Remnants of early Earth differentiation in the deepest mantle-derived lavas

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The noble gas isotope systematics of ocean island basalts suggest the existence of primordial mantle signatures in the deep mantle. Yet, the isotopic compositions of lithophile elements (Sr, Nd, Hf) in these lavas require derivation from a mantle source that is geochemically depleted by melt extraction rather than primitive. Here, this apparent contradiction is resolved by employing a compilation of the Sr, Nd, and Hf isotope composition of kimberlites—volcanic rocks that originate at great depth beneath continents. This compilation includes kimberlites as old as 2.06 billion years and shows that kimberlites do not derive from a primitive mantle source but sample the same geochemically depleted component (where geochemical depletion refers to ancient melt extraction) common to most oceanic island basalts, previously called PREMA (prevalent mantle) or FOZO (focal zone). Extrapolation of the Nd and Hf isotopic compositions of the kimberlite source to the age of Earth formation yields a 143Nd/144Nd, 176Hf/177Hf composition within error of chondritic meteorites, which include the likely parent bodies of Earth. This supports a hypothesis where the source of kimberlites and ocean island basalts contains a long-lived component that formed by melt extraction from a domain with chondritic 143Nd/144Nd and 176Hf/177Hf shortly after Earth accretion. The geographic distribution of kimberlites containing the PREMA component suggests that these remnants of early Earth differentiation are located in large seismically anomalous regions corresponding to thermochemical piles above the core–mantle boundary. PREMA could have been stored in these structures for most of Earth’s history, partially shielded from convective homogenization.

Oceanic basalts provide a more direct approach to investigate Earth’s convecting mantle than mantle-derived continental magmas, as they erupt on oceanic lithosphere, which is considerably thinner and less enriched in mantle-incompatible elements than the lithosphere of continental plates. Hence, most of what is currently known about Earth’s convecting mantle—the most voluminous domain of our planet—derives from the study of oceanic basaltic. One obvious drawback is that this knowledge is largely limited to the last 150 to 200 My (i.e., the oldest age of oceanic lithosphere before it is subducted).

Ocean island basalts (OIBs) derive from partial melting of mantle plumes, the majority of which are associated with seismically anomalous regions called large low shear-wave velocity provinces (LLSVPs) located above the core–mantle boundary (1, 2). OIBs exhibit He isotope compositions that can extend to considerably less radiogenic values (i.e., higher 3He/4He ratios) compared with mid-ocean ridge basalts (MORBs), which has been widely advocated as evidence that the source of OIBs contains a primordial component preserved since Earth accretion (3). The Xe isotope systematics of some high-3He/4He OIBs further indicate that their source region became separated from the MORB source within the first 100 My of Earth accretion (4), where the MORB source occupies most of Earth’s convecting mantle and is geochemically depleted in incompatible elements due to continuous extraction of oceanic and continental crust from the mantle (5, 6). Elevated 3He/4He ratios in OIBs appear to be exclusively associated with plumes originating from the LLSVPs (7, 8), thus suggesting a possible spatial link between early Earth remnants and these seismically anomalous regions above the core–mantle boundary.

Elevated 3He/4He ratios may be a common feature of the prevalent mantle (PREMA) (9, 10). This mantle component was originally defined using the narrow range of Nd and Sr isotope ratios (e.g., 143Nd/144Nd ~ 0.5129 to 0.5130) shown by several OIBs (10). In Sr-Nd-Pb isotope plots, OIBs from each island form compositional trends that converge from variously enriched compositions to a common moderately depleted mantle component dubbed focal zone [FOZO (9)], which has a radiogenic isotope composition like that of PREMA (10, 11) (Fig. 1). This implies that FOZO and PREMA are essentially equivalent, and we treat them as such in this manuscript. These observations have been widely employed to argue that PREMA represents a fundamental and abundant constituent of Earth’s convecting mantle, which contributes to the genesis of most OIBs [and also some MORBs (12, 13)]. This interpretation is reinforced by the common occurrence of PREMA-like compositions in juvenile continental magmas (10, 11, 14, 15) and as we will show, in kimberlites dating back to more than ~2 Ga.

The association between primordial high-3He/4He compositions with nonchondritic high-143Nd/144Nd ratios—indicative of long-term depletion in PREMA—apparently negates a primitive origin of PREMA (16). However, these apparently contradictory geochemical features could be reconciled if PREMA represents a depleted mantle residue that formed by silicate melt extraction in the early Earth (10). Alternatively, PREMA could originate from extensive recycling of oceanic and continental crust from the mantle (5, 6).

Significance

Understanding how the Earth evolved from its accretion to the present-day conditions is a major quest of the Earth sciences. This contribution focuses on the evolution of the deepest realms of our planet sampled by basalts in ocean islands (such as Hawaii) during the last ~100 to 150 million years and diamond-bearing kimberlites emplaced in continents since ~2 billion years ago. Radiogenic isotope ratios are employed to demonstrate that these lavas share a common source, which includes a component that originated from melt extraction soon after Earth accretion. These findings help reconcile contrasting geochemical observations in ocean island basalts and provide constraints on the composition and evolution of the deepest and most ancient parts of Earth’s mantle.

Author contributions: A.G. designed research; A.G. and M.G.J. performed research; A.G., A.F., and H.D. analyzed data; and A.G. and M.G.J. wrote the paper with contributions from A.F. and H.D.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2015211118/-/DCSupplemental.

Published December 28, 2020.

PNAS 2021 Vol. 118 No. 1 e2015211118

https://doi.org/10.1073/pnas.2015211118 | 1 of 9
Fig. 1. Present-day Sr-Nd-Hf isotope compositions of MORB and OIBs including the overlapping positions of the OIB-based PREMA or FOZO and depleted kimberlite source. (A) $^{143}$Nd/$^{144}$Nd vs. $^{176}$Hf/$^{177}$Hf; (B) $^{87}$Sr/$^{86}$Sr vs. $^{143}$Nd/$^{144}$Nd. The OIB-PREMA corresponds to the Geochemical Centre of Konter et al. (33) (Materials and Methods show the calculation of $^{176}$Hf/$^{177}$Hf), while the depleted kimberlite source is from this study (Fig. 2); the PREMA ellipses represent calculated values ±2σ uncertainties. MORB and OIB values are from the compilation of Stracke (11).

The Radiogenic Isotope Record of Kimberlites through Time

In order to evaluate the time evolution of kimberlites, it is important to first define a suite of kimberlitic compositions that best reflect their respective mantle sources. The term “kimberlite” has been previously (and incorrectly) employed to describe different types of diamond-bearing magmas, including rocks (e.g., group II kimberlites, also called orangeites) with an affinity to magmas derived from metasomatized (i.e., geochemically enriched) lithospheric mantle sources (24). In this paper, a robust screening based on a strict definition of kimberlites is applied (27) (Materials and Methods). This compilation includes Nd and Hf isotope compositions of bulk kimberlite samples, including some Nd isotope ratios for perovskite separates, from worldwide localities (SI Appendix, Fig. S1) with well-constrained emplacement ages (Dataset S1). The Sr isotope data are less comprehensive because they are restricted to analyses of perovskite, a robust magmatic phase, given that crustal contamination commonly modifies the magmatic Sr isotope signature of kimberlite rocks (24). We attempted to address the influence of crustal contamination on bulk rock Nd and Hf isotope compositions by applying major and trace element-based filters (e.g., Si/Al, Nb/Th, Ba/Nb, Ce/Pb) that are extremely sensitive to continental crust contributions (28, 29). With rare exceptions (30), major and trace element ratios are not correlated to the Nd-Hf isotopic compositions in kimberlites (SI Appendix, Figs. S2–S6). This observation is consistent with the occurrence of magmatic, mantle, and crustal components in bulk kimberlites (27). However, kimberlite
magnas are highly enriched in Nd and to a lesser extent, Hf compared with common mantle and crustal rocks (24, 28, 29). Any contribution from crustal or enriched (i.e., metasomatized) lithospheric mantle components would lower the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ and increase the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of kimberlite magnas (26, 30). Also, hydrothermal alteration, which is common in kimberlites (27), is likely to modify bulk rock Sm/Nd and Lu/Hf ratios due to the fluid-immobile behavior of these elements. Therefore, rather than filtering the bulk kimberlite Nd-Hf isotopic data for crustal or lithospheric mantle contamination using major and trace element ratios, only the most radiogenic bulk rock $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ value and the least radiogenic perovskite $\text{Sr}^{87}/\text{Sr}^{86}$ value in each kimberlite province are considered, as these are least likely to have been influenced by lithospheric contamination, including continental crust assimilation (Materials and Methods). These isotopic values are hereafter considered representative of the evolution of the deep, sublithospheric mantle source of kimberlites through time.

When the initial Sr, Nd, and Hf isotope compositions of all kimberlites are plotted as a function of time (Fig. 2), kimberlites from each province have compositions that range from moderately depleted (i.e., higher $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and lower $\text{Sr}^{87}/\text{Sr}^{86}$) corresponding to long-term evolution under high Sm/Nd and Lu/Hf and low Rb/Sr to more geochemically enriched isotopic values (i.e., lower $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and higher $\text{Sr}^{87}/\text{Sr}^{86}$). A first-order observation is that kimberlites do not exhibit extreme depletion and thus, never extend to DMM (i.e., MORB source) compositions. Some <200-Ma kimberlites (i.e., North America Central Corridor and Luc de Gras in Canada, Alto Paraiba in Brazil, and South Australia) are unusual in that they are geochemically enriched and exhibit isotopic compositions that overlap with the EM-1 (enriched mantle type-1; which contains deeply subducted crustal material) compositions in OIBs (SI Appendix, Fig. S7). In detail, Sr isotope compositions in these kimberlites are limited to higher $\text{Sr}^{87}/\text{Sr}^{86}$ (i.e., more geochemically enriched compositions) compared with other kimberlites and ultramafic lamprophyres of similar age (e.g., Tazania, Rosario do Sul [Brazil], Siberia Jurassic) (Fig. 2). This observation is in line with the interpretation of Woodhead et al. (19), where the sources of kimberlites emplaced in the past 200 Ma near the margins of Pangea are influenced by addition of deeply subducted, recycled crustal material. Whether or not this phenomenon has had a limited impact on kimberlites earlier in geologic time is unclear based on our database, which shows variability in initial $^{143}\text{Nd}/^{144}\text{Nd}$ and especially $\text{Sr}^{87}/\text{Sr}^{86}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios at any given time in the kimberlite record. After these anomalous, geochemically enriched kimberlites are excluded, a remarkable pattern becomes clear, wherein the most radiogenic Sr and most radiogenic Nd-Hf isotope compositions in each kimberlite province plot along a relatively narrow linear array through time (Fig. 2). This observation appears to indicate that a common, moderately depleted component (less depleted than the upper mantle source of MORB) has participated in the genesis of kimberlites since at least 2.06 Ga. The spread of isotopic values toward more geochemically enriched compositions (i.e., lower $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and higher $\text{Sr}^{87}/\text{Sr}^{86}$) recorded by kimberlites in each province at a given time can be related to different factors including crustal contamination (30), contribution by enriched lithospheric mantle (25, 31), or source pollution by recycled crustal material (19, 26, 32).

**Kimberlites and the Origin of PREMA**

Statistically robust regressions (Materials and Methods) through the common depleted component of kimberlites in plots of Sr-Nd-Hf isotope ratios vs. time (Fig. 2) yield present-day compositions ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512897 \pm 0.000060$ [2r]; i.e., $^{143}\text{Nd} = 5.2 \pm 1.2$; $^{176}\text{Hf}/^{177}\text{Hf} = 0.283013 \pm 0.000076$ [i.e., $^{176}\text{Hf} = 8.1 \pm 2.7$]; $\text{Sr}^{87}/\text{Sr}^{86} = 0.70335 \pm 0.00032$) within the PREMA (or FOZO) field sampled by OIBs ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512950 \pm 0.000143$ [2r]; $^{176}\text{Hf}/^{177}\text{Hf} = 0.283100 \pm 0.000125$; $\text{Sr}^{87}/\text{Sr}^{86} = 0.70330 \pm 0.00058$) (33) (Fig. 1). In detail, the depleted kimberlite source overlaps with the geochemically enriched side of the PREMA field, which may be consistent with the lower melting degree of kimberlites and hence, their sampling of more geochemically enriched components compared with OIBs; this is because geochemically enriched material is assumed to be more fusible and is hence preferentially sampled relative to less fusible (i.e., geochemically depleted) materials at lower degrees of melting. Regardless, the data show that, like OIBs, kimberlites sample a ubiquitous PREMA component in Earth’s mantle, not a component with primitive $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ (19).

This observation provides insights into the origin of PREMA. If PREMA compositions are widespread in kimberlites since ~2.06 Ga and in juvenile continental magmas since the Late Archean as previously reported by Stein and Hofmann (14), it seems a fortuitous coincidence that mixing of depleted and enriched mantle components in an evolving Earth can consistently generate such a remarkably homogeneous isotopic composition over geologic time. This is because the composition of subducted crustal material has undoubtedly changed throughout the last 2 billion years—e.g., progressive modification of ocean chemistry and marine sediments (34, 35) and widespread occurrence of oceanic crust rocks derived by subduction of oceanic crust (36). Likewise, the pressure and temperature conditions of metamorphism in subduction zones have also changed significantly throughout Earth history (37). The temperature and oxygen fugacity of the mantle have decreased (38) and increased (39) over time, respectively, which is reflected by the composition of mafic magmas through time (40). Given radical changes in subduction conditions and subducted protolith compositions, it is unlikely that subducted crust, when mixed with depleted mantle such as the MORB source, gives rise to the relatively narrow range of PREMA-like compositions consistently through time. This supports a hypothesis where PREMA is a long-lived primordial mantle domain, not a mixture of geochemically enriched and geochemically depleted domains.

The linear isotopic evolution of kimberlites through time (Fig. 2) allows us to extrapolate the composition of the geochemically depleted PREMA domain back in time and estimate its initial isotopic compositions. Critical parameters are the initial Hf isotopic evolution of the depleted kimberlite source to the approximate age of Earth formation (4.567 Ga) returns initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.50657 ± 0.00010 (1σ) and 0.27983 ± 0.00012, respectively, which are within uncertainty of chondrite initial values ($^{143}\text{Nd}/^{144}\text{Nd} = 0.50669 \pm 0.00004$; $^{176}\text{Hf}/^{177}\text{Hf} = 0.27979 \pm 0.00001$ (41)). If this extrapolation is valid, the kimberlite $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ data suggest that the PREMA domain, sampled by OIBs today and kimberlites over the past >2 billion years, could have been established not long after Earth’s accretion from chondritic material. Critically, however, the calculated $^{143}\text{Sm}/^{144}\text{Nd}$ (0.2086 ± 0.0022; 1σ) and $^{176}\text{Lu}/^{177}\text{Hf}$ (0.0358 ± 0.0010) ratios of the PREMA domain tapped by kimberlites must be suprachondritic to generate the geochemically depleted (i.e., high $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic compositions that characterize PREMA. Hence, kimberlites do not sample a primitive, circa-chondritic mantle reservoir as previously suggested (19) but rather, a domain (PREMA), which derived from early depletion of chondritic mantle.

These Sm/Nd and Lu/Hf ratios are remarkably similar to those of the Early Depleted Reservoir (EDR) modeled by Caro and Bourdon (42) (referred to as “Super-Chondritic Earth Model” in their paper). The EDR was originally conceived as the portion of mantle that experienced differentiation via silicate melt extraction within the first 30 My of Earth accretion, leaving behind an early geochemically depleted silicate reservoir with elevated (suprachondritic) Sm/Nd that evolved to higher than chondritic
143Nd/144Nd. This early silicate differentiation occurred during the lifetime of the short-lived isotope 146Sm (i.e., first 500 Ma of Earth’s history), and due to the decay of 146Sm to 142Nd (half-life ~ 10^3 My), the elevated Sm/Nd in the EDR also yields anomalously high 142Nd/144Nd in the accessible Earth (relative to certain classes of chondrites) (43). A complementary hidden enriched reservoir with low Sm/Nd, low 143Nd/144Nd, and low 142Nd/144Nd is also predicted by this model but has not yet been observed. In this model, continental crust was subsequently extracted from the EDR, thereby generating the depleted mantle source of MORB, explaining why MORBs and OIBs (which sample recycled crust) exhibit anomalously high 142Nd/144Nd compared to most chondrites. However, while this 142Nd/144Nd difference was interpreted to signal an early terrestrial silicate differentiation event (43), later work attributed the elevated 142Nd/144Nd in the accessible silicate Earth to poor mixing of nucleosynthetic heterogeneities during solar system formation—where the Earth formed from a region of the solar nebula with higher 142Nd/144Nd than most chondrites—rather than radioactive decay (44, 45). As a result, the existence of the EDR has been questioned.

Nonetheless, up to 10 ppm of the 142Nd/144Nd difference between Earth and enstatite chondrites (44–46) (i.e., the chondrites with isotopic compositions most similar to Earth) may be the result of 146Sm decay [discussion is in de Leeuw et al. (47) and Willhite et al. (48)]. Therefore, the 142Nd/144Nd difference between Earth and enstatite chondrites can be explained as the result of marginal suprachondritic Sm/Nd in the accessible Earth. In this model, the required Sm/Nd is sufficiently high to

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**Fig. 2.** Nd, Hf, and Sr isotope evolution of kimberlites and ultramafic lamprophyres through time. (A) 143Nd/144Nd vs. time, (B) 176Hf/177Hf vs. time, and (C) 87Sr/86Sr vs. time. D–F show the last 700 My of isotopic evolution for the Nd, Hf, and Sr isotope systems, respectively. All of the isotopic ratios represent initial values corrected for radiogenic ingrowth using the emplacement ages of kimberlites and ultramafic lamprophyres. The evolution of the depleted kimberlite source (dark blue lines with 2σ uncertainty envelope in lighter blue) represents a linear regression through the most radiogenic 143Nd/144Nd and 176Hf/177Hf values and least radiogenic 87Sr/86Sr ratios (i.e., larger symbols) of kimberlites (circles) and ultramafic lamprophyres (crosses) from each province (Dataset S2). The provinces that contain geochemically enriched kimberlites (diamonds) and transitional kimberlites (triangles) are excluded from these regressions because their isotopic compositions are dominated by recycled subducted and/or enriched lithospheric components (19, 26, 31). Three kimberlite provinces are also excluded from the regressions in 176Hf/177Hf vs. time charts (i.e., Limpopo-Zimbabwe, Premier, Slave-Cambrian) because their 176Hf/177Hf ratios are all moderately to highly unradiogenic probably due to the ubiquitous alteration of kimberlites from these provinces. All age and Nd-Hf-Sr isotopic values are reported in Dataset S1. Materials and Methods show the values employed to calculate the isotopic evolutions of the DMM and CHUR.
generate the suprachondritic $^{143}$Nd/$^{144}$Nd observed in PREMA domains (48). Alternatively, if $^{142}$Nd/$^{144}$Nd differences between Earth and chondrites reflect purely nucleosynthetic processes, then early formation of PREMA and its long-suprachondritic $^{143}$Nd/$^{144}$Nd composition could still be explained if Earth differentiation by silicate melt extraction and development of suprachondritic Sm/Nd was delayed until the abundance of short-lived $^{140}$Sm had been greatly diminished by decay. For example, if the Moon-forming impact at ∼4.45 to 4.40 Ga (49) triggered the global silicate differentiation event, which generated an early-formed depleted domain (50) and hence, PREMA, this delayed early differentiation event would not generate observable positive $^{142}$Nd/$^{144}$Nd anomalies in the depleted silicate Earth. In detail, the Sm/Nd ratio required to generate the present-day (kimberlite-based) PREMA $^{142}$Nd/$^{144}$Nd (i.e., ε$^{143}$Nd of +5.2) from differentiation of a chondritic mantle at ∼4.40 to 4.45 Ga would generate only a small $^{142}$Nd/$^{144}$Nd anomaly of a magnitude that is close to the external reproducibility of modern instruments (i.e., 5 ppm) and would be difficult to resolve analytically (47,50).

An even later silicate differentiation event (i.e., not linked to lunar formation) would further suppress generation of resolvable $^{142}$Nd/$^{144}$Nd anomalies while permitting formation of the suprachondritic $^{143}$Nd/$^{144}$Nd observed in PREMA. This might explain the lack of resolvable $^{142}$Nd/$^{144}$Nd anomalies in previously analyzed kimberlites (43). Hence, it is possible that PREMA represents a portion of an early depleted mantle domain that has not been modified since Early Hadean silicate Earth differentiation (51), and the isotopic compositions of kimberlites are best explained by episodic tapping of this PREMA composition over geologic time. An ancient origin for PREMA by silicate melt extraction would reconcile the apparently paradoxical association between primordial noble gas compositions, including elevated $^3$He/$^4$He ratios, and $^{142}$Nd/$^{144}$Nd-$^{176}$Hf/$^{177}$Hf ratios indicative of long-term depletion in the PREMA domain sampled by OIBs.

**Early Earth Remnants above the Core–Mantle Boundary**

Survival of a minimally modified portion of this early depleted mantle domain (i.e., PREMA) since shortly after Earth accretion requires (partial) isolation from convecting mixing, which is most readily achieved if this domain is located in the deep mantle where convective motions are slowed due to higher viscosity. This hypothesis might be supported by the observation that plumes generating most Phanerozoic kimberlites and modern volcanic hot spots, including OIBs, are dominantly sourced from large seismically anomalous regions (i.e., LLSVPs) above the core–mantle boundary (20,52). However, not all kimberlites are linked to the LLSVPs, and it is unknown if the geochemistry of kimberlites (i.e., PREMA compositions) varies as a function of their geographic relationship with the LLSVPs. To constrain whether PREMA-like kimberlites were spatially correlated with the LLSVPs at the time of their eruption, we have examined the geographic distribution of kimberlites and related ultramafic lamprophyres for which Sr-Nd-Hf isotope compositions are available. This survey is limited to the last ∼270 Ma, a time interval for which the assumption of LLSVP fixity (53,54) and the association between LLSVP and plumes from the core–mantle boundary seem to be well constrained (20, 52). Fig. 3 demonstrates that kimberlites with radiogenic isotope compositions typical of PREMA are exclusively associated with the LLSVPs, whereas kimberlites that lack a PREMA signature occur both above and far away from the LLSVPs. This observation supports the hypothesis that minimally modified remnants of early Earth differentiation are located within these seismically anomalous regions representing thermochemical piles above the core–mantle boundary and is consistent with the elevated (primordial) $^3$He/$^4$He ratio of OIBs sourced from mantle plumes rooted into the LLSVPs (8).

In conclusion, this study demonstrates that kimberlites and ultramafic lamprophyres as old as 2.1 Ga sample a similar PREMA component as that occurring in OIBs and that this component likely represents a remnant of early Earth differentiation. This can explain the association of primordial noble gas signatures in kimberlites and OIBs with Nd-Hf isotope

![Fig. 3. Geographic distribution of the depleted kimberlite source (PREMA) in Earth’s mantle. Kimberlites and ultramafic lamprophyre provinces within the last 270 My and with available Sr-Nd-Hf isotope compositions are reconstructed to their location at time of eruption and compared with the position of LLSVPs above the core mantle boundary using the GPlates software (78) paired with the continent rotation model of Torsvik et al. (54). LLSVPs are defined based on the 1% (±0.5%; dv/v: shear-wave velocity variation) slow contour of the Savani tomography model (79) at a depth of ∼2,800 km. Kimberlites and ultramafic lamprophyres containing the PREMA component (yellow circles) overlap the LLSVPs at time of eruption, with the notable exception of Siberian kimberlites, which are proximal to the Perm low shear-wave anomaly above the core–mantle boundary (80). Conversely, kimberlites lacking the PREMA component (black diamonds) do not exhibit any preferential geographical association with the LLSVPs. These results are independent of the employed seismic tomography model as shown in SI Appendix, Fig. S11.](https://doi.org/10.1073/pnas.2015211118)
compositions indicative of long-term depletion. Derivation of kimberlites and OIBs from common deep sources is supported not only by the common PREMA contribution to both magma types but also, the occurrence of similar enriched components in OIBs and kimberlites younger than 200 Ma, including EM-1 (SI Appendix, Fig. S7) and HIMU (i.e., high U/Pb-type) compositions (55). Although no EM-2 (enriched mantle type-2) compositions have so far been observed in kimberlites, it should be noted that EM-2 OIBs are restricted to the Pacific LLSPV (56), whereas no kimberlites of Mesozoic or younger age were located above the Pacific LLSPV at the time of eruption (20). The exclusive association of PREMA-like kimberlites in the last ~270 Ma with the LLSPVs suggests that this early Earth component is stored in the LLSPVs, and therefore, the origin of these structures could date back to the time of early Earth differentiation (57). Additional studies of Paleoproterozoic and Archean alkaline ultramafic magmas will be required to augment the isotopic record of kimberlites and ultramafic lamprophyres presented herein, thus improving available constraints on the evolution of the deep mantle in the first half of Earth evolution. Kimberlites hold unique clues of early Earth differentiation, and future examination of their noble gas, 182W, and 142Nd isotope systematics is likely to yield fundamental insights into the evolution and dynamics of Earth’s mantle.

Materials and Methods

Database. The initial dataset includes bulk sample 146Nd/144Nd and 176Hf/177Hf and perovskite 87Sr/86Sr isotope compositions for rocks that were labeled kimberlites or carbonate-rich ultramafic lamprophyres (dominantly aillikites) in the original publications. Carbonate-rich ultramafic lamprophyres have similar mineralogical and geochemical compositions to kimberlites, including radiogenic isotope systematics (24, 25, 58-61). The similarity is such that some of these lamprophyres were incorrectly classified as kimberlites when these datasets were originally reported (see below). In this study, kimberlites and carbonate-rich ultramafic lamprophyres are considered to be derived from similar sources even though we recognize that the actual petrogenetic relationship between these magmas is unclear. In this compilation, we do not consider group II kimberlites, subsequently renamed orangeites (62), transitional kimberlites, and lamproites (67-84), or ultramafic lamprophyres; i.e., aillikites; and South Australia (kimberlites and ultramafic lamprophyres). Archetypal kimberlites and ultramafic lamprophyres can contain components derived from enriched lithospheric mantle (25, 31). However, by considering the most radiogenic 146Nd/144Nd and 176Hf/177Hf and least radiogenic 87Sr/86Sr values in each province, these contributions can be filtered out (see below).

Filtering for Crustal Contamination. Kimberlites are hybrid rocks that contain crustal and mantle-derived fragments (i.e., xenoliths) and hydrothermal alteration that are not mantle derived (27). The fusion of the crust and mantle is especially problematic for radiogenic isotope studies of kimberlites as shown, for example, by the commonly higher 87Sr/86Sr ratios of bulk kimberlite samples compared with those of perovskite, a robust magmatic phase (24, 30, 71). To mitigate this issue, the 87Sr/86Sr isotope data we have considered herein are restricted to analyses of perovskite. Even though kimberlite magmas are highly enriched in Nd and to a lesser extent, Hf compared with crustal rocks (24, 28, 29), crustal contamination can also affect the 143Nd/144Nd and 176Hf/177Hf isotope compositions of bulk kimberlite samples (26, 30). For this reason, we have applied several filters based on major and trace element ratios (Si/Al, Nb/Ti, Nb/U, Ba/Nb, Ba/Ti, Rb/Ti, Ce/Pb, Yb/Gd), which are sensitive to crustal contamination based on previous studies of kimberlite and mafic magmas (28, 29, 48). For each filter, the upper and lower bounds of the primitive value (P) were determined as 1.26 times the crustal value (73) were first calculated. Next, bins were assigned for values above the larger and below the smaller values of the two aforementioned endmembers (i.e., primitive mantle and continental crust); finally, further bins were determined by splitting the difference between the two endmembers into evenly sized bins, typically five. Kimberlite and ultramafic lamprophyre samples (for which bulk sample major and trace element results were available together with Nd and/or Hf isotope compositions) in the entire database were placed into these bins according to their bulk major and trace element compositions (SI Appendix, Figs. S2-S6).

We observe no correlation between major or trace element ratios and Nd or Hf isotope compositions on a global scale (SI Appendix, Figs. S2 and S3) or in individual provinces (e.g., southern Africa Cretaceous, Lac de Gras) (SI Appendix, Figs. S4-S6). This observation is not unexpected because a range of crustal, mantle, and depleted core components are reflected in these compositions. Given that this approach of screening for crustal contamination did not produce appreciable results, we have adopted a different strategy as outlined in the next section.

Filtering for Lithospheric Contribution. In the following, “province” is considered to include one or more clusters and/or fields of kimberlites (and/or ultramafic lamprophyres) from the same geographic region, which were emplaced in a restricted time window (typically ~100 My). Kimberlites in each province can, therefore, be traced back to the same source region in the sublithospheric mantle. To understand the source of isotopic variability in each province, we have only considered provinces for which at least three analyses of kimberlites or carbonate-rich ultramafic lamprophyres are available for at least one of the three isotopic systems examined herein. In most provinces, kimberlites show variable radiogenic isotope compositions despite their similar emplacement ages (Fig. 2 and SI Appendix, Figs. S8 and S9). This variability can be attributed to one or more of the following: 1) source heterogeneity in the sublithospheric mantle, most likely related to recycling of subducted or delaminated lithospheric material (19, 26); 2) incorporation of enriched lithospheric mantle material during magma ascent (25, 31); and 3) crustal contamination (26, 30). The common effect of these processes is that the 143Nd/144Nd and 176Hf/177Hf ratios in kimberlites. Textbook examples of the geochemical consequences of these processes include the aillikite dykes at Torngat, Labrador [whose Nd and Hf isotopic compositions form a linear trend from moderately high to
low values attributed to increasing contribution from metasomatized lithospheric mantle (25) and the Premier kimberlite in South Africa (where 143Nd/144Nd is higher than 0.512, consistent with SiO2 content, increasing crustal contamination (30)). Therefore, to screen the dataset from the effects of any lithospheric contribution, be it crustal or lithospheric mantle, we have only considered the most radiogenic 143Nd/144Nd and 176Hf/177Hf, and least radiogenic 87Sr/86Sr values in each kimberlite province. Commonly, the selected analyses with most radiogenic 143Nd/144Nd do not correspond to the most radiogenic 176Hf/177Hf ratio for the same Kimberlite province because there are considerably more Nd isotopes than Hf isotopes available, and some Nd isotope compositions are of perovskite separates, which do not have associated Hf isotopic ratios, and 2) Nd isotopes in bulk Kimberlite samples are more resistant to crustal or lithospheric mantle contamination than Hf isotopes, which results in occasional decoupling between these two isotopic systems in bulk Kimberlite rocks. We acknowledge that this approach can also filter out the potential contributions of deeply subducted material in the kimberlite sources. However, our aim is to address the origin of the moderately depleted mantle component, least influenced by crustal recycling processes, that is evident in the majority of Kimberlites worldwide (large symbols in Fig. 2). In this sense, some Kimberlites appear to be anomalous because they apparently lack this depleted component (see below), or the component exists but the appropriate samples have not been analyzed.

Screening of Geochronically Enriched Kimberlites. The transitional Kimberlites identified above based on petrographic and mineral chemical criteria typically feature geochemically enriched isotopic signatures (i.e., moderately to strongly radiogenic 143Nd/144Nd and 176Hf/177Hf ratios) combined with high 87Sr/86Sr values (triangles in Fig. 2). Kimberlites from four young (<200 My) provinces (Lac de Gras and North America Central Corridor in Canada, Alto Paraíba in Brazil, and South Australia) exhibit 87Sr/86Sr ratios that are moderately to strongly radiogenic (North America Central Corridor, Alto Paraíba) and never extend to the unradiogenic compositions of Kimberlites elsewhere with similar ages (diamonds in Fig. 2). However, these geochemically enriched Kimberlites do not exhibit mineralogical or mineral chemical features of transitional Kimberlites. They are located in proximity of the paleomargins of Pangaea, and their sources were probably enriched by subduction of oceanic lithosphere in the convecting mantle (19, 26) as also indicated by studies of sublithospheric diamonds in other Cretaceous kimberlites from Brazil (74, 75). Kimberlites with such geochemical characteristics are not commonly observed prior to 200 My, perhaps due to limited contribution of recycled lithospheric material to the deep source of Kimberlites (19). As the aim of this work is to identify the long-term evolution of the depleted component in the Kimberlite sources, samples from these four provinces have been screened out from calculation of the long-term 143Nd/144Nd and 176Hf/177Hf Kimberlite source composition (but are shown in the figures to provide important context). While other provinces also include Kimberlites with moderately radiogenic 87Sr/86Sr ratios (e.g., southern Africa Cretaceous, Great Bear Province) (Fig. 2), the Kimberlites from these provinces do not feature isochronally depleted compositions, which are here considered to be representative of the depleted mantle component occurring in the majority of Kimberlites worldwide. Hence, these provinces have been retained in the calculations below.

Statistical Treatment of Data. To understand the present-day composition of the deep Kimberlite source (i.e., its depleted component) and its evolution with time, we have calculated linear regressions through the most radiogenic 143Nd/144Nd and 176Hf/177Hf, and least radiogenic 87Sr/86Sr values in each kimberlite province (Fig. 2 and SI Appendix, Fig. 510). These regressions allow derivation of present-day 143Nd/144Nd, 176Hf/177Hf, and 87Sr/86Sr values at any time (Fig. 2 and SI Appendix, Fig. 510). These regressions allow derivation of present-day 143Nd/144Nd, 176Hf/177Hf, and 87Sr/86Sr values as well as time-integrated 143Nd/144Nd, 176Hf/177Hf, and 87Sr/86Sr ratios in the Kimberlite source least influenced by recycled crustal material.

We employed four different methods for calculating linear regressions using the Python programming language (“numpy.polyfit,” “smols,” “scipy.stats.linregress,” and “np.linalg.lstsq”). These functions calculate a least squares polynomial or linear fit through the data and attempts to minimize the squared errors from the regression. Outputs also include the covariances of the gradient and the y intercept. The results of these calculations are broadly similar, and those from polyfit and linregress are compared in SI Appendix, Fig. 510. All of the data points were included in the linear regressions calculated for 143Nd/144Nd vs. age and 87Sr/86Sr vs. age, whereas three low-176Hf/177Hf data points (Limpopo-Zimbabwe, Premier, Slave-Cambrian) were removed from the 176Hf/177Hf vs. age regression because they fell outside the 2σ envelope of the regression. The majority of Kimberlites in these provinces are altered, which suggests that the depleted Hf component of these Kimberlites could not be correctly identified. Nonetheless, inclusion of these results would not alter the output of this model but rather, generate considerably larger uncertainties (e.g., present-day 176Hf/177Hf = 0.282993 ± 0.000196 [2σ] compared with 0.283013 ± 0.000076 when the outliers are removed).

The apparently robust correlations between age and isotopic compositions in Fig. 2 (i.e., $R^2 = 0.998$, 0.993, and 0.882 for Nd, Hf, and Sr isotopes, respectively) were then subjected to the standard two-tailed Student’s t test for the null hypothesis that the correlations between variables occur by chance. We calculated $t$ values at the 99% level of confidence using the relationship $t = r \sqrt{ n - 2}$, where $n$ is the number of data points and $r$ is the correlation coefficient. None of the correlations examined are likely to have occurred by chance because calculated $t$ values are significantly higher than critical $t$ values (i.e., Nd isotopes: $n = 26$, $t_{calc} = 109 > t_{test} (0.01; 26) = 3.7$; Hf isotopes: $n = 15$, $t_{calc} = 43 > t_{test} (0.01; 4; 13) = 4.1$; Sr isotopes: $n = 13$, $t_{calc} = 9.1 > t_{test} (0.01; 13) = 4.2$). The regression results generated using linregress are reported in Fig. 2 and have been employed for modeling the origin and evolution of the Kimberlite source, including its present-day composition.

Linear regression models were also run on Minatab 19 with the Predict function used to extrapolate the initial 143Nd/144Nd and 176Hf/177Hf compositions of the Kimberlite source to 4.567 Ga. This software was also employed to determine the uncertainties of the initial values based on the confidence and prediction intervals of the regression model.

Comparison with Other Geochemical Reservoirs. The present-day isotopic composition of the Kimberlite source obtained from the regressions above is compared with the compositions of other mantle end-members (e.g., DMM, PREMA, or FOZO) in Fig. 1. The present-day 143Nd/144Nd and 87Sr/86Sr composition of PREMA is taken from Koster et al. (33), whose Geochemical Centre represents the volume where the trends formed by each ocean island chain converge in Sr-Nd-Pls isotope space. The PREMA 176Hf/177Hf ratio (and 2σ variability) is then calculated using the Geochemical Centre 143Nd/144Nd value and the Nd-Hf mantle array of Chauvel et al. (76). This comparison shows that the present-day isotopic composition of the depleted Kimberlite source is indistinguishable from the OIB-based PREMA (Fig. 1).

In Fig. 2, the isotopic evolution of the DMM with time is calculated following the method of Stracke et al. (77) and assuming differentiation occurred at ~4.4 Ga. We employed present-day DMM values of 0.51320 for 143Nd/144Nd, 0.28335 for 176Hf/177Hf, and 0.70270 for 87Sr/86Sr. For the Nd-Hf isotope evolution of the Chondrite Uniform Reservoir (CHUR), we employed the model of Bouvier et al. (41), while for Sr isotopes, we used the following values: 87Sr/86Sr = present day = 0.7045 and $Rb Sr$ = 0.0827.

Finally, the initial 143Nd/144Nd and 176Hf/177Hf compositions of the Kimberlite source at 4.567 Ga calculated using linregress and Predict (see above) were compared with the initial CHUR composition of Bouvier et al. (41): 143Nd/144Nd = 0.50663 ± 0.00005, 176Hf/177Hf = 0.27983 ± 0.00012, 87Sr/86Sr = 0.70270 ± 0.00007, and 176Hf/177Hf = 0.27978 ± 0.00007.

These results indicate that the 143Nd/144Nd and 176Hf/177Hf compositions of the depleted Kimberlite source are within uncertainty of CHUR values at the approximate time of Earth formation and suggest that the depleted Kimberlite source derived from differentiation of a mantle with chondritic composition via silicate melt extraction not long after Earth accretion.

Data Availability. All study data are included in the article and supporting information.

ACKNOWLEDGMENTS. We thank Jon Woodhead, Janet Hergt, Rick Carlson, Paolo Sossi, Brad Peters, and Andreas Stracke for discussions and Matteo Desiderio for proofreading this manuscript. Comments from the editor and two anonymous reviewers have improved the clarity of this contribution. This research was funded by Swiss National Science Foundation Ambizione Fellowship PZ00P2_180126/1 (to A.G.) and NSF Grant NSF EAR-1900652 (to M.G.J.)


