



**HAL**  
open science

# The Mercury Isotopic Composition of Earth's Mantle and the Use of Mass Independently Fractionated Hg to Test for Recycled Crust

Frederic Moynier, Matthew G Jackson, Ke Zhang, Hongming Cai, Saemundur Ari Halldórsson, Raphael Pik, James M D Day, Jiubin Chen

► **To cite this version:**

Frederic Moynier, Matthew G Jackson, Ke Zhang, Hongming Cai, Saemundur Ari Halldórsson, et al.. The Mercury Isotopic Composition of Earth's Mantle and the Use of Mass Independently Fractionated Hg to Test for Recycled Crust. *Geophysical Research Letters*, In press, 10.1029/2021GL094301 . hal-03321622

**HAL Id: hal-03321622**

**<https://hal.science/hal-03321622v1>**

Submitted on 17 Aug 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1           **The Mercury Isotopic Composition of Earth's Mantle and the Use of Mass**  
2           **Independently Fractionated Hg to Test for Recycled Crust**

3   **Frédéric Moynier<sup>1,2\*</sup>, Matthew G. Jackson<sup>3</sup>, Ke Zhang<sup>4</sup>, Hongming Cai<sup>4</sup>, Sæmundur Ari**  
4   **Halldórsson<sup>5</sup>, Raphael Pik<sup>6</sup>, James M.D. Day<sup>7</sup>, Jiubin Chen<sup>2,4\*</sup>**

5   <sup>1</sup>Université de Paris, Institut de Physique du Globe de Paris, CNRS, 1 rue Jussieu, Paris 75005, France

6   <sup>2</sup>State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University  
7   of Geosciences, Wuhan 430074, China

8   <sup>3</sup>Department of Earth Science, University of California, Santa Barbara, CA 93106

9   <sup>4</sup>Institute of Surface-Earth System Science, Tianjin University

10   <sup>5</sup>Nordic Volcanological Center, Institute of Earth Sciences, University of Iceland, Reykjavík, Iceland.

11   <sup>6</sup>Centre de Recherche Pétrographique et Géochimique, CNRS, Université de Lorraine, Nancy.

12   <sup>7</sup>Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093-0244, USA

13  
14   \*Corresponding authors:

15   Corresponding authors: Frederic Moynier ([moynier@ipgp.fr](mailto:moynier@ipgp.fr)) and Jiubin Chen  
16   ([jbchen@tju.edu.cn](mailto:jbchen@tju.edu.cn))

17   **Key Points:**

- 18       • The Hg isotopic composition of the primitive mantle determined by analysing lavas from  
19       the Samoa and Iceland hotspots  
20       • Key samples from the canonical mantle endmember analyzed to track crustal recycling in  
21       the mantle.  
22       • We demonstrate the presence of recycled oceanic and continental materials in the source  
23       of ocean island basalts.

24

25

26 **Abstract**

27 **The element mercury (Hg) can develop large mass-independent fractionation (MIF) ( $\Delta^{199}\text{Hg}$ )**  
28 **due to photo-chemical reactions at Earth's surface. This results in globally negative  $\Delta^{199}\text{Hg}$**   
29 **for terrestrial sub-aerially-derived materials and positive  $\Delta^{199}\text{Hg}$  for sub-aqueously-derived**  
30 **marine sediments. The mantle composition least affected by crustal recycling is estimated**  
31 **from high- $^3\text{He}/^4\text{He}$  lavas from Samoa and Iceland, providing an average of**  
32  **$\Delta^{199}\text{Hg}=0.00\pm 0.10$ ,  $\Delta^{201}\text{Hg}=-0.02\pm 0.09$ ,  $\delta^{202}\text{Hg}=-1.7\pm 1.2$ ; 2SD, N=11. By comparison, a**  
33 **HIMU-type lava from Tubuai exhibits positive  $\Delta^{199}\text{Hg}$ , consistent with altered oceanic crust**  
34 **in its mantle source. A Samoan (EM2) lava has negative  $\Delta^{199}\text{Hg}$  reflecting incorporation of**  
35 **continental crust materials into its source. Three Pitcairn lavas exhibit positive  $\Delta^{199}\text{Hg}$  which**  
36 **correlate with  $^{87}\text{Sr}/^{86}\text{Sr}$ , consistent with variable proportions of continental (low  $\Delta^{199}\text{Hg}$  and**  
37 **high  $^{87}\text{Sr}/^{86}\text{Sr}$ ) and oceanic (high  $\Delta^{199}\text{Hg}$  and low  $^{87}\text{Sr}/^{86}\text{Sr}$ ) crustal material in their mantle**  
38 **sources. These observations indicate that MIF signatures offer a powerful tool for examining**  
39 **atmosphere-deep Earth interactions.**

40

41 **Plain language summary:**

42 **While Earth's mantle is continuously chemically and isotopically stirred by convection, some**  
43 **ocean island lavas preserve isotopic anomalies. Their most likely origin is the recycling of**  
44 **crustal material into Earth's mantle by subduction. A question is then whether these crustal**  
45 **materials originate from the ocean or the continents. By using mercury stable isotopic**  
46 **compositions, which have specific signatures in ocean and continent materials, we identify**  
47 **whether these anomalies are due to continental or oceanic crustal material in various ocean**  
48 **island basalts.**

49

**50 1 Introduction**

51 The composition of Earth's mantle is in part known through the chemical and isotopic analyses  
52 of lavas from different tectonic settings such as mid-ocean ridge basalts (MORB) and ocean  
53 island basalts (OIB) [e.g. Hofmann, 2013]. The variable isotopic compositions of OIB are  
54 usually interpreted to reflect mantle heterogeneity formed by recycling of surface material back  
55 into the mantle through subduction, the contribution of Earth's core into the deep source of  
56 certain lavas, or the survival of early-formed heterogeneities in the mantle [e.g. Hauri and Hart,  
57 1993; Hofmann, 1997; Hofmann and White, 1982; Mukhopadhyay and Parai, 2019; Mundl-  
58 Petermeier et al., 2020; Rizo et al., 2019]. Identifying the geological origin of such mantle  
59 sources is paramount to understand mantle dynamics through time.

60 Mantle heterogeneities have been defined and traditionally traced by using radiogenic isotopes  
61 such as Sr, Nd, Hf and Pb [e.g. Blichert-Toft et al., 1999; Blichert-Toft et al., 2003; Chauvel et  
62 al., 1992; Hofmann, 1988; 1997; White and Hofmann, 1982; Zindler and Hart, 1986], and  
63 several end-members have been defined : EM-1 (Enriched-Mantle 1, intermediate  $^{87}\text{Sr}/^{86}\text{Sr}$  and  
64 low  $^{206}\text{Pb}/^{204}\text{Pb}$ ), EM-2 (Enriched-Mantle 2, high  $^{87}\text{Sr}/^{86}\text{Sr}$  and intermediate  $^{206}\text{Pb}/^{204}\text{Pb}$ ), and  
65 HIMU (defined by low  $^{87}\text{Sr}/^{86}\text{Sr}$  and high  $^{206}\text{Pb}/^{204}\text{Pb}$ ). There is a general consensus emerging for  
66 the origin of EM-2 from continental crust materials (e.g. Jackson et al., 2007; White and  
67 Hofmann, 1982) and HIMU as oceanic crust and lithosphere or marine carbonates (e.g. Cabral et  
68 al., 2013; Chauvel et al., 1992; Hofmann and White, 1982), but the origin of EM-1 is debated  
69 (e.g. continental crust, pelagic sediments, delaminated sub-continental lithosphere or a common  
70 origin with EM-2 as terrestrial sediments; Castillo, 2017; Delavault et al., 2016; Eisele et al.,  
71 2012; Garapic et al., 2015) and understanding its origin represents an important challenge. Stable

72 isotope systems can give complementary information to radiogenic systems, but the potential  
73 sources of isotopic fractionation are diverse (e.g. magmatic differentiation, surficial processes),  
74 and their interpretation can be somewhat ambiguous.

75 A few stable isotope systems, the most notable being S, O and Hg, exhibit mass-independent  
76 isotopic fractionations (MIF) in naturally-occurring mantle-derived samples that are not strongly  
77 modified by high temperature processes [e.g. Cabral et al., 2013; Delavault et al., 2016; Moynier  
78 et al., 2020]. For example, the presence of MIF sulfur in Mangaia (Cook Islands, Polynesia) and  
79 Pitcairn lavas demonstrated the presence of an Archean atmosphere-derived sulfur component in  
80 their mantle source [Cabral et al., 2013; Delavault et al., 2016]. Mercury is the most volatile  
81 among the moderately volatile elements [Lodders, 2013] and exhibits large mass-dependent  
82 isotopic fractionations (MDF) and MIF. The MIF-Hg signatures of odd isotopes (odd-MIF) are  
83 due to magnetic isotope effects [e.g. Bergquist and Blum, 2007], or a nuclear field shift effect  
84 [Estrade et al., 2009] in surficial environments [e.g. Bergquist and Blum, 2007; Blum et al.,  
85 2013; Chen et al., 2012; Estrade et al., 2010; Foucher and Hintelmann, 2006; Sherman et al.,  
86 2010; Sonke et al., 2010], producing  $> \%$  effects. High temperature processes such as magmatic  
87 degassing produce limited ( $<10\text{ppm}$ ) Hg-MIF [Moynier et al., 2020].

88 Mercury isotopes are mass-independently fractionated in surface samples and exhibit specific  
89 signatures related to different environments, showing potential application to study the nature of  
90 recycled materials in the mantle sources of lavas. This is due to the distinct MIF signatures of  
91 terrestrial surface environments whereby sub-aerially formed terrestrial reservoirs having  
92 generally negative odd-isotopes MIF [e.g. Blum et al., 2014] while the oceanic environment,  
93 including sediments and seawater, shows positive odd-isotope MIF [Meng et al., 2020; Meng et  
94 al., 2019; Yin et al., 2015]. In particular, it may be possible to test whether EM1 lavas sample a

95 component of deeply recycled terrestrial sediments [Castillo, 2017; Eisele et al., 2012; Garapic et  
96 al., 2015].

97 A recent landmark study showed that Hg from gold deposits associated with arc magmatism had  
98 positive odd-isotope MIF associated with recycling of marine Hg from the subduction zone into  
99 the mantle source of arc lavas [Deng et al., 2020]. This highlights the utility for Hg isotopes to  
100 serve as a tracer of deep recycling processes, from subduction zones to hotspots. Here, we test  
101 the origin of the material present in various end-member signatures (EM1, EM2, and HIMU) of  
102 OIB using Hg isotopes.

103 Due to the high volatility of mercury, constraints on its isotopic composition within Earth's  
104 mantle are critical for evaluating the origin of terrestrial volatile elements by means of  
105 comparison with the isotopic composition of primitive meteorites [Meier et al., 2016; Moynier et  
106 al., 2020]. However, the Hg isotopic composition of the mantle has been estimated from only  
107 four basaltic rocks [Geng et al., 2018; Moynier et al., 2020], and these samples may not be  
108 ideally suited for evaluating the composition of the primitive mantle. A primary hurdle for Hg  
109 isotopic characterization of mantle-derived lavas is their low Hg contents (a few ppb). We have  
110 recently developed a method that yields high precision data on less than 5ng of Hg, which  
111 enables isotope characterization with just a few grams of material [Moynier et al., 2020]. This  
112 allows targeting of a key set of mantle-derived lavas to evaluate the Hg isotopic composition of  
113 the mantle least impacted by crustal recycling, and place key constraints on the origin of the  
114 volatile element Hg on Earth.

115 To evaluate the Hg isotopic composition of the mantle least affected by crustal recycling, we  
116 selected lavas with least degassed signatures reflected by their high- $^3\text{He}/^4\text{He}$  ( $>13$  atmospheric

117 ratio,  $R_A$ ), including four samples from Samoa [Jackson et al., 2007], and seven from Iceland  
118 [Füri et al. 2010 and Halldórsson et al. 2016b]. To further characterize the composition of the  
119 mantle we analysed three additional Icelandic samples [Óskarsson et al. 1982] and six basalts  
120 from the Afar (Ethiopia) [Deng et al., 2018; Pik et al., 2006]. To search for deep recycling of  
121 surface-derived Hg, samples from the three canonical mantle endmembers thought to reflect  
122 deep recycling of crustal materials: EM1 (Pitcairn, N=3), HIMU (Tubuai, N=1), EM2 (Samoa,  
123 N=1) were selected.

## 124 **2 Materials and Methods**

### 125 **2.1 Sample descriptions**

126 We report isotopic data on international rock standards to assess data quality and intra-laboratory  
127 data comparisons: USGS samples: BCR-2 (basalt, USA), RGM-2 (Rhyolite, USA) and STM-2  
128 (syenite, USA) and three Icelandic samples used as internal standards at the University of  
129 Iceland (I-ICE, A-ALK, B-ALK, Óskarsson et al. 1982), all of which are available upon request.  
130 The Hg isotopic composition of BCR-2 has been reported previously [Geng et al., 2018]. One  
131 trachyandesite from the Samoa hotspot (ALIA-115-21) [Adams et al., 2021], three basalt  
132 samples from Pitcairn [Garapic et al., 2015], and one basalt sample from Tubuai [Hauri and Hart,  
133 1993] were selected to represent the EM2, EM1 and HIMU mantle end-members, respectively.  
134 Four samples from Ofu island (Samoa [Jackson et al., 2007]) and seven samples from several  
135 different regions (Eastern Rift Zone, Reykjanes Peninsula, Western Rift Zone, and Northern Rift  
136 Zone) of Iceland [Halldórsson et al., 2016ab; Jackson et al., 2020; Macpherson et al., 2005;  
137 Rasmussen et al., 2019] were taken to represent the high- $^3\text{He}/^4\text{He}$  mantle ( $>13R_A$ ). Six basalt  
138 samples from the Stratoid Series in the Afar hotspot [Deng et al., 2018; Pik et al., 2006] were

139 selected to further estimate the mantle composition. While the  $^3\text{He}/^4\text{He}$  of the Afar samples have  
140 not been characterized, the composition of samples from this region is  $\sim 10\text{-}13 R_A$  [Marty et al.,  
141 1996; Medynsky et al., 2013]. The UM-Almedén cinnabar standard was also analysed for inter-  
142 laboratory comparison.

## 143 **2.2 Methods**

144 The method follows the same protocol as in Moynier et al. [2020]. The Hg isotopic analysis was  
145 carried out using a MC-ICP-MS (Nu-Plasma-3D, Nu-Instruments) [Chen et al., 2010; Huang et  
146 al., 2015; Yuan et al., 2018; Zhang et al., 2020]. The instrumental mass bias was corrected by an  
147 internal NIST-SRM-997-Tl standard using the standard-sample bracketing method. All samples  
148 were analyzed in three blocks (33 cycles). A 10-minute washout time in between samples



149 ensured blank levels <0.2% of the preceding sample signals. Signal intensities were 2.5V on  
 150  $^{202}\text{Hg}$  (1 ppb solution).

151 The data for Hg-MDF is reported as  $\delta^x\text{Hg}$  :

$$152 \quad \delta^x\text{Hg} (\%) = [({}^x\text{Hg}/{}^{198}\text{Hg})_{\text{sample}} / ({}^x\text{Hg}/{}^{198}\text{Hg})_{\text{NIST SRM 3133}} - 1] \times 1000 \quad (\text{Eq. 1})$$

153 where x refers to 199, 200, 201, or 202.  $\delta^{202}\text{Hg}$  is used for the discussion of MDF. The MIF data  
 154 are defined as the deviation of the  $\delta^x\text{Hg}$  from the theoretical value based on kinetic isotopic  
 155 fractionation [e.g. Blum and Johnson, 2017]:

$$156 \quad \Delta^x\text{Hg} (\%) = \delta^x\text{Hg} (\%) - \beta^x \times \delta^{202}\text{Hg} \quad (\text{Eq. 2})$$

157 where the mass dependent scaling factor  $\beta^x$  is 0.2520, 0.5024 and 0.7520 for  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$  and  
 158  $^{201}\text{Hg}$ , respectively.

159 Errors are reported as twice the standard deviation from the replicates of the same solution, and  
 160 are typically 0.08‰, 0.03‰, 0.03‰, 0.05‰ for  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ,  
 161 respectively. Long-term measurements of UM-Almadén Hg and CRM-GBW07405 standards  
 162 give identical values for Hg isotopic composition (both MDF and MIF) to literature [Chen et al.  
 163 2010; Moynier et al. 2020; Huang et al. 2019], attesting the quality of Hg isotope analysis.

### 164 **3 Results**

165 Isotopic data for samples are reported in Table S1 and the  $\Delta^{199}\text{Hg}$  values are reported  
 166 against  $\delta^{202}\text{Hg}$  values in Figure 1. The isotopic composition of BCR-2 is identical within error to  
 167 literature values [Geng et al., 2018].

168 The terrestrial igneous rock samples show variable  $\delta^{202}\text{Hg}$  values, from -3.23 to -0.01,  
169 consistent with literature data [Geng et al., 2018; Moynier et al., 2020] (Figure 1). High  $^3\text{He}/^4\text{He}$   
170 localities - Ofu island and Iceland- do not exhibit any MIF, and the Afar samples also lack MIF-  
171 Hg signatures. By contrast, the HIMU sample from Tubuai has a positive odd-isotope-MIF  
172 ( $\Delta^{199}\text{Hg}=+0.23\pm 0.07$ ). The extreme EM2 Samoa ALIA-115-21 sample has a distinct negative odd-  
173 isotope-MIF signature ( $\Delta^{199}\text{Hg}=-0.14\pm 0.02$ ). In the Pitcairn lava suite, there is a positive  
174 correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and MIF-Hg: two Pitcairn lavas with the less extreme EM1 signatures  
175 have clear negative odd-isotope-MIF-Hg ( $\Delta^{199}\text{Hg}$  down to  $-0.45\pm 0.01$ ), while the Pitcairn sample  
176 with the most extreme EM1 signature has no resolvable MIF (Figure 2). No samples exhibit even-  
177 isotope-MIF signatures.

## 178 **4. Discussion**

### 179 **4.1 The isotopic composition of the primitive mantle.**

180 Before discussing the potential effects of recycling of surficial material on the Hg isotopic  
181 composition of mantle sources, it is critical to establish the composition of the primitive mantle.  
182 OIB with the highest  $^3\text{He}/^4\text{He}$  are inferred to sample mantle sources that are least degassed [Craig  
183 and Lupton, 1976; Mukhopadhyay and Parai, 2019] and the least modified by crustal recycling  
184 [Jackson et al., 2020; White, 2015]. Making the assumption that these samples represent materials  
185 with Hg isotopic compositions consistent with the most “pristine” mantle domain, we can then  
186 establish the impact of crustal subduction and recycling on the Hg systematics of mantle-derived  
187 lavas.

188 The Ofu island samples have high- $^3\text{He}/^4\text{He}$  ( $22R_A$  to  $34R_A$ , see Table S1) [Jackson et al.,  
189 2007] and are inferred to sample an ancient mantle domain [Mundl-Petermeier et al., 2020] less  
190 impacted by crustal recycling than other Samoan lavas [Jackson et al., 2020]. Given that the high-

191  $^3\text{He}/^4\text{He}$  reservoir is least impacted by recycling, and the discovery that some high- $^3\text{He}/^4\text{He}$  lavas  
192 preserve early-Hadean signatures identified using several different short-lived isotope systems -  
193  $^{129}\text{Xe}/^{130}\text{Xe}$  [Mukhopadhyay and Parai, 2019],  $^{142}\text{Nd}/^{144}\text{Nd}$  [Peters et al., 2018], and  $^{182}\text{W}/^{184}\text{W}$   
194 [Mundl-Petermeier et al., 2020; Rizo et al., 2019]-this mantle reservoir is most likely to preserve  
195 signatures associated with terrestrial accretion. Indeed, arguments have been made that the high-  
196  $^3\text{He}/^4\text{He}$  reservoir is the oldest domain that has survived in Earth's mantle [Giuliani et al., 2020;  
197 Jackson et al., 2010] but alternative views exist [e.g. Mukhopadhyay and Parai, 2019]. Therefore,  
198 the absence of Hg-MIF in the high- $^3\text{He}/^4\text{He}$  samples suggests that Earth's mantle accreted Hg  
199 devoid of MIF, and therefore any observed MIF are the consequence of terrestrial fractionation.  
200 Combining Hg isotope data from the Ofu (N=4) with Iceland samples for which  $^3\text{He}/^4\text{He}$  are  
201 available (N=7, all of which have  $13 < ^3\text{He}/^4\text{He} < 34$ ), return an average Hg isotopic composition for  
202 the mantle of  $\Delta^{199}\text{Hg}=0.00\pm 0.10$  and  $\Delta^{201}\text{Hg}=-0.02\pm 0.09$  (2SD, N=11). This represents the  
203 current best estimate of the terrestrial "primitive mantle" composition. The  $\delta^{202}\text{Hg}$  values are more  
204 variable within these samples. Since Hg is highly volatile, degassing during magma ascent can  
205 induce isotopic fractionation [e.g. Zambardi et al. 2009], and further isotopic fractionation could  
206 also occur during igneous processes. Therefore, compared to MIF-Hg signatures, which should  
207 not be significantly impacted by high temperature magmatic and degassing processes, the  $\delta^{202}\text{Hg}$   
208 values are likely more impacted by the processes leading to the formation of the basalts.  
209 Nevertheless, the  $\delta^{202}\text{Hg}$  of the 11 high- $^3\text{He}/^4\text{He}$  samples from Ofu island and Iceland show limited  
210 variation, with an average  $-1.7\pm 1.2$  (2SD, N=11), which compare well with a previous estimate of  
211 the mantle composition based on only a few unrelated igneous rocks ( $\delta^{202}\text{Hg} < -2.35$ , [Moynier et  
212 al., 2020], see Figure S1). Furthermore, samples from the Afar ( $^3\text{He}/^4\text{He} \sim 10\text{-}13 \text{ Ra}$ , [Marty et al.,

213 1996; Medynsky et al., 2013]) (N=6) have similar Hg isotopic composition within error,  
214 suggesting a large-scale homogeneity of Earth's modern mantle.

215 Our estimate of the primitive mantle Hg isotopic composition falls within the range defined  
216 by chondrites (Figure 3). While the large uncertainties on the Hg concentration of the Earth's  
217 mantle prevent an accurate estimate the amount of terrestrial Hg that is stored into the Earth's core,  
218 the present chondritic isotopic composition of the Earth's primitive mantle is an argument that late  
219 accretion of chondritic material delivered the present mantle Hg (and other volatile elements) (see  
220 discussion in Moynier et al. [2020]). This conclusion is consistent with observations made from  
221 C, N and noble gas isotopes [Marty, 2012] and the volatile and chalcophile elements S, Se and Te  
222 [Wang and Becker 2013; Varas-Reus et al. 2019].

223

#### 224 **4.2. Evidence for Hg recycling?**

225 Considering the Hg isotopic composition of high- $^3\text{He}/^4\text{He}$  lavas defined above as representative of  
226 the mantle domains the least modified by crustal recycling, we can compare our estimate for the  
227 Hg isotopic composition for low- $^3\text{He}/^4\text{He}$  mantle endmembers that are suggested to host recycled  
228 surface materials—EM1 Pitcairn (EM1), Samoa (EM2), and Tubuai (HIMU)—and then identify  
229 Hg isotope signatures associated with recycling in the mantle sources of these lavas.

230 Three OIB samples examined in this study that represent mantle end-member  
231 compositions— TBA-B3 (Tubuai HIMU), ALIA-115-21 (Samoa EM2), and two Pitcairn lavas  
232 (Pit-6 and Pit-8)—show clearly resolvable odd-MIF. The correlation between  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$   
233 values with a slope of  $\sim 1$  (Figure 4), typical of surface photochemical reactions on Hg [Bergquist  
234 and Blum, 2007], suggests that the three samples share likely a similar origin for the MIF  
235 signatures in surficial environments. The Hg-MIF signatures in OIB therefore provides evidence

236 for recycling of shallow geochemical reservoirs into the deep sources of hotspots. This correlation  
237 between  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  values also provides further confidence on the quality of the data as  
238 isobaric interference would produce isotopic signatures that lie outside of this range.

239 Photochemical reduction of aqueous  $\text{Hg(II)}$  to  $\text{Hg(0)}$  vapor is the major source of odd-MIF,  
240 and is the main pathway of transfer of Hg from the ocean (surface) to the atmosphere [e.g.  
241 Bergquist and Blum, 2007]. During the photochemical reduction, a positive  $\Delta^{199}\text{Hg}$  [ $\text{Hg(II)}$ ] is  
242 retained in the marine environment while the complementary negative  $\Delta^{199}\text{Hg}$  [ $\text{Hg(0)}$ ] is released  
243 into the atmosphere [e.g. Bergquist and Blum, 2007]. Given the short residence time of  $\text{Hg(0)}$  in  
244 the atmosphere ( $\sim 1$  year), its quick subsequent deposition confers a globally negative  $\Delta^{199}\text{Hg}$  to  
245 the terrestrial reservoirs, while marine environments are characterized by positive  $\Delta^{199}\text{Hg}$  [e.g.  
246 Biswas et al., 2008; Blum et al., 2014; Demers et al., 2015; Grasby et al., 2017; Jiskra et al., 2017].  
247 How a negative  $\Delta^{199}\text{Hg}$  preserved in terrestrial material is then transported into the ocean through  
248 time is unclear at present. Further work is required to test the robustness of this negative signature  
249 on long timescales necessary for this material to be recycled within the mantle. This difference  
250 between terrestrial and marine settings is well reflected in sediments, with generally negative  
251  $\Delta^{199}\text{Hg}$  in coastal sediments (which originate via erosion of nearby terrestrial materials) and  
252 positive  $\Delta^{199}\text{Hg}$  for open sea marine sediments [e.g. Meng et al., 2019; Yin et al., 2015]. The odd-  
253 MIF of ALIA-115-21 (Samoa EM2), TBA-B3 (Tubuai HIMU), and Pit-6 and Pit-8 (Pitcairn)  
254 therefore likely reflect a marine Hg isotopic signature in Tubuai, and continental Hg signatures  
255 Samoan EM2 lavas (Figure 4). As discussed below, Pitcairn lavas exhibit Hg isotopic evidence for  
256 recycled marine and terrestrial materials.

257 The presence of marine and continental signatures in the mantle sources of Tubuai HIMU and  
258 Samoa EM2 lavas, respectively, is consistent with traditional interpretations based on radiogenic

259 isotope signatures. Tubuai exhibits a HIMU signature, which is considered to result from recycling  
260 of ancient oceanic crust into the mantle [Hofmann and White, 1982]. The geochemically-depleted  
261  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  signatures in HIMU lavas globally precludes a significant sediment  
262 (terrigenous or marine) contribution to their mantle sources, but transfer of positive  $\Delta^{199}\text{Hg}$  isotope  
263 compositions of seawater to oceanic crust during hydrothermal circulation at a mid-ocean ridge  
264 could explain the MIF signatures in Tubuai HIMU OIB. A potential caveat with this model is the  
265 low abundance of Hg in seawater compared to fresh basalts that would require a water/rock ratio  
266 of  $\sim 1000$  to transfer the Hg isotopic composition of seawater to oceanic crust. However, the  
267 absence of data on Hg behavior during seawater alteration of oceanic crust (e.g., Hg concentration  
268 measurements on altered oceanic crust, including serpentinites) limits our ability to quantitatively  
269 model this scenario. An additional complexity is that a fraction of the slab Hg budget would be  
270 lost during subduction dehydration, but relevant data are not yet available to quantify this. By  
271 contrast, Samoan EM2 lavas exhibit geochemically-enriched (high)  $^{87}\text{Sr}/^{86}\text{Sr}$  and (low)  $^{143}\text{Nd}/^{144}\text{Nd}$   
272 signatures consistent with the input of recycled terrigenous materials [Jackson et al., 2007;  
273 Workman et al., 2008], consistent with the slightly negative  $\Delta^{199}\text{Hg}$  terrestrial signature.

274 The presence of negative  $\Delta^{199}\text{Hg}$  in the source of Pitcairn EM1 OIB suggests that, like EM2,  
275 EM1 contains a fraction of recycled terrigenous material [Castillo, 2017; Delavault et al., 2016;  
276 Stracke, 2012]. However, there is complexity in the MIF present in the Pitcairn suite that is not  
277 explained by our simple model: the correlation between the  $\Delta^{199}\text{Hg}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  for the three  
278 Pitcairn samples (Figure 2) is puzzling, as we would expect the sample with the highest  $^{87}\text{Sr}/^{86}\text{Sr}$   
279 to host the largest fraction of continent-derived material and, therefore, the lowest  $\Delta^{199}\text{Hg}$ . Instead,  
280 the Pitcairn lava with the weakest EM1 signature has the strongest negative  $\Delta^{199}\text{Hg}$ , and the most  
281 extreme EM1 Pitcairn lava has no resolvable  $\Delta^{199}\text{Hg}$  signature. The positive correlation between

282  $\Delta^{199}\text{Hg}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  is unlikely to be explained by seawater alteration, a mechanism that would  
283 increase both  $\Delta^{199}\text{Hg}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ . This is because 1)  $\Delta^{199}\text{Hg}$  also exhibit a negative correlation  
284 with  $^{143}\text{Nd}/^{144}\text{Nd}$  (Figure S2), a radiogenic isotope system immune to seawater influence, and 2)  
285 the selected Pitcairn lavas are young ( $<1.0\text{Ma}$ ; [Duncan et al., 1974]) and fresh (i.e., no signs of  
286 visible alteration). Therefore, we explore a mantle source origin for the correlation between  
287  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\Delta^{199}\text{Hg}$ , acknowledging that this relationship is only for three samples.

288 Unlike Samoan EM2 (which is a melt of a peridotite mantle source that hosts recycled  
289 terrigenous material) [Jackson and Shirey, 2011] and Tubuai HIMU (which is a melt of a  
290 mantle source with recycled oceanic crust) [Hauri and Hart, 1993], extreme Pitcairn EM1 is  
291 suggested to host both recycled oceanic crust and terrigenous materials [Eisele et al., 2003]. A  
292 mixture of both recycled oceanic crust and terrigenous materials can help to explain the correlation  
293 between  $\Delta^{199}\text{Hg}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  (Figure 2), where Pitcairn's extreme EM1 endmember  
294 (highest  $^{87}\text{Sr}/^{86}\text{Sr}$ ) lacks a clear odd-MIF, and the Pitcairn lava with the weakest EM1 signature  
295 (lowest  $^{87}\text{Sr}/^{86}\text{Sr}$ ) has a negative  $\Delta^{199}\text{Hg}$ . Because recycled oceanic crust and terrigenous materials  
296 have complementary positive and negative  $\Delta^{199}\text{Hg}$  signatures, respectively, it is possible for their  
297 mixture to generate in a near-zero  $\Delta^{199}\text{Hg}$  value like that observed in the extreme Pitcairn EM1  
298 sample. In this case, the presence of terrigenous materials explains the high  $^{87}\text{Sr}/^{86}\text{Sr}$  in the extreme  
299 EM1 Pitcairn lava. In contrast, the Pitcairn lava with the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  (weakest EM1  
300 signature) is explained by a smaller fraction of recycled terrigenous material, and the very negative  
301  $\Delta^{199}\text{Hg}$  in this lava can explained by the absence (or near absence) of oceanic crust (which would  
302 have a positive  $\Delta^{199}\text{Hg}$  values): the remaining contribution of recycled terrigenous material has  
303 strongly negative  $\Delta^{199}\text{Hg}$ , and explains the negative  $\Delta^{199}\text{Hg}$  values determined in lavas. In this  
304 way, the relative proportions and absolute abundances of recycled terrigenous and oceanic crust

305 materials can be modulated to explain the magnitude and sign of the  $\Delta^{199}\text{Hg}$  values, and its  
306 relationship with radiogenic isotopes.

307

## 308 **5. Conclusions**

309 To estimate the Hg isotopic composition of the mantle that is least affected by crustal  
310 recycling, we analysed high- $^3\text{He}/^4\text{He}$  lavas from Samoa and Iceland. We obtained an average  
311  $\Delta^{199}\text{Hg}=0.00\pm 0.10$ ,  $\Delta^{201}\text{Hg}=-0.02\pm 0.09$  and  $\delta^{202}\text{Hg}=-1.7\pm 1.2$  (2SD, N=11), which is the best  
312 estimate for the composition of the primitive mantle.

313 HIMU lavas from Tubuai exhibit positive Hg-MIF, likely reflecting a transfer of the  
314 isotope compositions of seawater to oceanic crust during hydrothermal circulation at a mid-ocean  
315 ridge; positive Hg-MIF therefore signals the presence of altered oceanic crust in its mantle source.  
316 The negative MIF observed for EM2 lava from Samoa is consistent with assimilation of  
317 continental crust material. The negative MIF for the Pitcairn lavas, and the positive correlation of  
318  $\Delta^{199}\text{Hg}$  values with  $^{87}\text{Sr}/^{86}\text{Sr}$ , provides an independent argument in favor of mixture between  
319 terrestrial and marine materials in the mantle source of EM1.

## 320 **Acknowledgments, Samples, and Data**

321 Runsheng Yin and Michael Bizimis are thanked for insightful reviews that have improved this  
322 manuscript. This study was supported by the National Natural Science Foundation of China  
323 (41625012, 41961144028, U1612442, 41830647) to JB.C and by the China National Space  
324 Administration (No. D020205) to ZW. FM thanks Yongsheng Liu for making the visit at CUG  
325 Wuhan possible. MGJ thanks IGP for providing a stimulating academic home during sabbatical,  
326 and acknowledges partial support from NSF EAR-1900652 and OCE-1928970.

## 327 **Open Research section**



328 All the data are presently provided as a supplementary table and will be deposit on the CNRS HAL  
329 website as well as on the database Earthchem: <https://earthchem.org/>

330  
331 **References:**

- 332 Adams, J., J. M., F. Spera, A. Price, B. Byerly, G. Seward, and J. Cottle (2021), Extreme isotopic  
333 heterogeneity in Samoan clinopyroxenes constrains sediment recycling, *Nature com.*, 12, 1234.  
334 Bergquist, B. A., and J. D. Blum (2007), Mass-dependent and-independent fractionation of Hg  
335 isotopes by photoreduction in aquatic systems, *Science*, 318, 417-420.  
336 Biswas, A., J. D. Blum, B. A. Bergquist, G. J. Keeler, and Z. Xie (2008), Natural mercury isotope  
337 variation in coal deposits and organic soils, *Env. Sci. & Tech.*, 42, 8303-8309.  
338 Blichert-Toft, J., F. A. Frey, and F. Albarède (1999), Hf isotope evidence for pelagic sediments in  
339 the source of Hawaiian basalts, *Science*, 285, 879-882.  
340 Blichert-Toft, J., D. Weis, C. Maerschalk, A. Agranier, and F. Albarède (2003), Hawaiian hot spot  
341 dynamics as inferred from the Hf and Pb isotope evolution of Mauna Kea volcano, *Geochem.*  
342 *Geophys. Geosyst.*, 4, doi:10.1029/2002GC000340.  
343 Blum, J., and M. Johnson, W. (2017), Recent developments in mercury stable isotopes analysis,  
344 in *Non-traditional stable isotopes*, edited by F.-Z. Teng, J. Watkins and N. Dauphas, pp. 733-757,  
345 Mineralogical society of America.  
346 Blum, J., B. Popp, J. Drazen, C. Choy, and M. Johnson (2013), Evidence for methylmercury  
347 production below the mixed layer in the central North Pacific Ocean, *Nat. Geosci.*, 6, 879-884.  
348 Blum, J., L. Sherman, and M. W. Johnson (2014), Mercury Isotopes in Earth and Environmental  
349 Sciences, *A. Rev. Earth and Plane. Sci.*, 42, 249-269.  
350 Cabral, R., M. Jackson, E. Rose-Koga, K. Koga, M. Whitehouse, M. Antonelli, J. Farquhar, J. Day,  
351 and E. Hauri (2013), Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of  
352 Archaean crust, *Nature*, 496, 490-493.  
353 Castillo, P. (2017), An alternative explanation for the Hf-Nd mantle array, *Science Bulletin*, 62,  
354 974-975.  
355 Chauvel, C., A. W. Hofmann, and P. Vidal (1992), HIMU-EM: The French Polynesian connection,  
356 *Earth Planet. Sci. Lett.*, 110, 99-119.  
357 Chen, J., H. Hintelmann, and B. Dimock (2010), Chromatographic pre-concentration of Hg from  
358 dilute aqueous solutions for isotopic measurement by MC-ICP-MS, *J. Anal. Atom. Spec.*, 25,  
359 1402-1409.  
360 Chen, J., H. Hintelmann, X. Feng, and B. Dimock (2012), Unusual fractionation of both odd and  
361 even mercury isotopes in precipitation from Peterborough, ON, Canada, *Geochim. Cosmochim.*  
362 *Acta*, 90, 33-46.  
363 Craig, H., and J. E. Lupton (1976), Primordial neon, helium, and hydrogen in oceanic basalts,  
364 *Earth Planet. Sci. Lett.*, 31, 369-385.  
365 Delavault, H., C. Chauvel, E. Thomassot, C. Devey, and B. Dazas (2016), Sulfur and lead isotopic  
366 evidence of relic Archean sediments in the Pitcairn mantle plume, *Proc. Nat. Ac. Sci.*, 113,  
367 12952-12956.

- 368 Demers, J. D., J. Blum, and D. Zac (2015), Mercury isotopes in a forested ecosystem:  
369 Implications for air-surface exchange dynamics and the global mercury cycle., *Adv. Earth Space*  
370 *Sci.* 27, 222-238.
- 371 Deng, C., G. Sun, Y. Rong, R. Sun, D. Sun, B. Lehmann, and R. S. Yin (2020), Recycling of mercury  
372 from the atmosphere-ocean system into volcanic arc associated epithermal gold systems.  
373 *Geology*, 49, 309–313.
- 374 Deng, Z., M. Chaussidon, P. Savage, F. Robert, R. Pik, and F. Moynier (2018), Titanium isotopes  
375 as a tracer for the plume or island arc affinity of felsic rocks, *Proc. Nat. Ac. Sci.*, 116, 1132-1135.
- 376 Duncan, R., McDougall, I., Carter, R., Coombs, D., 1974. Pitcairn island— another Pacific hot  
377 spot? *Nature* 251, 619–682.
- 378 Eisele, J., W. Abouchami, S. J. G. Galer, and A. W. Hofmann (2003), The 320 kyr Pb isotope  
379 evolution of Mauna Kea lavas recorded in the HSDP-2 drill core, *Geochem. Geophys. Geosyst.*,  
380 4, doi: 10.1029/2002GC000339.
- 381 Eisele, J., M. Sharma, S. J. G. Galer, J. Blichert-Toft, C. Devey, and A. W. Hofmann (2012), The  
382 role of sediment recycling in EM-1 inferred from Os, Pb, Hf, Nd, Sr isotope and trace element  
383 systematics of the Pitcairn hotspot, *Earth Planet. Sci. Lett.*, 196, 197-212.
- 384 Estrade, E., J. Carignan, J. E. Sonke, and O. Donard (2009), Mercury isotope fractionation during  
385 liquid-vapor evaporation experiments, *Geochim. Cosmochim. Acta*, 73, 2693-2711.
- 386 Estrade, N., J. Carignan, and O. Donard (2010), Isotope tracing of atmospheric mercury sources  
387 in an urban area of northeastern France, *Environ. Sci. Technol.*, , 44, 6062-6067.
- 388 Foucher, D., and H. Hintelmann (2006), High-precision measurement of mercury isotope ratios  
389 in sediments using cold-vapor generation multi-collector inductively coupled plasma mass  
390 spectrometry, *Anal. Bioanal. Chem.*, 384, 1470-1478.
- 391 Füre, E., D. Hilton, S. Halldórsson, P. Barry, D. Hahm, T. Fischer, and K. Grönvold (2010),  
392 Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: The role of  
393 He depletion, melt mixing, degassing fractionation and air interaction, *Geochim. Cosmochim.*  
394 *Acta*, 74, 3307–3332.
- 395 Garapic, G., M. Jackson, E. Hauri, S. R. Hart, K. A. Farley, J. Blusztajn, and J. Woodhead (2015), A  
396 radiogenic isotopic (He-Sr-Nd-Pb-Os) study of lavas from the Pitcairn hotspot: Implications for  
397 the origin of EM-1 (enriched mantle 1), *Lithos*, 228, 1-11.
- 398 Geng, H., R. S. Yin, and X. Li (2018), An optimized protocol for high precision measurement of  
399 Hg isotopic compositions in samples with low concentrations of Hg using MC-ICP-MS, *J. Anal.*  
400 *Atom. Spec*, 33, 1932-1940.
- 401 Giuliani, A., M. G. Jackson, A. Fitzpyane, and H. Dalton (2020), Remnants of early Earth  
402 differentiation in the deepest mantle-derived lavas., *Proc. Nat. Ac. Sci*, 118, e2015211118.
- 403 Grasby, S. E., W. Shen, R. Yin, J. D. Gleason, J. D. Blum, and R. F. Lepak (2017), Isotopic  
404 signatures of mercury contamination in latest Permian oceans, *Geology*, 45, 55-58.
- 405 Halldórsson, S., J. Barnes, A. Stefánsson, D. Hilton, E. Hauri, and E. Marshall (2016a), Subducted  
406 lithosphere controls halogen enrichments in the Iceland mantle plume source, *Geology*, 44,  
407 679-682.
- 408 Halldórsson, S., D. Hilton, P. Barry, E. Füre, and K. Grönvold (2016b), Recycling of crustal material  
409 by the Iceland mantle plume: new evidence from nitrogen elemental and isotope systematics of  
410 subglacial basalts, *Geochim. Cosmochim. Acta*, 176, 206-226.

- 411 Hauri, E. H., and S. R. Hart (1993), Re-Os isotope systematics of EMII and HIMU oceanic basalts  
412 from the south Pacific Ocean, *Earth Planet. Sci. Lett.*, 114, 353-371.
- 413 Hofmann, A. W. (1988), Chemical differentiation of the Earth: the relationship between mantle  
414 continental crust, and oceanic crust, *Earth Planet. Sci. Letters*, 90, 297-314.
- 415 Hofmann, A. W. (1997), Mantle geochemistry: the message from oceanic volcanism, *Nature*,  
416 385, 219-229.
- 417 Hofmann, A. W. (2013), Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and  
418 Trace Elements, in *Treatise on Geochemistry*, edited by H. D. Holland and K. K. Turekian, pp. 61-  
419 101, Elsevier.
- 420 Hofmann, A. W., and W. M. White (1982), Mantle plumes from ancient oceanic crust, *Earth*  
421 *Planet. Sci. Lett.*, 57, 421-436.
- 422 Huang, Q., Y. Liu, J. Chen, X. Feng, W. Huang, S. Yuan, H. Cai, and X. Fu (2015), An improved  
423 dual-stage protocol to pre-concentrate mercury from airborne particles for precise isotopic  
424 measurement., *J. Anal. Atom. Spectr.*, 30, 957-966.
- 425 Huang, Q., Chen, J., Huang, W., Reinfeldt, J.R., Fu, P., Yuan, S., Wang, Z., Yuan, W., Cai, H.,  
426 Ren, H., 2019. Diel variation in mercury stable isotope ratios records photo-reduction of PM 2.5-  
427 bound mercury. *Atmos. Chem. Phys.* 10, 315-325.
- 428 Jackson, M., S. R. Hart, A. Koppers, H. Staudigel, J. Konter, J. Blusztajn, M. Kurz, and J. Russell  
429 (2007), The return of subducted continental crust in Samoan lavas, *Nature* 448, 684-687.
- 430 Jackson, M. G., et al. (2020), Ancient He and W isotopic signatures preserved in mantle domains  
431 least modified by crustal recycling, *PNAS*, 117, 30993-31001.
- 432 Jackson, M. G., R. Carlson, M. Kurz, P. D. Kempton, D. Francis, and J. Blusztajn (2010), Evidence  
433 for the survival of the oldest terrestrial mantle reservoir., *Nature*, 466, 853-856.
- 434 Jackson, M. G., and S. B. Shirey (2011), Re-Os isotope systematics in Samoan shield lavas and  
435 the use of Os-isotopes in olivine phenocrysts to determine primary magmatic compositions,  
436 *Earth Planet. Sci. Lett.*, 312, 91-101.
- 437 Jiskra, M., J. G. Wiederhold, U. Skjellberg, R. M. Kronberg, and R. Kretzschmar (2017), Source  
438 tracing of natural organic matter bound mercury in boreal forest runoff with mercury stable  
439 isotopes, *Environmental Science: Processes & Impacts*, 19, 1235-1248.
- 440 Macpherson, C. C., D. Hilton, J. Day, D. Lowry, and K. Gronvold (2005), High- $^3\text{He}/^4\text{He}$ , depleted  
441 mantle and low  $\text{d}^{18}\text{O}$ , recycled oceanic lithosphere in the source of central Iceland magmatism,  
442 *Earth Planet. Sci. Lett.*, 233, 411-427.
- 443 Marty, B. (2012), The origins and concentrations of water, carbon, nitrogen and noble gases on  
444 Earth, *Earth Planet. Sci. Lett.*, 314, 56-66.
- 445 Marty, B., R. Pik, and Y. Gezahegn (1996), Helium isotopic variations in Ethiopian plume lavas:  
446 nature of magmatic sources and limit on lower mantle contribution, *Earth Planet. Sci. Lett.*, 144,  
447 223-237.
- 448 Medynsky, S., et al. (2013), Control on magmatic cycles and development of rift topography of the  
449 Manda Hararo segment (Afar, Ethiopia): Insights from cosmogenic  $^3\text{He}$   
450 investigation of landscape evolution, *Earth Planet. Sci. Lett.*, 367, 133-145.
- 451 Meier, M., C. Cloquet, and B. Marty (2016), Mercury (Hg) in meteorites: Variations in  
452 abundance, thermal release profile, mass-dependent and mass-independent isotopic  
453 fractionation, *Geochim Cosmochim Acta*, 182, 55-72.

- 454 Meng, M., R. Sun, H. Liou, B. Yu, Y. Yin, L. Hu, J. Chen, J. Shi, and G. Jiang (2020), Mercury  
455 isotope variations within the marine food web of Chinese Bohai Sea: Implications for mercury  
456 sources and biogeochemical cycling, *J. of Haz. Mat.*, 384, 121379.
- 457 Meng, M., R. Y. Sun, H. W. Liu, B. Yu, Y. G. Yin, L. G. Hu, J. B. Shi, and G. B. Jiang (2019), An  
458 integrated model for input and migration of mercury in Chinese coastal sediments, *Environ. Sci.*  
459 *Technol.*, 53, 2460-2471.
- 460 Moynier, F., J. Chen, K. Zhang, H. Cai, Z. Wang, M. G. Jackson, and J. Day (2020), Chondritic  
461 mercury isotopic composition of Earth and evidence for evaporative equilibrium degassing  
462 during the formation of eucrites, *Earth Planet. Sci. Lett.*, 551, 116544.
- 463 Mukhopadhyay, S., and R. Parai (2019), Noble Gases: A Record of Earth's Evolution and Mantle  
464 Dynamics, *Annual Rev. Earth Planet. Sci.*, 47, 389-419.
- 465 Mundl-Petermeier, A., R. J. Walker, R. A. Fischer, V. Lekic, M. Jackson, and M. Kurz (2020),  
466 Anomalous  $^{182}\text{W}$  in high  $^3\text{He}/^4\text{He}$  ocean island basalts: fingerprints of Earth's core?, *Geochim.*  
467 *Cosmochim. Acta* 194–211.
- 468 Óskarsson, N., Sigvaldason, G.E., and Steinthorsson, S., 1982, A dynamic-model of rift-zone  
469 petrogenesis and the regional petrology of Iceland: *Journal of Petrology*, v. 23, p. 28–74, doi: 10  
470 .1093 /petrology /23 .1 .28.
- 471 Peters, B. J., R. Carlson, J. M. D. Day, and M. F. Horan (2018), Hadean silicate differentiation  
472 preserved by anomalous  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios in the Réunion hotspot source., 555, 89-93.
- 473 Pik, R., B. Marty, and D. Hilton (2006), How many mantle plumes in Africa? The geochemical  
474 point of view, *Chem. Geol.*, 226, 100-114.
- 475 Rasmussen, M. B., S. A. Halldórsson, S. A. Gibson, and G. H. Guðfinnsson (2019), Olivine  
476 chemistry reveals compositional source heterogeneities within a tilted mantle plume beneath  
477 Iceland, *Earth Planet. Sci. Lett.*, 531, 116008.
- 478 Rizo, H., D. Andrault, N. Bennet, M. Humayun, A. Brandon, I. Vlastelic, B. Moine, A. Poirier, M.  
479 Bouhifd, and D. Murphy (2019),  $^{182}\text{W}$  evidence for core-mantle interaction in the source of  
480 mantle plumes., *Geochem. Perspect. Lett.*, 11, 6-11.
- 481 Sherman, L., J. Blum, K. Johnson, G. Keeler, J. Barres, and T. Douglas (2010), Mass-independent  
482 fractionation  
483 of mercury isotopes in Arctic snow driven by sunlight, *Nat. Geosci.*, 3, 173-177.
- 484 Sonke, J., J. Schafer, J. Chmeleff, S. Audry, G. Blanc, and B. Dupre (2010), Sedimentary mercury  
485 stable isotope  
486 records of atmospheric and riverine pollution from two major European heavy metal refineries,  
487 *Chem. Geol.*, 279, 90-100.
- 488 Stracke, A. (2012), Earth's heterogeneous mantle: A product of convection-driven interaction  
489 between crust and mantle, *Chem. Geol.*, 330, 274-299.
- 490 Varas-Reus, M. I., S. König, A. Yierpan, J. P. Lorand, and R. Schoenberg (2019), Selenium  
491 isotopes as tracers of a late volatile contribution to Earth from the outer Solar System, *Nature*  
492 *Geosci.*, 12, 779–782.
- 493 Wang, Z. Z., and H. Becker (2013), Ratios of S, Se and Te in the silicate Earth require a volatile-  
494 rich late veneer, *Nature*, 499, 328-331.
- 495 White, W. (2015), Isotopes, DUPAL, LLSVPs, and Anekantavada., *Chem. Geol.*, 419, 10–28.
- 496 White, W. M., and A. W. Hofmann (1982), Sr and Nd isotope geochemistry of oceanic basalts  
497 and mantle evolution, *Nature*, 296, 821-825.

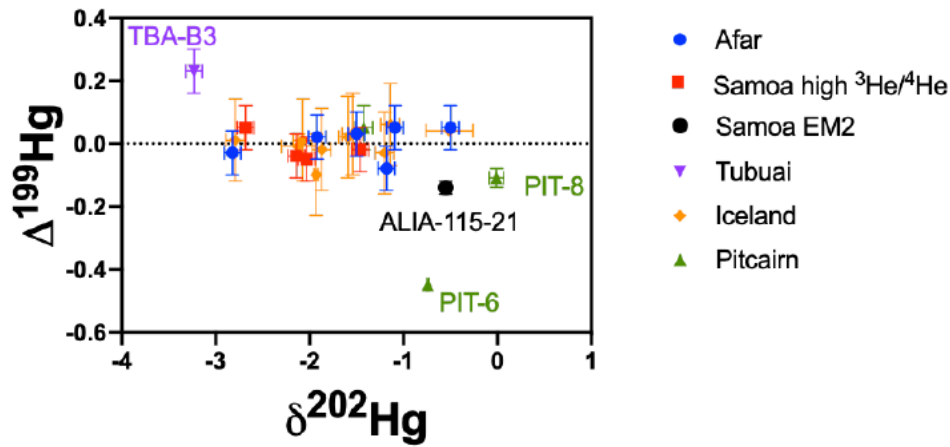
498 Workman, R. K., S. Hart, J. Eiler, and M. Jackson (2008), Oxygen isotopes in Samoan lavas:  
499 confirmation of continent recycling, *Geology*, 36, 551-554.  
500 Yin, R. S., X. B. Feng, B. Chen, J. Zheng, W. Wang, and X. Li (2015), Identifying the source and  
501 processes of mercury in subtropical estuarine and ocean sediments using Hg isotopic  
502 composition., *Environ. Sci. Tech.*, 49, 1347-1355.  
503 Yuan, S., J. Chen, H. Cai, W. Yuan, Z. Wang, Q. Huang, Y. Liu, and X. Wu (2018), Sequential  
504 samples reveal significant variation of mercury isotope ratios during single rainfall events., *Sci.*  
505 *Total Environ.*, 624, 133-144.  
506 Zambardi, T., J. Sonke, J.-P. Toutain, F. Sortnob, and H. Shinoharac (2009), Mercury emissions  
507 and stable isotopic compositions at Vulcano Island (Italy), *Earth Planet. Sci. Lett.*, 277, 236-243.  
508 Zhang, Y., et al. (2020), Mercury isotope compositions in large anthropogenically impacted  
509 Pearl River, South China., *Ecotox. Environ. Safety*, 191, 110229.  
510 Zindler, A. W., and S. R. Hart (1986), Chemical Geodynamics, *Ann. Rev. Earth Planet. Sci.*, 14,  
511 493-571.  
512  
513

#### 514 **References From the Supporting Information**

515 Jackson, M., S. R. Hart, A. Koppers, H. Staudigel, J. Konter, J. Blusztajn, M. Kurz, and J. Russell  
516 (2007), The return of subducted continental crust in Samoan lavas, *Nature* 448, 684-687.  
517 Jackson, M. G., et al. (2020), Ancient He and W isotopic signatures preserved in mantle domains  
518 least modified by crustal recycling, *PNAS*, 117, 30993-31001.  
519 Macpherson, C. C., D. Hilton, J. Day, D. Lowry, and K. Gronvold (2005), High- $^3\text{He}/^4\text{He}$ , depleted  
520 mantle and low  $\text{d}^{18}\text{O}$ , recycled oceanic lithosphere in the source of central Iceland magmatism,  
521 *Earth Planet. Sci. Lett.*, 233, 411-427  
522 Furi, E., D. Hilton, S. Halldórsson, P. Barry, D. Hahm, T. Fischer, and K. Grönvold (2010),  
523 Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: The role of  
524 He depletion, melt mixing, degassing fractionation and air interaction, *Geochim. Cosmochim.*  
525 *Acta*, 74, 3307-3332.  
526 Garapic, G., M. Jackson, E. Hauri, S. R. Hart, K. A. Farley, J. Blusztajn, and J. Woodhead (2015), A  
527 radiogenic isotopic (He-Sr-Nd-Pb-Os) study of lavas from the Pitcairn hotspot: Implications for  
528 the origin of EM-1 (enriched mantle 1), *Lithos*, 228, 1-11.  
529

530 Figure Caption:

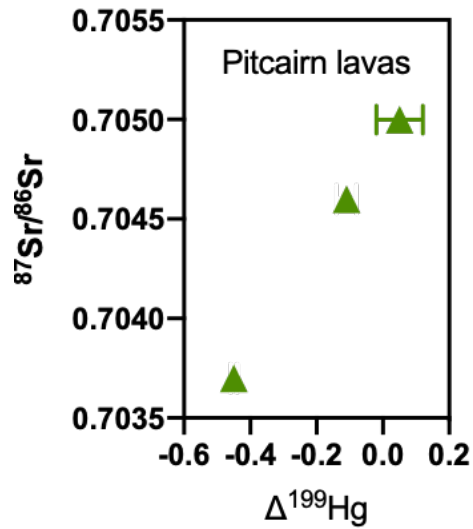
531 Figure 1:  $\Delta^{199}\text{Hg}$  versus  $\delta^{202}\text{Hg}$  for all samples analyzed here. Samples from the Afar, Ofu island, and Iceland have  
 532 similar  $\Delta^{199}\text{Hg}$  that cluster around zero and variable  $\delta^{202}\text{Hg}$  values. A sample from Tubuai has a positive  $\Delta^{199}\text{Hg}$   
 533 value, whereas two Pitcairn samples and one Samoan sample with recycling signatures have negative  $\Delta^{199}\text{Hg}$ .  
 534



535  
 536  
 537  
 538  
 539  
 540  
 541  
 542  
 543  
 544  
 545  
 546  
 547

548 Figure 2:  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $\Delta^{199}\text{Hg}$  for Pitcairn lavas. The correlation of  $\Delta^{199}\text{Hg}$  values with  $^{87}\text{Sr}/^{86}\text{Sr}$  suggests a  
549 mixture of both recycled oceanic crust (high  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\Delta^{199}\text{Hg}$ ) and terrigenous materials (low  $^{87}\text{Sr}/^{86}\text{Sr}$  and  
550  $\Delta^{199}\text{Hg}$ ) in the Pitcairn mantle source.  $^{87}\text{Sr}/^{86}\text{Sr}$  data from Garapic et al. [2015].

551



552

553

554

555

556

557

558

559

560

561

562

563

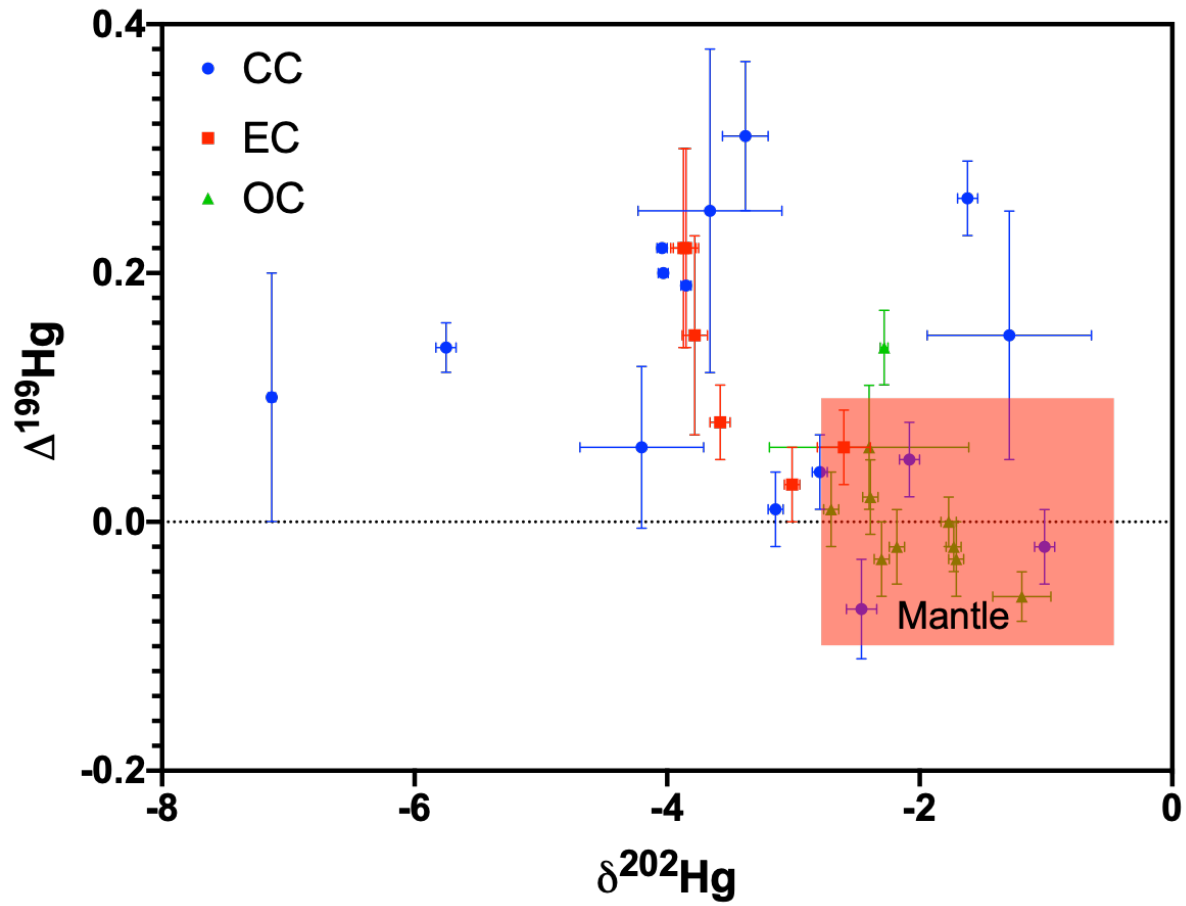
564

565

566

567

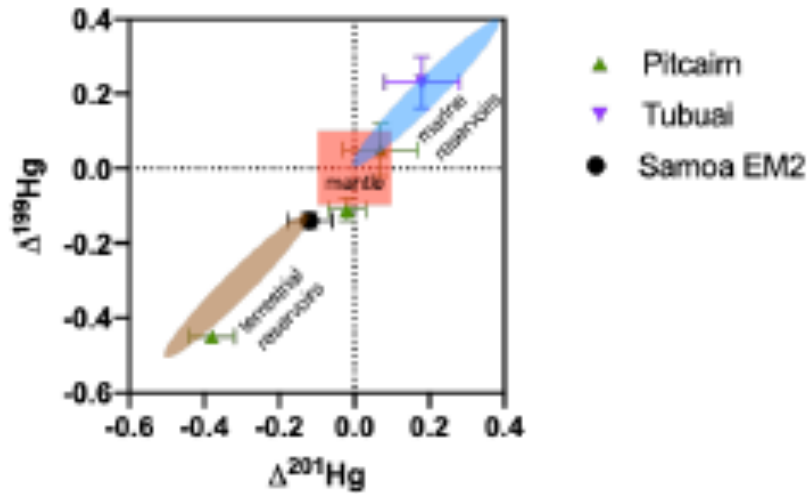
568 Figure 3: Mercury isotopic composition of the Earth's mantle (red box, defined by high  $^3\text{He}/^4\text{He}$  lavas from Samoa  
 569 and Iceland) compared to chondrites (CC=carbonaceous chondrites, EC=enstatite chondrites, OC=ordinary  
 570 chondrites). Mantle-derived lavas exhibit no clear signatures for crustal recycling and fall within the chondritic  
 571 range..  
 572



573  
 574  
 575  
 576  
 577  
 578  
 579  
 580



581 Figure 4:  $\Delta^{199}\text{Hg}$  versus  $\Delta^{201}\text{Hg}$  for the Earth's mantle (red box, defined by high  $^3\text{He}/^4\text{He}$  lavas from Samoa and  
 582 Iceland), Pitcairn, Tubuai and Samoa lavas. HIMU (Tubuai), EM-1 (Pitcairn) and EM-2 (Samoa) deviates from the  
 583 mantle composition, reflecting a contribution of recycled surface materials in their mantle sources (marine material  
 584 for Tubuai, continental material for Samoa, and both marine and continental material in the Pitcairn mantle).



585  
 586  
 587  
 588  
 589  
 590  
 591  
 592  
 593  
 594  
 595  
 596  
 597  
 598  
 599  
 600

601 Table S1

602 **Introduction** This table contains the mercury isotopic composition the samples analysed in this study. The full data  
 603 table can be found in supplementary materials (Table S1) and the Figure S1 (our Hg isotope data plotted against Nd  
 604 isotope ratios). Helium isotopic data are from [Jackson *et al.*, 2007; Jackson *et al.*, 2020; Macpherson *et al.*, 2005;  
 605 Furi *et al.* 2010]. All the data were collected in 2021 on a Nu Instruments Multi-collectors inductively-coupled-  
 606 plasma mass-spectrometer.

607

608

609

610

611

612 **Table S1:**

613

Samples	$\delta^{202}\text{Hg}$	2SD	$\Delta^{199}\text{Hg}$	2SD	$\Delta^{200}\text{Hg}$	2SD	$\Delta^{201}\text{Hg}$	2SD	$\Delta^{204}\text{Hg}$	2SD	$^3\text{He}/^4\text{He}$ (Ra)
<b>Afar</b>											
AF13-339	-0.50	0.09	0.05	0.07	0.05	0.07	0.08	0.10	-0.02	0.18	
AF13-356	-1.50	0.09	0.03	0.07	0.01	0.07	-0.02	0.10	-0.07	0.18	
AF13-44	-1.09	0.09	0.05	0.07	0.03	0.07	0.05	0.10	-0.03	0.18	
AF13-48	-1.92	0.09	0.02	0.07	0.02	0.07	0.06	0.10	-0.11	0.18	
AF13-56	-1.18	0.09	-0.08	0.07	-0.07	0.07	0.01	0.10	-0.02	0.18	
AF13-90	-2.82	0.09	-0.03	0.07	0.09	0.07	0.05	0.10	-0.05	0.18	
<b>Samoa</b>											
ALIA-115-21	-0.55	0.03	-0.14	0.02	0.02	0.02	-0.12	0.06	-0.04	0.07	
Ofu-04-03	-2.03	0.09	-0.05	0.07	-0.02	0.07	-0.03	0.10	0.03	0.18	24
Ofu-04-06	-2.68	0.09	0.05	0.07	0.10	0.07	-0.07	0.10	-0.02	0.18	34
Ofu-04-10	-2.14	0.09	-0.04	0.07	0.01	0.07	-0.07	0.10	-0.22	0.18	22
Ofu-04-15	-1.46	0.09	-0.02	0.07	0.01	0.07	-0.03	0.10	-0.02	0.18	30
<b>Pitcairn</b>											
PIT-13	-1.42	0.09	0.05	0.07	0.05	0.07	0.07	0.10	0.00	0.18	9
PIT-6	-0.74	0.01	-0.45	0.01	-0.01	0.05	-0.38	0.06	0.05	0.05	
PIT-8	-0.01	0.08	-0.11	0.03	0.03	0.03	-0.02	0.05	-0.03	0.09	8
<b>Tubuai</b>											
TBA-B3	-3.23	0.09	0.23	0.07	0.04	0.07	0.18	0.10	-0.10	0.18	7
<b>Iceland</b>											
<i>Eastern Rift Zone</i>											
A11	-0.51	0.25	0.04	0.01	0.00	0.02	-0.01	0.10	0.00	0.25	24
A24	-2.07	0.10	0.01	0.13	0.03	0.08	0.01	0.10	-0.16	0.25	26
<i>Reykjanes Peninsula and Western Rift Zone</i>											
STAP-1	-1.87	0.10	-0.02	0.13	0.02	0.08	0.01	0.10	-0.01	0.25	14
VIF-1	-1.59	0.10	0.02	0.13	0.07	0.08	0.06	0.10	-0.10	0.25	13

MID-1	-1.54	0.11	0.03	0.13	0.05	0.08	0.02	0.16	0.17	0.07	17
<i>Northern Rift Zone</i>											
NAL-625	-1.93	0.02	-0.10	0.13	0.06	0.03	-0.08	0.02	0.03	0.03	34
<i>South Iceland Volcanic Zone</i>											
SAL-601	-1.14	0.10	0.06	0.13	0.06	0.08	0.01	0.10	0.04	0.25	19
<b>Geostandards</b>											
BCR-2	-2.18	0.09	-0.01	0.07	0.02	0.07	0.00	0.10	0.02	0.18	
BCR-2 (Geng et al.)	-2.08	0.08	0.00	0.14	0.01	0.08	0.00	0.14			
RGM-2	-0.98	0.09	-0.02	0.07	0.02	0.07	-0.03	0.10	0.02	0.18	
STM-2	-1.11	0.09	0.00	0.07	0.01	0.07	-0.01	0.10	-0.12	0.18	
BE-N	-3.08	0.08	0	0.03	0.01	0.03	-0.02	0.05	-0.01	0.09	
<i>Uol internal standards</i>											
I-ICE	-2.12	0.18	-0.01	0.04	0.01	0.03	-0.04	0.02	0.00	0.10	
A-ALK	-1.20	0.10	-0.03	0.13	-0.02	0.08	-0.06	0.10	0.00	0.25	
B-ALK	-2.79	0.10	0.01	0.13	0.08	0.08	-0.03	0.10	-0.01	0.25	

614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632

## References:

- Jackson, M., S. R. Hart, A. Koppers, H. Staudigel, J. Konter, J. Blusztajn, M. Kurz, and J. Russell (2007), The return of subducted continental crust in Samoan lavas, *Nature* **448**, 684–687.
- Jackson, M. G., et al. (2020), Ancient He and W isotopic signatures preserved in mantle domains least modified by crustal recycling, *PNAS*, **117**, 30993–31001.
- Macpherson, C. C., D. Hilton, J. Day, D. Lowry, and K. Grönvold (2005), High-<sup>3</sup>He/<sup>4</sup>He, depleted mantle and low d<sup>18</sup>O, recycled oceanic lithosphere in the source of central Iceland magmatism, *Earth Planet. Sci. Lett.*, **233**, 411–427
- Füri, E., D. Hilton, S. Halldórsson, P. Barry, D. Hahm, T. Fischer, and K. Grönvold (2010), Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: The role of He depletion, melt mixing, degassing fractionation and air interaction, *Geochim. Cosmochim. Acta*, **74**, 3307–3332.