1	Pre-Cordilleran mantle metasomatism preserved in alkali basalts of Isla
2	Isabel, México
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17 Abstract

The presence of HIMU (high-²³⁸U/²⁰⁴Pb) signatures in ocean island basalts has long been used to argue 18 19 that ancient oceanic crust has been tectonically recycled into the mantle sources of plume-derived 20 volcanic hotspots such as St. Helena or Mangaia. However, alternative hypotheses regarding the origins of HIMU signatures have also been put forward. This paper addresses the origins of HIMU-like Pb 21 22 isotopic signatures in Isla Isabel, a small (~1 km²) intraplate volcanic island located off the western coast of México, southeast of the southern tip of Baja California. The Nd-Hf isotopic signatures of Isla Isabel 23 24 are nearly identical to St. Helena and Mangaia, however since there is no mantle plume underlying Isla 25 Isabel it is unlikely that these signatures derive from recycled oceanic crust. We argue that Isla Isabel 26 lavas were instead produced by mixing of depleted mantle-like material and continental lithospheric 27 mantle that was metasomatized ≥ 600 Ma ago, an age that overlaps with the regional breakup of Rodinia. 28 Such preservation of ancient tectonic events is remarkable, since the exposed geological record in 29 continental México preserves a very limited record of geological events older than the Mexican Cordillera (<165 Ma). Isla Isabel therefore illustrates that the origins of HIMU-type intraplate lavas are 30 not limited to ancient recycled oceanic crust. Rather, they can also preserve information about the 31 evolution of the upper mantle through large-scale tectonic cycles, even when these events have been 32 otherwise erased from the surficial rock record. 33

34 Introduction

35 Isla Isabel is an intraplate volcanic island overlying the western México continental shelf (Fig. 1) that 36 hosts HIMU-like isotopic signatures with undetermined provenance (Housh et al., 2010). The geological 37 history of the region surrounding Isla Isabel is complex. Subduction of the Farallon Plate generated 38 volcanism in northwestern México until 12 Ma ago, when seafloor spreading along the Pacific-39 Guadalupe Ridge ended and subduction in this region ceased (Lonsdale, 1991). Subsequently, the volcanic arc migrated southward to the presently active Trans-Mexican Volcanic Belt (TMVB; e.g., 40 Ferrari et al., 2012) and northwestern México transitioned to an extensional tectonic regime, marked 41 most notably by the opening of the Gulf of California (Lonsdale, 1991). Isla Isabel lies on the extended 42 43 strike of the TMVB onto the continental shelf, toward the Gulf of California, and is located ca. 100 km north of the northernmost extent of the subduction zone. Thus, it is considered unlikely the ca. 5 Ma 44 45 volcanic history of Isla Isabel is related to regional subduction; rather, it is thought to be related to local 46 extension from the prior regional tectonic reorganization (Housh et al., 2010).

47 Intraplate basalts with broadly similar geochemical compositions to Isla Isabel occur in northwestern mainland México (Aranda-Gómez et al., 2007) and within the TMVB (Díaz-Bravo et al., 2014). The 48 49 radiogenic Pb isotopic and olivine major element compositions of these rocks have been attributed to 50 metasomatism of the mantle wedge underlying the active and paleo-volcanic arcs and to crustal 51 assimilation. Isla Isabel presents a complementary perspective on the sub-Mexican mantle in that its 52 geochemistry is largely unaffected by either subduction or crustal assimilation processes (Housh et al., 53 2010). Alkali basalts are also found on islands several hundred km southwest of Isla Isabel that overlie oceanic, rather than continental lithosphere. Two of these islands, Socorro and Guadalupe, are generated 54 by mantle plumes imaged by seismic tomography that extend through 30-40% of the total mantle depth 55 (e.g., Koppers et al., 2021); by contrast, no mantle plume is known to underlie Isla Isabel. 56

A previous study of Isla Isabel basalts identified their distinct geochemical and isotopic compositions 57 compared to the arc-related volcanic rocks of the TMVB (Housh et al., 2010). Notably, like intraplate-58 type basalts from the TVMB (Díaz-Bravo et al., 2014), their Pb isotope signatures trend toward those 59 of HIMU (high $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) ocean island basalts (OIB; Housh et al., 2010). HIMU is one of several 60 theoretical mantle components, which among OIB is most commonly associated with recycling of 61 62 ancient (>2 Ga old) subducted oceanic crust (e.g., Chauvel et al., 1995; Stracke et al., 2005; Nebel et al., 2013). The HIMU component is classically found in OIB from Mangaia and St. Helena (Zindler and 63 64 Hart, 1986; Stracke et al., 2005), although the Pb isotopic signature of Isla Isabel lavas is not as 65 radiogenic as in these localities (Housh et al., 2010). HIMU-like isotope compositions have also been 66 identified in continental intraplate rocks unrelated to recycled subducted crust, and ancient mantle 67 metasomatism has been proposed for an alternative mechanism to generate highly radiogenic Pb signatures (Ballentine et al., 1997; Rooney et al., 2014; cf., Díaz-Bravo et al., 2014). This paper uses 68 69 combined Sr-Nd-Hf-Pb isotopic and trace element compositions to clarify the origins of the HIMU-like

isotope signatures of Isla Isabel lavas and to determine whether intraplate magmas can provide
 constraints on the geochemical evolution of the mantle during tectonic reorganization processes.

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73 Methods and Results

Nine Isla Isabel samples, originally studied by Housh et al. (2010) were analyzed for their ⁸⁷Sr-¹⁴³Nd-74 176Hf-206,207,208Pb isotopic compositions. Full details of analytical methods are given in the 75 76 Supplementary Information. Isla Isabel samples have homogeneous Sr-Nd-Hf-Pb isotopic compositions 77 (Table 1). The combined Sr-Nd-Pb isotopic signatures of Isla Isabel lavas plot at the edge of the TMVB 78 arrays or extend these arrays and overlap the compositional fields of global non-hotspot intraplate basalts (Fig. 2). Their Sr and Nd isotopic compositions are intermediate between depleted mid-ocean ridge 79 basalt (MORB) mantle (DMM, e.g., East Pacific Rise MORB) and highly enriched isotopic 80 compositions (EM) and are dissimilar to HIMU-type OIB (Fig. 2a). The average ²⁰⁶Pb/²⁰⁴Pb ratio of Isla 81 Isabel basalts is 19.330 ±0.027 (2 s.d.), significantly less radiogenic than classical HIMU-type OIB but 82 more radiogenic than DMM or TMVB lavas (Fig. 2b). The ²⁰⁸Pb*/²⁰⁶Pb* compositions of Isla Isabel 83 lavas also differ from both DMM and classical HIMU lavas (Fig. 2c). By contrast, their Nd and Hf 84 85 isotopic signatures fall below the mantle array and are almost identical to the Nd-Hf isotopic signatures of classical HIMU hotspots (Fig. 2d), making them clearly distinct from nearly all other global non-86 87 hotspot intraplate lavas.

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89 Discussion

90 Comparison of HIMU-like signatures in Isla Isabel

91 The Nd-Hf isotopic compositions of Isla Isabel lavas (Fig. 2d) imply that they may share a common 92 history with classical HIMU OIB. The location of the samples below the mantle array indicates their 93 sources tap a mantle component that has experienced a past enrichment event that produced lower 94 Sm/Nd and Lu/Hf ratios compared to the sources of lavas that lie on the mantle array. The less radiogenic ¹⁷⁶Hf/¹⁷⁷Hf for a given ¹⁴³Nd/¹⁴⁴Nd ratio exhibited by HIMU lavas relative to other OIB has been 95 96 previously attributed to fractionation events that were more extreme with respect to Lu-Hf than Sm-Nd, resulting in long-term decoupling of the two isotope ratios (cf., Nebel et al., 2013). The amount of 97 98 decoupling depends on both the timing and the degree of fractionation between the corresponding parent and daughter elements (Chauvel et al., 2008). Classical HIMU are generally associated with geologically 99 old (>2 Ga) sources, because this allows simultaneous generation of very radiogenic Pb and relatively 100 unradiogenic Sr, Nd, and Hf isotopic signatures. However, an alternative hypothesis holds that HIMU-101 like isotopic signatures can be generated by mantle metasomatism in little as 200 Ma (e.g., McCoy-West 102 103 et al., 2016).

Isla Isabel lavas possess less radiogenic Pb isotopic signatures (Fig. 2c) compared to HIMU OIB 104 localities. Additionally, their combined ²⁰⁸Pb*/²⁰⁶Pb* compositions, which record the long-term Th/U 105 ratio of its mantle source, are incompatible with mixing between DMM and an OIB HIMU component 106 107 (Figs. 1c, S1). Instead, the Pb isotopic compositions of Isla Isabel lavas lie along an array of global nonhotspot intraplate lavas with ²⁰⁷Pb/²⁰⁴Pb-²⁰⁶Pb/²⁰⁴Pb compositions that link depleted isotopic signatures 108 (e.g., MORB) with an ancient enriched Pb isotopic signature (Fig. S2). For example, the Isla Isabel Pb 109 110 isotopic signature can be modeled as a mixture of EPR-like depleted material and an enriched Pb isotopic component that was introduced 600 Ma ago and raised both the Pb isotopic ratios and the U/Pb ratio of 111 the Isla Isabel mantle source (Fig. S2). Introduction of this component at ages like those expected for 112 113 HIMU OIB would instead require that the Isla Isabel source has a low U/Pb ratio, less than that of the 114 depleted mantle. Further, Isla Isabel lavas lack the strongly positive Nb anomalies associated with recycled crust (e.g., Cordier et al., 2021); instead, they have Ce/Pb and Nb_N/Nb* ratios that resemble 115 DMM (e.g., Arevalo & McDonough, 2010; Fig. S3). Finally, Isla Isabel olivine have high CaO and low 116 NiO compositions (Housh et al., 2010; Fig. S4) that require their derivation from peridotite rather than 117 118 mantle pyroxenite associated with subducted oceanic crust (e.g., Herzberg et al., 2014). A similar 119 observation was previously reported for intraplate-type basalts from the TMVB (Díaz-Bravo et al., 120 2014), implying that pyroxenite signatures are generally absent from the regional mantle.

Modern HIMU-type OIB associated with geochemical signatures of recycled oceanic crust are spatially 121 122 associated with deep mantle plumes (Jackson et al., 2018). By contrast, there is no known mantle plume 123 beneath Isla Isabel or in the region of northwestern México (Smith, 1999; Mora-Klepeis, 2021; Koppers 124 et al., 2021) that would be capable of delivering deeply recycled oceanic crust to the melting region of 125 Isla Isabel. Recycling of subducted crust at shallower mantle depths is also unlikely due to the higher 126 density of subducted crust, which transforms to eclogite in subduction zones, compared to upper mantle peridotites (Brandenburg et al., 2008). Alternatively, ancient mantle plumes and fluids released during 127 subduction can metasomatize the upper mantle and change local isotopic evolution pathways (e.g., 128 129 Homrighausen et al., 2018). For example, a CO₂-rich metasomatic origin for the classical HIMU island 130 Mangaia was also evaluated (Weiss et al., 2016), and a single analysis of CO_2 in a basaltic glass from Isla Isabel (Housh et al., 2010) yielded a CO_2 abundance similar to those of melt inclusions from 131 132 Mangaia (Cabral et al., 2014). Therefore, an ancient metasomatic origin is most likely for Isla Isabel. This interpretation has also been invoked for other non-hotspot intraplate basalts, for example HIMU-133 like intraplate lavas from Africa are argued to be related to melting of amphibole-rich metasomes that 134 135 were generated 700 Ma ago (Rooney et al., 2014).

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137 A pre-Cordilleran metasomatic origin of Isla Isabel HIMU signatures

To determine the origin of Isla Isabel's distinct isotope composition, a solid-state mixing model between convecting, depleted upper mantle (DMM; compositions from Salters & Stracke, 2004 and Workman

- 140 & Hart, 2005) and metasomatized continental lithospheric mantle (CLM; compositions based on Wittig
- 141 et al., 2010, see Supplementary Information) is applied to the collected data. The calculated $\Delta \epsilon^{176}$ Hf and
- 142 ²⁰⁷Pb/²⁰⁶Pb compositions of the metasomatized component depend in part on the time this metasomatism
- 143 occurred, with earlier metasomatism producing lower $\Delta \epsilon^{176}$ Hf and 207 Pb/ 206 Pb if the effect of
- 144 metasomatism on parent-daughter ratios is held constant. One constraint on this age is provided by the
- 145 Hf model ages of the Isla Isabel samples ($\tau_{176} = 616 \pm 35$ Ma, 2 s.d.). Although this likely provides only
- a minimum age for the time of metasomatism (Supplementary Information), it is the only contextualized
- age information available for the mantle source of Isla Isabel.
- 148 This model produces a mixing curve between modern DMM and metasomatized CLM that passes 149 through both the Isla Isabel data and, at higher proportions of metasomatized mantle, also passes through literature data for Mangaia (Fig. 3). A relatively high proportion of a fusible, metasomatized CLM 150 151 component beneath Isla Isabel may have promoted mantle melting when the mantle lithosphere was reactivated by recent tectonic reorganization (cf., Hoernle et al., 2011), thus providing an explanation 152 for localized volcanism. By contrast, a model representing 3 Ga old recycled oceanic crust (cf., Nebel 153 154 et al., 2013) can also reproduce the isotopic composition of Mangaia and St. Helena rocks (cf., Nebel et al. (2013), but not Isla Isabel signatures. In both cases, the model uses a global average DMM value as 155 156 the depleted mixing component, although MORB from a geographically close location to Isla Isabel, e.g., the northern East Pacific Rise (NEPR), have slightly negative $\Delta \varepsilon^{176}$ Hf values. These compositions 157 can be explained analogously to those of Isla Isabel, however in this case the metasomatic CLM 158 component must be either older or possess more enriched Lu/Hf-Sm/Nd ratios (cf., Fig. 3, "alternative" 159 model). In this context, the $\Delta \epsilon^{176}$ Hf compositions of Isla Isabel and NEPR samples may reflect pervasive 160 161 dispersion of variably metasomatized Mexican CLM throughout the continental and oceanic lithosphere 162 along the Mexican margin.
- 163 The origin of the Isla Isabel mantle metasomatic component cannot be related to the modern subduction zone, since the Hf isotopic compositions of the Isla Isabel rocks likely require that their mantle source 164 differentiated from the depleted mantle at least 600 Ma ago, whereas the Farallon Plate is likely less 165 than 165 Ma old (e.g., Engebretson et al., 1985). By contrast, surficial volcanic rocks in México provide 166 167 only a limited record of tectonic events prior to the generation of the Mexican Cordillera. For example, collisional-extensional regimes related to the assembly and breakup of the Precambrian supercontinent 168 Rodinia are preserved only by the Oaxaquia microplate of southern México, ca. 1200 km SE of Isla 169 Isabel (e.g., Keppie and Ortega-Gutiérrez, 2010). The last of these preserved extensional events occurred 170 171 between 750 and 545 Ma ago, an age that overlaps the Hf model ages of the studied Isla Isabel samples and thus provides a potential explanation for their negative $\Delta \epsilon^{176}$ Hf compositions (Fig. 3). The 172 lithospheric mantle beneath Isla Isabel may therefore preserve a geochemical memory of events related 173 174 to ancient supercontinent cycles that have been largely overprinted on the Mexican mainland. Dispersed 175 metasomatized CLM in other localities may similarly preserve geochemical information about ancient

tectonic events but this is only exceptionally unlocked by non-hotspot intraplate volcanoes such as IslaIsabel.

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179 Conclusion

Combined Sr-Nd-Hf-Pb isotopic compositions for the intraplate volcanic island Isla Isabel reflect a 180 HIMU-type mantle source that was likely generated by ancient metasomatic event affecting Mexican 181 CLM. Dispersal of this component to a relatively high degree under Isla Isabel, and possibly to a lesser 182 extent throughout the regional oceanic mantle, generated the HIMU-like isotopic characteristics Isla 183 Isabel basalts. Hafnium isotopic compositions constrain the age of the metasomatic event to be older 184 than Mesozoic-to-recent subduction of the Farallon Plate that produced the Mexican Cordillera. This 185 demonstrates that the utility of HIMU-type intraplate lavas is not limited to understanding ancient 186 subduction of oceanic crust; rather, they can provide critical access to other ancient tectonic processes 187 for which few remnants remain in the accessible geological record. 188

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Table and Figures 195

196 Table 1. Sr, Nd, Hf and Pb isotope data of Isla Isabel samples.

Sample	⁸⁷ Sr/ ⁸⁶ Sr	2SD	$n(n_{\rm d})^{\rm a}$	εNd ^b	2SD	$n(n_{\rm d})^{\rm a}$	εHf ^b	2SD	$n(n_d)^a$	²⁰⁶ Pb/ ²⁰⁴ Pb	2SD	²⁰⁷ Pb/ ²⁰⁴ Pb	2SD	²⁰⁸ Pb/ ²⁰⁴ Pb	2SD	$n(n_d)^a$
NAY-2	0.703267	0.000009	1 (1)	5.14	0.05	4 (1)	4.66	0.54	2 (1)	19.3049	0.0012	15.6430	0.0013	38.9373	0.0042	7(1)
NAY-3	0.703285	0.000009	3 (2)	5.03	0.05	4 (2)	5.55	0.09	7 (2)	19.3559	0.0010	15.6488	0.0009	39.0148	0.0030	12 (2)
NAY-4	0.703260	0.000009	1 (1)	4.97	0.07	2 (1)	5.38	0.27	2(1)	19.3269	0.0012	15.6465	0.0015	38.9600	0.0054	7(1)
NAY-13	0.703251	0.000009	1 (1)	4.92	0.07	2 (1)	4.96	0.25	2(1)	19.3317	0.0006	15.6507	0.0006	38.9762	0.0022	7(1)
NAY-14	0.703245	0.000009	1 (1)	4.92	0.07	2 (1)	5.59	0.27	2(1)	19.3364	0.0026	15.6566	0.0031	38.9952	0.0101	8 (1)
NAY-15	0.703253	0.000009	1 (1)	5.00	0.08	2 (1)	5.49	0.24	2(1)	19.3324	0.0011	15.6483	0.0012	38.9688	0.0041	6(1)
NAY-31	0.703256	0.000009	1 (1)	4.96	0.07	2(1)	5.62	0.17	2(1)	19.3275	0.0009	15.6450	0.0009	38.9567	0.0029	7(1)
NAY-32	0.703224	0.000009	1 (1)	5.13	0.07	2(1)	5.75	0.17	2(1)	19.3234	0.0009	15.6392	0.0011	38.9282	0.0036	7(1)
NAY-35	0.703250	0.000009	1(1)	4.95	0.07	2(1)	5.46	0.17	2(1)	19.3287	0.0010	15.6468	0.0010	38.9637	0.0034	11 (1)
BHVO-2 °	0.703470	0.000009	1 (1)	6.99	0.04	8 (1)	10.81	0.10	6(1)	18.5980	0.0003	15.5368	0.0004	38.1930	0.0010	7(1)

Notes: 198

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199 ^a n refers to number of individual analyses, n_d refers to number of separate digestions of a given sample.

^b Epsilon notation normalised to CHUR values 176 Hf/ 177 Hf = 0.282785 and 143 Nd/ 144 Nd = 0.512630 (Bouvier et al., 2008). 200

^c Measured BHVO-2 values are within reference values reported by Weis et al. (2005): 176 Hf/ 177 Hf= 0.283096 ±20, 143 Nd/ 144 Nd = 0.512983 ±10, 206 Pb/ 204 Pb = 18.6173 ±465, 207 Pb/ 204 Pb = 15.5355 ±54, 208 Pb/ 204 Pb = 38.2108 ±384. 201





Figure 1. Map of the location of Isla Isabel, showing also relevant tectonic features (TF = Tamayo fault;
SBF = San Blás fault; SBT = San Blás Trough; MMR = María Magdalena Rise). Cities (M = Mazatlán;
SB = San Blás; TE = Tepic; G = Guadalajara; PV = Puerto Vallarta) and volcanoes of the western
TMVB (SJ = San Juan; Sa = Sangangüey; Te = Tepetiltic; Ce = Ceboruco; Teq = Tequila; LP = Sierra
La Primavera) are shown. The blue point on the inset map is the island Guadalupe. Features shown have
been adapted from Housh et al. (2010), bathymetry grid data obtained from GEBCO
(https://www.gebco.net/) (GEBCO Compilation Group, 2021).



Figure 1. Isotope composition of Isla Isabel lavas. a) 87 Sr/ 86 Sr vs ${\epsilon}^{143}$ Nd, b) 206 Pb/ 204 Pb vs 207 Pb/ 204 Pb, c) 208 Pb ${}^{*/206}$ Pb * vs 87 Sr/ 86 Sr, the 208 Pb ${}^{*/206}$ Pb * ratio is calculated as described in Stracke et al., 2005, d) ${\epsilon}^{143}$ Nd vs ${\epsilon}^{176}$ Hf with mantle array according to Chauvel et al. (2008). For comparison, isotopic data from MORB, HIMU OIB, TMVB (intraplate lavas, where available), and African-Arabian intraplate rocks are plotted. Approximate compositions of OIB mantle components (DMM, HIMU, EM) are shown. The references for literature data are given in the Supplementary Information.



Figure 2. Mixing model for the $\Delta \epsilon^{176}$ Hf (deviation of the ϵ^{176} Hf compositions of a sample from the mantle array given the sample ϵ^{143} Hf) versus 207 Pb/ 206 Pb compositions of DMM and metasomatized CLM compared to Isla Isabel and literature data. The blue lines represent the model mixing lines, for both best fit and alternative metasomatism models, as well as for a model for 3 Ga old recycled subducted oceanic crust (after Nebel et al. 2013). Symbols on the mixing lines represent the fraction metasomatized CLM component added. Comparison data are the same as in Fig. 2.

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1	Supplementary information and figures for:
2	Pre-Cordilleran mantle metasomatism preserved in alkali basalts of Isla Isabel, México
3	
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7	Submitted to Geology
8	This is a non-peer reviewed preprint uploaded to EarthArXiv

9 1. Methods

The nine analyzed Isla Isabel samples are the same as in Housh et al. (2010) and were provided by the 10 Smithsonian Museum of Natural History. The GPS coordinates for sample collection locations are 11 12 provided in Table 1 of Housh et al. (2010) and replicated in Table S1. Housh et al. (2010) only reported 13 isotopic data for four samples and no Hf isotopic data. All sample powders, except for that for BHVO-2, were repetitively leached with 2M HCl in an ultrasonic bath in 20-minute intervals. After each 14 15 leaching interval, the acid and all suspended fine particles were removed with a pipette. The leaching was repeated until the acid solution remained transparent after the 20-minute ultrasonication. At this 16 17 point, the leachate was again removed, and the leach was stopped by adding mQ H₂O to the sample and ultrasonicating the sample for a further 20 minutes. Subsequently, the H₂O was decanted from the 18 19 sample with a pipette and the sample residues were gently dried. They were subsequently digested in a 4:1 mixture of concentrated, distilled HF and concentrated, double-distilled HNO₃ for >3 days. 20

21 The separation method for Hf was adapted from Münker et al. (2001) and completed on a separate aliquot from the same sample digestion used for Sr-Nd-Pb separations. First, high field strength elements 22 23 (HFSE), including Hf, were separated from matrix elements in 1M HCl-0.1M HF on BioRad AG50-X8, 200-400 mesh cation exchange resin. The sample aliquots were then dried and repetitively dissolved in 24 25 drops of concentrated, high-purity HClO₄ to oxidize Ti. Following this, Hf was separated from other HFSE on 50-100 µm Eichrom Ln resin. The Hf collection procedure was calibrated, which was 26 accomplished using the basaltic reference material BCR-2. This second column step encompasses 27 28 separation of Ti (in 0.09M HCit-0.45M HNO₃-1 wt% H₂O₂) and Zr (in 2M HCl-0.1M HF) and finally 29 the collection of Hf isotopes using 6M HCl-0.04M HF. Lead was separated from matrix elements using 30 BioRad AG1-X8 anion exchange resin using 0.5N HBr (matrix) and 0.5M HNO₃ (Pb). Following this, Nd was separated from the Pb matrix fraction in two steps using BioRad AG50-X8, 200-400 mesh cation 31 exchange resin and 50-100 um Eichrom Ln resin. Strontium was separated from the sample matrix on 32 33 Eichrom Sr resin using the matrix fraction collected in the first step of Nd separation.

34 The Nd, Hf, and Pb isotopic compositions of the Isla Isabel samples were measured using the Thermo Scientific Neptune multi-collector inductively coupled plasma source mass spectrometry (MC-ICP-MS) 35 in the Isotope Geochemistry and Cosmochemistry group at ETH Zürich. Neodymium isotopic compositions were normalized to ${}^{146}Nd/{}^{144}Nd = 0.7219$ and ${}^{142}Nd/{}^{144}Nd = 1.141876$ using a ${}^{142}Ce/{}^{140}Ce$ 36 37 ratio that was empirically calculated from the offset in fractionation-corrected ¹⁴³Nd/¹⁴⁴Nd ratios 38 between the JNdi-1 standard with and without an added Ce dopant. The corrected ¹⁴³Nd/¹⁴⁴Nd ratios 39 were then normalized to a reference JNdi-1¹⁴³Nd/¹⁴⁴Nd value of 0.512115 (Tanaka et al., 2004) on a 40 per-session basis. Hafnium isotopic compositions were normalized to 179 Hf/ 177 Hf = 0.7325 and corrected 41 ¹⁷⁷Hf/¹⁷⁶Hf ratios were normalized to a reference value of 0.282160 for the JMC475 standard (Blichert-42 Toft et al., 1997). Lead isotopic compositions were corrected for mass bias using Tl doping and a 43 ²⁰³Tl/²⁰⁵Tl ratio calculated to produce a total offset of zero between measured ^{206,207,208}Pb/²⁰⁴Pb and 44 ^{207,208}Pb/²⁰⁶Pb ratios and the reference values of Baker et al. (2004). External precisions (estimated as 45 the 2σ s.d. of all measured standards in one measurement session) were 0.06-0.09 for ϵ^{143} Nd (two 46 measurement sessions), 0.24 for ϵ^{176} Hf (one measurement session), 0.0009-0.0010 for 206 Pb/ 204 Pb, 47 0.0008-0.0012 for ²⁰⁷Pb/²⁰⁴Pb, and 0.0020-0.0032 for ²⁰⁸Pb/²⁰⁴Pb (three measurement sessions). The 48 obtained isotopic compositions for BHVO-2 digested and processed with the Isla Isabel samples agree 49 with literature reference values (Table 1). 50

51 Strontium isotopic compositions were measured using the Thermo Scientific Triton thermal ionization 52 mass spectrometer (TIMS) in the Isotope Geochemistry and Cosmochemistry group at ETH Zürich. The 53 data were normalized to ⁸⁸Sr/⁸⁶Sr = 8.375209 and the corrected ⁸⁷Sr/⁸⁶Sr values were normalized to a 54 reference ⁸⁷Sr/⁸⁶Sr ratio of 0.710245 for the NBS987 standard (mean of published values on the 55 GeoREM database). The external precision for ⁸⁷Sr/⁸⁶Sr ratios, estimated as the s.d. of all measured 56 standards, was 0.000009. Measured isotopic compositions for BHVO-2 digested and chemically 57 separated with the Isla Isabel samples agree with literature reference values (**Table 1**).

For all samples and isotopic systems, uncertainties of single measurements are expressed as the larger of (i) the 2σ standard error of the measurement and (ii) the 2σ standard deviation of all measured standards as reported in the sections above. The reported values and uncertainties of replicated standard and sample measurements are the weighted average and 2σ standard deviation of individual runs, weighted by the uncertainty of individual measurements as previously defined.

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2. Model age calculations

The timing of the metasomatic event that generated the Nd-Hf-Pb isotopic signatures associated with 65 66 HIMU OIB can be constrained with the help of the Lu-Hf and Sm-Nd isotopic systems, and through this potentially linked to tectonic or magmatic events. To determine the age constraints for the model 67 68 calculations, the closing time of the systems τ was calculated based on the collected isotope data. Since 69 the Lu-Hf isotope system experiences very small amounts of fractionation between parent and daughter elements during partial melting of intraplate basalts from metasomatized mantle, measured Lu/Hf ratios 70 of the rocks are assumed to be the same as in the magma source (cf., Pilet et al., 2008; Rooney et al., 71 72 2014):

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$$\tau_{176} = \frac{1}{\lambda} * ln \left(\frac{\frac{176}{177}Hf}{\frac{177}{Hf}_{sample}} - \frac{\frac{176}{177}Hf}{\frac{177}{Hf}_{DMM}} + 1 \right)$$

74

75 The average τ_{176} value based on the Isla Isabel isotope data is $\tau_{176} = 616 \pm 35$ Ma. The same calculations 76 for the Sm-Nd system result in a younger age of $\tau_{143} = 376 \pm 27$ Ma, both of which reflect pre-Cordilleran ages. The average τ_{143} age is somewhat older than the age of mantle metasomatism inferred from the Nd 77 78 isotopic compositions of mantle xenoliths in northwest México, approximately 700 km NNE of Isla 79 Isabel (<227 Ma; Nimz et al., 1995). The difference in the ages implied by the two isotope systems is 80 likely related to differences in the closed system behavior of Hf isotopes compared to Nd isotopes. It has been observed that although the two isotope systems have similar compatibility behaviors, among 81 82 mantle lithologies the Sm-Nd system seems to be more sensitive to later-stage disturbances, like meltrock interactions, than the Lu-Hf system (Stracke et al., 2011). Thus, the Lu-Hf system is considered the 83 84 more robust indicator of the timing of the metasomatic or other enrichment event affecting the Isla Isabel 85 mantle source. A geologically parsimonious explanation for the differing model ages is that they reflect 86 distinct events that affected the Sm-Nd and Lu-Hf systems differently. For example, the >735 Ma mantle depletion age inferred from the least metasomatized mantle xenoliths of Nimz et al. (1995, from 87 88 northwest México ca. 700 km NNE of Isla Isabel), along with the average Hf depletion age of Isla Isabel 89 samples (616 Ma) may reflect collision-rifting cycles associated with the supercontinent Rodinia (e.g., Keppie and Ortega-Gutiérrez, 2010). The Paleozoic Nd model ages of the northwest México mantle 90 91 xenoliths (Nimz et al., 1995) and the Isla Isabel samples may reflect distinct episodes of smaller-scale magmatism that are recorded for example in the Coahuila terrane of northwestern México and the 92 93 southern United States (e.g., Denison et al., 1969).

94 It is important to note that these model ages do not necessarily directly reflect the time at which the regional continental lithospheric mantle (CLM) was metasomatized, since they reflect the measured 95 96 ϵ^{176} Hf and Lu/Hf ratios of the samples, which represent the composition mixed mantle source (DMM + 97 CLM) and not the composition of the metasomatic CLM component itself. Since the $\Delta \varepsilon^{176}$ Hf composition of Isla Isabel basalts is a mixture of depleted mantle ($\Delta \epsilon^{176}$ Hf near 0) and the metasomatized 98 component, the latter must have a $\Delta \epsilon^{176}$ Hf composition that is more negative than Isla Isabel. More 99 negative $\Delta \epsilon^{176}$ Hf signatures would require more time to evolve from a pre-metasomatic peridotite that 100 is DMM-like compared to less negative $\Delta \epsilon^{176}$ Hf signatures, unless the Lu/Hf ratio of the more negative 101 $\Delta \epsilon^{176}$ Hf domain is low enough to allow the negative $\Delta \epsilon^{176}$ Hf signatures to develop in a shorter time. For 102 example, Woodhead et al. (2017) reported Hf isotopic data for a global assemblage of mantle-derived 103 104 zircon, which, due to their very low Lu/Hf ratios and relatively young ages (<120 Ma), preserve their initial Hf compositions. Within their "group A," in which Hf isotopic compositions are correlated with age, a kernel density estimate reveals a peak ϵ^{176} Hf composition of ca. -3. Assuming the most extreme 105 106 case of Lu/Hf = 0, which will produce the youngest possible τ_{176} age, if the metasomatized CLM 107 contributing to the Isla Isabel source possessed a ϵ^{176} Hf of -3, its τ_{176} would be ca. 750 Ma. In the most 108

extreme possible example for Isla Isabel, a metasomatized CLM source with Lu/Hf = 0 and ϵ^{176} Hf \approx 109 110 +0.4 would produce a τ_{176} virtually identical to the average τ_{176} of the samples. However, this would require that the metasomatized CLM contributes ca. 55% of the Hf budget of Isla Isabel basalts. Such a 111 high proportion would more likely produce a more volatile-rich mafic lithology, approaching a lamproite 112 or a carbonatite, than the alkali basalts that characterize Isla Isabel. The Isla Isabel samples would also 113 likely possess trace element characteristics that are common in these rock types, such as enrichments in 114 Th and Ba (e.g., Hoernle et al., 2002), which are absent in the Isla Isabel basalts. Thus, utilizing the 115 116 Lu/Hf ratios of the Isla Isabel samples to calculate the age of CLM metasomatism likely underestimates the age of regional CLM metasomatism. There are no regional constraints on the Lu/Hf and ratio of the 117 118 CLM that would permit the model to be constructed otherwise, however mantle xenoliths from northwestern México (ca. 700 km NNE of Isla Isabel; Nimz et al., 1995) similarly preserve a pre-119 Cordilleran model age of >735 Ma in their Nd model ages. Further, there are no direct constraints on 120 the U,Pb/Th ratios or Pb isotopic compositions of the regional lithospheric mantle that could be used to 121 complete the model into its form in Fig. 3. 122

123

3. Model fitting of the metasomatized component

125 Determining the starting composition of the enriched component of the Isla Isabel magma source is difficult as combined data for the Sm-Nd, Lu-Hf, and U, Th-Pb isotopic systems is relatively scarce for 126 lithospheric mantle xenoliths. Compositions able to generate the required isotope compositions can be 127 found by model fitting and using literature data for global xenoliths of CLM. For the Pb isotope 128 compositions, a ²³⁸U/²⁰⁴Pb of 56.3 (Wittig et al., 2010) observed in metasomatized continental mantle 129 xenoliths reproduce the isotopic compositions of Isla Isabel lavas assuming a starting age of 616 Ma 130 (i.e. the average Lu-Hf model age of the samples). However, the Lu/Hf and Sm/Nd ratios of the same 131 rocks are not able to reproduce the observed Nd and Hf isotopic compositions of Isla Isabel lavas; 132 133 instead, the component requires a more enriched Lu/Hf ratio compared to the depleted mantle than the enrichment of Sm/Nd ratios compared to the depleted mantle. This incongruous enrichment can be 134 observed in the same metasomatized mantle samples from Wittig et al. (2010), but the enrichment is not 135 extreme enough (e.g., ${}^{176}Lu/{}^{177}Hf = 0.02$ and ${}^{147}Sm/{}^{144}Nd = 0.21$; Wittig et al., 2010) to produce Nd-Hf 136 isotopic compositions as far below the mantle array as what is observed for Isla Isabel lavas. In order to 137 produce a fit to the Isla Isabel data, the Lu/Hf ratio of their most extreme sample was thus adjusted 138 139 downwards, and its Sm/Nd ratio was proportionally adjusted upwards. This represents an artificial arithmetic adjustment; however, it mimics the same metasomatic enrichment process observed in the 140 141 samples of Wittig et al. (2010), but to a higher degree.

142 The best fit mixing line for the Isla Isabel samples also passes through samples from Gerba Guracha, 143 which have been suggested to originate from melting of amphibole-rich lithospheric metasomes, 144 resulting in their HIMU-like compositions (Rooney et al., 2014). Isla Isabel samples have similar 145 $^{207}Pb/^{206}Pb$ and $\Delta\epsilon^{176}$ Hf values to the lavas from Gerba Guracha (Fig. 2), which speaks for the possibility

- 146 of a similar metasomatic component being involved in the island's magma source.
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149 Supplementary table and figures

150	Supplementary	Table S1.	GPS	collection	coordinates	for sam	ples used	l in th	nis study	7.
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Sample	Latitude	Longitude
NAY-2	21.8436	-105.8794
NAY-3	21.8436	-105.8794
NAY-4	21.8500	-105.8878
NAY-13	21.8463	-105.8844
NAY-14	21.8491	-105.8851
NAY-15	21.8492	-105.8888
NAY-31	21.8480	-105.8879
NAY-32	21.8433	-105.8864
NAY-35	21.8445	-105.8861





154 Supplementary Figure S1. 87Sr/86Sr versus ²⁰⁸Pb*/²⁰⁶Pb* non-linear isotope mixing model. Points and numbers indicate the fraction of HIMU component in the mixture. This simple model indicates that 155 mixing between enriched (e.g., HIMU component originating from recycled subducted oceanic crust) 156 and a depleted (e.g., DMM) endmembers is unable to produce Isla Isabel isotope compositions. 157 Endmember isotopic compositions are derived from the literature (DMM: ${}^{87}Sr/{}^{86}Sr = 0.7026$, ${}^{206}Pb/{}^{204}Pb$ 158 = 18.23, ${}^{208}Pb/{}^{204}Pb = 37.84$, Workman and Hart, 2005; HIMU: ${}^{87}Sr/{}^{86}Sr = 0.7033$, ${}^{206}Pb/{}^{204}Pb = 22$, 159 208 Pb/ 204 Pb = 40.8, Stracke et al., 2005). The choice of Pb and Sr elemental abundances in the mixing 160 model is arbitrary, since there is no possible mixing line that would pass through the Isla Isabel data; the 161 162 displayed mixing line is thus only illustrative.



Supplementary Figure S2. Isotope model of ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb isochrons adapted from 164 Rooney et al. (2014). The model compares the evolution of Pb-Pb isochrons with varying µ values at a 165 fixed time (ca. 600 Ma) based on the Isla Isabel Hf isotope data (τ_{176}). The reference depleted isochron 166 starts with an initial composition representing DMM Pb isotope signatures (Workman and Hart, 2005) 167 using µ ranges from 0-35. This isochron lies below the Isla Isabel data. The adjusted, enriched isochron 168 is fitted to the most extreme Isla Isabel value by increasing the initial value of ²⁰⁷Pb/²⁰⁴Pb from 15.486 169 to 15.598. This increase could represent a geochemical enrichment event affecting DMM material, 170 generated for example by incorporation of subducted oceanic crust or metasomatized CLM. Along with 171 the Isla Isabel samples, intraplate rocks that have metasomatized mantle sources are plotted for 172 reference. Together, they illustrate a broad mixing line between the two isochrons. 173



Supplementary Figure S3. Ce/Pb versus Nb_N/Nb* (Nb_{PM} / (La_{PM} * Th_{PM})^{1/2}, where PM indicates 175 normalization to the primitive mantle composition of McDonough & Sun, 1995) for Isla Isabel and 176 177 comparison data from literature. These trace element ratios can be used to infer information about the 178 sources of intraplate magmas because they are relatively unaffected by partial melting and fractional 179 crystallization and have distinct values in continental curst and mantle material. Trace element compositions of Isla Isabel (Housh et al., 2010) overall overlap with depleted mantle values (22 ± 10 ; 180 181 Arevalo and McDonough, 2010), while classical HIMU rocks such as Mangaia and St. Helena, which are thought to derive from recycled, subducted oceanic crust and tend to have high Nb_N/Nb* and Ce/Pb 182 183 values (Cordier et al., 2021). The vertical dashed line represents the boundary between the Pitis (depleted) and Muru (recycled) group lavas within the Pitcairn-Gambier hotspot chain, as proposed by 184 185 Cordier et al. (2021). The lack of strongly elevated Ce/Pb and Nb_N/Nb* ratios, producing a dissimilarity with the Muru group, indicates that a classical HIMU origin is unlikely for the Isla Isabel isotope 186 composition. 187



Supplementary Figure S4. Olivine compositions of Isla Isabel (Housh et al., 2010) compared to 189 190 literature data: a) CaO versus forsterite (Fo) content; b) NiO versus forsterite content. Isla Isabel olivines have low NiO and high CaO contents, overlapping with both olivines from MORB (Sobolev et al., 2007) 191 and the TMVB (Díaz-Bravo et al., 2014). These data are consistent with derivation of Isla Isabel lavas 192 from partial melting of peridotite source (e.g., high CaO, low NiO; Díaz-Bravo et al., 2014). The 193 194 recycling of oceanic crust tends to generate hybrid pyroxenite mantle lithologies, which produce low CaO, high NiO olivines when melted, as observed in the Ko'olau (Hawai'i) and Gambier (French 195 Polynesia) olivines. The lack of evidence for a pyroxenite component in the Isla Isabel olivine 196 compositions argues against derivation of Isla Isabel lavas from recycled oceanic crust, and rather 197 198 implies the involvement of metasomatized mantle lithologies, for example with carbonatitic melts (McCoy-West et al., 2016; Weiss et al., 2016). 199

200

201 Literature data

- For comparison with the Isla Isabel data, literature values from lavas of different locations and origin were plotted.
- Figures 2, 3, and S2: MORB (Castillo et al., 2000; Niu et al., 2002; Debaille et al., 2006; Waters et al., 2011; Mougel et al., 2014; Mallick et al., 2019), TMVB (Pier et al., 1992; Petrone et al., 2003; ValdezMoreno et al., 2006; Díaz-Bravo et al., 2014), African and Arabian intraplate rocks (Bertrand et al., 2003; Lucassen et al., 2008; Rooney et al., 2014), St. Helena (Hanyu et al., 2014) and Mangaia (Woodhead, 1996; Nebel et al., 2013)
- Supplementary Figure S3: DMM (Salters and Stracke, 2004), Pacific islands (Cordier et al., 2021), St.
 Helena (DIGIS Team, 2021), Mangaia (DIGIS Team, 2021), Isla Isabel (Housh et al., 2010)
- Supplementary Figure S4: MORB (Sobolev et al., 2007), Koolau (Sobolev et al., 2007), Gambier
 (Delavault et al., 2015), TMVB (Díaz-Bravo et al., 2014), Mangaia (Herzberg et al., 2014), Isla Isabel
- 213 (Housh et al., 2010)
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215 Supplementary References

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