Recycled ancient ghost carbonate in the Pitcairn mantle plume

Xiao-Jun Wang, Li-Hui Chen, Albrecht W. Hofmann, Takeshi Hanyu, Hiroshi Kawabata, Yuan Zhong, Lie-Wen Xie, Jin-Hua Shi, Takashi Miyazaki, Yuka Hirahara, Toshiro Takahashi, Ryoko Senda, Qing Chang, Bogdan S. Vaglarov, and Jun-Ichi Kimura

*State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, 210023 Nanjing, China; †Abteilung Klimageochemie, Max-Planck-Institut für Chemie, D-55128 Mainz, Germany; ‡Department of Solid Earth Geochemistry, Japan Agency for Marine-Earth Science and Technology, 237-0061 Yokosuka, Japan; ‡Faculty of Science and Technology, Kochi University, 780-8520 Kochi, Japan; and *State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, 100029 Beijing, China

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The extreme Sr, Nd, Hf, and Pb isotopic compositions found in Pitcairn Island basalts have been labeled enriched mantle 1 (EM1), characterizing them as one of the isotopic mantle end members. The EM1 origin has been vigorously debated for over 25 years, with interpretations ranging from delaminated subcontinental lithosphere, to recycled lower continental crust, to recycled oceanic crust carrying ancient pelagic sediments, all of which may potentially generate the requisite radiogenic isotopic composition. Here we find that δ26Mg ratios in Pitcairn EM1 basalts are significantly lower than in normal mantle and are the lowest values so far recorded in oceanic basalts. A global survey of Mg isotopic compositions of potentially recycled components shows that marine carbonates constitute the most common and typical reservoir invariably characterized by extremely low δ26Mg values. We therefore infer that the subnormal δ26Mg of the Pitcairn EM1 component originates from subducted marine carbonates. This, combined with previously published evidence showing exceptionally radiogenic Pb as well as sulfur isotopes affected by mass-independent fractionation, suggests that the Pitcairn EM1 component is most likely derived from late Archean subducted carbonate-bearing sediments. However, the low Ca/Al ratios of Pitcairn lavas are inconsistent with experimental evidence showing high Ca/Al ratios in melts derived from carbonate-bearing mantle sources. We suggest that carbonate–silicate reactions in the late Archean subducted sediments exhausted the carbonates, but the isotopically light magnesium of the carbonate was incorporated in the silicates, which then entered the lower mantle and ultimately became the Pitcairn plume source.

Pitcairn mantle plume | EM1 | magnesium isotopes | ancient carbonate-bearing sediments

The geochemical and isotopic diversity of ocean island basalts (OIBs) erupted at hot spots is generated by partial melting of heterogeneous mantle sources that contain recycled crustal and/or lithospheric mantle materials (1, 2). Specific recycled components generally show radiogenic isotope ratios distinct from the ambient mantle, and radiogenic isotopes are therefore widely used tools for tracing them. However, this tool can be compromised by the fact that similar radiogenic isotope features can appear in different geological reservoirs. Thus, the exceptionally radiogenic Pb isotopes observed in intraplate enriched mantle 1 [EM1 (3)] lavas have been variously attributed to recycled ancient pelagic sediments (4–7), subducted oceanic plateau (8), recycled lower continental crust (LCC) (9), delaminated subcontinental lithospheric mantle (10), and recycled mafic sediments (11). Fortunately, a combination of stable and radiogenic isotopes can sometimes be used to discriminate the nature of recycled materials less ambiguously. Recently, Delavault et al. (7) demonstrated the presence of sulfur isotopes affected by mass-independent fractionation in sulfides contained by Pitcairn lavas, which are likely to have been introduced into the Pitcairn source by subduction of ancient sediments. Here we use a stable isotope tracer, magnesium, which undergoes strong isotopic fractionation during precipitation of carbonate from seawater/pore fluids (12), producing distinctively low δ26Mg values in marine carbonates. Because of this, it appears to be an excellent tracer of a more specific recycled component than, for example, oxygen isotopes.

There are many models for the creation of chemical heterogeneity in the source regions of OIBs that invoke the recycling of oceanic crust and lithologically different sediments through the mantle (5, 13–15). The existing Mg isotope data show that marine sediments and altered oceanic crust have variable Mg isotopic signatures that differ significantly from those of normal peridotitic mantle (Fig. 1). In particular, marine carbonates stand out by their extremely light Mg isotopes, reaching values of δ26Mg as low as −5‰. This provides the opportunity to use anomalous Mg isotopic signatures in erupted OIBs as tracers of their sources. A recent Mg isotopic study on Hawaii and Louisville basalts presented a first test of this proposition, showing small but significant differences in δ26Mg (16). However, the current Mg isotope database for OIBs is still very small, and the Mg isotope characteristics of the several classical mantle species, i.e., HIMU (high μ = 238U/204Pb), EM1, and enriched mantle 2 (3), remain to be evaluated. Here we focus on

Significance

Lavas from Pitcairn Island are the best candidates for exploring the origin of the enigmatic EM1 component found in some mantle plumes because they show the most extreme isotopic compositions of Sr, Nd, Hf, and Pb that define the EM1 component. We find that these lavas have the lowest δ26Mg values so far recorded in oceanic basalts. Subducted late Archean dolomite-bearing sediments are the most plausible source of the low-δ26Mg feature of Pitcairn lavas. This requires that an ancient, originally sedimentary component has been emplaced near the core–mantle boundary to ultimately become part of the Pitcairn plume source.


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on the EM1 end member by presenting whole-rock Mg isotope analyses of Rarotonga and Pitcairn Island lavas. The combination of Mg isotopes with Sr–Nd–Hf–Pb isotopes provides critical evidence for the return of ancient, subducted dolomite-derived magnesium in EM1 lavas erupted at Earth’s surface.

Pitcairn mantle plume has recently been identified as a category 1–primary plume, by French and Romanowicz (17), who used waveform seismic tomography to trace it down to the core–mantle boundary. Identifying the nature and age of surface-derived geochemical signatures in such a plume therefore provides important constraints on the nature and time scale of deep mantle circulation processes.

Results

We analyzed 12 samples from Pitcairn Island (SI Appendix, Fig. S1). Seven of the samples come from the shield-building Tiedsva volcanics, and five others are from the late-stage, posterosional volcanics including Pulawana, Christians Cave Formation, and Adamstown volcanics. Duncan et al. (18) reported K-Ar ages for Tiedsva and late-stage volcanics of 0.95–0.76 and 0.67–0.45 Ma, respectively. The whole-rock Mg isotopic compositions, and newly measured major and trace elements, as well as the Sr–Nd–Hf–Pb isotope ratios are reported in Datasets S1–S3. For comparison, we also analyzed Mg isotopes of four well-characterized samples (19) from Rarotonga Island (SI Appendix, Fig. S1), which show Sr–Nd–Hf–Pb isotope ratios trending toward the EM1 endmember (5, 19). All of our samples belong to the alkaline series, and most of them are relatively unevolved rocks with SiO₂ < 52 wt % (SI Appendix, Fig. S2). The Tiedsva basalt has robust EM1 endmember isotopic signatures compared with the late-stage Pitcairn lavas and Rarotonga basalts (SI Appendix, Fig. S3).

The δ²⁶Mg values of Tiedsva basalts range from −0.40 to −0.31‰, clearly lower than those of the late-stage Pitcairn lavas (−0.30 to −0.16‰), peridotitic mantle δ²⁶Mg = −0.23 ± 0.04‰ (20) or δ²⁶Mg = −0.25 ± 0.04‰ (21), and other typical OIBs (Hawaii, Louisville, and Rarotonga) (Fig. 2). The lower end of the Pitcairn range is the lowest value observed so far in OIBs (see the compilation in ref. 21) and is close to the upper bound of the continental intraplate EM1 end member basalt from Wudalianchi and Erkeshan [hereafter referred to as “intracontinental EM1 basalts”; δ²⁶Mg = −0.57 to −0.45‰ (22, 23)] in northeast China (Fig. 3). The δ²⁶Mg values of Pitcairn and Rarotonga EM1 basalts, taken together, exhibit significant negative correlations with ⁸⁷Sr/⁸⁶Sr and positive correlations with ²⁰⁶Pb/²⁰⁴Pb, εNd, and εHf (Fig. 3). Inclusion of the intraplate EM1 basalts strengthens these correlations and further extends their range to even lower δ²⁶Mg values. A common heritage of oceanic and continental EM1 magmas is further substantiated by the correlation between δ²⁶Mg and CaO/Al₂O₃ (Fig. 4). Oceanic EM1 lavas exhibit the lowest CaO/Al₂O₃ ratios within the global OIB association (24), and the intraplate EM1 basalts have even lower CaO/Al₂O₃ ratios. Therefore, we consider all these EM1-type intraplate lavas as a group to explore the origin of the characteristic EM1 component.

Discussion

Subnormal δ²⁶Mg of the EM1 Mantle Sources. The analyzed OIB samples are fresh, and no secondary carbonates can be observed (SI Appendix, Fig. S4). Their loss on ignition (LOI) values are very low (mostly <1.0 wt %; Dataset S2), and there is no correlation between δ²⁶Mg and LOI, precluding any obvious chemical weathering. Seawater has lower δ²⁶Mg [−0.85‰ (21)] value than reported values of OIBs (16, 21); thus, seawater contamination might potentially modify the Mg isotopic composition of OIBs. However, seawater has much lower Mg concentrations [0.128 wt % (25)] than our basaltic samples with low δ²⁶Mg values, and more than 90% of seawater would have to be added to the basalt to shift the δ²⁶Mg of basalt from −0.25 to −0.40‰. This can be ruled out because of the low LOI of our samples. Hence, the low δ²⁶Mg values of Tiedsva basalts are unlikely to be the result of postmagmatic alteration.

Fractionation of olivine, pyroxene, and plagioclase dominate the major element variations of Pitcairn lavas with MgO > 4 wt %, and fractionation of Fe–Ti–rich phases (e.g., ilmenite) is apparent in lavas with MgO < 4 wt % (SI Appendix, Fig. S2). Fractionation of the former group of phases can induce very minor (<0.07‰ (26) Mg isotope fractionation, but that of the latter may lead to considerable fractionation (27). Therefore, because Mg isotopic variation in the two highly evolved samples (MgO < 3 wt %; Fig. 2) might be largely controlled by fractionation of Fe–Ti–oxides, we ignore these samples hereafter. Overall, crystal fractionation cannot be responsible for lowering δ²⁶Mg values, because the lowest δ²⁶Mg (−0.40‰) values appear in high-MgO (>8 wt %) Tiedsva samples, and these should reflect the inherent properties of the primary magmas. For Pitcairn lavas, their high MgO
contents (Fig. 2 and SI Appendix, Fig. S2) indicate that their normal mantle-like δ²⁶Mg values are those of the respective primary melts. Isotope fractionation during partial melting also cannot produce the low-δ²⁶Mg feature of Tedside samples, because the largest δ²⁶Mg difference between partial melts and solid residue is less than 0.1‰, no matter whether the initial source is a garnet pyroxenite or a peridote (16). In summary, neither crystallization nor partial melting effects can explain the observed low δ²⁶Mg values (as low as −0.40‰) in EM1-type OIBs, and the subnormal δ²⁶Mg lavas require an isotopically light mantle source component, as was also the case for the intracontinental EM1 basalts (22). Given the correlations between δ²⁶Mg and Sr-Nd-Hf-Pb isotope ratios of EM1 lavas (Fig. 3), we conclude that the unradiogenic isotope ratios of Pb, Nd, and Hf, together with the elevated ⁸⁷Sr/⁸⁶Sr ratios, are all coupled with subnormal δ²⁶Mg values in the EM1 component.

The Origin of EM1. The low δ²⁶Mg values of Pitcairn lavas are clearly at odds with some of the earlier models advocating delaminated subcontinental lithosphere or recycled LCC, given that neither of these reservoirs have primary subnormal δ²⁶Mg (21, 22). A summary of Mg isotope data for 160 global peridotite xenoliths that sample the subcontinental lithospheric mantle with various parageneses, chemical compositions, and ages definitely shows no evidence for subnormal δ²⁶Mg values that would qualify them as the EM1 source component (Fig. 1). Although some peridotite xenoliths have been extensively metasomatized by carbonatite or CO₂-rich silicate melts, they still maintain mantle-like δ²⁶Mg values [−0.27 to −0.16‰ (28)]. The δ²⁶Mg values of cratonic eclogites are highly heterogeneous and can be as low as −1.0‰ (29), and such rocks may thus potentially constitute a low-δ²⁶Mg origin. However, such eclogites are only a minor (<1 vol %) component of subcontinental lithospheric mantle (30). They are usually thought to represent the composition of recycled ancient oceanic crust (29, 31, 32). The reconstructed bulk compositions of these eclogites, as represented by the 2.9-Ga Lace basaltic eclogites, yield median Sm/Nd and Lu/Hf ratios of 0.40 and 0.27, respectively (32). These are higher than the average values of midocean ridge basalts (MORB) [Sm/Nd = 0.326 and Lu/Hf = 0.195 (33)]. Therefore, the long-term isotopic evolution of the cratonic eclogites in the mantle should lead to highly radiogenic Nd-Hf isotopic compositions (32) rather than the observed, unradiogenic EMI-type end member. A collection of LCC xenoliths that have not been affected by carbonatic metasomatism indicates that normal LCC also has mantle-like δ²⁶Mg value [δ²⁶Mg = −0.26 ± 0.06‰ (34)], although a few of the intensively metasomatized low-MgO samples do have δ²⁶Mg values as low as −0.7‰ (34). Therefore, on balance, models invoking delaminated subcontinental lithosphere and/or LCC are difficult to reconcile with the consistently subnormal δ²⁶Mg of the EM1 sources.

Recycled ancient ocean plateaul material, which contains cumulus gabбро, has also been suggested to be the origin of Pitcairn EM1 source (8). This possibility is inconsistent with the

![Fig. 3](image_url)

**Fig. 3.** δ²⁶Mg versus (A) ⁸⁷Sr/⁸⁶Sr, (B) ⁴⁰K/³⁹Ar, and (C) εNd and (D) εHf isotopic arrays for mixing of ambient peridotite and recycled material. Recycled material is the mix of recycled oceanic crust (R) and residual sediment component (S) in various mixing proportions. For details of how the composition of the residual sediment component (S) is derived, see Discussion and SI Appendix, Part 2. Mixing curves are marked in 10% increments. An enlarged figure (SI Appendix, Fig. S6) showing mixtures of all of the three end members is given in SI Appendix. The modeling parameters can be found in SI Appendix, Table S1. Also plotted are data for intracontinental EM1 basalt compared to the average MORB (see SI Appendix, Part 3 for data sources). A separate mixing curve for these lavas is required in B because the estimated age and δ²⁶Mg value (22) of the subducted sediments that evolved into the EM1 component in their source are different from those of the Pitcairn EM1 component (7). For average MORB, the δ²⁶Mg value (−0.25 ± 0.06‰ (2 SD) is from ref. 59, and radiogenic isotope ratios are the mean (±95% confidence interval on the mean) given in ref. 33. Others are as in Fig. 2.

![Fig. 4](image_url)

**Fig. 4.** Extreme EM1 lavas show exceptionally low CaO/Al₂O₃ and δ²⁶Mg values. The late-stage Pitcairn lavas are omitted here because their CaO/Al₂O₃ ratios have been severely modified by fractionation of clinopyroxene and plagioclase. Also plotted are literature data for other types of basalts (see SI Appendix, Part 3 for data sources). Shaded regions labeled I (gray) and II (green) denote the CaO/Al₂O₃ ranges for experimental partial melts of pyroxenite (53, 56) and carbonatite eclogite (44). For Pitcairn primary magmas, the CaO/Al₂O₃ ratio is from ref. 24; for average MORB, it is the calculated mean (±95% confidence interval on the mean) based on the data in ref. 33. Others are as in Fig. 3.
低-26Mg特征的Pitcairn EMI源因为Mg同位素组成与玄武岩和橄榄石之间存在差异。类似地，被回收的镁质沉积物由橄榄石和靶氧化物组成，以及它们的熔体产品（即，石英）（11）并不期待以符合的σ alteration signature of the Pitcairn EMI component, because these minerals show mantle-like or even higher 26Mg values (21).

回收的海底沉积物已反复被引用为EM1 mantle sources (4–7). This interpretation is supported here by the systematically lowered Nb/Th ratios and the positive correlations in the plots of εNd and 268/26Pb versus Nb/Th for Pitcairn Island basalts (SI Appendix, Fig. S5), which require some recent discovery of mass-independent fractionation of sulfur isotopes (S-MIF) down to ΔS = −0.8‰ in sul-
fides contained by Pitcairn lavas, along with three-stage Pb isotope growth modeling, has constrained the late Archean age (2.5–2.6 Ga) of the recycled sediments incorporated into the Pitcairn EMI source (7). Our results are fully consistent with this interpretation, but they add an additional constraint that further specifies the nature of the recycled sediments. Thus, the recycled sediments must initially contain significant amounts of carbonates, to satisfy the low-26Mg feature of Pitcairn EMI component. Among poten-
tially subducted materials, marine carbonates identify the low-
26Mg end member by their extremely light Mg isotopic compo-
sitions, which are remarkably distinct from other Mg reservoirs
and sedimentary rocks (1). Accordingly, marine carbonates
with extremely low 26Mg values, especially for the Mg-rich car-
bonates (dolomite), appear to be the unique reservoir capable of
dominating the Mg isotopic compositions of bulk sediments. Be-
cause the metamorphic equivalents of the subducted sediments
tend to preserve their original Mg isotopic compositions (37),
recycled Archean dolomite-bearing sediments provide a likely
origin of the low-26Mg feature of EMI component. In the fol-
lowing sections, we discuss additional aspects of this proposi-
tion.

Archean Carbonate Deposits. How common are marine carbonate
deposits in Archean time? Veizer et al. (38) reviewed the geo-
chemistry of Archean carbonates with geological attributes of
marine sediments and noted that they are “a minor component of
the Archean greenstone belts.” Nevertheless, they do occur in
many such greenstone belts, including the Yellowknife Super-
group; the Abitibi, Michipicoten, Uchi, and Wabigoon Green-
stone Belts in Canada; the Main Greenstone Belt of Zimbabwe;
the Sargur Marbles of India; the Warrawoona Group of Australia
(38, 39); and the Neoarchean Transvaal carbonate platform,
South Africa (40). Most of these deposits appear to have been
originally formed as urarinitic limestone, but many have been
replaced by dolomite and/or ankerite during sedimentation and
diagenesis (38, 41), thus constituting a significant Mg reservoir
with isotopically light magnesium. We conclude that although such
carbonates may indeed be minor constituents of Archean sedi-
mentary sequences, they are by no means uncommon. In this
context, it is important to remember that extreme EM1 end
member basalts are also rare in the oceanic basalts family.

Ghost Carbonate in the Pitcairn Source. Another question is, how was
the isotopically light Mg of dolomite in originally subducted sedi-
ments introduced into the EMI source? One possible way is that the
bulk subducted dolomite, together with its surrounding silicate
sediments, was directly incorporated into the Pitcairn EMI source.
However, this can be largely ruled out by the major element com-
positions of Pitcairn EMI lavas. These lavas are characterized by the
lowest CaO and CaO/Al2O3 ratios but among the highest SiO2
contents in the global OIB database (24, 42, 43). Their low CaO/
Al2O3 ratios (0.5–0.6) are not induced by extensive fractionation
of clinopyroxene and plagioclase, and the estimated CaO/Al2O3 ratio
of their primary melts is as low as 0.54 (24). By contrast, experi-
mental work has shown that partial melting of carbonate-bearing
mantle rocks (peridotite/pyroxene) produces melts with high CaO
and low SiO2 contents (44, 45). Notably, the HIMU-like low-26Mg
basalts from New Zealand, which were suggested to derive from a
carbonated eclogite source (28), show extremely high CaO/Al2O3
and low SiO2 (Fig. 4 and ref. 46), features that are distinct from the
low-26Mg EM1 basalts. Accordingly, the low CaO and CaO/Al2O3
of Pitcairn lavas are inconsistent with the presence of carbonate in
the direct mantle source. An alternative possibility is that the iso-
topically light Mg remains in the EMI source as a “ghost” of the
originally subducted dolomite, but the carbonate component of
the dolomite has been lost. This is somewhat analogous to the in-
terpretations of Hawaii and Mangaia hot spot lavas, where it has been
shown that the original chemical or isotopic identity of recycled
crustal materials may be present only as a ghost or phantom
signature in the mantle source, whereas their actual lithological iden-
tity has been completely lost (47, 48). In the present case, a
prerequisite is that the isotopically light Mg of dolomite in the
originally subducted sediments must be inherited by Mg-silicate
and then be incorporated into the EMI source. Below, we discuss pos-
sible mechanisms for such processes.

Possible Decarbonation Mechanisms. As suggested above, the low-
26Mg feature of Pitcairn EMI component is inferred to be de-
rived from dolomite in Archean subducted sediments. Because the
Archean subduction zones are hot, such sediments are prone to
losing their carbon inventory during subduction, through carbon-
ete melting or subsolidus decarbonation (49). According to ex-
perimentally determined solidi (50), carbonate-bearing sediments
may possibly melt within the pressure range of 6–9 GPa in hot
subduction zones. Because the carbonate melts produced by
melting of carbonate-bearing sediments in the pressure range of
6–9 GPa are Ca-rich and Mg-poor (50), most of the dolomite-
derived Mg budget will remain in the silicate residue after melt
extraction. Therefore, the original low-26Mg signature is expected
to be transferred to the silicate residue, thus providing one pos-
sible solution to the ghost carbonate Mg isotopic signature of
the Pitcairn EMI source. However, the extraction of carbonate melts
from subducted dolomite-bearing sediments would also remove
large proportions of incompatible trace elements, and this should
deplete the residual source in incompatible trace elements to such
an extent that it would no longer be capable of generating highly
trace element-enriched (Pitcairn-type) basalts. Therefore, car-
bonate melting is not a suitable decarbonizing mechanism to
generate the particular EMI source of Pitcairn lavas.

Another plausible mechanism is decarbonation reaction during
subduction. The dolomite-bearing sediments are SiO2-rich, and they
will be transformed into assemblages mainly consisting of dolomite
+ quartz/coesite at intermediate depths [−150 km (50)] or mag-
sesite + coesite at greater depths [−150 km (50)]. During sub-
duction of these assemblages, the following decarbonation reactions
will easily occur under suitable P–T conditions (51–53):

\[
\begin{align*}
\text{CaMg(CO}_3\text{)}_2 & \text{ (dolomite) + 2SiO}_2 \text{ (coesite)} \\
\rightarrow & \text{CaMg}_2\text{Si}_2\text{O}_6 \text{ (diopside) + 2CO}_2 \\
\text{CaMg(CO}_3\text{)}_2 & \text{ (dolomite) + 2SiO}_2 \text{ (coesite)} \\
\rightarrow & \text{CaMg}_2\text{Si}_2\text{O}_6 \text{ (diopside) + 2C(graphite/diamond) + 2O}_2 \\
\text{MgCO}_3 & \text{ (magnesite) + SiO}_2 \text{ (coesite)} \\
\rightarrow & \text{MgSiO}_3 \text{ (enstatite) + CO}_2.
\end{align*}
\]

Through these reactions, the silicate products (diopside and ensta-
tite) can accommodate the Mg released by carbonate reactants,
providing a feasible mechanism whereby the light Mg isotopic
compositions of the original dolomite can be inherited by silicate

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products to form an isotopically light silicate component (21). Meanwhile, incompatible elements, including rare earth elements, can also be hosted in the silicate products, e.g., diopside. This silicate residue, bearing a ghost carbonate Mg isotopic signature inherited from the subducted carbonate, will ultimately become the plume source for the Pitcairn EM1 magmas. **Quantitative Evaluation of the Subducted Carbonate.** A three-component mixture of ancient sediment, old recycled oceanic crust, and ambient mantle peridotite has been suggested to constitute the Pitcairn mantle source by several previous studies proposing sediment recycling (4–7). Based on the Mg isotopic constraint in this study, we suggest that the ancient sediment component is the silicate residue of Archean (~2.5 Ga) subducted dolomite-bearing sediments after dolomite was completely decarbonated during subduction (hereafter referred to as “residual sediment component”). Here the proportion of dolomite ($\delta^{26}\text{Mg} = -2.68\%$; SI Appendix, Table S1) in originally subducted sediments is assumed to be as high as 50%, so as to provide sufficient isotopically light Mg to affect the Pitcairn source. Thus, the residual sediment component has evolved from a late Archean (~2.5 Ga) mixture initially consisting of 50% of dolomite and 50% of silicate sediments. To constrain the amount of originally subducted dolomite, we quantitatively modeled the mixing of ambient peridotite, recycled oceanic crust, and residual sediment component (Fig. 3 and SI Appendix, Fig. S6; see SI Appendix, Part 2 for details). However, we find that the unmodified mixture of dolomite and calcic sediment would not generate present-day isotopic compositions (SI Appendix, Table S1) consistent with the Pitcairn isotopic data (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$). We assume that this inconsistency is the result of trace element mobilization during subduction, and we therefore modified the trace element concentrations and parent/daughter isotopic ratios of the original mixture to obtain an appropriate residual sediment component whose isotopic compositions fit the mixing arrays in Fig. 3 and SI Appendix, Fig. S6. The final geochemical composition of the residual sediment component at ~2.5 Ga (SI Appendix, Table S1) was determined by mixing the chemical and isotopic compositions of ~2.5-Ga dolomites and ~2.5-Ga silicate sediments and then removing a fraction of the total trace element budget (see SI Appendix, Part 2 for the detailed proportions of the removed part). After long-term (~2.5 Gyr) isolation, the isotopic evolution, this sediment component can generate the extreme Pitcairn EM1 component. Considering the high uncertainty of the element fractions mobilized during dehydration/melting of subducting slabs (54), we argue that the modification of the trace element concentrations of the above mixture and the mixing modeling is reasonable. According to the modeling results (Fig. 3), the proportion of recycled materials (oceanic crust + sediment) in the Pitcairn source is about 3-36%, and the corresponding percentage of the residual sediment component varies from ~1.5 to 18%. This means that the maximum amount of originally subducted dolomite ($\delta^{26}\text{Mg} = -2.68\%$) required to generate the low $\delta^{26}\text{Mg}$ value of the Pitcairn source is ~9%. A new question arises whether the addition of CaO, inherited from the decomposed carbonate, to the Pitcairn source might increase the CaO/Al$_2$O$_3$ ratio of the Pitcairn lavas. A striking feature of the Pitcairn EM1 basalts is their exceptionally low CaO/Al$_2$O$_3$ ratios (Fig. 4). These are lower than the respective ratios found in MORB, in other types of OIBs, and in intracratonic HIMU-like basalts, and thus, they point to a pyroxenitic rather than peridotitic or carbonated eclogite source lithology (Fig. 4; see also refs. 24, 55, and 56). Thus, we can answer the above question by estimating the effect of adding CaO released by ~9% of originally subducted dolomite to a pyroxenite on the final melt composition produced by melting of this mix. In the absence of specific experiments addressing this question, we have approached the problem using pMELTS (57) (for detail, see SI Appendix, Fig. S7). The major element compositions of the mixed lithology were calculated by mixing of 91% of the chemical compositions of the MIX1G pyroxene (55) and 9% of the chemical composition of dolomite (MgO = 21.86 wt % and CaO = 30.41 wt %; excluding CO$_2$) and then normalized to 100%. The assumed melting pressure is 3 GPa. We plot the estimated residual modal abundances and CaO and CaO/Al$_2$O$_3$ values of the melts produced by 0–40% melting of the mixed lithology and the MIX1G pyroxene in SI Appendix, Fig. S7. Results show that the addition of CaO to a pyroxenitic source increases the modal proportion of clinopyroxene at the expense of garnet (SI Appendix, Fig. S7A), but this has little effect on the CaO content and CaO/Al$_2$O$_3$ ratio of partial melts formed from this assemblage (SI Appendix, Fig. S7 B and C). **Comparison Between Oceanic and Subcontinental EM1 Sources.** The common element characterizing Pitcairn basalts and the intracontinental EM1 basalts is the involvement of an ancient, low-$\delta^{26}\text{Mg}$ EM1 component in their mantle sources. The difference between the two settings may lie in the mechanism and location of the decarbonation processes required to account for the low CaO/Al$_2$O$_3$ ratios characterizing all EM1 basalts. For Pitcairn basalts, decarbonation proceeded most likely through carbonate-silicate reactions during subduction of dolomite-bearing sediments, as explained above. Intracratonic EM1 sources, on the other hand, were more likely decarbonated in the transition zone through the melting of carbonate melts in the presence of K-feldspar (22), to account for their excess Rb and high K/U and Ba/Th ratios, as well as their positive Zr–Hf anomalies, features that distinguish the intracontinental EM1 basalts from Pitcairn basalts (SI Appendix, Fig. S8). In any case, in both settings the magnesium isotopes are the main carbonate memory left in the EM1 source, and neither setting supports actual subduction of substantial amounts of carbonates into the lower mantle, at least not during late Archean or early Proterozoic time when the subduction zones were presumably hotter than in geologically more recent times (49). **Materials and Methods** **Major Oxides, Trace Elements, and Radiogenic Isotopes.** All rock samples were powdered in an alumina mill. Whole-rock geochemical compositions other than Mg isotopes were determined at the Japan Agency for Marine-Earth Science and Technology. Major and trace element compositions of whole-rock samples were analyzed by X-ray fluorescence spectrometry and inductively coupled plasma–quadrupole mass spectrometry (ICP-QMS). Pb, Sr, Nd, and Hf isotope ratios were measured on rock powders, after acid leaching, by thermal ionization mass spectrometry for Sr and Nd isotopes and multiple-collector ICP-MS for Pb and Hf isotopes. The detailed descriptions for sample preparation, chemical treatment, and analytical conditions are given in SI Appendix, Part 1. **Mg Isotopes.** Mg isotope analyses were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences, following previously well-established procedures (58). All samples and US Geological Survey (USGS) rock reference materials were weighed in Savillex screw-top beakers and then digested by using concentrated acids in the following sequence: (i) HF-HNO$_3$ (3:2, vol/vol), (ii) HCl-HNO$_3$ (3:1, vol/vol), and (iii) HNO$_3$ until they were completely dissolved. The clear solutions were dried and dissolved in 2 mol HNO$_3$ to obtain Mg concentrations of 20 ppm. Mg purification was achieved by cation exchange chromatography in Savillex microcolumns loaded with 2 mL of Bio-Rad AG50W-X12 (38-74 μm) resin. Each sample solution containing 20 μg Mg was loaded onto the resin. The same column procedure was carried out twice to obtain pure Mg solutions. One or two synthetic Mg solutions (IGGMg1-A) and at least two USGS rock reference materials were processed through the same column procedure with our investigated samples for checking the column chemistry. Purified sample and standard solutions were diluted to 2 ppm Mg using the same batch of 2% HNO$_3$. After column chemistry, the Mg yields were ≥99.8% for all reference materials and unknown samples. The total procedural Mg blank during this study was less than 6 ng. Mg isotopic compositions were measured by the sample-standard bracketing method on a Thermo Scientific Neptune MC-ICP-MS. A quartz dual cyclonic spray chamber combined with an Elemental Scientific Inc. 50 μL min$^{-1}$ PFA Microflow Teflon nebulizer was used as the introduction system. Each sample was measured at least four times and then averaged. Mg isotopic compositions are expressed in δ notation as per mil (‰) deviation from DSM3: $\delta^{26}\text{Mg} = \left[\text{Mg}^{26}_{\text{sample}}/\text{Mg}^{26}_{\text{SMOW}}\right]^{-1} \times 1,000$, where X = 25 or 26. The
long-term external precision was determined by repeated analyses of the international standards (D53M and Cambridge 1), in-house Mg standards (IGG Mg1 and SRM980), and various rock reference materials, and this value is better than +0.06% (2 SD) for $^{26}$Mg. Replicated measurements of the Cambridge 1 and IGG Mg1 at different dates yielded average $^{26}$Mg values of −2.62 ± 0.05% (2 SD, n = 26) and −1.75 ± 0.05% (2 SD, n = 34), respectively. Comparison between our results of standards/USGS rock reference materials and published values is summarized in Dataset S4. In a plot of $^{26}$Mg vs. $^{28}$Mg (SI Appendix, Fig. S9), all samples fall along the mass-dependent fractionation line for Mg isotopes.

The data supporting the findings of this study are available in either the SI Appendix or the published works cited.

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