al., 2016, Kruijer and Kleine, 2018). Small variations in extinct isotopic systems represent either potential contributions from early-formed material or core interactions with the plume source. c | 129Xe/130Xe in mantle sources for Iceland (Mukhopadhyay, 2012), the Samoa Rochambeau Rift (Peto et al., 2013) and the Galápagos (accumulated gas (Péron et al., 2021)). Error bars are 1SD following convention in the noble gas literature. The depleted mantle source (solid grey line) is 129 Xe/ 130 Xe = 7.8 from mid-ocean ridge basalts (MORBs) and well gases (Moreira et al., 1998; Holland and Ballentine, 2006; Parai et al., 2012; Tucker et al., 2012). The atmospheric source (dashed grey line) is ¹²⁹Xe/¹³⁰Xe = 6.496 (Basford et al., 1973), which is distinctly lower than ¹²⁹Xe/¹³⁰Xe determined for OIB and MORB mantle sources. Noble gas systematics highlight the compositional differences between the MORB and OIB mantle sources. d | Step-crush data with 1SD error bars are shown for Iceland, Samoa and N. Atlantic MORB (Moreira et al., 1998; Mukhopadhyay, 2012; Peto et al., 2013; Parai and Mukhopadhyay, 2021). Neither post-eruptive atmospheric contaminated mantle (illustrated by the trends toward atmospheric values in the step-crush data) nor incorporation of regassed atmospheric Xe into the mantle can explain the OIB data arrays in ¹²⁹Xe/¹³⁰Xe–³He/¹³⁰Xe space. The low ¹²⁹Xe/¹³⁰Xe in OIB mantle sources are thus interpreted to reflect a lower I/Xe ratio during the lifetime of ¹²⁹I compared to the upper mantle (Moreira et al., 1998; Parai and Mukhopadhyay, 2021). Shortlived isotopic decay products indicate OIB sample early-formed reservoirs, and provide insight into early Earth evolution processes. Concerted efforts to measure $\mu^{142}Nd$, $\mu^{182}W$ and Xe isotopes in the same samples are needed to better understand what processes generated these early-formed signatures and how they have been preserved in the mantle.

Figure 5: Mantle convection simulations in two-dimensional spherical annulus geometry Numerical simulations of mantle plumes showing contributions of materials with distinct compositions (see composition triangle) initially forming a layer of thickness D_{prim} , the primordial layer thickness (1650 km in **a** and 1617 km in **b**): Basalt (blue); Harzburgite (beige); a bridgmanitic primordial material (dark red), which is rheologically more viscous (primordial lower mantle viscosity contrast λ_{prim} (100 in **a** and 50 in **b**)). B is the primordial buoyancy ratio, varying between 0.07-0.78 (0.28 in both panels here). The model also features an ancient FeOrich basal layer (magenta) with the same physical properties as basalt. The color scale bar shows the age of the material forming the basal piles. These models illustrate that mantle convection over 4.5 Gyr yields a strongly heterogeneous mantle that is capable of producing the wide range

of compositional variations observed in OIBs around the world. Part a and b are adapted from ref. (Gülcher et al., 2021), CC BY 4.0.

Box 1: Mantle plumes and LIPs

Geodynamic models and analog experiments indicate that when plumes begin to rise through the mantle, upwelling material takes the form of a mushroom, with a large, semicircular head trailed by a narrow tail (Richards et al., 1989; Farnetani et al., 2002; Kerr and Mériaux, 2004; Lin and van Keken, 2006). Initial melt production is high, owing to the large volume of the plume head. When the plume head melts, it produces Large Igneous Provinces (LIPs) on land (for example, Deccan, Siberian Traps), below sea level (such as, Shatsky, Ontong–Java, Manihiki oceanic plateaus), or both (Kerguelen). This LIP phase is usually brief (1-3 Myr), but can last longer and involves large mantle volumes. Part a of the figure shows the minimum and maximum relative volumes of several LIPs as cross-sections of spheres scaled to estimates of the volume of partial melting during their emplacement (Coffin and Eldholm, 1994). The LIP phase of plume activity is followed by a reduction in melt production, which yields oceanic island basalts (OIBs) sourced from the plume tail; this phase often lasts millions of years (White and McKenzie, 1989; Sleep, 1990; Campbell and Griffiths, 1990; White, 1993; Kumagai et al., 2008). NAIP: North Atlantic Igneous Province; CRFB: Columbia River Flood Basalts.

The sheer size of plume heads requires a large volume of material from the lower mantle. Indeed, mantle plumes are associated with low seismic velocities, reflecting the elevated temperature of ascending mantle material (Montelli et al., 2006; Putirka et al., 2007). As a result of findings from seismic studies of the lower mantle (Dziewonski and Woodhouse, 1987; Garnero, 2000; Masters et al., 2000; Garnero et al., 2007) mantle plume models have evolved from the classical mushroom-shaped, thermal model toward more complex thermo-chemical structures. The internal dynamics of thermo-chemical plumes reflect the interplay between positive (thermal) and negative (compositional) buoyancy forces. The symmetrical geometry is often lost (Tackley, 1998; Davaille, 1999, Farnetani and Samuel, 2005) because some parts of the plume conduit sink (Kumagai et al., 2008) whereas others ascend slowly.

The geochemical signatures of LIP phases reflect the complex relationship between compositional heterogeneity and the internal structures of mantle plumes. Components sampled by LIP melts include the plume material itself, upper mantle, and even lithospheric material. Such signals are often more strongly observed in LIPs emplaced on continents than in submarine settings. Geochemical contributions to LIPs can be identified using alteration-resistant, so-called immobile elements, which include Th, Ti, Yb, and Nb. During mantle melting, these elements behave similarly and predictably, making them useful both as proxies for common mechanisms that affect mantle-derived melts and for different mantle and/or crustal components (Pearce et al., 2021). Elevated Th/Nb ratios in LIP melts (part **b** of the figure) reflect increased crustal contamination. The TiO₂/Yb ratio increases with depth of melt generation (more melting in the garnet region of the mantle, >80 km) (Doucet et al., 2005; Frey et al., 2002; Yang et al., 1998); this ratio also increases as the partial melting extent decreases, a signature frequently observed in the OIB (plume tail) phase, when considerably less melt is being generated than during the LIP stage.

The Kerguelen mantle plume produced a hybrid LIP, consisting of continental flood basalts in the early stages (>120 Ma), followed by an oceanic plateau (119-95 Ma), then a plume trail (82-38 Ma), the Kerguelen Archipelago (30 Ma-now) and Heard Island (Frey et al., 2002). Kerguelen lavas preserve signatures of multiple components whose origins vary from the lower mantle to the crust, providing a valuable cross-section of the mantle reservoirs supplying the Kerguelen plume. Kerguelen melts are predominantly within the oceanic field (red circles in part **b** of the figure), overlapping with other LIP fields and extending slightly into the transitional area between MORB-dominant and OIB-dominant LIP melts (Weis and Frey, 2002). A few older samples also overlap with the EM–OIB and lithospheric fields, the latter of which is interpreted as crustal contamination of LIP melts, a phenomenon commonly observed in continental settings (Pearce et al., 2021). SZLM: Subduction Zone-Lithospheric Mantle; OPB: Ocean Plateau Basalt; EM: Enriched Mantle; MORB: Mid-Ocean Ridge Basalt.

Box 2: An introduction to isotopes and isotopic analysis

Isotopes of a chemical element have the same number of protons in their nucleus but differ in their number of neutrons. The relative abundance of one isotope to another is measured by a mass spectrometer. Isotopes can be classified on the basis of their stability and formation pathways.

[bH1] Radiogenic isotopes

Radioactive isotopes have unstable atomic nuclei that emit radiation and spontaneously transform into another isotope, the radiogenic product. Their decay rate is characterized by the half-life ($T_{1/2}$), which is the time for half of a given amount of the parent isotope to decay. In geological settings, time is primarily responsible for differences in radiogenic isotopic compositions. Isotopes with $T_{1/2} > 100$ Myr, such as 87 Rb and 147 Sm, are still decaying today (see figure). The resulting variations in the abundances of daughter products take millions to billions of years to develop, and are measured relative to a stable isotope of the same element (87 Sr/ 86 Sr and 143 Nd/ 144 Nd) using mass spectrometry (Box 3). Such long-lived isotopic systems are used for geochronology and fingerprinting sources of materials. Conversely, radioactive isotopes with $T_{1/2} < 100$ Myr have now fully decayed and are extinct, providing information about events that happened very early in Earth's history.

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

Unlike trace elements (defined as elements that are not structural components of major mantle minerals and have abundances <0.1 wt.%), radiogenic isotopic compositions are not affected by the degree of partial melting or the crystallization history of a melt. Therefore, radiogenic

isotopic ratios (such as ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ²⁰⁶Pb/²⁰⁴Pb, ⁴He/³He, or ¹⁷⁷Hf/¹⁷⁶Hf) of a basalt represent the composition of the material that melted to produce the basalt, providing time-integrated information about its origin. In contrast, variations of extinct radiogenic isotopic systems (such as, ¹⁴²Nd/¹⁴⁴Nd, ¹⁸²W/¹⁸⁴W, ¹²⁹Xe/¹³⁰Xe) indicate the presence of material that differentiated from the rest of the mantle during accretion.

[bH1] Stable Isotopes

Isotopes with a stable nucleus have invariant isotopic abundances. Some of these isotopes, especially light elements, can be fractionated by physical, biological, and sometimes chemical processes, and are used to trace fractionation processes rather than the long-term evolution of the lava source. Examples include atmospheric weathering (O), groundwater interaction (H, O, C), sediment recycling (Li, Tl), and redox changes (Fe).

[bH1] Noble Gases

All noble gases have radiogenic and stable isotopes. For many radioactive systems (Supplementary Table 2), parent–daughter fractionation by gas loss within the lifetime of the radioactive isotope generates variations in radiogenic noble gas isotope signatures over time. For example, ³He is primordial, because it is a stable, non-radiogenic isotope whose abundance was established during accretion; any primordial isotopes lost to the atmosphere are not replaced in Earth's noble gas budget. Primordial noble gas isotopes are no different from the stable, nonradiogenic normalizing isotopes used in other decay systems (such as ²⁰⁴Pb). Accordingly, the less commonly used notation ⁴He/³He is consistent with radiogenic isotope convention, but helium isotopic ratios are usually reported as the inverse, ³He/⁴He. In contrast with other isotopic systems, however, ⁴He is continuously produced by radioactive decay of ²³⁵U, ²³⁸U, and ²³²Th. Unradiogenic He isotopic ratios sample reservoirs that have experienced less degassing (transport of gas from the mantle to the atmosphere associated with mantle processing by partial melting and volcanism). A less-degassed mantle reservoir has relatively high ³He/⁴He (or low ⁴He/³He) because it has retained more of its primordial He, and the impact of radiogenic ingrowth of ⁴He is muted compared to the rest of the mantle. Furthermore, a less-degassed reservoir is not necessarily primordial mantle. Regassing (transport of atmospheric gases into the mantle via subducted slabs) of He is negligible as it is light enough to escape to the atmosphere. Atmospheric contamination during or after sample formation affects Ne, Ar, Kr and Xe isotopic compositions measured in all OIBs. Corrections are needed to determine the mantle source composition and assess whether regassing has affected the mantle being sampled in any given analysis.

Box 3 Analytical precision in the determination of radiogenic isotopic ratios

¹⁴²Nd/¹⁴⁴Nd and ¹⁸²W/¹⁸⁴W ratios are mainly determined using thermal-ionization mass spectrometry (TIMS) techniques that allow high precision analysis, but they also require considerable time and effort to achieve successfully. Analytical artifacts can produce small isotopic variations in TIMS measurements, which can be linked to factors such as isotopic ratios not following the exponential law (Upadhyay et al., 2008), the rate of mass fractionation being too high for dynamic measurements (Roth et al., 2014), mixing of different sample reservoirs on the filaments (Upadhyay et al., 2008, Roth et al., 2014), non-mass dependent isotopic variations caused by the chemical separation protocol (Garçon et al., 2018; Kruijer and Kleine, 2018; Saji

et al., 2016), and the need to improve the determination of O isotope composition for TIMS measurements of W isotope in oxide form (Trinquier et al., 2016). Deviations in the 142 Nd/ 144 Nd and 182 W/ 184 W systems are small; therefore, they are expressed in μ -notation (deviation in parts per million relative to the average ratio measured in the terrestrial standard).

High precision isotopic ratio measurements reveal small differences between the terrestrial standards commonly used in the different laboratories (O'Neil et al., 2008; Saji et al., 2016), as exemplified by the variation of a few parts per million in ¹⁴²Nd/¹⁴⁴Nd ratios measured in La Jolla, JNdi-1, and AMES Nd. A multi-mass-step acquisition scheme enables all isotopic ratios of the element to be determined in dynamic mode, with subsequent application of quality-control criteria (Garçon et al., 2018).

When publishing isotopic data, analytical uncertainty is reported as 2SD (standard deviation, calculated from repeated measurements of the same sample) or 2SE (standard error, where 2SE = $2SD/\sqrt{N}$ and N is the number of measurements). The SE corresponds to the internal error when the sample is measured once. The scientific community has debated the significance of a deviation relative to its analytical precision extensively, without a clear resolution. Regardless of the choice of 2SD or 2SE, publications claiming high-precision isotopic measurements should thoroughly describe the analytical protocols used and all data associated with the measurement, and should also present the results for international, cross-calibrated reference standard materials. A rigorous analysis requires that an appropriate number of duplicate, replicate, and total blank measurements be performed and their results reported in the publication.

To achieve high-precision isotopic OIB measurements it is important to measure only the original, magmatic composition of the basalt, which is achieved primarily through appropriate sample preparation procedures. For example, Rb–Sr, U–Pb, and stable Li isotopic systems are susceptible to perturbation by seawater alteration, and Tl and Pb isotopic measurements are sensitive to ferromanganese precipitation. These secondary products must be removed by physical separation and cleaning followed by careful, systematic acid leaching procedures (Manhès et al., 1978; Dupré and Allègre, 1980; McDonough and Chauvel, 1991; Abouchami et al., 2000; Weis et al., 2006, 2007; Hanano et al., 2009; Nobre Silva et al., 2009, 2010; Williamson et al., 2021). Finally, older OIB samples (>7–10 Ma) must be age-corrected for insitu decay since their eruption (Harrison et al., 2017; Harrison and Weis, 2018). Age correction requires measurements of the elemental parent–daughter ratio of the unleached sample. For the U-Th-Pb system in particular, care must be taken to estimate the primary U concentration in submarine OIB properly, as U is susceptible to secondary alteration. For example, primary U can be estimated using the Th/U of unaltered samples (Nobre Silva et al., 2013b; Harrison et al., 2017).

In OIB studies it is difficult to compare data on the same samples when measured using different instruments, methods, and/or analytical laboratories. These comparisons require geochemists to apply a normalization scheme based on published values for standards and reference materials (Weis et al., 2011, 2020). It is essential that the same standard and reference values are used otherwise spurious correlations can occur.

TOC blurb:

The Earth's mantle influences many dynamic processes such as crust formation, recycling, and mantle convection. This Review explores modern isotopic methods used to characterize plume-derived basalts and therefore gain insight into the mantle's composition.