Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume

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The isotopic diversity of oceanic island basalts (OIB) is usually attributed to the influence, in their sources, of ancient material recycled into the mantle, although the nature, age, and quantities of this material remain controversial. The unradiogenic Pb isotope signature of the enriched mantle I (EM I) source of basalts from, for example, Pitcairn or Walvis Ridge has been variously attributed to recycled pelagic sediments, lower continental crust, or recycled subcontinental lithosphere. Our study helps resolve this debate by showing that Pitcairn lavas contain sulfides whose sulfur isotopic compositions are affected by mass-independent fractionation (S-MIF down to Δ33S = −0.8), something which is thought to have occurred on Earth only before 2.45 Ga, constrain the youngest possible age of the EM I source component. With this independent age constraint and a Monte Carlo refinement modeling of lead isotopes, we place the likely Pitcairn source age at 2.5 Ga to 2.6 Ga. The Pb, Sr, Nd, and Hf isotopic mixing arrays show that the Archean EM I material was poor in trace elements, resembling Archean sediment. After subduction, this Archean sediment apparently remained stored in the deep Earth for billions of years before returning to the surface as Pitcairn’s characteristic EM I signature. The presence of negative S-MIF in the deep mantle may also help resolve the problem of an apparent deficit of negative Δ34S anomalies so far found in subduction source.

Results and Discussion

The sulfur isotopic data measured on sulfide inclusions in olivines, plagioclases, and matrix material at Centre de Recherche Pétrographiques et Géochimiques (CRPG) in Nancy are given in SI Appendix, Table S1 and shown in Fig. 2. The sulfur isotopic constraint and a Monte Carlo refinements of lead isotopes, we place the likely Pitcairn source age at 2.5 Ga to 2.6 Ga. The Pb, Sr, Nd, and Hf isotopic mixing arrays show that the Archean EM I material was poor in trace elements, resembling Archean sediment. After subduction, this Archean sediment apparently remained stored in the deep Earth for billions of years before returning to the surface as Pitcairn’s characteristic EM I signature. The presence of negative S-MIF in the deep mantle may also help resolve the problem of an apparent deficit of negative Δ34S anomalies so far found in subduction reservoirs.

O ceanic island basalts (OIB) are isotopically diverse (1) and, in radiogenic (Sr, Nd, Pb, Hf) isotopic spaces, define trends to extreme mantle compositions (“endmembers”) such as HIMU (high μ, with μ = 238U/204Pb) and the two enriched mantles EM I and II (EM I with low 206Pb/204Pb and EM II with high 87Sr/86Sr). These endmembers are all thought to have been generated by subduction of material into the asthenosphere over time (2), so determining the age and geological nature of their precursors is important to understand the geochemical evolution of the Earth. Although there appears to be consensus on the presence of recycled ancient oceanic crust in the source of HIMU (3, 4) and ancient clastic continental sediments in the source of EM II (5), the origin of the EM I signature is more controversial.

The Polynesian chains show examples of all these type of source signatures (3, 6–9). For example, Mangaia and Tubuai Islands in the Cook-Austral chain have the elevated 206Pb/204Pb ratios typical of HIMU compositions, islands from both the Society and Marquesas chains have the high 87Sr/86Sr that define EM II compositions, and Pitcairn lavas in the Pitcairn-Gambier chain have the very low 206Pb/204Pb at high 208Pb/204Pb that characterize EM I isotopic signatures.

Here we focus on EM I of Pitcairn Island [0.95 My to 0.62 My (10)] and the Pitcairn Seamounts (11), which constitute the most recent volcanism of the Pitcairn-Gambier chain, located on the southeast side of the Polynesian Superplume (Fig. 1). Previous studies of both the island and the seamounts led to various interpretations for the origin of the EM I source: recycled oceanic crust carrying 0.7- to 2-Ga pelagic sediment (12, 13), delaminated subcontinental lithospheric mantle (14), and delaminated lower continental crust (15). Each of these suggestions was an attempt to explain the peculiar Pb isotopic compositions of Pitcairn basalts, but all remain model-dependent, as the problem is underdetermined. Independent constraints on either the age or the nature of the source component are therefore required to choose the best candidate.

Here we revisit the possible origin of the EM I signature by presenting in situ sulfur isotopic analyses of Pitcairn samples that provide independent constraints on a minimum age. Combining these data with modeling of new high-precision Pb isotopic data and Sr, Nd, and Hf isotopes allows us to constrain the nature of the material involved in their source.

Significance

The source material for mantle plume volcanism is generally agreed to show geochemical signatures of former oceanic lithosphere (crust and/or sediments) recycled into the mantle by subduction. The specific nature and ages of these materials remains, however, controversial. This study shows that the source of Pitcairn basalts contains Archean sediments (i.e., >2.45 Ga) that have remained chemically isolated in Earth’s mantle for billions of years.

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young, $\Delta^{34}S = 0$ material, probably from seawater; this may be the result of syneruptive or post eruptive seawater infiltration into the basaltic matrix. None of the inclusions in minerals show $\Delta^{34}S > 0$, which we suspect is a result of the better resistance of mineral structures to such syneruptive or post eruptive seawater infiltration.

Negative $\Delta^{34}S$ values have been previously reported for pyrite included in Archean barite bedded formations (16, 17), Neo-Archean carbonates (18, 19), exhalites in Archean greenstone belts (20), or Archean sandstones and conglomerates (21). S-MIF only occurred in Earth’s atmosphere before the Great Oxygenation Event at ca. 2.45 Ga (22), so its presence in at least part of the Pitcairn plume source places a strong lower limit on the age of that source. The association of nonchondritic $^{34}S$ (between $-6.1\%$ and $-2.3\%$) with negative $\Delta^{34}S$ is an unambiguous signal of a contribution of Archean supracrustal material to the plume source.

Cabral et al. (23) reported small negative S-MIF anomalies for sulfides in HIMU basalts from Mangaia Island (Fig. 2), which they attributed to hydrothermal processes occurring in Archean basaltic crust. Interestingly, at both Pitcairn and Mangaia, $\Delta^{34}S$ are always negative, in contrast to values found in sulfi thorospheric sulfide included in diamonds.

Previous modeling (3, 12, 13) suggested that the Pitcairn source includes recycled surface material, although with a young age (0.7 Ga to 2 Ga). To investigate the elemental and isotopic composition of the Pitcairn component, we developed a mixing model using our new Pb, Sr, Nd, and Hf data for Pitcairn (see Materials and Methods and SI Appendix, Table S2 and Fig. S2). This model constrains the isotopic ratios and Pb, Sr, Nd, and Hf concentrations of the Pitcairn component by assuming that it is the unknown member of a three-component mix (along with old subducted crust and ambient peridotite mantle). The composition of the Pitcairn component (shown by the yellow star on Fig. 3 and SI Appendix, Fig. S3) is determined with no assumption about its geological origin but by simply adjusting its isotopic ratios and trace element concentrations so that its calculated percentage in the source of each individual Pitcairn lava is the same for all available isotopic systems (Pb, Sr, Nd, and Hf).

Our mixing model provides two important pieces of information: (i) that the percentage of the Pitcairn component in the source of the individual lavas varies between $-2.5\%$ and $-18\%$ and (ii) that the Pitcairn component has a trace element composition (see SI Appendix, Table S3) that is significantly depleted relative to that modeled, for example, as a source component for the Gambier Island basalts (24), located upstream along the Pitcairn chain (also listed in SI Appendix, Table S3 and Fig. 1). The Gambier Island source was suggested to consist of 1.5-Ga recycled material (basaltic crust + average oceanic sediment) and ambient peridotite.

Using the modeled Pb isotopic composition of the Pitcairn component and the evidence for S-MIF at Pitcairn, we can use a three-stage Pb growth model including a Monte Carlo refinement procedure to constrain its age (T) and $\mu$ ($^{238}\text{U}/^{204}\text{Pb}$) and $\kappa$ ($^{232}\text{Th}/^{238}\text{U}$) ratios. The Monte Carlo refinement technique (25) searches possible combinations of $\mu$ ($^{238}\text{U}/^{204}\text{Pb}$), $\kappa$ ($^{232}\text{Th}/^{238}\text{U}$), and age for the three stages that reproduce the targeted Pitcairn component Pb isotopic values (see Materials and Methods and SI Appendix, Fig. S4). The method randomly tests potential growth-model results (for model equations, see Materials and Methods) with a criteria function (Eq. 4) and either accepts or rejects the results depending on their match to the target value, here the yellow star in Fig. 3. The method is intrinsically not very different from the Monte Carlo simulation of Eisele et al. (13), but their target composition was different in two significant ways: (i) a $^{208}\text{Pb}/^{204}\text{Pb}$ lower than 17.6 when ours is 17.04, and (ii) variable $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ $^{207}\text{Pb}/^{204}\text{Pb}$ ratio within $\mp0.005$ from the array in $^{207}\text{Pb}$, $^{204}\text{Pb}$ vs. $^{206}\text{Pb}$, $^{204}\text{Pb}$ space and $^{208}\text{Pb}/^{204}\text{Pb}$ between 38.8 and 39.1) when ours are 15.45 and 39.0.

The three steps of our model are distinguished using subscripts 1, 2, and 3 for $T$, $\mu$, and $\kappa$. $T_1$ corresponds to the age of the Earth (4.55 Ga), $T_2$ represents the onset of the crustal history, and $T_3$...
represents the age of the onset of the surface material history. To limit the number of possible solutions, we set four values, the age of the Earth \( T_1 \) and the initial composition of its mantle \( [\mu_1 = 8.3 \text{ and } k_1 = 3.8 \text{ (26)}] \) together with the age \( T_2 \) of the onset of crustal history [here 3 Ga (27, 28)] (see Materials and Methods for the choice of parameters). Results are shown in Fig. 4 in both \( \mu_2 - k_2 - k_3 \) and \( \mu_2 - k_2 - T_3 \) space, and other interdependences between \( \mu_2, k_2, \mu_3, k_3, \) and \( T_3 \) are shown in SI Appendix, Fig. S5. Fig. 4 shows that a large number of \( \mu - k - T \) combinations (all dots in Fig. 4) can reproduce the target composition but that, by limiting the range of \( \mu_2 \) and \( k_2 \) values reasonable for the continental crust \( [9 \leq \mu_2 \leq 11.6 \text{ and } 4 \leq k_2 \leq 5 \text{ (29–33); see Fig. 4A}] \), the field is drastically reduced (as shown by the red dots). We can use the presence of S-MIF in the Pitcairn component to place a lower limit of 2.45 Ga on \( T_2 \) (the onset of sedimentary history); the \( \mu_2 \) and \( k_2 \) constraints outlined above give an upper age limit for \( T_3 \) of 2.75 Ga, with a maximum of solutions around 2.5 Ga to 2.6 Ga. This Archean age for the Pitcairn component differs greatly from the 0.7- to 2-Ga model ages suggested previously (12, 13). This difference results from the combined effects of the different composition of the Pitcairn component, the older onset of crustal evolution (3.7 Ga), and, mainly, the lower \( \mu \) and higher \( k \) values for the early mantle (13) used in previous modeling.

Our model provides constraints on the \( \mu \) and \( k \) values of the sedimentary material formed at \( T_3 \) and recycled later on into the mantle. The calculated low values for \( \mu_3 \) (6.3 to 6.4) and high values for \( k_3 \) (6.3 to 6.7) are needed to produce the high \( 208\text{Pb}/204\text{Pb} \) at low \( 206\text{Pb}/204\text{Pb} \) that characterize EM I. We also tested the model for variations in the age of onset of crustal history \( T_2 \) ranging from 2.5 Ga to 3.8 Ga to evaluate the impact of this parameter on the final results. The main findings are (i) when the age of the crustal history onset increases from 2.5 Ga to 3.8 Ga, \( k_3 \) (the sedimentary component value) needs to decrease from 6.6 through 7.4 (\( T_2 = 2.5 \text{ Ga} \)) to 5.3 through 5.8 (\( T_2 = 3.8 \text{ Ga} \)) but remains at high values (see SI Appendix, Fig. S6); (ii) in all cases, the age of onset of the sedimentary history \( T_3 \) is Archean or very early Proterozoic (\( \sim 2.3 \text{ Ga if } T_2 = 2.5 \text{ Ga and } \sim 3.5 \text{ Ga if } T_2 = 3.8 \text{ Ga} \)) (see SI Appendix, Fig. S6); and (iii) the overall probability of the model reproducing the lead isotopic values of the Pitcairn component decreases significantly when \( T_2 \) increases (with an increase of \( T_2 \) from 2.5 Ga to 3.8 Ga, the probability of successful results decreases from \( \sim 25\% \) to \( \sim 2.5\% \); see SI Appendix, Fig. S6).

Together with its low \( \mu \) and high \( k \) (and ancient negative \( \Delta^{33}\text{S} \)), the Archean Pitcairn component has very low Pb, Nd, and Hf concentrations and rather low Sr contents (see SI Appendix, Fig. S5 and Table S3). Equivalent concentrations are not seen in modern oceanic
All samples were crushed in an agate mortar, and the $^{232}\text{Th}/^{204}\text{Pb} = 17.04$, $^{207}\text{Pb}/^{206}\text{Pb} = 15.45$, and $^{208}\text{Pb}/^{206}\text{Pb} = 39$) are represented (see Results and Discussion and Materials and Methods for more details). Model limits are described in Results and Discussion and in Materials and Methods. The red fields show our preferred range of $\mu_2$ (9 to 11.6) and $\kappa_3$ (4, 5) for continental crust, and the red dots highlight solutions with values in these ranges that also have $T_3$ ages $>2.45$ Ga in accordance with the S-MIF evidence.

Materials and Methods

Radiogenic Isotopes. All samples were crushed in an agate mortar, and the pure Nd, Hf, Pb, and Sr fractions were isolated using ion exchange chromatography techniques. Nd, Hf, and Pb isotopic ratios were measured using a high-resolution multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS; Nu Instrument 500 HR) at ENS Lyon, and Sr isotopic ratios using a thermal ionization mass spectrometer (TIMS, Thermo Scientific Triton) at PSO-IUEM (Pôle de Spectrométrie Océan, Institut Universitaire Européen de la Mer) in Brest (see SI Appendix for more details).

Sulfur Isotopes. Multiple sulfur isotope analyses ($\delta^{34}\text{S}, \delta^{33}\text{S}, \Delta^{33}\text{S}$) were performed in situ on thin sections using a high-resolution secondary ion mass spectrometer (CAMECA 1280-HR, CRPG-Nancy) (see SI Appendix for more details).

Monte Carlo Refinement Method. The three-stage Pb isotopic growth is described by Eqs. 1–3 for the three isotopic ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$, where $T_i$ is the age of the Earth (4.55 Ga), and $T_j$ and $T_k$ represent the onset of the crustal ($T_j$) and sedimentary ($T_k$) histories; ($^{206}\text{Pb}/^{204}\text{Pb}$) is the isotopic ratio at Earth’s formation, taken as that of Canyon Diablo Troilite; $\lambda_3$, $\lambda_4$, and $\lambda_5$ are the decay constants of $^{238}\text{U}$, $^{235}\text{U}$, and $^{232}\text{Th}$, respectively; $\mu = ^{238}\text{U}/^{204}\text{Pb}$, $\omega = ^{232}\text{Th}/^{208}\text{Pb}$, and $\kappa =$.

To reproduce the Pb isotopic ratios of the Pitcairn component as listed in SI Appendix, Table S3, we performed a Monte Carlo refinement of the possible combinations of $\mu$ ($^{238}\text{U}/^{204}\text{Pb}$), $\lambda$ ($^{232}\text{Th}/^{208}\text{Pb}$), and $\kappa$ that fulfill the three equations given above. The method consists in generating random values for each unknown parameter in Eq. 1–3. A comparison between calculated results for each random set of values and the problem statement (Pb isotopic composition of the Pitcairn component) allows the input parameters to be accepted or rejected. We performed a total of $1 \times 10^{11}$ calculations. The results shown in Fig. 3 correspond to the 9,366 successful combinations. The only fixed parameters were age of the Earth at 4.55 Ga ($T_1$), initial mantle $\mu_1$ and $\kappa_1$ at 83.3 and 3.8 (26), and $\mu_2$ (the $\mu_2$ corresponds to the average of values listed by Asmerom and Jacobsen (26) after removal the two outliers), and $T_3$ of 3 Ga for the time at which large volumes of continental crust already existed (27, 28). The unknown values are therefore $\mu_2$, $\kappa_3$, $\mu_5$, $\kappa_5$, and $T_5$. To investigate the variability of results, parameter
boundaries were set as follows: $\mu_2$ was allowed to vary between 1 and 12, $\mu_2$ was allowed to vary between 4 and 7, $\mu_2$ was allowed to vary between 1 and 12, and $\mu_2$ was allowed to vary between 4 and 7. Randomly generated lots of values were accepted as plausible only when the difference between the calculated Pb isotopic values and the target isotopic values of the Piccairn component was less than 0.01.

\[
\begin{align*}
\text{abs}\left(\frac{\text{Pb}}{\text{target}} - \frac{\text{Pb}}{\text{observed}}\right) + \text{abs}\left(\frac{\text{Pb}}{\text{target}} - \frac{\text{Pb}}{\text{observed}}\right) & < 0.01, \\
\end{align*}
\]

where the subscript "target" represents the Piccairn component value and the subscripts $a$, $b$, and the target are the results of Eqs. 1–3, respectively, defined above. The Matlab code used for this model is available as Dataset S1.

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