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1 Heavy Mo isotope enrichment in the Pitcairn plume: implications for the
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3 subduction cycle of anoxic sediments
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43 recycling, subduction zones*
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Abstract

Subduction redistributes elements between Earth's principal geochemical reservoirs, modifying the chemical composition of Earth's mantle, crust, atmosphere, and hydrosphere, and consequently having an impact on the evolution of life itself. Subduction of surface material that has been geochemically modified by low-temperature processes leads to mineralogical and chemical heterogeneities in mantle reservoirs over time and is recorded in modern ocean island basalts. One of the principal geochemical end members of the heterogeneous deep mantle, the enriched mantle 1 (EM-1) source of Pitcairn Island, has been attributed to the contribution of crustal material with vastly different chemical compositions and ages. The Mo isotope composition of lavas from Pitcairn Island constrains the nature of this recycled crustal component. Pitcairn lavas have elevated $\delta^{98/95}\text{Mo}$ relative to the depleted mantle. The high $\delta^{98/95}\text{Mo}$ is associated with high time-integrated $^{232}\text{Th}/^{238}\text{U}$ and $^{87}\text{Rb}/^{86}\text{Sr}$, and low time-integrated $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{238}\text{U}/^{204}\text{Pb}$. These characteristics can be attributed to the recycling of nearly pristine pelagic sediments that were deposited in a Proterozoic anoxic deep-ocean into the sources of the Pitcairn Island lavas. The isotope composition of these lavas is similar to that of EM-1 hotspots from the South Atlantic, indicating the addition of reduced sediments in both of Earth's large low shear wave velocity provinces (LLSVPs). Consistent data from both locations imply that the subduction cycling of sedimentary redox-sensitive elements such as Mo, S, Se, and U into arc magmas was in these cases inefficient in the Precambrian and the chemical and isotopic signature of reduced sediments is preserved in the source of ocean island basalts bearing the EM-1 characteristics.

Introduction

Plate tectonics and Earth's surface oxygenation are intimately linked and influence the Earth's principal geochemical reservoirs by redistributing elements over time (e.g., Kump and Barley, 2007; Campbell and Allen, 2008; Keller and Schoene, 2012; Lee et al., 2016; Smit and Mezger, 2017). Chemical fractionation processes during subduction determine the composition of Earth's mantle, crust, atmosphere, and hydrosphere, and consequently have an impact on the distribution of elements

46 essential for life (Zerkle, 2018). The subduction of material which has been geochemically modified
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3 47 by near-surface, low-temperature processes leads to distinct chemical heterogeneities in Earth's
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5 48 interior. Melts derived from such heterogeneities can provide complementary information about
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7 49 secular changes in the surface redox conditions (e.g., Cabral et al., 2013; Andersen et al., 2015;
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9 50 Gaschnig et al., 2017, 2021b; Stolper and Bucholz, 2019; Liu et al., 2019; Dottin et al., 2020; Yierpan
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11 et al., 2020; Ahmad et al., 2022). The variation in the isotope composition of redox-sensitive stable
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13 51 metal isotopes in plume-influenced mid-ocean ridge basalts (MORB) and ocean island basalts (OIB)
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15 52 can be used to further constrain the origin, nature, and scale of compositional heterogeneity in the
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17 53 Earth's deep mantle, which has conventionally been constrained by major- and trace-element, and
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19 54 radiogenic isotope systematics.
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25 56 The elemental and isotope signatures of Mo are distinct between the mantle and surface reservoirs due
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27 57 to the incompatible behavior of Mo during magmatic processes (e.g., Newsom et al., 1986) and its
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29 58 redox-dependent aqueous mobility and mass-dependent fractionation (e.g., Bali et al., 2012; Freymuth
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31 et al., 2015; König et al., 2016; Kendall et al., 2017; Chen et al., 2019; Villalobos-Orchard et al., 2020;
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33 59 Ahmad et al., 2021). Therefore, Mo isotopes can track the subduction of variously redox-affected,
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35 60 surface-derived material into the mantle (e.g., Gaschnig et al., 2021b; Ma et al., 2022; Ahmad et al.,
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37 61 2022; Hin et al., 2022). The Mo isotope systematics are particularly suitable to study element transfer
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39 62 among different surface and mantle reservoirs because the extent of Mo isotope fractionation during
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41 63 prograde subduction metamorphism depends on the Mo mobility (e.g., Chen et al., 2019; Ahmad et
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43 64 al., 2021, 2022), which in turn depends on the oxygen fugacity (fO_2) in the associated subduction zone
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45 65 fluids (Bali et al., 2012; Skora et al., 2017; Chowdhury et al., 2022). Thus, the stable Mo isotope ratio
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47 66 of a subducted slab integrates the redox-dependent aqueous mobility of Mo during subduction
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49 67 processes (Ahmad et al., 2022).
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55 69 From a global perspective, the redox state of subducting sediments is a reflection of Earth's surface
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57 70 O_2 budget (e.g., Evans, 2012). This leads to distinct Mo elemental abundances and isotopic
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71 compositions of arc magmas depending on the redox conditions of the respective subducted sediments
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72 (Freymuth et al., 2016; Gaschnig et al., 2017; Ahmad et al., 2021). This surface signature can also
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73 modify deep mantle domains and is recorded in melts derived from plumes that sample these domains
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74 (Gaschnig et al., 2021b; Ahmad et al., 2022). These melts that potentially carry a recycled oceanic
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75 sediment component in turn can provide insights into redox conditions during ancient sediment
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176 deposition, which is known to have changed over Earth's history from dominantly anoxic to oxic
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77 conditions, and subsequent sediment subduction (Ahmad et al., 2022). While oxic sediments are
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178 expected to have low Mo concentrations and low $\delta^{98/95}\text{Mo}$ (down to -1.5 ‰) due to prominent loss of
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79 isotopically heavy Mo^{6+} during early subduction (Ahmad et al., 2021), anoxic sediments preserve pre-
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80 subduction Mo isotope signatures and elemental abundances due to the immobile behavior of Mo in
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81 anoxic subduction settings (Ahmad et al., 2022). Due to the prevailing anoxic deep-ocean conditions
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82 during the Precambrian, the lower Mo mobility and availability, the small/non-existent oxic sink (i.e.
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83 Fe-Mn oxide-rich sediments enriched in light Mo), Precambrian deep-ocean anoxic sediments are
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84 expected to have Mo isotope compositions and elemental abundances similar to the upper continental
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85 crust (UCC; $\delta^{98/95}\text{Mo} \approx +0.05$ to 0.15 ‰; Willbold and Elliot, 2017 and references therein), while
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86 Phanerozoic anoxic sediments exhibit higher enrichments of heavy Mo (e.g., Kendall et al., 2017;
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87 Gaschnig et al., 2021b; Ahmad et al., 2022). Therefore, the Mo concentration and isotope composition
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88 of the subducted sediment layer indirectly records the oxidation state of the Earth's surface (Ahmad et
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89 al., 2022). This study provides constraints on the origin and genesis of the Pitcairn mantle source using
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90 variations of the stable isotopes of Mo in basalts collected from active submarine volcanoes about 80
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91 km east of the island of Pitcairn in the South-Pacific Ocean during the Polynaut cruise (1999)
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92 (Hekinian et al., 2003).

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93 Pitcairn Island represents one of the end member type-localities of the compositionally heterogeneous
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94 deep mantle, the enriched mantle 1 (EM-1) domain, and is associated with the Pacific large low shear
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95 wave velocity province (LLSVPs) (e.g., French and Romanowicz, 2015; Jackson et al., 2021). Pitcairn
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96 Island basalts have close to primordial Ne isotope ratios (Honda and Woodhead, 2005) associated with
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97 highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and some of the least radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ among known
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98 OIBs (Woodhead and Devey, 1993). This enriched component requires a low time-integrated μ
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99 ($^{238}\text{U}/^{204}\text{Pb}$) associated with high time-integrated κ ($^{232}\text{Th}/^{238}\text{U}$) and $^{87}\text{Rb}/^{86}\text{Sr}$. Different recycled
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100 geochemical reservoirs have been proposed to explain the enriched mantle source of Pitcairn Island,
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101 including metasomatized lithospheric mantle, pelagic sediments, marine carbonates, and lower
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102 continental crust (e.g., Woodhead and McCulloch, 1989; Eisele et al., 2002; Stracke, 2012; Garapić et
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103 al., 2015; Delavault et al., 2016; Wang et al., 2018; Labidi et al., 2022). The age of potentially recycled
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104 subducted sediments was interpreted to be Precambrian based on radiogenic isotopes and stable S
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105 isotopes (Eisele et al., 2002; Garapić et al., 2015; Delavault et al., 2016; Labidi et al., 2022). The
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106 occurrence of a sediment component in the source of the Pitcairn basalts can be tested using Mo
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107 isotopes. Due to the redox-sensitive behavior of Mo, recycled anoxic (Precambrian) deep-sea
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108 sediments will exhibit a Mo isotope composition that is heavier than the depleted mantle (Ahmad et
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109 al., 2022). Previously analyzed samples from Pitcairn Island include only subaerial lavas. They display
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110 $\delta^{98/95}\text{Mo}$ lower than the depleted mantle (Gaschnig et al., 2021b). The light isotopic signature,
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111 however, was explained by the influence of tropical weathering due to the correlation with Mo/Ce
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112 ratios and a secular disequilibrium recorded by $^{238}\text{U}/^{234}\text{U}$ ratios (Gaschnig et al., 2021b). Therefore, it
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113 was not possible to constrain the primary Mo isotope signature of the Pitcairn mantle plume. The active
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114 seamounts studied here offer fresh basaltic glassy material that is likely not affected by secondary
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115 alteration after the eruption and thus can be expected to preserve the geochemical characteristics of the
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116 hotspot. In order to ensure that the chemical signature of the volcanic material is primary, only glassy
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117 rims of pillow basalts were analyzed. The material was collected with the Nautilie submersible from
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118 the flanks of the seamounts “Bounty” and “Volcano 5”. All samples are well-characterized in terms of
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119 radiogenic isotopes (Sr, Nd, and Pb), S isotopes, volatile abundances, and major element abundances
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120 (Labidi et al., 2022). Furthermore, selected trace element data are available (Clog, 2010) making this
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121 material ideal to study the EM-1 end member component of the Pitcairn mantle source with Mo
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122 isotopes.
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123 Analytical methods 5 6 7

124 Molybdenum purification and isotope analyses were conducted in the clean laboratory facilities at the
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125 Institute of Geological Sciences, University of Bern. Enough sample powder was weighed into pre-
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126 cleaned Savillex™ Teflon® vials to obtain 100 to 500 ng Mo for each analysis. The samples were
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127 spiked with an enriched isotope tracer solution (⁹⁷Mo-¹⁰⁰Mo double spike) prior to dissolution. The
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128 samples were dissolved in concentrated single-distilled HF-HNO₃ (1.5 mL:0.5 mL mixture) at 100°C
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129 for at least 24 h. To suppress fluoride formation, additional 0.5 mL of concentrated HNO₃ was added
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130 to the sample during evaporation. The dry residue was then re-dissolved in 6 M HCl and evaporated
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131 after being heated for at least 24 h. To dissolve all precipitated fluorides, this step was conducted three
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132 times, with increasing heating temperature during each of these steps in the order: (i) 100 °C, (ii) 120
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133 °C, (iii) 140 °C.
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134 The dissolved samples were processed through anion- and cation exchange columns to obtain a clean
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135 Mo separate (Wille et al., 2013). In the first step, samples were taken up in 3 ml 4 M HCl + 0.15%
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136 H₂O₂ and passed through 1.5 ml Dowex 1X8, 200-400 mesh, anion resin (ca. 10 mm column width).
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137 Additional 4 ml of the loading acid and 2 ml of 18.2 MΩ·cm deionized water were used to elute most
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138 matrix elements except for Fe, which was subsequently eluted with 6 ml 3 M HNO₃ together with Mo.
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139 In a second step, the sample material was taken up in 2 ml of 0.5 M HCl + 0.10% H₂O₂ and passed
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140 through 2 ml Dowex 50WX8 200-400 mesh cation exchange resin (ca. 10 mm column width) to
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141 separate Fe. Additional 5 ml of the loading acid were used to recover Mo quantitatively. Measurement
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142 of stable Mo isotopes were carried out on a Neptune Plus MC-ICP-MS coupled with an Aridus II
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143 desolvating nebulizer with an uptake rate of 100 μl·min⁻¹ (details are provided in Ahmad et al., 2021).
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144 Six Mo isotopes (⁹⁴Mo, ⁹⁵Mo, ⁹⁶Mo, ⁹⁷Mo, ⁹⁸Mo, and ¹⁰⁰Mo) were measured simultaneously as well
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145 as ⁹⁹Ru and ¹⁰¹Ru to monitor potential isobaric interferences. All isotopes were measured with 10⁻¹¹ Ω
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146 resistors with the exception of ^{101}Ru , which was measured using a $10^{-12} \Omega$ resistor. A combination of
147 ‘H’ Ni sampler cone and ‘H’ Ni skimmer cone for analyses provided a signal intensity of ~ 45 V/ppm
148 on ^{95}Mo . A double spike correction method based on an iterative calculation procedure (see Siebert et
149 al., 2001) was used to obtain the natural isotope ratios of the sample. The total procedural blank was
150 0.71 to 0.74 ng, which is less than 1 % of the total analyzed Mo. Mo isotope compositions are presented
151 in the δ -notation relative to NIST SRM 3134 in ‰ (Greber et al., 2012; Goldberg et al., 2013) with an
152 interference correction based on ^{99}Ru :

$$\delta^{98/95}\text{Mo} = \left(\frac{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{Sample}}}{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{NIST SRM 3134}}} - 1 \right) * 1,000$$

156 $\delta^{98/95}\text{Mo}$ values corrected for Ru interferences using ^{99}Ru and ^{101}Ru were compared to ensure accurate
157 correction for Ru interference on Mo ($\Delta^{98/95}\text{Mo}_{^{99}\text{Ru}-^{101}\text{Ru}} < 0.01$ ‰). To correct for background Mo,
158 sample measurements were bracketed by measurements of a 0.5 M HNO_3 carrier solution on-peak.
159 Molybdenum isotope signals in the background solution were 10^4 times smaller than during the sample
160 measurement. Sample and background analyses consisted of 80 and 10 cycles, respectively, with a
161 signal integration time of 4.194 s for each cycle. Repeated measurements of the standard NIST SRM
162 3134 and an in-house J&M standard solution (JMCBern) lot 602332B gave an isotopic difference of
163 $\Delta^{98/95}\text{Mo} = 0.260 \pm 0.023$ ‰ (2 SD, $n = 10$), in agreement with other studies (Greber et al., 2012;
164 Ahmad et al., 2021, 2022; Kaufmann et al., 2021; O'Sullivan et al., 2021). Solution standards were
165 measured at a concentration of 50 ppb. Chemically purified whole-rock reference materials AGV-2
166 and BHVO-2 yielded a $\delta^{98/95}\text{Mo}$ of -0.175 ± 0.037 ‰ (2 SD, $n = 3$) and -0.077 ± 0.024 ‰ (2 SD, $n =$
167 3) (Table S-1). The values are within uncertainty of those determined previously (e.g., Burkhardt et
168 al., 2014; Willbold et al., 2016; Zhao et al., 2016). Individual measurements of whole rock reference

169 materials (Table S-1) are within the long-term 2SD external reproducibility of ± 0.05 ‰ as determined
170 by previous measurements of BHVO-2 (Ahmad et al., 2021, 2022).

171 Including previous BHVO-2 measurements (-0.09 ± 0.05 ‰; $n = 11$), we consider ± 0.05 ‰ as the
172 long-term 2 SD external reproducibility of the sample measurements. All samples and whole-rock
173 reference materials were measured multiple times (after one single digestion and chemical separation)
174 and the obtained $\delta^{98/95}\text{Mo}$ values were averaged for data presentation and interpretation (Table S-1).

175 All individual sample measurements differ less than ± 0.05 ‰ from their average $\delta^{98/95}\text{Mo}$.

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Results

The $\delta^{98/95}\text{Mo}$ values of Pitcairn basaltic glass samples exhibit a small range between -0.12‰ and -0.09‰ ($n=10$), with an average of -0.11‰ (Table 1; Fig. 1, 2). The variations among Pitcairn basalts are smaller than the external 2SD reproducibility of $\pm 0.05\text{‰}$ (Table 1). Within analytical uncertainty, all samples are isotopically heavier than the depleted mantle ($\delta^{98/95}\text{Mo} \approx -0.20\text{‰}$; Bezard et al., 2016; McCoy-West et al., 2019; Hin et al., 2022). These results differ from previously published Mo isotope data of Pitcairn Island lavas that were measured on material that was influenced by subaerial weathering (Gaschnig et al., 2021b). Overall, Mo concentrations range between 1.26 and 4.40 $\mu\text{g/g}$ and are higher than average MORB (log mean = $\sim 0.38^{+0.95}_{-0.27}$ $\mu\text{g/g}$, 2SD; Gale et al., 2013). Only considering the least differentiated samples, with MgO content ranging from 4.6 to 5.6 wt%, a large [Mo] variability from 1.26 to 2.93 $\mu\text{g/g}$ is observed. Furthermore, Mo/Ce ratios are variable (0.022 to 0.038) overlapping with average MORB Mo/Ce ($\sim 0.035 \pm 0.02$, 2SD; Gale et al., 2013) (Fig. 2). The samples have $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios that are characteristic of the EM-1 mantle reservoir (Labidi et al., 2022). The radiogenic isotope signatures of the basalts are similar to the most enriched EM-1 influenced MORBs from the South-Mid Atlantic Ridge (Fig. 3).

193 **Table 1.** Mo concentration and isotope data for Pitcairn Island lavas. Literature data from Labidi et
 194 al. (2022), except (A) (Bourdon and Van Orman, 2009). La/Sm and Ce concentrations are available
 195 for selected samples (Clog, 2010). Element oxides are in wt%, minor and trace elements are in µg/g.

sample ID	pn03-01	pn03-02	pn03-03	pn03-05	pn03-07	pn03-08	pn03-10	pn03-11	pn08-07	pn14-04
seamount	Bounty	Bounty	Bounty	Bounty	Bounty	Bounty	Bounty	Bounty	Volcano 5	Bounty
depth (mbsl)	2508	2508	2500	2408	2276	2250	2165	1957		1705
Na ₂ O	4.2	4.2	4.2	3.8	3.9	4.2	3.5	4.0	4.2	4.2
SiO ₂	47.8	47.9	47.7	47.8	47.6	48.8	50.6	48.9	54.4	54.2
K ₂ O	1.4	1.4	1.5	1.4	1.4	1.6	0.8	1.6	2.7	2.3
Al ₂ O ₃	16.0	16.0	15.8	15.4	15.3	16.2	15.1	15.3	16.1	15.3
CaO	9.1	9.1	9.1	9.8	9.7	8.1	8.6	8.7	4.9	5.4
MgO	5.4	5.5	4.8	5.2	5.4	5.0	5.6	4.6	2.6	2.6
P ₂ O ₅	0.7	0.7	0.8	0.7	0.7	0.8	0.5	0.8	1.2	1.2
FeO	9.7	9.8	9.7	9.9	10.0	9.7	9.6	9.7	9.1	9.5
MnO	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2
TiO ₂	2.9	2.9	3.0	3.1	3.1	3.3	3.1	3.4	1.9	2.2
total	97.5	97.6	96.8	97.2	97.1	97.9	97.6	97.2	97.2	97.0
Mo	2.47	1.26	2.45	2.23	1.53	2.93	1.38	2.41	4.40	4.22
Cl	502	494	498	426	424	459	324	417	493	750
Cu	59	50	52	50	56	33	37	50	3	11
H ₂ O	9192	9807	9662	8512	8125	9099	5696	5667		12123
S ²⁻	1279	1299	1133	953	875	738	1017	569	602	507
Ce				70.4	69.7	77.0	48.9	69.9		
K ₂ O/TiO ₂	0.49	0.48	0.49	0.44	0.45	0.49	0.27	0.47	1.40	1.06
CaO/Al ₂ O ₃	0.57	0.57	0.58	0.63	0.63	0.50	0.57	0.57	0.30	0.36
Cl/K	0.04	0.04	0.04	0.04	0.04	0.03	0.05	0.03	0.02	0.04
S ²⁻ /S _{tot}	0.97	0.98	0.80	0.95	0.91	1.00	0.95	0.72	1.00	0.99
Mo/Ce				0.032	0.022	0.038	0.028	0.034		
(La/Sm) _N				2.66	2.64	3.17	2.07	3.17		
δ ^{98/95} Mo (‰)	-0.121	-0.121	-0.112	-0.113	-0.111	-0.119	-0.115	-0.111	-0.097	-0.093
δ ³⁴ S (‰)	0.1	0.2	-1.0	-1.2	-1.3	-1.0	-1.2	-1.2	1.6	0.7
Δ ³³ S (‰)	0.020	0.028	0.025	0.028	0.012	0.027	0.030	0.031	0.026	0.007
Δ ³⁶ S (‰)	0.08	0.08	0.05	0.13	0.08	0.06	0.06	0.06	0.02	-0.06
²⁰⁶ Pb/ ²⁰⁴ Pb	17.742	17.742	17.749	17.816	17.809	17.747	17.926	17.770		18.198
²⁰⁷ Pb/ ²⁰⁴ Pb	15.470	15.470	15.474	15.482	15.479	15.475	15.493	15.479		15.516
²⁰⁸ Pb/ ²⁰⁴ Pb	38.569	38.570	38.579	38.645	38.658	38.644	38.798	38.668		38.916
¹⁴³ Nd/ ¹⁴⁴ Nd			0.512567	0.512599	0.512583	0.512537		0.512944		0.512762
⁸⁷ Sr/ ⁸⁶ Sr	0.704483	0.704477	0.704485	0.704482	0.704498	0.704624	0.704481	0.704531		0.704002
⁸⁷ Sr/ ⁸⁶ Sr ^A				0.70446		0.70463	0.70447		0.70530	

Discussion

The Pitcairn lavas define the end member of the EM-1 component. Their composition is a result of a complex history of mixing processes prior to eruption, including mantle source enrichment, low degrees of partial mantle melting, followed by magmatic differentiation and sulfide segregation, and variable extents of volatile loss via degassing (e.g., Woodhead and McCulloch, 1989; Eisele et al., 2002; Garapić et al., 2015; Delavault et al., 2016; Wang et al., 2018; Labidi et al., 2022). All these processes can potentially affect the Mo isotopic composition of the erupted melts.

The potential effect of secondary and magmatic processes on $\delta^{98/95}\text{Mo}$

The primary isotope composition of Mo preserved in rocks and minerals can be modified by direct or indirect interaction with seawater. Although careful separation of fresh glass avoids the former, it is not possible to detect visually magmatic assimilation of altered oceanic crust (AOC) that happened en route to the surface or to eliminate all traces of Fe-Mn coating in picked samples. The Cl/K ratios are < 0.05 for Bounty lavas and < 0.02 for Volcano 5 samples (Labidi et al., 2022) (Table 1), which is below the threshold of 0.10, above which lavas are considered to be contaminated significantly by Cl-rich brines (Michael and Cornell, 1998). These low Cl/K ratios exclude Cl enrichment by assimilation of hydrated oceanic crust, interaction with brine, and seawater alteration. Furthermore, seawater alteration should affect the sample $^{87}\text{Sr}/^{86}\text{Sr}$, while $^{143}\text{Nd}/^{144}\text{Nd}$ remains unchanged (e.g., Labidi et al., 2013), which is not observed in subaerial Pitcairn lavas (not shown; Garapić et al., 2015). Isotope effects caused by Mo adsorbed on Fe-Mn oxides can be excluded as well, because this would have shifted the Mo isotope composition towards $\delta^{98/95}\text{Mo} < \text{depleted mantle}$ ($\delta^{98/95}\text{Mo} \approx -0.20\%$; Bezard et al., 2016; McCoy-West et al., 2019; Hin et al., 2022). It is also unlikely that seafloor alteration, oceanic crust assimilation, or Mn-oxide contribution would generate a statistically homogeneous $\delta^{98/95}\text{Mo}$ in all investigated samples derived from different sampling depths (Table 1).

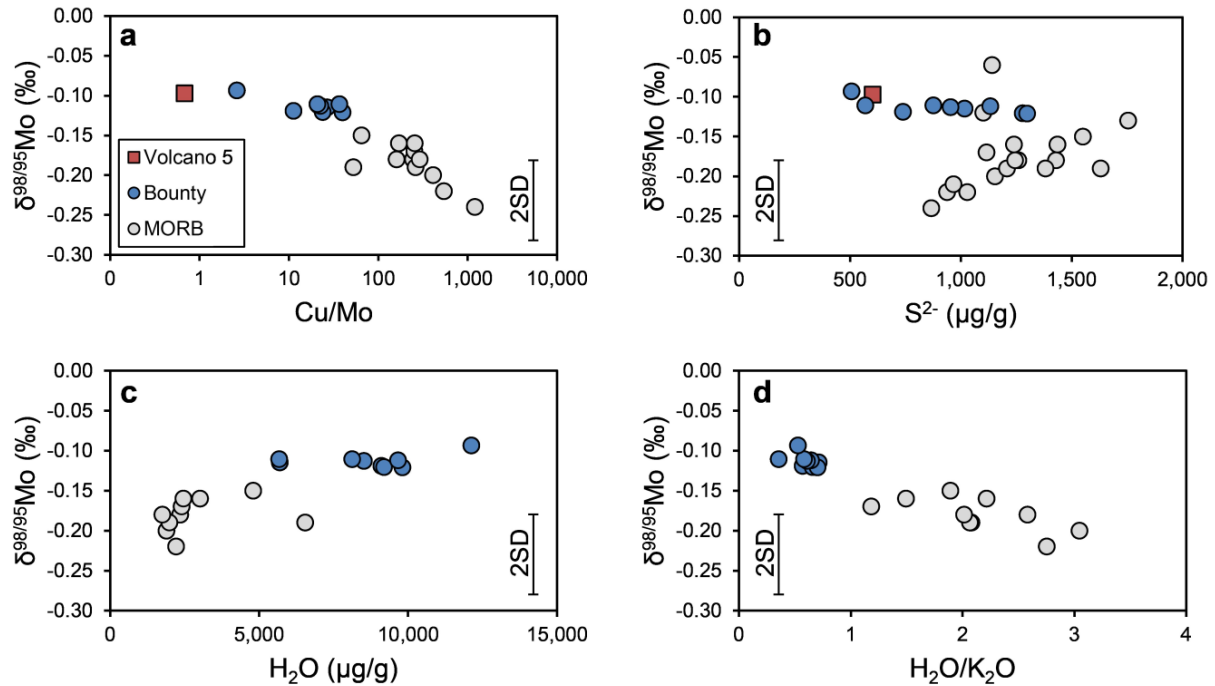
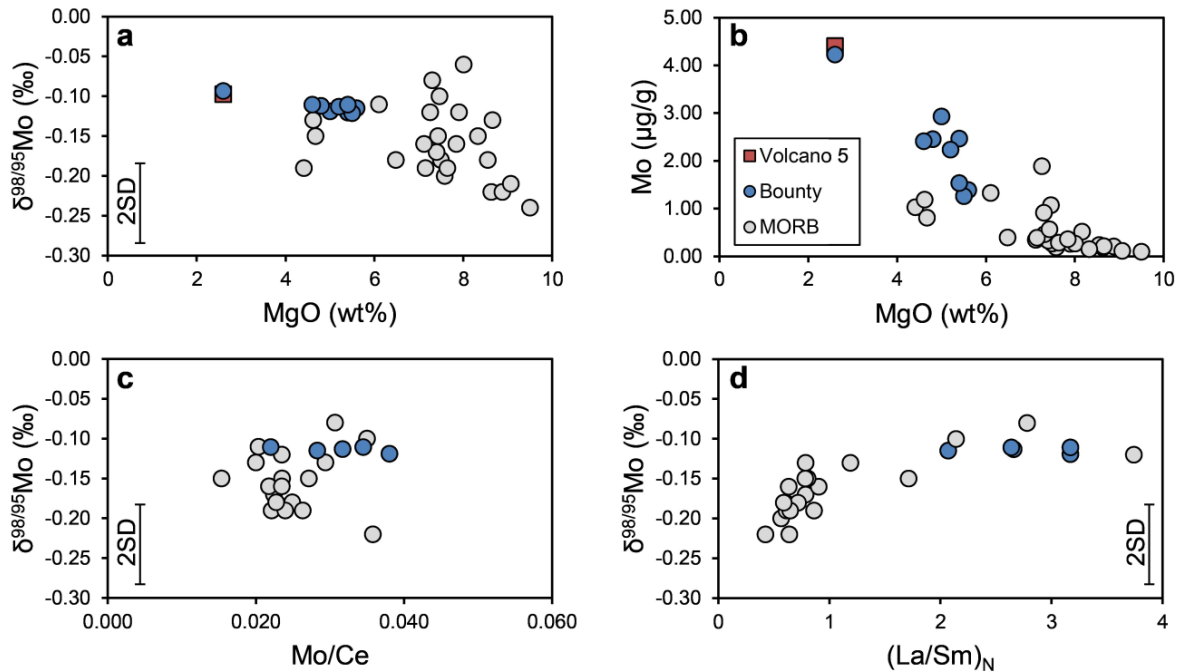


Figure 1. Plots of $\delta^{98/95}\text{Mo}$ vs. (a) Cu/Mo ; (b) S^{2-} ; (c) H_2O ; (d) $\text{H}_2\text{O}/\text{K}_2\text{O}$. Error bars indicate 2 SD external reproducibility. MORB data is from the literature (Clog et al., 2013; Labidi et al., 2014; Bezaud et al., 2016). Three isotopically heavy outliers from Bezaud et al. (2016) are excluded.

The variability of the bulk S contents in Pitcairn lavas is attributed to continuous tholeiite-like sulfide segregation and magmatic degassing (Labidi et al., 2022) that may have also affected the Mo isotope composition of the residual silicate melt (e.g., Greber et al., 2014; Liang et al., 2017; Kaufmann et al., 2021; Hin et al., 2022). Increasing sulfide melt segregation, indicated by decreasing Cu/Mo ratios in the silicate melt, due to the more chalcophile affinity of Cu does not show any covariation with $\delta^{98/95}\text{Mo}$ while previously reported MORB display an overall trend (Fig. 1). Furthermore, no control of magmatic degassing on the Mo isotope composition is observed, because the variable H_2O (and $\text{H}_2\text{O}/\text{K}_2\text{O}$) and S contents of the basaltic glass samples, which correlate with water depth (Labidi et al., 2022), are decoupled from Mo isotopes (Fig. 1).

No measurable isotopic difference among the least and most primitive samples (i.e. pn03-10 and pn14-04; Fig. 2, Fig S-1) is observed indicating that the effect of fractional crystallization (e.g., Voegelin et al., 2014; Wille et al., 2018) is negligible on the Mo isotope composition of the Pitcairn samples. This

236 observation has been made in other magmatic systems (e.g., Yang et al., 2015; Bezard et al., 2016;
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 237 Nebel-Jacobsen et al., 2021; Gaschnig et al., 2021a).



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 240 **Figure 2.** Plots of (a) $\delta^{98/95}\text{Mo}$ vs. MgO; (b) Mo vs. MgO; (c) $\delta^{98/95}\text{Mo}$ vs. Mo/Ce; (d) $\delta^{98/95}\text{Mo}$ vs.
 241 $(\text{La}/\text{Sm})_N$. Error bars indicate 2 SD external reproducibility. MORB data is from Bezard et al. (2016).
 242 Three isotopically heavy outliers from Bezard et al. (2016) are excluded.

243 The Mo/Ce and La/Sm ratios vary significantly in the samples from Pitcairn Island (Fig 2), potentially
 244 indicating different extents of low-degree partial melting of their source. Low-degree melting would
 245 result in high $\delta^{98/95}\text{Mo}$ (McCoy-West et al., 2019; Chen et al., 2022), due to the presence of both, Mo^{6+}
 246 and Mo^{4+} in the mantle, and associated higher incompatibility of isotopically heavy Mo^{6+} over light
 247 Mo^{4+} during mantle melting. The homogeneous $\delta^{98/95}\text{Mo}$ values of the basaltic lavas indicate that low-
 248 degree mantle melting had an insignificant effect on the Mo isotope composition of investigated lavas.
 249 This indicates a minor influence of low-degree melts on the Mo isotope composition of plume-
 250 influenced OIBs compared to MORB settings (e.g., East Pacific Rise; Chen et al., 2022). This can be
 251 explained by melting at higher temperatures along the hotter plume-adiabat (e.g., Putirka, 2008;
 252 Ahmad et al., 2022) or by Mo being present in only one oxidation state ($\text{Mo}^{6+}/\Sigma\text{Mo} = 1$), resulting in
 253 negligible effects on Mo isotope fractionation during mantle melting.

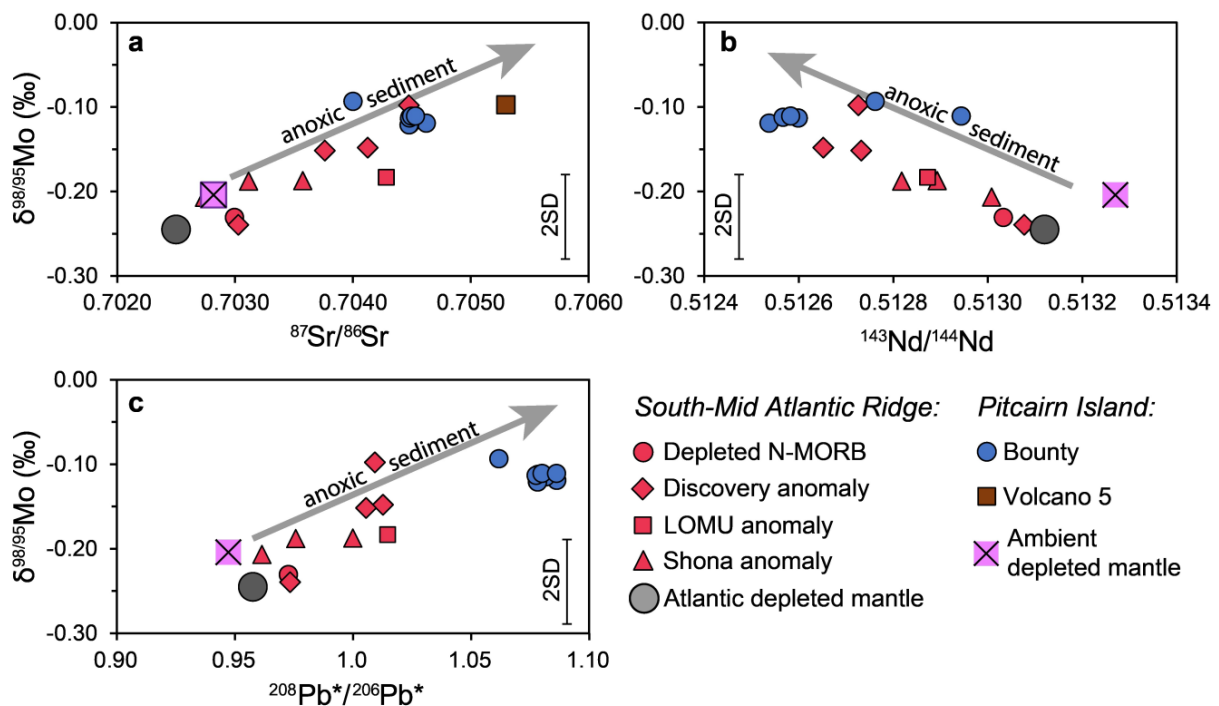
254 The potential role of recycled components

255 As the heavy Mo isotope composition of Pitcairn Island basalts cannot be attributed to assimilation or
256 mineral fractionation, the enrichment of the EM-1 component in ^{98}Mo is most likely a mantle source
257 feature. Various recycled plate materials have been proposed to contribute to EM-1 plume sources,
258 including metasomatized lithospheric mantle, oceanic sediments, and components from the lower
259 continental crust (e.g., Woodhead and McCulloch, 1989; Eisele et al., 2002; Stracke, 2012; Garapić et
260 al., 2015; Delavault et al., 2016; Wang et al., 2018; Labidi et al., 2022).

261 Processes involving fluid-driven enrichments of isotopically heavy Mo in the subcontinental mantle
262 in convergent plate settings (e.g., Freymuth et al., 2015; König et al., 2016; Chen et al., 2019; Ahmad
263 et al., 2021) could in principle account for the data. A similar model was proposed to explain the O
264 isotope data of Pitcairn Island phenocrysts (Eiler et al., 1995). However, systematic enrichments or
265 depletions of fluid mobile elements are not observed in the Pitcairn Island source (Willbold and
266 Stracke, 2006), in line with Mo/Ce ratios not significantly exceeding MORB values (e.g., Freymuth et
267 al., 2015; König et al., 2016; Villalobos-Orchard et al., 2020). Recycled lower continental crust (LCC)
268 material has been suggested to be a major component of the Pitcairn Island mantle source (e.g., Stracke,
269 2012 and references therein). There is no estimate of $\delta^{98/95}\text{Mo}$ of the LCC. Cumulates that possibly
270 reside in the LCC, however, likely have light Mo isotope signatures (Wille et al., 2018; Nebel-Jacobsen
271 et al., 2021) and are unsuitable candidates to explain the observed Mo isotope compositions in the
272 basalt samples. Isotopically heavy arc-derived cumulates that can be explained by slab-derived fluid
273 contamination (Storck et al., 2023), are not in line with fluid mobile element systematics, as discussed
274 above.

275 Furthermore, the low time-integrated $^{238}\text{U}/^{204}\text{Pb}$, which is characteristic of the Pitcairn EM-1 mantle
276 source, and overall unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ indicate that recycled isotopically variable altered oceanic
277 crust (Freymuth et al., 2015; Ahmad et al., 2021) cannot produce the EM-1 characteristics. Phanerozoic
278 subducted sediments and mafic oceanic crust are isotopically light (Chen et al., 2019; Ahmad et al.,

279 2021) and can also not contribute to the isotopically heavy composition of the EM-1 component.
 280 Previous studies have attributed the radiogenic isotope and stable Mg isotope composition of the
 281 Pitcairn Island mantle source to the recycling of (Precambrian) subducted marine carbonates
 282 (Delavault et al., 2016; Wang et al., 2018). The recycling of carbonate components has likely an
 283 undetectable effect on the Mo isotope ratio of an enriched mantle component due to the low distribution
 284 of dissolved Mo during authigenic carbonate formation leading to low Mo concentrations ($\ll 100$
 285 ng/g) in pure carbonate (e.g., Voegelin et al., 2009, 2010; Thoby et al., 2019). Furthermore,
 286 Precambrian seawater contained even less dissolved Mo (e.g., Anbar, 2008) that could be extracted by
 287 carbonate formation. Therefore, depending on marine deposition conditions, the Mo signature in
 288 carbonate successions is often dominated by clastic and organic phases.



291 **Figure 3.** Covariation diagram of EM-1 influenced lavas from South-Mid Atlantic Ridge (Douglass et
 292 al., 1999; Ahmad et al., 2022) and Pitcairn Island (this study). (a) $\delta^{98/95}\text{Mo}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$; (b) $\delta^{98/95}\text{Mo}$
 293 vs. $^{143}\text{Nd}/^{144}\text{Nd}$; $\delta^{98/95}\text{Mo}$ vs. $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ (time-integrated Th/U). Error bars indicate 2 SD external
 294 reproducibility. Values for Atlantic and ambient depleted mantle are in Table S-2.

295 When compared with radiogenic isotopes and other EM-1 mantle plume influenced lavas from the
 296 South-Mid Atlantic Ridge (S-MAR), a general trend towards an enriched mantle source is evident

297 (Fig. 3). This covariation was previously interpreted as a result of the recycling of Mid-Proterozoic
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298 anoxic deep-ocean sediments into the mantle source (Ahmad et al., 2022). To infer the hypothetical
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299 sediment end member, a misfit model (Supplementary Information) using Sr isotope and elemental
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300 systematics of the ambient mantle and a model Mid-Proterozoic sediment was applied. This is
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301 necessary to visualize different mixing lines/hyperbolas due to various potential combinations of [Mo]
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302 and $\delta^{98/95}\text{Mo}$ in the sediment end member. The misfit model suggests that a Precambrian pelagic
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303 sediment contributed to the observed Mo isotope systematics (Fig. 4).
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304 Different ages for the recycled sediments in the mantle source of Pitcairn Island lavas have been
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305 proposed. Labidi et al. (2022) argued that based on the small range of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Table 1) most
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306 likely Proterozoic (reduced) sediments were recycled into the mantle source of Pitcairn Island. The
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307 Proterozoic ocean was redox-stratified (e.g., Canfield, 1998) with oxygenated shallow waters and
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308 higher organic matter (OM) input closer to the continents, while the deep-sea remained anoxic with
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309 lower input of OM (e.g., Lyons et al., 2014; Laakso and Schrag, 2019). The literature data of
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310 Proterozoic OM-rich sediments (Fig. 4; Table S-2) represent mostly shallow-marine (continental
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311 shelf/closed basins) sediments from anoxic/euxinic settings, where e.g., sulfate reduction leads to
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312 higher authigenic accumulation of isotopically variable Mo from seawater compared to lower Mo
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313 accumulation in the anoxic deep-sea. In these deep waters, the Mo isotope signature and concentration
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314 of the sedimentary end member is expected to be close to UCC (Fig. 4; Ahmad et al., 2022). The best
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315 fit of the sedimentary end member of the Pitcairn mantle source (blue curve in Fig. 4) is located in the
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316 lower 1 SD (lower than 4.10 $\mu\text{g/g}$) of the compiled Proterozoic OM-rich sediment data (Supplementary
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317 Information) close to the UCC composition. This suggests that the Pitcairn mantle source is
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318 contaminated by Proterozoic deep-ocean sediments with limited heavy Mo isotope enrichment. An
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319 addition of less than 2 % of this sedimentary material is needed to account for the heavy Mo signature
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320 of the Pitcairn Island mantle source (2 component mixing between UCC and DM; Table S-2).
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321 Although mantle-like O isotope signatures within basalt phenocrysts have been used to argue against
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322 a sedimentary origin for the EM-1 source of Pitcairn Island (Eiler et al., 1995, 1997), a sediment
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323 contribution below ~2% remains undetected with stable O isotopes (Eiler et al., 1995). In addition,
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324 modeling of a sedimentary end member based on S-isotope as well as radiogenic isotope data of the
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325 Pitcairn samples (Table 1; Table S-2) (Labidi et al., 2022), suggests that a contribution of $\leq 2\%$ anoxic
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326 Proterozoic deep-sea sediments can fulfill the trace element and isotope systematics of the EM-1
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327 source of Pitcairn Island. Due to the increased compatibility of Mo^{4+} in stable Mo-bearing hosts such
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328 as rutile or sulfides (see Bali et al., 2012; Skora et al., 2017; Chowdhury et al., 2022) in the anoxic
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329 subducted sedimentary units, it is expected that Mo is immobile in reduced sediments during prograde
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330 subduction metamorphism. Therefore, no significant isotope fractionation during the subduction of
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331 reduced sediment is expected. Thus, the original sedimentary Mo isotope signatures and element
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332 abundances are preserved in the deep mantle (Ahmad et al., 2022). Such behavior is not expected for
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333 Mo in Phanerozoic oxidized sediments because of the prominent loss of heavy Mo^{6+} during (early)
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334 prograde subduction metamorphism (Ahmad et al., 2021).
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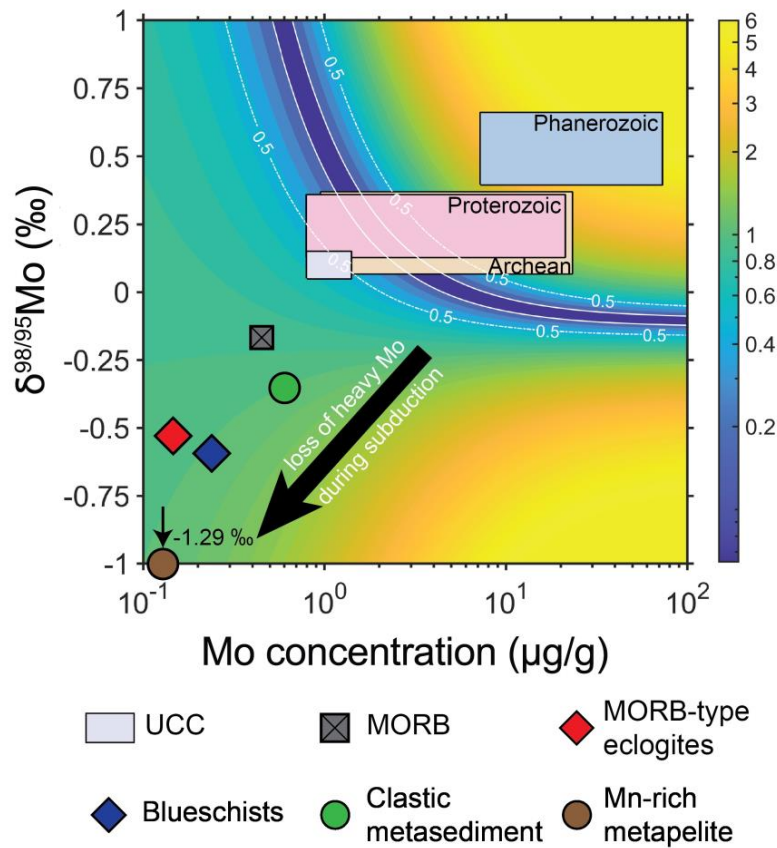


Figure 4. Least squares error ($\Delta^{98/95}\text{Mo}$ in ‰; up to 6 ‰) between calculated mixing lines and analyzed samples (after Ahmad et al., 2022). The best fit is indicated by the blue field. Variables are the $\delta^{98/95}\text{Mo}$ and $[\text{Mo}]$ values derived from the $\delta^{98/95}\text{Mo}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ relationship (Fig. 3). Literature values for potential (concentration averaged) recycled lithologies, and anoxic sediments sorted by age intervals are shown for comparison. See Supplementary Information for references, mixing parameters, and further details.

Anoxic pelagic sediments as a source for EM-1

The contribution of (Mid-)Proterozoic sediments to the source of the Pitcairn hotspot is supported by other studies (e.g., Woodhead and McCulloch, 1989; Eisele et al., 2002; Delavault et al., 2015). A (Mid-)Proterozoic pelagic sediment end member has also been identified for EM-1 influenced lavas from the S-MAR that interact with the Discovery- and Shona mantle plumes, based on correlations between radiogenic isotopes of Sr, Nd, and Hf, and $f\text{O}_2$ -sensitive stable isotope variations of S, Se, and Mo (Douglass et al., 1999; Andres et al., 2002; le Roux et al., 2002; Labidi et al., 2013; Yierpan et al., 2020; Ahmad et al., 2022) (Fig 3). The Mo and radiogenic isotope systematics of the Pitcairn lavas are

351 similar to S-MAR (Fig. 3). A cross-plot of $\delta^{98/95}\text{Mo}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ (time-
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352 integrated Th/U) shows that the Pitcairn lavas influenced by the EM-1 component extend the
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353 covariation recorded in S-MAR samples, pointing towards a similar Proterozoic pelagic sedimentary
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354 end member with a Mo isotopic composition heavier than the depleted mantle (Fig. 3). It is likely that
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355 Proterozoic deep-ocean processes under anoxic conditions also controlled the Th/U ratios of the
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356 sedimentary end member producing the EM-1 Pb-isotope signatures in Pitcairn Island and S-MAR
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357 lavas (Fig 3c). Under reducing conditions, U is immobile and shows a geochemical behavior very
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358 similar to Th. However, Th is much more particle-reactive than U, independently of ocean redox
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359 conditions, leading to higher Th enrichments over U in deep-sea pelagic sediments similar to present-
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360 day pelagic clays (Plank and Langmuir, 1998). The chemical composition of modern pelagic sediments
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361 differs from those deposited in Precambrian anoxic deep waters, because potential U hosts such as
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362 biogenic phosphate (bone and teeth debris) and Fe-Mn oxides were absent. The absence of these U
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363 hosts together with a much lower concentration of dissolved U in the ocean reservoir (Lyons et al.,
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364 2014) lowered the U flux into deep-sea sediments. The redox-stratified Proterozoic ocean instead
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365 probably favored significant U accumulation in organic matter (OM)-rich settings close to the
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366 continents (e.g., Lyons et al., 2014; Laakso and Schrag, 2019). Therefore, it can be argued that the
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367 EM-1 source signature reflects the contamination by pelagic sediments with elevated Th/U, low U/Pb,
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368 and high $\delta^{98/95}\text{Mo}$ from a continental source with enrichments of particle-reactive Th and Pb from a
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369 Mo- and U-depleted Proterozoic redox-stratified ocean. Furthermore, deep-mantle contamination with
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370 anoxic material is supported by C isotope data of CO_2 degassed at Pitcairn Island and other OIBs.
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371 These C isotope data are consistent with recycled reduced C in the mantle source of the lavas (Eguchi
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372 et al., 2020). The sequestration of reduced sediments into the deep mantle can also have enabled the
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373 oxygenation of Earth's surface (Duncan and Dasgupta, 2017).
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374 The global occurrence of anoxic deep-ocean bottom waters over most of the Proterozoic (e.g., Lyons
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375 et al., 2014) together with the low abundances of passive margins during the formation and
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376 stabilization of the Columbia supercontinent during the Mid-Proterozoic (e.g., Bradley, 2011)
377 probably provided the potential for widespread accumulation of anoxic pelagic sediments with
378 potentially high $\delta^{98/95}\text{Mo}$ and Th/U. The fact that two EM-1 influenced suites (i.e. Pitcairn and
379 Shona/Discovery plumes) from two different LLSVPs, i.e. the Pacific and the African, show an input
380 with a common radiogenic and Mo isotope composition (Fig. 3) suggests widespread recycling of
381 (Mid-) Proterozoic anoxic pelagic sediments into the deep mantle, most likely at the subduction girdle
382 surrounding the supercontinent (see Li et al., 2019). This is further supported by the geologic record,
383 where Precambrian deep-ocean sediments are generally absent due to subduction of the oceanic crust
384 (Patchett et al., 1984; Sperling et al., 2015).

385 Hin et al. (2022) suggested that the subchondritic $\delta^{98/95}\text{Mo}$ observed for the upper mantle (-0.20 ± 0.01
386 ‰) is the result of the continuous recycling of an isotopically light subduction-modified oceanic crust.
387 In their model, the subduction of different proportions of oceanic crust and sediment on different time
388 scales (1.1 to 3.9 Gyr) can explain the isotopically light composition of the upper mantle or the mantle
389 as a whole. Our findings show that mixing of the upper mantle with oceanic crust and sediments would
390 have opposing effects on the Mo isotopic signature of a mantle source, as subducted Precambrian
391 sediments are expected to possess a heavy UCC-like isotopic signature, while the subducted oceanic
392 crust has possibly a light isotope composition (Chen et al., 2019; Ahmad et al., 2021). Furthermore,
393 the widespread accumulation of Precambrian sediments in the LLSVPs suggests that a significant
394 proportion of crustal material is not recycled back to the bulk (or upper) mantle by convective stirring.
395 The higher density of the underlying subducted oceanic crust favored large scale deposition of ancient
396 subducted oceanic crust in the LLSVPs (Jones et al., 2020; Niu, 2018; Wang et al., 2020) preventing
397 its effective mixing into the bulk mantle. Therefore, there are contrasting effects of prograde
398 subduction metamorphism on the sediment elemental and isotope signature depending on the
399 prevailing redox state of the ocean (Ahmad et al., 2021, 2022) and an inefficient homogenization of
400 the mantle. This is not an argument against a subducted crustal component in the upper mantle,

401 however, but this suggests that the calculated recycling time scales and volumes may need to be
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402 refined.
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403 Implications for subduction cycling of redox-sensitive elements 7

404 These findings support the model that the redox structure of Earth's surface is directly connected to
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405 the deep-mantle compositional differences in $\delta^{98/95}\text{Mo}$ (Gaschnig et al., 2021b), which in turn inform
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406 about redox conditions of subducted material (Ahmad et al., 2022). Phanerozoic subducted Mn-Fe rich
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407 sediments can efficiently buffer subduction zone fluids towards oxidizing conditions (see Ague et al.,
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408 2022). On the other hand, subducted anoxic sediments, which were abundant in the Precambrian,
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409 buffer redox conditions during prograde subduction metamorphism to reduced conditions (Ahmad et
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410 al., 2022; Padron-Navarta et al., 2023). The widespread subduction of anoxic material and the
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411 preservation of isotopic signatures of Mo, Se, and S characteristic of sediments in EM-1 sources
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412 (Labidi et al., 2013; Yierpan et al., 2020; Ahmad et al., 2022) suggests a stable sulfide (and possibly
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403 rutile) phase during the related Precambrian subduction and negligible mobilization of these elements
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414 during prograde subduction metamorphism. As a consequence, decreased subduction recycling
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415 efficiency into the mantle wedge and ultimately arc magmatism is expected for these (and probably
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416 other) redox-sensitive elements during the Proterozoic compared to the times of dominant oxidized
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417 sediment subduction in the Phanerozoic. This is supported by Mo elemental and isotope systematics
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418 from the Lesser Antilles Arc suggesting a limited transfer of anoxic sediment-derived Mo to the mantle
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419 wedge (Freymuth et al., 2016; Gaschnig et al., 2017). Other redox-sensitive element systematics
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420 suggest inefficient subduction recycling of e.g., U during the Precambrian except during the major
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421 oxidation events (Liu et al., 2019) and limited redox transfer to the mantle wedge as indicated by
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422 $\text{Fe}^{3+}/\text{Fe}^{2+}$ and V/Sc ratios in arc lavas, which systematically rose only after the Neoproterozoic
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423 Oxidation Event when oxidation made sulfates in the deep-ocean available for subduction (Stolper and
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424 Bucholz, 2019). This further supports the notion that subducted anoxic sediments act as a redox filter
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425 that could buffer fluids from the underlying AOC and serpentinites to reducing conditions independent
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426 of their original fO_2 (Padron-Navarta et al., 2023). This low fO_2 consequently leads to suppressed redox
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427 budget transfer into arc magmas as well as mobility of e.g., Mo, Se, S, and U. This potentially results
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428 in changing abundances of these elements in continent-forming magmatic rocks over deep time,
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429 depending on the redox budget of subducted lithologies, which in turn is related to Earth's surface
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430 oxygenation.
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431 Conclusion 12 13 14

432 The lavas from Pitcairn Island define the known end member of the EM-1 mantle component. This
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433 makes them particularly suitable to constrain the chemical and isotopic composition of this distinct
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434 and important mantle component and elucidate its genesis. Applying mixing models using combined
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435 Mo and radiogenic isotopes from fresh Pitcairn hotspot basalts suggests that <2% of Proterozoic
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436 pelagic sediments formed near the anoxic base of a stratified ocean are a plausible contaminant to
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437 explain the Mo isotopic signature of the Pitcairn mantle source. This conclusion is in line with EM-1
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438 influenced lavas from the South Atlantic, where a recycled anoxic sediment contribution was proposed
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439 previously (Ahmad et al., 2022). Radiogenic isotopes and stable Mo isotopes from both settings
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440 suggest a common origin of the widespread contamination of Earth's LLSVPs, likely caused by the
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441 subduction of Proterozoic anoxic pelagic sediments. These findings complement those of Hin et al.
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442 (2022), who inferred predominantly light Mo isotope signatures recycled to the (bulk) mantle by
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443 adding anoxic Precambrian sediments. The addition of this anoxic and isotopically heavy material to
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444 the core-mantle boundary, which is not largely recycled back to the bulk mantle by convective stirring,
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445 may therefore be critical in refined models of silicate Earth evolution driven by subduction recycling
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446 through time. This further confirms that the Mo isotope signature of enriched hotspot lavas with a
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447 recycled sedimentary component can constrain the redox state before and during the subduction of
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448 those. The preservation of pre-subducted sedimentary Mo and S isotope signatures in the EM-1 mantle
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449 source suggests decreased subduction recycling of redox-sensitive elements like Mo, Se, S, and U from
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450 these sediments into the mantle wedge during the Precambrian. In addition, it supports the
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451 interpretation that the EM-1 component of the mantle includes ancient surface material.

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