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Light calcium isotope anomaly in the Pitcairn mantle plume: a signal of pyroxenite melting

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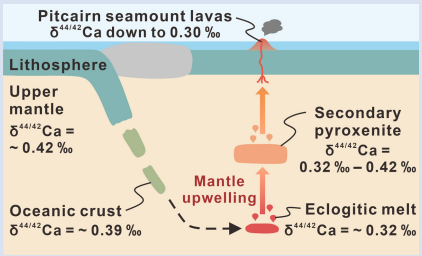
Abstract



The light calcium (Ca) isotope anomaly observed in ocean island basalts (OIBs) compared to mid-ocean ridge lavas has typically been attributed to recycling of carbonate-bearing sediments, partial melting of garnet-rich lithologies or a combination of both. This study presents Ca isotopic data for lavas from Pitcairn Island and nearby seamounts, yielding a $\delta^{44/42}$Ca variation (0.30 ± 0.02 ‰ to 0.40 ± 0.02 ‰) similar to that found in global OIBs. This $\delta^{44/42}$Ca variation cannot be attributed to post-eruption alteration, magmatic differentiation or recycling of carbonate-bearing sediments. Instead, correlations of $\delta^{44/42}$Ca with Sr/Nd and Eu/Eu* suggest that the light Ca isotope anomaly in Pitcairn lavas most likely reflects derivation from a pyroxenite source akin to the lower part of the recycled oceanic crust. Modelling suggests that the low $\delta^{44/42}$Ca end member can be explained by multiple-stage pyroxenite melting without requiring recycled carbonate-bearing sediments, offering new insights into using Ca isotopes to trace crust-mantle interactions.

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Introduction

Ocean island basalts (OIBs), as melting products of upwelling mantle plumes, provide critical insights into mantle heterogeneity. In recent decades, calcium (Ca) isotopes have shown great potential for tracing recycled carbonates and lithological diversity in the deep mantle. A light Ca isotope anomaly was first observed in Hawaiian basalts and was attributed to recycled ancient carbonates, which have significantly higher CaO contents and lighter Ca isotopic compositions than the upper mantle (Huang *et al.*, 2011). Similar light Ca isotope anomalies identified in mantle-derived magmas have been suggested to be related to source hybridisation by subducted carbonates (Liu *et al.*, 2017; He *et al.*, 2023; Wang *et al.*, 2023), and have now been observed in many more hotspots such as Pitcairn, Tristan da Cunha, and Kerguelen (enriched mantle-1, EM-1), Samoa, Society (enriched mantle-2, EM-2) and the Canaries (high-^{238}U/^{204}Pb, HIMU), confirming substantial Ca isotope variations as a common phenomenon among global OIBs (Eriksen and Jacobsen, 2022; Eriksen *et al.*, 2024). A number of recent studies favour a lithological control on Ca isotopic composition and invoke isotopic fractionation during melting of garnet-rich pyroxenites (Eriksen and Jacobsen, 2022; Eriksen *et al.*, 2024), as garnet is rich in both Ca and heavy Ca isotopes compared with other mantle minerals (Wang *et al.*, 2019; Antonelli *et al.*, 2021a). Nevertheless, independent evidence (including carbonatitic inclusions in olivine phenocrysts, the presence of associated carbonatite, trace element patterns typical of carbonatitic metasomatism in the source, enriched Sr-Nd-Pb isotopic compositions, as well as light Mg and heavy Zn isotope anomalies) suggests that recycled components, possibly containing carbonates, are prevalent in the sources of OIBs with light Ca isotope compositions (*e.g.*, Eisele *et al.*, 2002; Castillo, 2015; Wang *et al.*, 2018; Zhang *et al.*, 2022). Therefore, it remains a subject of debate as to what extent recycling of isotopically light Ca crustal components (*e.g.*, carbonates) and isotopic fractionation during melting of garnet-bearing lithologies contribute to Ca isotope variations in OIBs.

Here we examine this puzzle by measuring a suite of well-characterised lavas from the Pitcairn mantle plume, which exhibits significant chemical and isotopic variability ranging from a typical EM-1 end member to a markedly depleted one (Woodhead and McCulloch, 1989; Woodhead and Devey, 1993). The EM-1 component is typically defined by high ^{87}Sr/^{86}Sr, low ^{143}Nd/^{144}Nd and unradiogenic Pb isotopic compositions (Zindler and Hart, 1986). This sample diversity in a single plume enables us to distinguish between the contributions of recycled carbonate sediments and isotopic fractionation during partial melting to the Ca isotope variation. Our results identify a Ca isotope variation almost as large as that found in global OIBs. Combined with published data, we show that the isotopically light end member of Pitcairn lavas is akin to recycling of the lower (gabbroic) oceanic crust and suggest a dominant role of isotopic fractionation during multi-stage pyroxenite melting in its source (*e.g.*, Nebel *et al.*, 2019).

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Samples and Analytical Method

The samples measured in this study include five Tedside shield-building basalts and three post-erosional basalts from Pitcairn Island (Woodhead and McCulloch, 1989) and seven seamount lavas from Volcano 2 erupted on the adjacent ocean floor (Woodhead and Devey, 1993). Phenocrysts primarily consist of olivine, clinopyroxene, and plagioclase. The CaO-MgO diagram suggests that olivine was the dominant liquidus phase during early differentiation (*e.g.*, MgO ≥ 3.8 wt. %), transitioning to clinopyroxene dominance in more evolved lavas (Fig. S-1). Al_2O_3 behaves as an incompatible element until MgO content drops below ~1 wt. % (Fig. S-1), suggesting limited plagioclase control on the samples analysed here (*i.e.* all have MgO ≥ 1.18 wt. %). Tedside samples are characterised by notably high $^{87}Sr/^{86}Sr$, low $^{143}Nd/^{144}Nd$ and low $^{206}Pb/^{204}Pb$ ratios, whereas the post-erosional and seamount samples exhibit variable degrees of depletion in Sr-Nd-Pb isotopic compositions, suggesting mixing between an enriched EM-1 component and a more depleted component (Fig. S-1; Woodhead and Devey, 1993; Eisele *et al.*, 2002).

Calcium isotope analyses followed He *et al.* (2017) and were performed at the Isotope Geochemistry Laboratory, China University of Geosciences, Beijing. Stable Ca isotopic compositions and radiogenic ^{40}Ca excesses/deficits are reported in δ and ε notations, respectively, relative to SRM915a, with $\varepsilon^{40/44}Ca$ calculated from $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$ using the exponential law (Farkaš *et al.*, 2011; He *et al.*, 2017). To minimise possible effects of radiogenic ^{40}Ca, we discuss stable Ca isotopes primarily in terms of $\delta^{44/42}Ca$. Analytical procedures and full datasets for samples and reference materials are given in the Supplementary Information and Tables S-1 and S-2.

Results

The Pitcairn samples exhibit a $\delta^{44/42}Ca$ range from a mid-ocean ridge basalt (MORB)-like value of 0.40 ± 0.02 ‰ to as low as 0.30 ± 0.03 ‰ ($\delta^{44/40}Ca = 0.68 \pm 0.08$ ‰ to 0.84 ± 0.04 ‰; Fig. 1; Table S-1). Five enriched Tedside samples, characterised by high $^{87}Sr/^{86}Sr$ and low $^{143}Nd/^{144}Nd$ ratios indicative of EM-1 mantle components (Woodhead and McCulloch, 1989), have a mean $\delta^{44/42}Ca$ value of 0.37 ± 0.02 ‰ (2 s.d., $n = 5$). No systematic correlations are observed between $\delta^{44/42}Ca$ and Sr-Nd-Pb isotopic ratios or differentiation indices such as MgO and CaO (Figs. S-2 and S-3; Table S-3). $\varepsilon^{40/44}Ca$ values range from −1.3 ± 0.5 to +0.4 ± 0.3 (Table S-1). $\varepsilon^{40/44}Ca$ values in the Tedside samples are systematically higher than the BSE value (*e.g.*, −1.2; Antonelli *et al.*, 2021b), likely reflecting the contribution of a recycled component within the Pitcairn mantle plume (Fig. S-4). Detailed discussion of these results is provided in the Supplementary Information, and our subsequent discussion focuses on stable Ca isotopes ($\delta^{44/42}Ca$).

Role of post-extraction processes

All Pitcairn samples analysed in this study are fresh (LOI < 0.5 wt. %), indicating negligible post-eruption alteration. However, these samples have undergone varying degrees of magmatic differentiation. During early differentiation, olivine was the dominant crystallising phase (Fig. S-1), which likely had little effect on the $\delta^{44/42}Ca$ values of samples with MgO ≥ 3.8 wt. % (Fig. S-4). Three more-evolved lavas (P1, 45DS1, and 51DS4), with MgO < 3.8 wt. %, underwent substantial clinopyroxene crystallisation. Because clinopyroxene has slightly higher $\delta^{44/42}Ca$ values than its co-existing melt (Zhang *et al.*, 2018; Eriksen and Jacobsen, 2022), its crystallisation may have led to a minor decrease in the $\delta^{44/42}Ca$ value of the remaining melt (Zhang *et al.*, 2018; Wang *et al.*, 2023). Nevertheless, relatively heavy $\delta^{44/42}Ca$ values are observed in these three evolved samples, suggesting slightly higher primary $\delta^{44/42}Ca$ values than measured. Negative correlations of $\delta^{44/42}Ca$ with Sr/Nd and Eu/Eu* may suggest a role for plagioclase crystallisation (Fig. 2; Table S-4); however, this can be ruled out by the incompatible behaviour of Al_2O_3 during differentiation of the Pitcairn lavas measured here (Fig. S-1). Thus, the decreased $\delta^{44/42}Ca$ values in Pitcairn samples are not a consequence of magmatic differentiation but most likely reflects primary source characteristics.

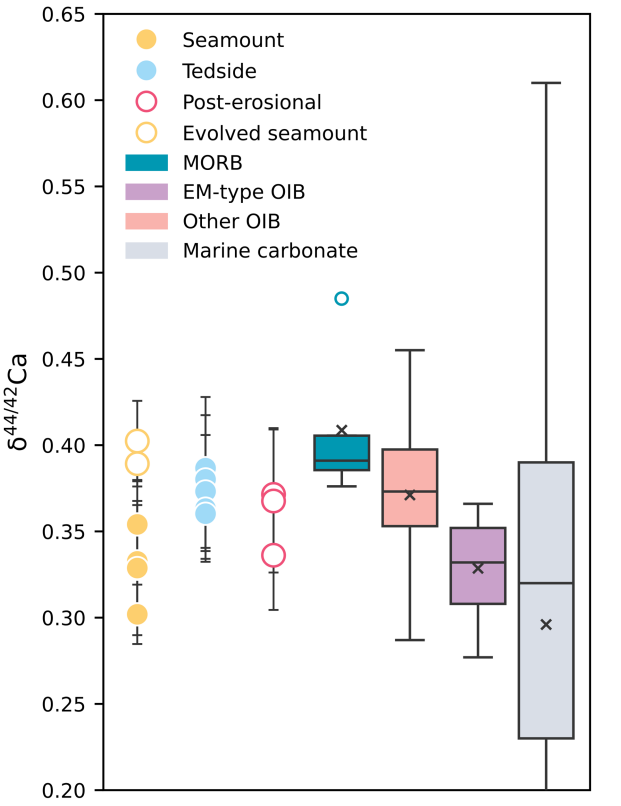

Figure 1 $\delta^{44/42}Ca$ for Pitcairn basalts. MORB, EM-type OIBs (EM-1/EM-2; enriched radiogenic isotopes), other OIBs and marine carbonates are shown for comparison. MORB and OIB data are from Eriksen and Jacobsen (2022) and Eriksen *et al.* (2024); marine carbonate data are from Fantle and Tipper (2014).

Origin of light Ca isotope anomaly among Pitcairn lavas

Low MgO (<3.8 wt. %) samples may be at risk of having experienced significant fractional crystallisation (Fig. S-1) and three post-erosional samples (erupted ~0.3 Myr after Tedside) do not follow the main Sr-Nd isotopic trend (Woodhead and McCulloch, 1989). We therefore focus our discussion of the origin of the Pitcairn source primarily on the ten Tedside and seamount samples with MgO ≥ 3.8 wt. % in order to minimise the influence of late stage processes and source heterogeneity, although these samples define the same trends in $\delta^{44/42}Ca$ *versus* Sr/Nd and Eu/Eu* plots. Accordingly, because (i) the early crystallising (MgO ≥ 3.8 wt. %) assemblage is dominated by olivine ± clinopyroxene with no plagioclase involvement (Fig. S-1) and (ii) melting occurred at garnet-facies pressures where plagioclase is unstable, the observed Sr/Nd and Eu/Eu* variations

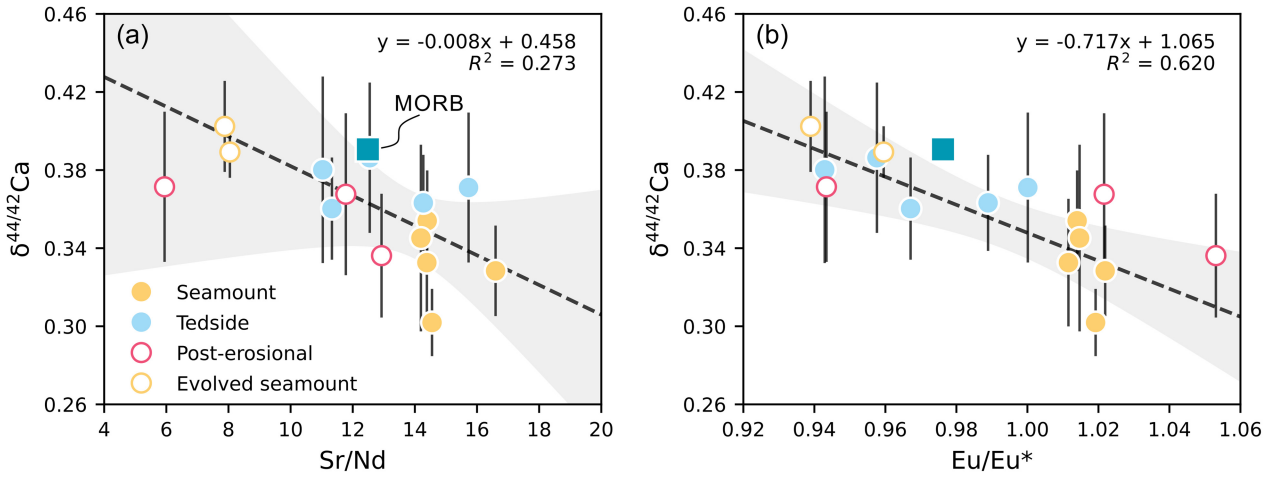

Figure 2 $\delta^{44/42}$Ca *versus* **(a)** Sr/Nb and **(b)** Eu/Eu* for Pitcairn basalts. Eu/Eu* = $Eu_N/(Sm_N \times Gd_N)^{0.5}$, where the subscript 'N' denotes chondrite-normalised values (Sun and McDonough, 1989). Trace element data are from Woodhead and McCulloch (1989) and Woodhead and Devey (1993). Filled symbols, Tedside + seamount samples with MgO ≥ 3.8 wt. % (used in fits); open symbols, post-erosional and evolved samples with MgO < 3.8 wt. % (excluded). Black line, linear regression fit to Tedside + seamount samples (MgO ≥ 3.8 wt. %); grey band, 95 % CI. MORB $\delta^{44/42}$Ca values are from Eriksen and Jacobsen (2022). Pitcairn trace elements are corrected for olivine accumulation following Nebel *et al.* (2019) (Table S-4), except for those with MgO < 3.8 wt. %, for which an effective clinopyroxene correction is unavailable.

record source metasomatism by at least two groups of crustal components, rather than magmatic processes. One group has sub-chondritic Sr/Nd and Eu/Eu* < 1, akin to sediments and the differentiated upper oceanic crust that has undergone plagioclase crystallisation. The other has high Sr/Nd and Eu/Eu* > 1, similar to gabbros in the lower oceanic crust that have experienced plagioclase accumulation (Fig. S-5). The involvement of surface crustal materials in the Pitcairn plume source has been independently inferred from low δ^{26}Mg values (Wang *et al.*, 2018) and mass independent Hg isotope fractionations (Moynier *et al.*, 2021). Nevertheless, samples with the lowest Sr/Nd and Eu/Eu* values and enriched radiogenic isotopes display MORB-like $\delta^{44/42}$Ca values, whereas light Ca isotope anomalies are observed in the depleted end member (Fig. 2; Fig. S-2). These puzzling trends are inconsistent with incorporation of low $\delta^{44/42}$Ca recycled sediments, and require an alternative mechanism to explain the low $\delta^{44/42}$Ca values in Pitcairn OIBs.

Unlike surface crustal materials with fractionated $\delta^{44/42}$Ca values, the gabbroic lower oceanic crust has a mean $\delta^{44/42}$Ca value comparable to that of the upper mantle (Fig. S-6). Therefore, the low $\delta^{44/42}$Ca magma end member cannot result from simple binary mixing between gabbroic lower oceanic crust and upper mantle but instead reflects Ca isotope fractionation during mantle metasomatism and late partial melting. Partial melting of pyroxenites with abundant residual garnet provides a plausible mechanism for generating melts with low $\delta^{44/42}$Ca values (Wang *et al.*, 2019, 2023; Eriksen and Jacobsen, 2022).

To quantitatively evaluate isotopic fractionation during partial melting, we perform incremental non-modal batch melting modelling for various mantle lithologies, including spinel- and garnet-bearing peridotite, recycled MORB (*i.e.* eclogite), and secondary pyroxenites generated by reaction between eclogite-derived melts and peridotite. The initial $\delta^{44/42}$Ca values for mantle peridotite and eclogite were set at 0.42 ‰ (Kang *et al.*, 2017) and 0.39 ‰ (Eriksen and Jacobsen, 2022), respectively. Melting conditions and modes were based on relevant experimental studies. Details of the modelling calculation are provided in the Supplementary Information and Tables S-5 to S-10.

Our results suggest that Ca isotope fractionation is limited during partial melting of peridotites and secondary pyroxenites in which garnet, if present, is less abundant (Fig. 3a), mainly due to the buffering effect of Ca-rich clinopyroxene, which has only slightly heavier Ca isotopic compositions than co-existing melts (Zhang *et al.*, 2018; Eriksen and Jacobsen, 2022). Partial melting of either garnet peridotite or secondary pyroxenite with a mantle-like $\delta^{44/42}$Ca value can account for the heavy $\delta^{44/42}$Ca magma end member but fails to explain both the lightest $\delta^{44/42}$Ca values and the steep slope of Pitcairn basalts in $\delta^{44/42}$Ca *versus* $(Dy/Yb)_N$ space (Fig. 3a). The involvement of abundant partial melts of recycled oceanic crust has been suggested for the source of the isotopically light seamount lavas (Woodhead and Devey, 1993; Eisele *et al.*, 2002; Delavault *et al.*, 2016). Partial melting of eclogite at high pressure (*e.g.*, 3–5 GPa; Sobolev *et al.*, 2005) in the deep mantle can generate melts with much lower $\delta^{44/42}$Ca values around 0.31 ‰, as garnet is abundant in the residua and minimally involved in the melting process (Table S-7). However, the proportion of eclogite-derived melts directly contributing to OIBs is likely limited (Sobolev *et al.*, 2007), and modelling calculations show that the trace element compositions (*e.g.*, $(Dy/Yb)_N$) do not match the characteristics of Pitcairn basalts (Fig. 3a). Instead, hybridisation of peridotite with high proportions of high pressure eclogite-derived melts (HPEMs) can produce secondary pyroxenites with lower $\delta^{44/42}$Ca and $(Dy/Yb)_N$ values. For example, mixing peridotite and HPEM in a 1:1 ratio (similar to Koolau lavas in Hawaii; Sobolev *et al.*, 2005) yields a secondary pyroxenite with $\delta^{44/42}$Ca ≈ 0.34 ‰ and $(Dy/Yb)_N \approx 1.29$ (Table S-8). High degrees of partial melting of such lithologies can resemble both the $\delta^{44/42}$Ca and $(Dy/Yb)_N$ values of the low $\delta^{44/42}$Ca magma end member among Pitcairn lavas (Fig. 3a).

Olivine and whole-rock compositions also suggest the contribution of pyroxenite sources to Pitcairn lavas (*e.g.*, Delavault *et al.*, 2015; Garapić *et al.*, 2015). Pyroxenite in the source of Pitcairn lavas with MORB-like $\delta^{44/42}$Ca values may form either from low HPEM proportions (*e.g.*, ~5 %; Fig. 3) or by mechanical mixing between recycled eclogite and mantle peridotite (Fig. S-6c). Our model illustrates a simple binary mixing scenario between melts derived from two secondary pyroxenites that differ in HPEM proportion. The MORB-like $\delta^{44/42}$Ca end member is derived from a secondary pyroxenite formed by ~5 % HPEM. To reproduce the enriched $^{87}Sr/^{86}Sr$ of the Tedside

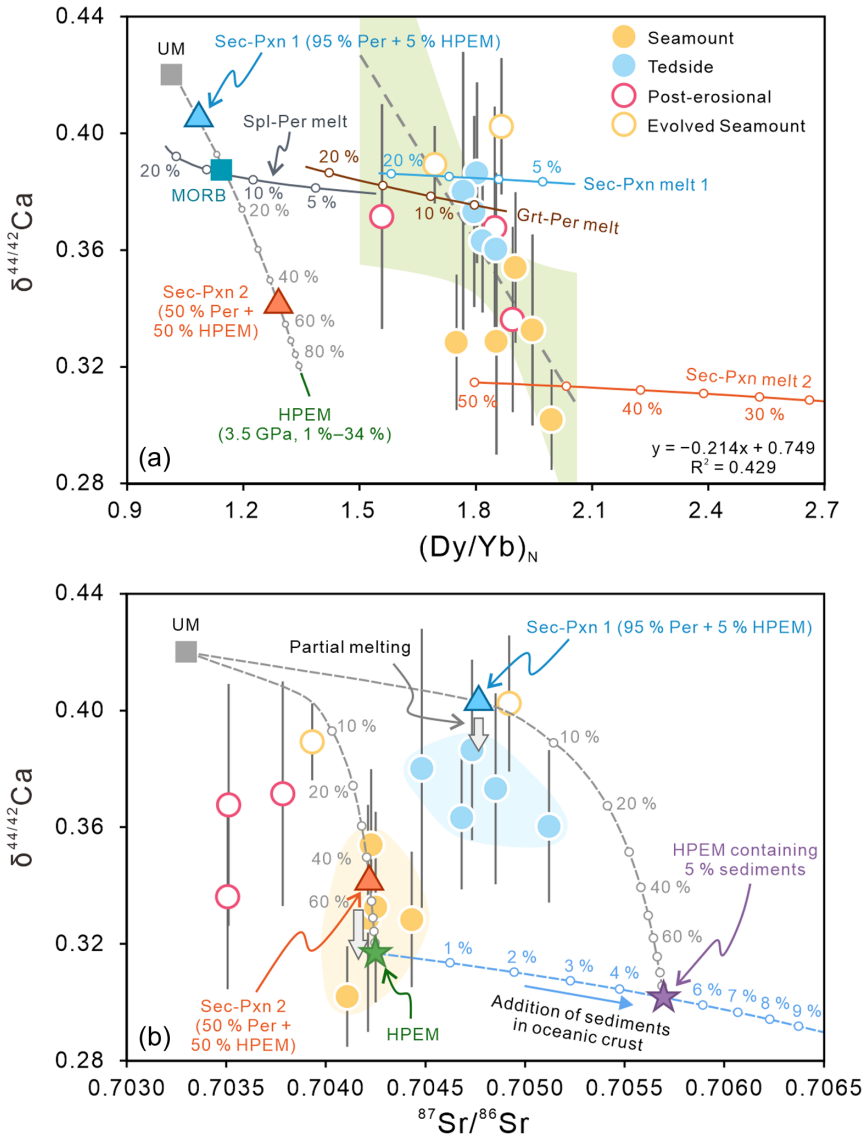

Figure 3 Model illustrating the origin of Ca isotope variations in the Pitcairn mantle plume. $\delta^{44/42}$Ca *versus* **(a)** $(Dy/Yb)_N$ and **(b)** $^{87}Sr/^{86}Sr$. Symbols and regression band are as in Figure 2. In **(a)**, grey and brown solid curves represent partial melting of spinel- and garnet-bearing peridotite, respectively, whereas blue and orange curves represent melting of two secondary pyroxenite end members. In **(b)**, the blue dashed line illustrates the effects of adding carbonate-bearing sediments to recycled oceanic crust to generate HPEM. In both panels, grey dashed lines represent the formation of secondary pyroxenites through interaction between HPEM and ambient peridotite at different proportions; blue and orange triangles indicate the resulting secondary pyroxenite end members. Abbreviations: Spl-Per, spinel peridotite; Grt-Per, garnet peridotite; Sec-Pxn, secondary pyroxenite; HPEM, high pressure eclogite-derived melt; UM, upper mantle. Modelling details are provided in the Supplementary Information and Tables S-5–S-10.

lavas, ~5 % carbonate-bearing sediments are included in the recycled oceanic crust generating the HPEM component. Because sediments contain much higher Sr concentrations than oceanic crust, this addition strongly influences $^{87}Sr/^{86}Sr$ but has only a negligible effect on $\delta^{44/42}$Ca (Fig. 3b; see the Supplementary Information). In contrast, the low $\delta^{44/42}$Ca end member, derived from a secondary pyroxenite containing ~50 % HPEM, displays higher Eu/Eu* and lower $^{87}Sr/^{86}Sr$, pointing to recycled lower oceanic crust with less sediments (Fig. 3b). Binary mixing between melts from these two pyroxenites reproduces the observed $\delta^{44/42}$Ca variations with trace element ratios (Figs. 2 and 3a) and radiogenic isotope ratios (Fig. 3b). Accordingly, secondary pyroxenite formed through interaction between HPEM and ambient mantle peridotite is likely a key control on the Ca isotopic variations of Pitcairn basalts. Whereas carbonatite melting can lower $\delta^{44/42}$Ca values in principle (Antonelli *et al.*, 2023), our Pitcairn lavas show no geochemical evidence for carbonatite involvement (*e.g.*, low CaO/Al_2O_3 and Ba/Nb, Fig. S-7), and the observed $\delta^{44/42}$Ca variations are fully explained by multi-stage melting and mixing among secondary pyroxenite melts at ~1400 °C. We therefore consider any carbonatite contribution to be minor at most and not required here.

Our study reaffirms the role of pyroxenite melting at pressures >3.0 GPa in generating metasomatic agents with low $\delta^{44/42}$Ca values but moderate $(Dy/Yb)_N$ ratios (Fig. 3). The Tedside basalts, representing the EM-1 end member, display higher $\delta^{44/42}$Ca values of 0.36–0.39 ‰, whereas the depleted seamount basalts exhibit notably lower $\delta^{44/42}$Ca values of 0.30–0.35 ‰. The lightest $\delta^{44/42}$Ca end member among the Pitcairn lavas shows geochemical signatures associated with the recycling of lower oceanic crust, which typically contains little

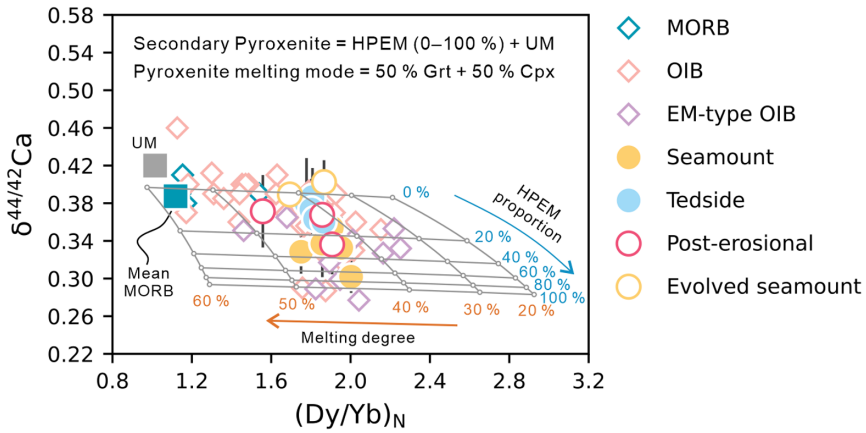

Figure 4 $\delta^{44/42}$Ca *versus* $(Dy/Yb)_N$ for global OIBs. Literature data are from Eriksen and Jacobsen (2022) and Eriksen et al. (2024). Symbols are as in Figure 2. Upper mantle and MORB $\delta^{44/42}$Ca references are as in Figure 3. The black grid represents our modelling of REEs and $\delta^{44/42}$Ca; see the Supplementary Information for details.

sediment and altered carbonate. Negative correlations with Sr/Nd and Eu/Eu* further indicate that this isotopically light Ca end member can be attributed to the recycling of lower gabbroic oceanic crust and isotopic fractionation during multi-stage pyroxenite melting. This study demonstrates that the lightest $\delta^{44/42}$Ca OIBs can be generated by partial melting of a mantle source involving a pyroxenitic component in the Pitcairn plume, rather than by contributions from recycled carbonate-bearing sediments. More broadly, the Pitcairn trend in $\delta^{44/42}$Ca *versus* $(Dy/Yb)_N$ space closely resembles the compositional range of global OIBs at the high $(Dy/Yb)_N$ end (Fig. 4), suggesting that similar processes involving HPEM and partial melting of its derivative secondary pyroxenite may also contribute to the origin of low $\delta^{44/42}$Ca signatures in other OIBs (Eriksen and Jacobsen, 2022; Eriksen *et al.*, 2024). This implies that interpretations of low $\delta^{44/42}$Ca signatures in OIBs as direct evidence for recycled carbonate-bearing sediments should be approached with caution (*e.g.*, Wang *et al.*, 2023).

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2613.

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