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1 Molybdenum mobility and isotopic fractionation during
2 subduction at the Mariana arc

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11 **Abstract**

12 The fate of crustal material returned to the convecting mantle by plate
13 tectonics is important for understanding the chemical and physical evolu-
14 tion of the planet. Marked isotopic variability of Mo at the Earth's surface
15 offers the promise of providing distinctive signatures of such recycled ma-
16 terial. However, characterisation of the behaviour of Mo during subduction
17 is needed to assess the potential of Mo isotope ratios as tracers for global
18 geochemical cycles. Here we present Mo isotope data for input and output
19 components of the archetypical Mariana arc: Mariana arc lavas, sediments
20 from ODP Sites 800, 801 and 802 near the Mariana trench and the altered
21 mafic, oceanic crust (AOC), from ODP Site 801, together with samples of
22 the deeper oceanic crust from ODP Site 1256. We also report new high pre-
23 cision Pb isotope data for the Mariana arc lavas and a dataset of Pb isotope
24 ratios from sediments from ODP Sites 800, 801 and 802. The Mariana arc
25 lavas are enriched in Mo compared to elements of similar incompatibility

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26 during upper mantle melting, and have distinct, isotopically heavy Mo (high
 27 $^{98}\text{Mo}/^{95}\text{Mo}$) relative to the upper mantle, by up to 0.3 parts per thousand.
 28 In contrast, the various subducting sediment lithologies dominantly host iso-
 29 topically light Mo. Coupled Pb and Mo enrichment in the Mariana arc lavas
 30 suggests a common source for these elements and we further use Pb isotopes
 31 to identify the origin of the isotopically heavy Mo. We infer that an aqueous
 32 fluid component with elevated [Mo], [Pb], high $^{98}\text{Mo}/^{95}\text{Mo}$ and unradiogenic
 33 Pb is derived from the subducting, mafic oceanic crust. Although the top few
 34 hundred metres of the subducting, mafic crust have a high $^{98}\text{Mo}/^{95}\text{Mo}$, as a
 35 result of seawater alteration, tightly defined Pb isotope arrays of the Mariana
 36 arc lavas extrapolate to a fluid component akin to fresh Pacific mid-ocean
 37 ridge basalts. This argues against a flux dominantly derived from the highly
 38 altered, uppermost mafic crust or indeed from an Indian-like mantle wedge.
 39 Thus we infer that the Pb and Mo budgets of the fluid component are dom-
 40 inated by contributions from the deeper, less altered (cooler) portion of the
 41 subducting Pacific crust. The high $^{98}\text{Mo}/^{95}\text{Mo}$ of this flux is likely caused
 42 by isotopic fractionation during dehydration and fluid flow in the slab. As a
 43 result, the residual mafic crust becomes isotopically lighter than the upper
 44 mantle from which it was derived. Our results suggest that the continen-
 45 tal crust produced by arc magmatism should have an isotopically heavy Mo
 46 composition compared to the mantle, whilst a contribution of deep recycled
 47 oceanic crust to the sources of some ocean island basalts might be evident
 48 from an isotopically light Mo signature.
 49 *Keywords:* Mo isotopes, subduction zones, Mariana arc, alteration, oceanic
 50 crust

51 1. Introduction

52 The Mo stable isotope system has, in the past decade, emerged as an im-
53 portant tool to reconstruct paleo-redox conditions in the ocean (e.g. Siebert
54 et al., 2003; Arnold et al., 2004). Fractionation of Mo isotopes has been
55 shown to occur between seawater ($\delta^{98/95}\text{Mo} = 2\text{‰}$ relative to NIST SRM
56 3134, Siebert et al., 2003) and oxic sediments (e.g. $\delta^{98/95}\text{Mo} \approx -1\text{‰}$ for
57 Fe-Mn crusts, Barling et al., 2001; Siebert et al., 2003), whereas anoxic sedi-
58 ments (such as black shales) incorporate Mo from seawater quantitatively and
59 therefore without isotopic fractionation (e.g. Arnold et al., 2004). Mo is also
60 removed from seawater during hydrothermal circulation at mid-ocean ridges
61 (Trefry et al., 1994), which could add an isotopically distinct Mo component
62 to the mafic oceanic crust. Oceanic crust therefore likely comprises altered
63 materials with isotopically highly variable Mo compositions, quite dis-similar
64 to mantle values (-0.2 to 0 ‰, Burkhardt et al., 2014). This suggests Mo
65 isotope measurements might provide a diagnostic tracer of surface material
66 returned to the Earth’s interior, which can be used to track the remixing of
67 subducted plates into the convecting mantle. Before such application, how-
68 ever, possibly modifications to the Mo isotope ratios of subducted material
69 need to be assessed.

70 Volcanic arc magmas contain components derived from subducted sedi-
71 ments and elements carried in a fluid phase that is released from the mafic,
72 altered oceanic crust (AOC) (Gill, 1981). The nature of this fluid phase,
73 aqueous fluid, supercritical fluid, or melt is debated but empirically it is com-
74 positionally distinct from the sediment component (Kay, 1980). Although
75 Noll et al. (1996) argued for minor fluid mobilisation of Mo during dehydra-

76 tion of subducting slabs, Green and Adam (2003) showed that Mo can be
77 highly mobile in aqueous fluids at temperatures and pressures relevant for
78 subduction zones. Mo transport in fluids derived from the subducted slab
79 has further been suggested to be responsible for Mo enrichment in volcanic
80 rocks from the Solomon arc (König et al., 2008). In addition, oxic oceanic
81 sediments can be highly enriched in Mo and upon subduction potentially
82 release Mo into the arc magma source. Volcanic arc magmas can therefore
83 be expected to obtain a significant Mo contribution from subducted compo-
84 nents.

85 As a consequence, Mo isotope measurements might act as a tracer for
86 components derived from subducted slabs in arc magmas. Release of Mo
87 from the subducted slabs in subduction zones also potentially alters the bulk
88 isotopic composition of material that is being transported beyond subduction
89 zones into deeper parts of the mantle. A comparison of the input material
90 into subduction zones (AOC and sediments) with the volcanic output can
91 provide information about the effect of these processes and the composition
92 of the residual, deep subducted material.

93 The Mariana arc (Fig. 1) is an ideal location to address these questions
94 because the islands of the Mariana arc are compositionally diverse, defin-
95 ing geochemical trends that implicate the variable influence of subducted
96 sediments and slab-derived fluids (e.g. Woodhead, 1989; Elliott et al., 1997)
97 (Fig. 2). In addition, samples of input material for the Mariana arc are avail-
98 able from ODP Sites 800, 801 and 802 (Fig. 1) which sampled the entire
99 sediment columns at these locations. Furthermore, ODP Site 801 provides
100 an unusually complete section through the upper AOC. Together, these sam-

101 ples allow us to constrain potential source components of the Mariana arc
102 lavas in exceptional detail. We complement the data from the upper AOC
103 with samples from ODP Site 1256, which is located further away from the
104 Mariana arc on the younger Cocos plate in the Eastern Pacific ocean but is
105 the stratigraphically deepest drill hole in the oceanic crust and thus allows
106 us to constrain the Mo isotope composition of deeper parts of the AOC. In
107 addition to Mo isotope ratios we present new Pb isotope data for the Mariana
108 arc lavas and for sediments from ODP Sites 800, 801 and 802. As another
109 chalcophile element, incompatible during mantle melting, Pb makes a useful
110 reference for the Mo data, especially since the isotopic composition of Pb has
111 long been used to trace the involvement of different subduction components
112 in arc lavas (Tatsumoto, 1969).

113 **2. Material and methods**

114 *2.1. Samples*

115 Sediment samples are from ODP Sites 800, 801 and 802 drilled during
116 ODP Leg 129 in the Western Pacific about 500-700 km East of the Mariana
117 trench (Fig. 1). The sediments range in age from the middle Jurassic to
118 recent (Lancelot et al., 1990) and are stratigraphically similar in the three
119 sites, starting with Mesozoic clay and radiolarites, followed by volcanoclastic
120 sediments, cherts and porcellanites, and pelagic clays deposited during the
121 Cenozoic (supplementary Table 1 and supplementary Fig. 1). However, the
122 thicknesses of the sediment sequences are variable between the three sites and
123 a sequence of Miocene volcanoclastic sediments, that presumably originates
124 from the Caroline Island volcanic chain (Lancelot et al., 1990), is only present

125 in the most southerly ODP Site 802. Volcaniclastic deposits are the volu-
126 metrically dominant sediment type (on average 55 % of the total sediment
127 thickness at the three ODP sites).

128 Samples of the mafic, AOC are taken from ODP Sites 801 and 1256 to
129 cover upper extrusive and lower intrusive sections of the crust, respectively.
130 ODP Site 801 (Fig. 1) has been re-visited and deepened during ODP Leg
131 185 and has a total penetration depth of 474 m into the 165 Ma old mafic
132 oceanic crust (Plank et al., 2000). It is a rare example of reasonable sample
133 recovery of the mafic oceanic crust to significant depth, that offers the possi-
134 bility of directly characterising the composition of the mafic crust subducting
135 at the Mariana trench. The samples analysed from this site are 'composites'
136 from 0-110 m and from 220-420 m depth within the mafic crust and the 'su-
137 per composite' (Kelley et al., 2003). These composites are mixed powders
138 representative of the various lithologies present in an interval of the crust
139 and its associated alteration. Three composites exist for each depth inter-
140 val: one that primarily samples less altered basaltic flows (FLO), one from
141 highly altered breccias (VCL) and a weighted mixture of both (ALL). The
142 super composite is a representative mixture of the entire top 420 m section of
143 oceanic crust sampled at Hole 801C. The use of composites provides a highly
144 effective means of determining an average for the heterogeneously altered
145 oceanic crust (Staudigel et al., 1995), especially valuable for time-intensive
146 isotopic analyses.

147 Drilling into the 15 Ma crust at ODP Site 1256 started during ODP
148 Leg 206 and the site has been re-visited and holes deepened during IODP
149 Expeditions 309, 312 and 335. It now penetrates a total depth of 1522

150 meters below sea level (mbsf) of which the top 251 m are sediments, fol-
151 lowed by 814 m of massive basalts and sheet flows, 345 m of sheeted dykes,
152 and a dike-gabbro transition zone at the bottom 113 m of the hole (Teagle
153 et al., 2012). Hole 1256D is the stratigraphically deepest hole drilled into
154 the mafic oceanic crust and gives us the opportunity to obtain information
155 about chemical and isotopic variation in deeper stratigraphic sections of the
156 oceanic crust, such as the hydrothermally altered dyke sequence and under-
157 lying gabbros. The samples used for this study are from 753-1494 m depth
158 (corresponding to 508-1249 m below the sediment cover) and so continue
159 our sample of the mafic AOC from ODP Site 801 to greater stratigraphic
160 depths. Lithologies analysed include sheet flows, sheeted dikes, and gabbros
161 (Supplementary Table 1).

162 Temperatures during alteration of the upper part of the oceanic crust
163 sampled at ODP Site 801 are below 100°C (Alt and Teagle, 2003). The
164 samples used in this study from ODP Site 1256 cross an alteration transition
165 zone (ATZ) at ~ 750 m depth within the mafic crust that separates an upper
166 section at low-temperature alteration ($<100^\circ\text{C}$) from a section of hydrother-
167 mal alteration with temperatures $>250^\circ\text{C}$ (Sano et al., 2008). Alteration of
168 the deep crust occurs by near axis, hydrothermal circulation which is most
169 strongly controlled by spreading rate (Purdy et al., 1992). Since ODP Sites
170 801 and 1256 both sample significantly off-axis crust produced from fast
171 spreading ridges, there is a rationale for the combination of these records
172 to produce a more complete estimate of crustal alteration, beyond simple
173 necessity of very limited access to the deep crust.

174 Samples from the Mariana islands analysed here (described in Elliott

175 et al., 1997) are from the four islands Guguan, Alamagan, Uracas, and Agri-
 176 gan, located in the Central Island province (CIP) of the Mariana arc (Fig. 1).
 177 They are from historic or morphologically very recent eruptions and therefore
 178 provide data for the contemporaneous geochemical variation within the arc.
 179 The islands of the Mariana arc are compositionally diverse with two end-
 180 members in trace elements and radiogenic isotopes that show the variable
 181 influence of a fluid- and sediment- components (e.g. high Ba/Th vs. low
 182 $^{143}\text{Nd}/^{144}\text{Nd}$ respectively, Fig. 2). These geochemical variability displayed
 183 by the lavas has been interpreted to reflect an approximately constant fluid
 184 contribution with variable amounts of sediment melts added to the mantle
 185 sources beneath different islands (Elliott et al., 1997).

186 *2.2. Analytical methods*

187 Mo isotope analyses was performed using a double spike technique using
 188 an approach similar to that described in Siebert et al. (2001). The ^{97}Mo -
 189 ^{100}Mo double spike calibrated and used by Archer and Vance (2008) was
 190 employed in this study and was added to all samples prior to dissolution.
 191 Sediment and AOC samples were initially treated with a mixture of HNO_3
 192 and H_2O_2 in order to decompose organic material. All samples were then
 193 dissolved in a $\text{HF-NH}_4\text{OH}$ mixture, followed by re-dissolution in HCl . The
 194 latter step was usually repeated and complete dissolution of the sample in
 195 HCl was ensured in order to achieve sample-spike equilibration.

196 We developed a new single pass anion exchange column procedure for
 197 separation of Mo from silicate matrices. Sediment and AOC samples were
 198 loaded onto 2 ml anion exchange resin in 3M HCl followed by removal of
 199 most of the matrix in 3M HCl , removal of the high field strength elements

200 in 0.5M HCl - 0.5% H_2O_2 , and collection of Mo in 3M HNO_3 . We later
 201 discovered that this procedure does not completely remove Zn which can
 202 lead to troublesome ZnCl interferences. The $^{64}\text{Zn}^{35}\text{Cl}$ species contributes
 203 to mass 99 and can lead to an over-correction of Ru interferences, which is
 204 calculated assuming all the mass 99 signal is Ru. Experiments showed that
 205 such ZnCl interferences are rarely significant, but in order to guard against
 206 possible artifacts, data were rejected when the total 'Ru correction' was more
 207 than 0.2 ‰ in $\delta^{98/95}\text{Mo}$. For analyses of arc lava samples an additional step
 208 was added to the column procedure in which Zn is eluted in 1M HF, prior
 209 to collection of Mo. In addition, Mo was eluted in 1M HCl rather than 3M
 210 HNO_3 , which yields better separation of Mo from Sn. The protocols are
 211 described in greater detail in Willbold et al. (in review).

212 Using the initial separation procedure, analyses of the BHVO-2 standard
 213 yielded $\delta^{98/95}\text{Mo} = -0.082 \pm 0.076$ ‰ and $c[\text{Mo}] = 3.44 \pm 2.5$ $\mu\text{g/g}$ ($n=14$)
 214 with Mo isotopic compositions reported as the parts per thousand deviation
 215 of the $^{98/95}\text{Mo}/^{95}\text{Mo}$ sample relative to NIST SRM 3134 (Greber et al., 2012;
 216 Goldberg et al., 2013). Note that the highly variable $c[\text{Mo}]$ is presumably
 217 a result of heterogeneous contamination of BHVO-2 during preparation of
 218 the powder (Weis et al., 2005). Analyses of BHVO-2 have been reported
 219 in a number of Mo isotope studies, making it valuable for cross-comparison,
 220 but the issue of its significant Mo contamination led us to use JB-2 as an
 221 additional rock standard. As a Japanese arc basalt, this standard is also
 222 particularly appropriate for this study. As processed using our modified
 223 Mo separation protocol JB-2 yielded $\delta^{98/95}\text{Mo} = 0.062 \pm 0.025$ ‰, $c[\text{Mo}] =$
 224 0.991 ± 0.003 $\mu\text{g/g}$ ($n=3$) and BHVO-2 $\delta^{98/95}\text{Mo} = -0.061 \pm 0.074$ ‰, $c[\text{Mo}] =$

225 $4.4991 \pm 3.393 \mu\text{g/g}$ ($n=3$). The uncertainties cited represent 2σ standard de-
 226 viations of repeat measurements and so are indicative of the reproducibilities
 227 of single measurements.

228 The Mariana arc lava samples were analysed for their Pb isotopic composi-
 229 tions by thermal ionisation, using a double spiking technique, as documented
 230 in detail in Taylor et al. (2015). These data significantly improve on the accu-
 231 racy and precision relative to the conventional thermal ionisation procedures
 232 employed by Elliott et al. (1997) and so supercede the data reported in this
 233 earlier study. For sediment samples, Pb was separated from the matrix by
 234 anion exchange with $50 \mu\text{L}$ columns of AG1-X8 resin using the approach of
 235 Strelow and Van der Walt (1981), further described by Galer (1986). Pb iso-
 236 tope ratios were corrected for mass bias by sample-standard bracketing with
 237 the NIST SRM 981 standard to ratios of NIST SRM 981 of $^{206}\text{Pb}/^{204}\text{Pb} =$
 238 16.9416 , $^{207}\text{Pb}/^{204}\text{Pb} = 15.4998$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.7249$ (Baker et al., 2004).
 239 Pb isotope ratios measured for the JB-2 standard were $^{206}\text{Pb}/^{204} = 18.343 \pm$
 240 0.008 ($n=5$), $^{207}\text{Pb}/^{204} = 15.562 \pm 0.006$ ($n=5$), $^{208}\text{Pb}/^{204} = 38.276 \pm 0.023$
 241 ($n=5$).

242 3. Results

243 3.1. Sediments

244 A plot of Mo isotopic compositions vs. Mo concentrations for sediment
 245 samples from ODP Sites 800, 801 and 802 is shown in Fig. 3a. These data
 246 are further plotted stratigraphically in the Electronic Supplement (Supple-
 247 mentary Table 1, Supplementary Fig. 1). The highest Mo concentrations
 248 ($>9 \mu\text{g/g}$ Mo) are present in the slowly accumulating Cenozoic clays while

249 concentrations are considerably lower in the other sediment lithologies, in-
 250 cluding the Mesozoic clays ($<3 \mu\text{g/g Mo}$). There is no systematic trend
 251 between Mo concentrations and Mo isotopic composition within or between
 252 sediment types. Mo isotopic compositions of the different sediment types vary
 253 from values similar to the mantle derived standards reported by Burkhardt
 254 et al. (2014) (-0.05 to -0.2 ‰) and our estimate of the mantle (-0.2 ‰ , see
 255 below) to notably lighter values (-1 to -2 ‰ in some clays). It has been
 256 argued on the basis of Pb and Sr isotope ratios (Avanzinelli et al., 2012) and
 257 Hf and Nd isotope ratios (Tollstrup and Gill, 2005) that the volcanoclastic
 258 sediments dominate the sediment signature contributed to the Mariana arc
 259 lavas. The three samples of volcanoclastic sediment analysed here have mod-
 260 est Mo concentrations of $0.50 \mu\text{g/g}$ and an average Mo isotopic composition
 261 that is lighter than the mantle reference ($\delta^{98/95}\text{Mo} = -0.40 \text{ ‰}$) (Fig. 3 a).
 262 The lithological and concentration weighted average Mo isotope composition
 263 of the sediments outboard of the Mariana arc is $\delta^{98/95}\text{Mo} = -0.29$ (Supple-
 264 mentary Table 1).

265 Pb isotope ratios in the sediment samples (Supplementary Table 2) are
 266 shown in Fig. 3b and Fig. 3c and compared to previous estimates for the Pb
 267 isotope composition of sediments subducted at the Mariana trench based on
 268 a smaller number of samples that were mostly analysed by thermal ionization
 269 mass spectrometry (Plank and Langmuir, 1998). Cenozoic pelagic clays have
 270 well-defined, unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ whereas the volcanoclastic sediments
 271 are higher and more variable in $^{206}\text{Pb}/^{204}\text{Pb}$. This reflects the diverse iso-
 272 topic compositions of the different seamount chains in the region (Koppers
 273 et al., 2003), which include so-called enriched mantle and HIMU components.

274 The latter is manifest in the radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values
 275 (Fig. 3b). Mesozoic radiolarites and clays, as well as cherts and porcellan-
 276 ites, are intermediate in Pb isotope ratios between the Cenozoic clays and the
 277 volcanoclastic sediments. The new and previously published data are largely
 278 comparable and the Pb isotope ratios of the average sediment, weighted by
 279 Pb concentration and relative sediment thickness, are very similar to the
 280 previous estimate based on a smaller set of analyses.

281 3.2. *Altered oceanic crust*

282 The Mo isotopic compositions and Mo concentrations in samples of the
 283 AOC from ODP Sites 801 and 1256 are reported in Supplementary Table 1
 284 and shown stratigraphically in Fig. 4a. Mo concentrations vary rather un-
 285 systematically from $\sim 0.1 - 1 \mu\text{g/g}$. Similarly, Mo isotopic variations with
 286 depth are erratic, but the isotopically heaviest samples are found in the up-
 287 permost mafic crust (Fig. 4a), which have $\delta^{98/95}\text{Mo}$ higher than any of the
 288 sedimentary samples.

289 We also show a plot of $\delta^{98/95}\text{Mo}$ vs. Ce/Mo in Fig. 4b for the AOC sam-
 290 ples to illustrate relative loss or gain of Mo during alteration and associated
 291 isotopic changes. The ratio Ce/Mo forms a useful reference as Mo has been
 292 found to be similarly incompatible during mantle melting and mafic differ-
 293 entiation to the light rare earth elements (Newsom et al., 1986). In Fig. 4b
 294 samples from different depths in ODP Site 801 show contrasting trends. In
 295 the uppermost (0-110 m) there is a linear trend between high $\delta^{98/95}\text{Mo}$, low
 296 Ce/Mo in the volcanoclastic rich composite (VCL) and lower $\delta^{98/95}\text{Mo}$, higher
 297 Ce/Mo in the composite comprised mainly of flows (FLO). These differences
 298 reflect contrasting intensity of alteration. The deeper (220-420 m) composites

299 have, on average, higher Ce/Mo ratios and form an approximately horizontal
 300 array at lower $\delta^{98/95}\text{Mo}$. Mo isotope ratios and Ce/Mo ratios of the low tem-
 301 perature altered samples from above the ATZ in ODP Site 1256 plot within
 302 the range of the 220-420 m composites from Hole 801C. Below the ATZ sam-
 303 ples from ODP Site 1256 have slightly lighter Mo isotopic compositions but
 304 have a similar range in Ce/Mo.

305 No systematic variations are observed in Mo isotopic compositions below
 306 the ATZ even though some variability occurs in Ce/Mo. This indicates that
 307 minor redistribution of Mo has occurred but on average the Mo isotope ratios
 308 are not greatly perturbed by alteration. We have therefore attempted to
 309 estimate the composition of unaltered mid-ocean ridge basalt (MORB) using
 310 the least altered AOC samples. A visual estimate of the degree of alteration
 311 is reported for ODP Site 1256 material (Expedition 309/312 Scientists, 2006),
 312 where samples are described as either 'slightly altered', 'moderately altered'
 313 or 'heavily altered'. The average Mo isotope ratios of the 'slightly altered'
 314 samples below the ATZ is $\delta^{98/95}\text{Mo} = -0.199 \pm 0.063$ ($n = 5$). While the
 315 Mo isotope ratios of these samples might be affected by a minor degree of
 316 alteration we consider this a useful reference for this study. It is also within
 317 the range of $\delta^{98/95}\text{Mo} = -0.15$ – -0.25 reported for handpicked MORB glasses
 318 (Hibbert et al., 2013).

319 3.3. Mariana arc lavas

320 Mo isotopic compositions and Mo concentrations in Mariana arc lavas are
 321 reported in Table 1. Molybdenum isotope ratios of the Mariana arc samples
 322 are plotted against MgO content in Fig. 5a. Compared to MORB, most
 323 Mariana arc lavas are substantially enriched in Mo over the similarly incom-

324 patible Ce (Fig. 5c). Similar observations have been made for samples from
 325 the Solomon arc (König et al., 2008), which mostly plot at the high Ce/Mo
 326 end of MORB but also extend to lower Ce/Mo (Fig. 5c). The Mariana arc
 327 lavas have significantly higher values of $\delta^{98/95}\text{Mo}$ than MORB (Fig. 6a). Pre-
 328 viously, Voegelin et al. (2014) reported $\delta^{98/95}\text{Mo}$ on a suit of continental arc
 329 lavas from Kos. Although they argued that $\delta^{98/95}\text{Mo}$ was perturbed during
 330 differentiation, even their least evolved samples have $\delta^{98/95}\text{Mo} \approx 0.05$, which
 331 is isotopically heavier than MORB and similar to the Mariana arc lavas.

332 Samples from Agrigan have lower $\delta^{98/95}\text{Mo}$ and higher Ce/Mo ratios com-
 333 pared to the other islands of the Mariana arc (Fig. 6a). Fig. 5c shows that
 334 the high Ce/Mo ratios reflect lower concentrations of Mo and slightly higher
 335 concentrations of Ce in the Agrigan samples compared to those in other is-
 336 lands. The Ce/Mo ratio of the Mariana arc lavas correlates with Ce/Pb
 337 (Fig. 6b), a ratio that reflects the high fluid-mobility of Pb compared to Ce
 338 and is commonly used as an indicator for fluid-enrichment in arc lavas (Miller
 339 et al., 1994).

340 The Mariana arc lavas form well-defined arrays in $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$
 341 and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 7). Samples from Uracas have sig-
 342 nificantly more radiogenic Pb isotope ratios than the other islands. Agrigan
 343 and Guguan plot at the unradiogenic end of the trend. The modest over-
 344 all variation in Pb isotope ratios means that the high precision analyses are
 345 necessary to clearly delineate these features.

346 4. Discussion

347 4.1. Controls on the Mo isotopic composition of oceanic sediments and al- 348 tered oceanic crust

349 The higher concentrations of Mo in the Cenozoic clays compared to the
350 Mesozoic clays and radiolarites (Fig. 3) can be explained by their slow sedi-
351 ment deposition rates and the associated higher percentage of Fe-Mn oxides
352 (Lancelot et al., 1990), which adsorb Mo from seawater. The isotopic com-
353 position of the Cenozoic clays relative to seawater (with $\delta^{98/95}\text{Mo} \approx 2.0 \text{ ‰}$
354 (Siebert et al., 2003)) indicates a similar isotopic fractionation to that ob-
355 served for the absorption of Mo to Mn oxyhydroxides (Barling et al., 2001).
356 However, the Cenozoic clays have a considerable range in Mo isotope ratios
357 which suggests that incorporation of Mo into pelagic clays is more complex
358 than simple scavenging of Mo by Fe-Mn oxides.

359 The effect of alteration in the uppermost oceanic crust on Mo isotope
360 ratios is shown by the 0-110 m composites from ODP Site 801 (Fig. 4).
361 That the most altered (VCL) composite has the lowest Ce/Mo and highest
362 $\delta^{98/95}\text{Mo}$ indicates incorporation of isotopically heavy, seawater-derived Mo
363 into the upper crust during alteration.

364 Alt and Teagle (2003) found that the style of alteration changes with
365 depth within the mafic oceanic crust of ODP Site 801. The top part is domi-
366 nated by the formation of celadonite halos and veins formed under oxidizing
367 conditions. Saponite and pyrite as well as carbonate veins are more abundant
368 in deeper sections which are generally more reducing. Mo is a redox-sensitive
369 element and the isotopically lighter compositions of the 220-420 m sections of
370 ODP Site 801 compared to the 0-110 m composites (Fig. 4) can thus poten-

371 tially be related to the different alteration assemblages and redox conditions.
372 The more reduced conditions might be anticipated to result in more quanti-
373 tative addition of Mo to the crust, with $\delta^{98/95}\text{Mo}$ closer to seawater, but this
374 is clearly not the case (Fig. 4). Instead the 220-420 m composites display a
375 range in $\delta^{98/95}\text{Mo}$ and Ce/Mo comparable to the dykes from ODP Site 1256.
376 The highly variable Ce/Mo at $\delta^{98/95}\text{Mo}$ only slightly heavier than MORB
377 suggests redistribution of Mo in a rock-buffered system at elevated tempera-
378 tures. Thus, addition of a seawater Mo component to the crust is only clearly
379 evident in the shallowest (highest porosity) sequence of extrusives.

380 *4.2. Incorporation of Mo from the subducted slab into Mariana arc magmas*

381 The possibility of Mo isotope fractionation during magma differentiation
382 has been discussed by Voegelin et al. (2014). Samples from Uracas and Agri-
383 gan have a wide range of MgO content but do not show any related variations
384 in $\delta^{98/95}\text{Mo}$ (Fig. 5a). Thus, fractional crystallization does not appear to sig-
385 nificantly affect their Mo isotope ratios. The Ce/Mo ratios of each island vary
386 little compared to the total range within the Mariana arc and do not change
387 systematically with the degree of differentiation (Fig. 5b), thus confirming
388 similar partitioning of Ce and Mo during crystallisation of basaltic melts.
389 An exception to this within-island consistency of Ce/Mo is seen in sample
390 GUG-6 from Guguan, which has a Ce/Mo ratio more than twice as high as
391 other samples from the same island. This is caused by a lower Mo concen-
392 tration in this sample (Fig. 5c). However, radiogenic and U-series isotopes
393 and most trace element systematics in this sample are indistinguishable from
394 other samples from Guguan (Elliott et al., 1997). One further variable that
395 distinguishes it from the other Guguan samples within the dataset of El-

396 liott et al. (1997) is a significantly lower concentrations of Pb (but without
 397 differences in Pb isotopes), which might be caused by the separation of an
 398 immiscible sulphide phase during fractional crystallization, a process that has
 399 been suggested to occur in the Mariana arc and backarc (Alt et al., 1993).
 400 It is likely that sulphide segregation also isotopically fractionates Mo and we
 401 attribute the somewhat heavier Mo isotopic composition of GUG-6 relative
 402 to otherwise very similar Guguan lavas to this process. Given we believe the
 403 Mo systematics of this sample are perturbed by differentiation, we exclude it
 404 from subsequent discussion of the influence of subduction processes on Mo.

405 The study by Noll et al. (1996) concluded that Mo is immobile in sub-
 406 duction zone fluids even though positive correlations were shown between
 407 Mo/Ce and B/La, the latter being used in the study as indicator for fluid
 408 enrichment. On the contrary, König et al. (2008) showed significant Mo en-
 409 richment in subduction related volcanic rocks from the Solomon islands and
 410 inferred that Mo can be mobile in subduction zone fluids. The mobility of
 411 Mo in fluids in subduction settings is also suggested by the experiments of
 412 Green and Adam (2003) on fluid-partitioning in equilibrium with MORB at
 413 3.0 GPa and 650-750°C. These show highly enriched concentrations of Mo in
 414 the fluid compared to the light rare earth elements. The experiments of Bali
 415 et al. (2012) focus specifically on the fluid-mobility of Mo and W at similar
 416 pressure and temperature conditions. They confirm the partitioning of Mo
 417 into fluids and show that the magnitude of Mo enrichment in fluids depends
 418 on the oxygen fugacity, fluid salinity and the amount of residual rutile, in
 419 which Mo is shown to be compatible. Based on these studies it is therefore
 420 likely that fluids released from the subducting slab carry significant amounts

421 of Mo and are enriched in Mo compared to Ce.

422 Transport of elements from the mafic portion of the oceanic crust in
423 the slab-derived fluid has been inferred from the unradiogenic Pb isotopic
424 composition of a low Ce/Pb component in lavas from Okmok, Aleutians
425 (Miller et al., 1994). This notion is explored for our Mariana arc samples in
426 Fig. 8. The oceanic crust subducting at the Mariana trench is of 'Pacific'
427 isotopic affinity while the subarc mantle has 'Indian' isotopic characteristics
428 (Pearce et al., 1999). The linear Pb isotope array formed by the Mariana
429 lavas backprojects through the field of Pacific, not Indian, MORB (Fig. 8).
430 This clearly links the origin of the unradiogenic Pb to the subducting slab
431 not the mantle wedge. As noted by Miller et al. (1994), this unradiogenic
432 component is also strongly enriched in Pb relative to the light rare earth
433 elements (e.g. low Ce/Pb), implying strong fractionation of these elements
434 from the MORB protolith in their transport by aqueous fluids. The same
435 holds for the Marianas and the samples from Guguan, in which the fluid
436 component is most evident (see Fig. 2), have the lowest Ce/Pb (Fig. 6).

437 Avanzinelli et al. (2012) argued that the Pb isotope systematics of the
438 Mariana arc lavas are inconsistent with the derivation of the fluid component
439 from the most altered, upper part of the oceanic crust. Instead, the Pb
440 sampled by the fluid needs to be dominantly sourced from the lower, less
441 altered part of the subducted oceanic crust that is compositionally similar
442 to fresh Pacific MORB. These points are further emphasised by our new
443 analyses (Fig. 8). That the aqueous fluid component samples Pb from the
444 unaltered mafic crust, implies that the fluid is sourced yet deeper, most
445 plausibly therefore from dehydration of underlying serpentinites (see review

446 by Spandler and Pirard, 2013) .

447 At the other end of the arc lava array, the average composition of the
448 sediment subducting at the Mariana trench is too low in $^{206}\text{Pb}/^{204}\text{Pb}$ to
449 represent the radiogenic end-member (Fig. 8). However, the volcanoclastic
450 sediments have suitable Pb isotope ratios to constitute this component, as
451 has been previously suggested (Tollstrup and Gill, 2005; Avanzinelli et al.,
452 2012). Alternatively, the radiogenic end-member could be a mixed slab melt
453 formed by the bulk sediment together with the top of the AOC.

454 The Pb isotope composition of the Mariana arc lavas thus reflects two
455 distinct components: a fluid that dominantly samples the less altered, cooler
456 part of the mafic crust and a melt that is produced by fluid addition to the
457 hotter, top of the slab. The sub-arc mantle, represented in Fig. 8 by Indian
458 MORB, does not significantly contribute to the Pb budget of the Mariana arc
459 lavas. Mo enrichment in the Mariana arc lavas correlates with Pb enrichment
460 (Fig. 6b), suggesting similar transport mechanisms for the two elements.
461 Thus Pb isotopic constraints on the origin of the slab components in the
462 Mariana lavas, as reviewed above, provide a useful background in accounting
463 for their Mo isotopic compositions.

464 Samples from Guguan, Alamagan, and Uracas form an approximately
465 horizontal trend in $\delta^{98/95}\text{Mo}$ against Ce/Mo (Fig. 6a). That the sediment-
466 rich lavas from Uracas and the sediment poor (hence fluid dominated) lavas
467 of Guguan both have $\delta^{98/95}\text{Mo} \sim 0.05$, implies the Mo isotopic composition
468 for two slab-derived components is similar and higher than either MORB or
469 sediment inputs to the subduction zone (Fig. 6a).

470 However, samples from Agrigan do not plot on the same trend as the

471 other Mariana arc lavas in Fig. 6a. To some extent this is not unexpected
 472 as it has previously been highlighted (Elliott et al., 1997; Avanzinelli et al.,
 473 2012) that although Agrigan samples have low Nd isotope ratios and Ba/Th
 474 ratios indicating a relatively large fraction of sediment melts in their sources
 475 (Fig. 2), they have unradiogenic Pb isotope ratios when compared to most
 476 other Mariana arc lavas (Fig. 6, 8). This has been argued to reflect the het-
 477 erogeneity in the Pb isotopic compositions of the subducting volcanoclastics
 478 (see Fig. 3). Yet Agrigan samples also have high Ce/Pb and Ce/Mo ratios
 479 (Fig. 6b). This requires further explanation and suggests an unusually low
 480 amount of fluid added to the Agrigan mantle source. Thus, the anomalous
 481 position of Agrigan lavas in Fig. 6a reflects both a compositionally different
 482 sediment component and a smaller fluid contribution compared to the other
 483 samples.

484 The slab melt component (for islands other than Agrigan) should plot
 485 at higher Ce/Mo along the horizontal extrapolation of the sample array in
 486 Fig. 6a. From Pb isotopes (Fig. 8), the slab melt was argued to be either
 487 dominantly derived from volcanoclastic sediments or a mixture of sediment
 488 melt and AOC melt. The latter explanation is the most straight-forwardly
 489 plausible from initial inspection of Fig. 6a, given a mixture of volcanoclastics
 490 and AOC can generate an appropriate high Ce/Mo endmember for the main
 491 arc lava array. However, it is possible that both Ce/Mo and even Mo isotopes
 492 fractionate during sediment melting and so we cannot rule out the former
 493 scenario from our current scant knowledge of the behaviour of Mo during
 494 sediment melting.

495 The geometry of Fig. 6a requires that the low Ce/Mo fluid component

496 has a $\delta^{98/95}\text{Mo} \sim 0.05$, which is markedly isotopically heavier than unaltered
 497 MORB (Fig. 6a). Although the uppermost part of the altered oceanic crust
 498 has elevated $\delta^{98/95}\text{Mo}$, as discussed above, the Pb isotope ratios in the Mari-
 499 ana arc lavas are inconsistent with the derivation of the fluid from this source.
 500 If the Mo in the fluids, as with Pb, is dominantly derived from the unaltered
 501 lower part of the oceanic crust then the heavy Mo isotope composition of the
 502 fluid requires the Mo transported in the fluid to be isotopically fractionated
 503 by this process. High temperature isotopic fractionation during the release
 504 of fluids in subduction zones is known to occur for other elements, e.g. for
 505 B (e.g. Marschall et al., 2007, and references therein). For heavier elements
 506 the amount of fractionation will generally be smaller but mass-dependent
 507 Mo isotopic differences have already been documented in magmatic mineral
 508 phases (Voegelin et al., 2014), showing that significant fractionation can oc-
 509 cur at temperatures higher than those in the AOC at sub-arc depth. This
 510 suggests that equilibrium fractionation of Mo isotopes during generation and
 511 passage of fluids through the oceanic crust is plausible. A mechanism for
 512 fractionating Mo isotopes could be equilibration with rutile, which has been
 513 found to incorporate Mo at 2.6 GPa and 600-800°C (Bali et al., 2012) and
 514 is a common phase in metabasalts and metagabbros, showing evidence for
 515 chemical exchange with fluids in eclogite veins (e.g. Spandler et al., 2011).
 516 Residual rutile is also widely inferred to be present during sediment melt-
 517 ing and so if rutile is responsible for the Mo isotopic fractionation in the
 518 fluid component, then fractionation may also occur during sediment melting.
 519 Alternatively, Mo isotope fractionation might occur via equilibration with
 520 sulfides, some of which are stable in the slab up to temperatures of $>750^\circ\text{C}$

521 (Tomkins and Evans, 2015).

522 4.3. Implications for the global Mo cycle

523 The average sediment subducted at the Mariana trench is isotopically
524 slightly lighter than the suggested composition of unaltered MORB (Fig. 6a).
525 The mafic oceanic crust (AOC + unaltered lower crust) initially has higher
526 $\delta^{98/95}\text{Mo}$ than unaltered MORB (Fig. 6a) but release of isotopically heavy
527 fluids from the mafic crust will lower the $\delta^{98/95}\text{Mo}$ of the residual crust.

528 The Mo isotope composition of the residual slab is explored further in
529 a simple mass balance calculation (see Supplementary Table 3 for details of
530 the calculation and input parameters). We acknowledge that many of the
531 input parameters, and indeed the bounds on their uncertainty, are poorly
532 known. Thus the quantification below is only meant as indication of the
533 potential magnitude of isotopic fractionation given widely used, best esti-
534 mates. Sediments dominate the mass of Mo transported into the subduction
535 zone with ca. $145 \text{ kg} \times \text{km}^{-3} \times \text{year}^{-1}$ while about $85 \text{ kg} \times \text{km}^{-3} \times \text{year}^{-1}$ of
536 Mo is subducted in the mafic crust at the Mariana arc. This compares to
537 a magmatic Mo output of approximately $82 \text{ kg} \times \text{km}^{-3} \times \text{year}^{-1}$. Thus, if
538 the mantle source of Mo in the Mariana arc is minor compared to the slab
539 source (Fig. 6a) then approximately 35 % of Mo is removed from the slab
540 and transferred to the arc magma source. Since the Mo removed from the
541 slab is isotopically heavy compared to the bulk crust (with $\delta^{98/95}\text{Mo} = -0.21$,
542 Fig. 6a) this will lower the Mo isotope ratios in the residual crust. With the
543 Mo isotope ratios of the material removed from the slab constrained by the
544 Mo isotope composition of the Mariana arc lavas (Fig. 5), the residual slab
545 that is transported beyond the subduction zone into the deeper mantle has

546 $\delta^{98/95}\text{Mo} = -0.27 - -0.36$, about 0.1–0.15 permil lower than the Mo isotope
 547 composition of unaltered MORB. Mo isotope measurements are therefore po-
 548 tentially useful as a tracer for deep recycled components, which we predict
 549 to have distinctly light $\delta^{98/95}\text{Mo}$. We note that seafloor sediments and sub-
 550 duction processed mafic crust might both have isotopically light Mo isotope
 551 signatures, but these components can be distinguished using more traditional
 552 radiogenic isotope tracers.

553 Subduction zones have been suggested to be the primary site of generation
 554 of continental crust (e.g. Taylor, 1967). The majority of Mariana arc lavas
 555 have heavy Mo isotopic compositions compared to MORB (Fig. 6a) and if
 556 this is typical of all arcs then we would expect that bulk continental crust
 557 should have high $\delta^{98/95}\text{Mo}$ relative to the mantle. The mantle should thus
 558 have evolved to lower $\delta^{98/95}\text{Mo}$ due to extraction of the continental crust. The
 559 composition of the bulk earth has been suggested by Burkhardt et al. (2014)
 560 to be $\delta^{98/95}\text{Mo} = -0.16 \pm 0.02$ based on an average of chondritic meteorites.
 561 This is at the higher end but within error of our preliminary estimate for the
 562 Mo isotope ratios of the mantle. More comprehensive determinations the
 563 $\delta^{98/95}\text{Mo}$ of the upper mantle and continental crust are necessary to assess if
 564 these reservoirs are complementary in terms of their Mo isotopic composition
 565 as we tentatively suggest from these initial data.

566 **5. Conclusions**

567 The diverse sediments from ODP Site 800, 801 and 802 in the Western
 568 Pacific Ocean have variable Mo isotopic compositions and Mo concentra-
 569 tions. The sediments tend towards isotopically light compositions relative to

570 the mantle, likely reflecting isotopic fractionation during absorption of Mo
 571 from seawater. Alteration of the mafic oceanic crust shows a contrasting
 572 influence on Mo systematics with depth. The top several hundred meters
 573 of the mafic crust are enriched in Mo and distinctly isotopically heavy com-
 574 pared to unaltered MORB, thus indicating incorporation of the isotopically
 575 heavy Mo from seawater with relatively little isotopic fractionation during
 576 low temperature alteration. Deeper parts of the mafic crust that were altered
 577 at higher temperatures have variable Ce/Mo but Mo isotope ratios that are
 578 little different from those in the least altered samples. This implies minor
 579 Mo re-distribution in a rock-buffered system and so this process does not sig-
 580 nificantly affect the Mo isotope composition of the mafic crust. The mafic,
 581 altered oceanic crust is therefore appears similar in $\delta^{98/95}\text{Mo}$ to unaltered
 582 MORB except for the isotopically heavy top few hundred meters.

583 The Mariana arc lavas are relatively enriched in Mo and have $\delta^{98/95}\text{Mo}$
 584 significantly greater than MORB (apart from the samples from the island of
 585 Agrigan). This implicates the addition of a Mo-rich fluid with $\delta^{98/95}\text{Mo} \sim$
 586 $+0.05\text{‰}$ to the mantle wedge beneath most islands. Pb isotopes further im-
 587 ply this component is dominantly derived from the little altered mafic oceanic
 588 crust, which requires Mo isotopic fractionation during slab dehydration and
 589 fluid transport. A rough mass balance suggests that removal of about 35
 590 % of the Mo from the oceanic crust can generate the Mo enrichment in the
 591 Mariana arc lavas. Since this flux is isotopically heavier than the initial sub-
 592 ducting slab composition, the residual slab should become isotopically light
 593 compared to MORB and subducted slabs transported into the deep mantle
 594 are therefore predicted to have distinctly light Mo isotope ratios. Heavy Mo

isotope ratios are predicted for the bulk continental crust. Thus, deep subducted slabs and the continental crust potentially form two complementary reservoirs for Mo isotopes.

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Figure 1: Map of the Mariana arc showing the location of sampled islands and proximal ODP Sites 800, 801 and 802. The basemap is from geomapapp (www.geomapapp.org).

Figure 2: Compositional variations of erupted magmas in the central island province (CIP) of the Mariana arc. Mariana arc lava samples used in this study are shown with large symbols. Other CIP data are from Woodhead (1989); Wade et al. (2005); Elliott et al. (1997) and Marske et al. (2011). Nd isotope composition of the average sediment subducted at the Mariana trench is from Plank and Langmuir (1998). The composition of the sub-arc mantle beneath the Mariana arc is based on the Mariana trough data from Woodhead et al. (2012) (average of their Nd isotope data, filtered by Woodhead et al. (2012) to exclude samples influenced by addition of subduction components) and Gale et al. (2013) (mean Ba/Th, weight ratio, of global MORB). The composition of slab-derived fluid from the mafic crust is inferred from the trend of the Mariana arc lavas and an arrow towards its approximate position is also indicated.

Figure 3: Mo and Pb isotope ratios in sediments from ODP Sites 800, 801 and 802. a) $\delta^{98/95}\text{Mo}$ vs. Mo concentration. The error bar for Mo isotope ratios shows the 2 sigma external reproducibility determined from multiple measurements of BHVO-2. Grey horizontal bar provides a reference for the Mo isotope composition of the mantle based on the range of terrestrial basalts reported by Burkhardt et al. (2014). It also includes our estimate for mid-ocean ridge basalts (MORB) (see text for details). b) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, c) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. The average sediment is weighted by Pb concentration and sediment thickness using Pb concentrations from Plank and Langmuir (1998). Previous estimates for the Pb isotope composition of sediments subducting at the Mariana trench are shown in b) and c) with inverse triangles (Plank and Langmuir, 1998). Errors of Pb isotope ratios are usually smaller than the symbol sizes.

Figure 4: Mo isotope ratios and Mo concentrations in AOC samples from ODP Sites 801 and 1256. a) depth profiles for Mo concentrations and Mo isotope ratios. Depth indicates meters below the top of the mafic part of the oceanic crust. The vertical grey and red bars indicate the estimates for Mo concentrations and Mo isotope ratios of unaltered MORB and average subducted sediment at the Mariana arc, respectively (see text for details). ATZ = alteration transition zone. b) $\delta^{98/95}\text{Mo}$ vs. Ce/Mo (weight ratio). Mo isotope ratio shown for MORB is the same as used in a) (error is about the size of the symbol) and the Ce/Mo ratio for MORB reports the average and standard deviation of the compilation of global MORB data from Gale et al. (2013). We did not include the Jenner and O'Neill (2012) MORB dataset because their invariant $[\text{Mo}]$ at low $[\text{Ce}]$ might indicate an uncorrected interference. The error bar for Mo isotope ratios shows the 2 sigma external reproducibility determined from multiple measurements of BHVO-2.

Figure 5: Mo isotope compositions and Ce/Mo ratios in Mariana arc lavas. Symbols for the Mariana arc lavas are the same as in Fig. 1. a) $\delta^{98/95}\text{Mo}$ vs. MgO (weight %). The error bar for Mo isotope ratios shows the 2σ external reproducibility determined from multiple measurements of JB-2. b) Ce/Mo (weight ratio) vs. MgO, c) [Mo] vs. [Ce]. Also shown are data for MORB (Gale et al., 2013) and the Solomon arc (Schuth et al., 2009). Lines labeled '9:1', '18:1' and '32:1' indicate Ce/Mo weight ratios.

Figure 6: Mo isotopic and trace element variation in Mariana arc lavas. a) $\delta^{98/95}\text{Mo}$ vs. Ce/Mo. 'Fluid' indicates the Mo isotope and Ce/Mo ratio suggested for slab-derived fluids, 'bulk oceanic crust' indicated on the y axis is the weighted Mo isotope composition of the oceanic crust (mafic crust + sediments) (calculated using parameters in Supplementary Table 3). b) Ce/Pb vs. Ce/Mo. Symbols are the same as in Fig. 1, 3 and 4. MORB in a) is from Fig. 4 and in b) from Gale et al. (2013).

Figure 7: Pb isotope ratios in Mariana arc lavas. a) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, b) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. Also shown are linear regression lines ($R^2 = 0.925$ in a), $R^2 = 0.885$ in b). Symbols are the same as in Fig. 1. Ellipses indicate 2σ external reproducibility.

Figure 8: Pb isotope ratios in Mariana arc lavas, sediments and AOC subducting at the Mariana trench. Also shown is the composition of Pacific and Indian MORB (compilation from Elliott et al., 1999). Symbols for sediments and AOC are the same as in Fig. 3 and Fig. 4. Data for sediments are averages for each sediment type, weighted by Pb concentration and sediment thickness using Pb concentrations from Plank and Langmuir (1998). Pb isotope ratios of the ODP Site 801 AOC are from Hauff et al. (2003). The average sediment is the same as in Fig. 3. Solid lines are regression lines from Fig. 6.

Table 1: Mo isotope ratios and Mo concentrations in Mariana arc lavas. $2SE = 2\sigma$ standard error

sample	$\delta^{98/95}\text{Mo}$ [‰]	$\pm 2SE$	Mo [$\mu\text{g/g}$]	MgO [wt.%]*
GUG6(1)	0.150	0.023	0.398	3.99
GUG9	0.067	0.020	0.776	4.23
GUG11	0.049	0.016	1.003	3.38
GUG12	0.021	0.025	0.894	3.49
GUG13	0.038	0.031	0.856	3.47
GUG13 (r)	0.020	0.020	0.905	3.47
ALAM2	0.082	0.021	1.277	4.40
ALAM5	0.047	0.014	1.072	4.86
AGR2	-0.092	0.018	0.492	4.98
AGR4b	-0.130	0.012	0.563	4.80
AGR4b (r)	-0.172	0.025	0.631	4.80
AGR5	-0.099	0.025	0.623	5.38
AGR8b	-0.113	0.014	0.595	3.55
AGR8b (r)	-0.122	0.022	0.629	3.55
MM-92-6 (AGR)	-0.083	0.022	0.998	3.15
URA5	0.059	0.015	0.710	6.13
URA5 (r)	0.069	0.019	0.746	6.13
URA7	0.054	0.017	0.907	2.71
URA12	0.043	0.022	0.909	2.68

(r) replicate analysis on separate dissolution of the sample powder

* MgO concentration is from Elliott et al. (1997)

Table 2: Pb isotope ratios in Mariana arc lavas. $2SE = 2\sigma$ standard error. Samples PAG3, ACR3, and SAG1 are from Pagan, Asuncion and Sagrigan, respectively. Pb isotope data for these samples are not plotted in Fig. 6 and Fig. 7 for consistency because no Mo isotope data are available for these islands. In addition, Sagrigan has previously been shown to have unusual Pb isotope ratios compared to the other Mariana arc volcanoes (Woodhead and Fraser, 1985).

sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2SE$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2SE$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2SE$
GUG3	18.8228	0.0009	15.5663	0.0008	38.4021	0.0026
GUG4	18.7818	0.0008	15.5574	0.0008	38.3458	0.0024
GUG6	18.7545	0.0008	15.5511	0.0008	38.3340	0.0024
GUG9	18.7553	0.0009	15.5509	0.0008	38.3351	0.0026
GUG11	18.7671	0.0012	15.5533	0.0010	38.3413	0.0033
GUG12	18.7743	0.0011	15.5496	0.0010	38.3310	0.0032
GUG13	18.7626	0.0013	15.5514	0.0010	38.3366	0.0036
ALAM2	18.7971	0.0035	15.5694	0.0031	38.4398	0.0099
AGR2	18.7674	0.0008	15.5469	0.0007	38.3696	0.0023
AGR4b	18.7809	0.0010	15.5503	0.0009	38.3767	0.0028
URA5	18.8719	0.0011	15.5736	0.0011	38.5102	0.0033
URA6	18.8604	0.0022	15.5774	0.0020	38.5062	0.0064
URA7	18.8712	0.0016	15.5796	0.0014	38.5110	0.0044
URA12	18.8672	0.0021	15.5749	0.0019	38.4978	0.0059
PAG3	18.8236	0.0011	15.5657	0.0010	38.4124	0.0030
ACR3	18.7443	0.0014	15.5532	0.0013	38.3876	0.0039
SAG1	18.9603	0.0011	15.5815	0.0010	38.4593	0.0031

Supplementary Table 1: Mo isotope ratios and Mo concentrations in sediments from ODP Sites 800, 801 and 802 and samples of the AOC from ODP Sites 801 and 1256.

sample	$\delta^{98/95}\text{Mo}$ [‰]	$\pm$ 2SE	Mo [$\mu\text{g/g}$]	depth [m below sea floor]	dominant lithology
<i>ODP Site 801 composite samples</i>					
801C FLO 0-110 m	0.270	0.038	0.42	55 (a)	less altered basaltic flows
801C ALL 0-110 m	0.385	0.032	0.39	55 (a)	basalt, average of 0-110 section
801C VCL 0-110 m	0.861	0.019	0.47	55 (a)	highly altered basalt breccias
801C FLO 220-420 m	0.044	0.060	0.16	320 (a)	less altered basaltic flows
801C ALL 220-420 m	0.043	0.033	0.23	320 (a)	basalt, average of 220-420 m section
801C VCL 220-420 m	-0.122	0.026	0.95	320 (a)	highly altered basalt breccias
801C super composite	0.359	0.024	0.37	210 (a)	composite for all ODP site 801 basalts
<i>ODP Site 1256 mafic crust</i>					
1256 75R-1 116-123	0.011	0.048	0.09	508 (b)	basalt, sheet flows, slightly altered
1256 99R-29-37	-0.018	0.011	0.53	663 (b)	basalt, sheet flows, slightly altered
1256 99R-2 101-120	-0.128	0.031	0.14	664 (b)	basalt, sheet flows, slightly altered
1256 120R-1 95-105	-0.292	0.024	0.17	773 (b)	basalt, sheet flows, slightly altered
1256D 129R-1 34-51	0.004	0.027	0.22	816 (b)	basalt, sheet flows, slightly altered
1256 132R-1 0-18	-0.140	0.023	0.17	830 (b)	basalt, sheeted dikes, slightly altered
1256 135R-1 27-30	-0.353	0.024	0.22	844 (b)	basalt, sheeted dikes, slightly altered
1256D 135R-1 54-64	-0.230	0.035	0.14	845 (b)	basalt, sheeted dikes, slightly altered
1256D 174R-1 73-79	-0.043	0.031	0.41	1021 (b)	basalt, sheeted dikes, moderately altered
1256 198R-1 0-18	-0.029	0.018	0.27	1125 (b)	basalt, sheeted dikes, moderately altered
1256D 216R-1 49-58	-0.292	0.048	0.05	1173 (b)	gabbro, moderately altered
1256D 232R-1 35-50	-0.882	0.025	0.10	1249 (b)	gabbro, highly altered
<i>ODP Site 800 sediments</i>					
800A-13R-1-46	-0.743	0.025	0.05	107	chert/porcellanite
800A-36R-3-28	-0.595	0.024	0.37	319	volcaniclastic
800A-53R-2-25/B	-1.871	0.018	1.75	467	radiolarite/claystone, Mesozoic
<i>ODP Site 801 sediments</i>					
801A-3R2-56-58	0.066	0.017	27.08	22	clay, Cenozoic
801A-3R2-145-150-WSF	0.091	0.031	36.96	23	clay, Cenozoic
801A-5R3-50-52	-0.921	0.024	9.88	43	clay, Cenozoic
801A-5R3-145	-1.122	0.021	15.58	44	clay, Cenozoic
801A-8R-1-1-3	-0.174	0.030	2.57	69	chert/porcellanite
801B-25R-1-49-53	-1.047	0.031	1.24	406	radiolarite/claystone, Mesozoic
801B-35R2-0-10-IWTF	-0.393	0.032	2.26	454	radiolarite/claystone, Mesozoic
<i>ODP Site 802 sediments</i>					
802A-15R-1-141-143	-0.152	0.037	0.34	124	volcaniclastic
802A-19R-2-67-72	-0.428	0.027	0.50	161	volcaniclastic
802A-26R-1-120-124	0.015	0.023	0.38	227	chalk
802A-38R-02W-51-53	-0.526	0.025	0.77	341	radiolarite/claystone, Mesozoic
802A-52R-01W-56-58	0.111	0.022	1.01	460	radiolarite/claystone, Mesozoic
802A-54R-01W-50-52	-0.263	0.030	0.28	479	limestone

Supplementary Table 1 – continued from previous page					
sample	$\delta^{98/95}\text{Mo}$ [‰]	$\pm$ 2SE	Mo [$\mu\text{g/g}$]	depth [m below sea floor]	dominant lithology
<i>average sediment compositions</i>					
Cenozoic clay	-0.23		22.37		
chert & porcellanite	-0.18		1.31		
volcaniclastics	-0.32		0.40		
Mesozoic radiolarite and claystone	-0.81		1.32		
average Mariana arc sedi- ment (c)	-0.29		2.49		

870 (a) average depth for the composite samples, depth is in m below the top of the mafic crust (total depth minus 520
 871 m of sediment cover)
 872 (b) depth is in m below the top of the mafic crust (total depth minus 245 m of sediment cover)
 873 (c) average of the four main sediment types, weighted by Mo concentration and stratigraphic thickness

874 Supplementary Table 2: Pb isotope ratios in sediments from ODP Sites
875 800, 801 and 802.

sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\text{SE}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\text{SE}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\text{SE}$	dominant lithology
ODP Site 800 sediments							
800A-4R-01-97	18.623	0.006	15.649	0.007	38.796	0.022	clay, Cenozoic
800A-13R-01-46	18.996	0.003	15.693	0.002	39.080	0.007	chert/porcellanite
800A-28R-2-48	19.387	0.006	15.696	0.007	39.316	0.024	volcaniclastic
800A-36-03-28	20.466	0.001	15.700	0.001	40.090	0.005	volcaniclastic
800A-39R-2-11	19.937	0.001	15.686	0.001	39.787	0.002	volcaniclastic
800A-50R-01-59	19.256	0.004	15.656	0.004	38.851	0.013	volcaniclastic
800A-53-02-25/B	18.783	0.001	15.652	0.001	38.757	0.005	radiolarite/claystone, Mesozoic
800A-55R-01-126	19.031	0.004	15.678	0.004	38.984	0.014	radiolarite/claystone, Mesozoic
ODP Site 801 sediments							
801A-3R02W-56-58	18.551	0.006	15.632	0.008	38.720	0.027	clay, Cenozoic
801A-3R2-145-150-WSF	18.547	0.005	15.649	0.004	38.769	0.011	clay, Cenozoic
801A-5R-03W-50-52	18.765	0.009	15.672	0.012	38.930	0.038	clay, Cenozoic
801A-5R3-145-150-IWSF	18.746	0.003	15.672	0.003	38.913	0.007	clay, Cenozoic
801A-8R-1-1-3	19.164	0.008	15.706	0.009	39.043	0.026	chert/porcellanite
801A-19R-01-55	21.209	0.003	15.880	0.003	39.187	0.008	volcaniclastic
801B-3R-01-100	31.286	0.007	16.897	0.004	39.337	0.010	volcaniclastic
801B-5R-01W-40-42	19.424	0.002	15.645	0.003	39.347	0.009	volcaniclastic
801B-6R-4-62	24.362	0.004	16.179	0.002	39.235	0.005	volcaniclastic
801B-7R-01W-35-37	19.234	0.001	15.640	0.001	39.150	0.003	volcaniclastic
801B-8R3-155	19.055	0.010	15.645	0.009	38.931	0.024	volcaniclastic
801B-25RI-49-53-x	18.769	0.001	15.651	0.001	38.835	0.002	radiolarite/claystone, Mesozoic
801B-35R2-0-10-IWTF	18.603	0.005	15.611	0.005	38.516	0.013	radiolarite/claystone, Mesozoic
ODP Site 802 sediments							
802A-4R-01-140-150	19.294	0.006	15.663	0.007	38.759	0.023	volcaniclastic
802A-15R-141-143	19.009	0.005	15.578	0.005	38.842	0.017	volcaniclastic
802A-16R-01-30-33	18.989	0.003	15.584	0.004	38.823	0.011	volcaniclastic
802A-19R-01-27-29	18.791	0.001	15.606	0.001	38.752	0.005	volcaniclastic
802A-19R-2-67-72	18.906	0.001	15.567	0.001	38.691	0.003	volcaniclastic
802A-38R-02W-51-53	18.739	0.001	15.669	0.002	38.893	0.006	radiolarite/claystone, Mesozoic
802A-40R-01W-87-89	19.018	0.001	15.675	0.001	39.074	0.004	volcaniclastic
802A-40R-02W-52-54	19.079	0.001	15.628	0.001	39.110	0.005	volcaniclastic
802A-43R-01W-57-59	18.958	0.003	15.658	0.003	39.013	0.013	volcaniclastic
802A-43R-03W-33-35	18.946	0.002	15.632	0.002	38.926	0.005	volcaniclastic
802A-47R-03W-52-54	19.021	0.001	15.610	0.000	38.970	0.001	volcaniclastic
802A-51R-03W-118-120	19.089	0.002	15.695	0.003	39.298	0.009	radiolarite/claystone, Mesozoic
802A-52R-01W-56-58	18.963	0.002	15.686	0.003	39.062	0.009	radiolarite/claystone, Mesozoic
802A-54R-01W-50-52	18.862	0.004	15.686	0.004	39.054	0.014	limestone

Supplementary Fig. 1: Depth profiles of Mo concentrations and Mo isotope compositions for sediment samples from ODP Sites 800, 801 and 802. Depths are in meters below sea floor [mbsf].

876

Supplementary Table 3: input parameters for Mo mass balance

	Mo [$\mu\text{g/g}$]	$\delta^{98/95}\text{Mo}$ [‰]	
AOC 0-400 m	0.37	0.36	(a)
AOC 400-1200 m	0.21	-0.14	(b)
AOC 1200-6000 m	0.08	-0.2	(c)
total AOC	0.12	-0.07	
sediments 0-500 m	2.49	-0.29	(d)
total oceanic crust 6500 m	0.30	-0.21	
primitive arc lavas	0.61	-0.1 - 0.07	(e, Fig. 6a)
MORB		-0.2	(f)
AOC crustal thickness	6000 m		(g)
subduction rate r_{sub}	4	cm/year	(g)
density AOC ρ_{AOC}	3	g/cm^3	(h)
arc magma production rate	45	$\text{km}^3 \times \text{km}^{-1} \times \text{Ma}^{-1}$	(i)

878

(a) composition of the ODP Hole 801 super composite (Supplementary
879 Table 1), (b) average of AOC samples for 420-1200 m depth (Supplementary
880 Table 1), (c) Mo isotope ratios of the 1200-6000 m section are assumed to
881 be similar to unaltered MORB ($\delta^{98/95}\text{Mo} = -0.2$ ‰, see text for details),
882 Mo concentrations are averages for the two samples of gabbro from ODP
883 Site 801 (table 2) and 7 samples of gabbro from the Hess Deep sampled on
884 cruise JC-21 (unpublished data F. Vils), (d) from supplementary Table 1 (e)
885 average for Mariana arc lavas with $\text{SiO}_2 < 52$ wt.% (this study). Samples
886 with this degree of differentiation are assumed to represent near primary
887 magmas (Marske et al., 2011), (f) see text for details of suggested Mo isotope
888 ratios of MORB, (g) from Chen (1992), (h) from Bird (2003), (i) for absolute

889 masses only, density cancels out in the procedure used for the mass balance
 890 calculation, (j) from Dimalanta et al. (2002)

891 The mass balance calculations were performed using the following proce-
 892 dure:

893 1) The Mo subduction rate per unit of arc length was calculated from the
 894 plate subduction rate, crustal thickness, density, and average Mo concentra-
 895 tion in the oceanic crust (AOC and sediments):

$$r(Mo)_{subducted} = r_{sub} \times d \times \rho_{AOC} \times c(Mo)_{OC} \quad (.1)$$

896 where $r_{subducted}$ = rate of subduction of the Pacific plate at the Mariana
 897 trench, d = crustal thickness, ρ_{OC} = density of the oceanic crust, $c(Mo)_{OC}$
 898 = concentration of Mo in the oceanic crust.

899 2) The Mo output rate per unit of arc length was calculated based on the
 900 Mo concentration in the least evolved arc magmas:

$$r(Mo)_{arc} = c(Mo)_{arc} \times r_{prod} \quad (.2)$$

901 where $c(Mo)_{arc}$ is the concentration of Mo in primitive Mariana arc mag-
 902 mas and r_{prod} is the arc magma production rate.

903 3) The fraction of Mo removed from the subducted crust was calculated
 904 by comparing the Mo subduction rate to the MO output rate:

$$f(Mo)_{removed} = r(Mo)_{subducted} / r(Mo)_{arc} \quad (.3)$$

905 4) The $\delta^{98/95}\text{Mo}$ of the residual oceanic crust was calculated:

$$\delta^{98/95}\text{Mo}_{residual\ crust} = \frac{\delta^{98/95}\text{Mo}_{total\ oceanic\ crust} - \delta^{98/95}\text{Mo}_{arc\ lavas} \times f(Mo)_{removed}}{1 - f(Mo)_{removed}} \quad (.4)$$

906 which is shown as a function of the $\delta^{98/95}\text{Mo}$ of the erupted volcanics for
907 different arc growth rates in in.