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Time scales and mechanisms of uranium uptake in altered ocean crust; observations from the \sim 15 million year-old site 1256 in the eastern equatorial Pacific

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Time scales and mechanisms of uranium uptake in altered ocean crust; observations

- from the ~15 million year-old Site 1256 in the Eastern Equatorial Pacific
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- 23
- 24 Abstract

25 The alteration of ocean crust through hydrothermal seawater circulation facilitates chemical exchange between Earth's surface and interior. Hydrothermal alteration leads 26 27 to uranium (U) removal from seawater and net U uptake by the ocean crust, particularly during low temperature alteration that occurs on the vast ocean ridge flanks away from 28 the spreading axes. Determining the timescales of U uptake and its associated ²³⁸U/²³⁵U 29 signature has important implications for understanding U exchange processes during 30 31 subduction and recycling into the mantle. Here we study the U systematics of ~15 million vear-old ocean crust drilled at Site 1256 on the eastern flank of the East Pacific Rise. 32 33 Analysis of cores from the upper ~1300 meters of intact ocean crust at this site, reveal large variability in U concentrations and ²³⁸U/²³⁵U ratios. Many of the samples from the 34 upper ~600 meters of extrusive lavas have elevated U concentrations and ²³⁸U/²³⁵U ratios 35 36 lower than seawater, consistent with mechanisms of U uptake under relatively oxidised conditions. Samples from the underlying sheeted dikes and gabbros show evidence for 37 hydrothermal U mobilisation, but negligible net U uptake. In contrast, in the transition 38 39 zone between the extrusive lavas and the sheeted dikes, samples revealed large U enrichments and high ²³⁸U/²³⁵U ratios above seawater. This is consistent with uptake of 40 the reduced U⁺⁴ species under relatively reducing conditions from seawater-derived 41 hydrothermal fluids. In addition, large secular disequilibrium in ²³⁴U/²³⁸U ratios from 42 43 samples in the lava-dike transition and upper sheeted dikes give evidence for U mobility 44 within the last ~1.5 million years, likely driven by deep channelled flow of seawaterderived hydrothermal fluids combined with preferential leaching of ²³⁴U from the rock 45 matrix. Both the total estimated U uptake and mean ²³⁸U/²³⁵U at Site 1256 is lower than 46 47 similar estimates from significantly older (>100 million years) altered ocean crusts at drill Sites 801 and 417/418. This shows the variable total U uptake and ²³⁸U/²³⁵U ratio in altered 48

49 ocean crust over time, which needs to be taken into consideration when estimating global
50 U budgets.

51

52 Keywords: altered ocean crust; uranium isotopes; Site 1256; IODP; 238U/235U; 234U/238U

53

54 **1. Introduction**

55 The formation of new ocean crust at mid-ocean ridge axes and its recycling into the mantle by subduction enables chemical exchanges between Earth's surface and mantle 56 57 reservoirs. These exchanges occur via high temperature (up to ~400°C) circulation of seawater-58 derived fluids at the spreading ridges driven by heat from the cooling and crystallisation of new 59 ocean crust, and lower temperature (<100°C) exchanges on the ocean ridge flanks (e.g. Alt, 60 1995; Elderfield and Schultz, 1996; Staudigel, 2014). These processes lead to seawater-driven weathering and alteration of the ocean crust, inducing chemical exchanges with potential losses 61 62 and gains of elements (e.g., magnesium, potassium, rubidium, uranium, carbon; Albarède and Michard, 1986; Alt and Teagle, 1999; Dunk et al., 2002; Staudigel, 2014). Characterisation of 63 the alteration signatures in the ocean crust is important for establishing the heat exchange 64 between mantle and the ocean (e.g. Elderfield and Schultz, 1996; Staudigel, 2014; Stein and 65 Stein, 1994), geochemical budgets of elements in the ocean (e.g. Albarède and Michard, 1986; 66 Staudigel, 2014) and the fluxes of surface-derived components into arc systems and the residual 67 proportion transported further into the mantle (e.g. Plank and Manning, 2019). These alteration 68 69 processes can be gauged from changes in geochemical signatures, either based on diagnostics in major and trace metal compositions or isotope systematics (e.g. Staudigel, 2014). For 70 71 example, the seawater and ocean crust exchange of strontium (Sr) during alteration has a major impact on the ⁸⁷Sr/⁸⁶Sr signature of seawater (e.g. Palmer and Edmond, 1989; Vance et al., 72 2009) and the distinctive $^{238}U/^{235}U$ ratios of the uranium (U) uptake in altered ocean crust has 73

been used to identify the recycling of surfaced-processed U into the mantle (Andersen et al., 2015). However, usage of such geochemical tools requires the rigorous characterisation of the variations in composition of altered ocean crust. Although relatively homogeneous compared to the continents, ocean crust still shows significant variations in alteration style with spreading rate and age as it cools, subsides and becomes covered by sediments with maturation away from the ocean ridges (e.g. Staudigel, 2014).

80 Uranium is a sensitive tracer of surface exchange processes because it has relatively high concentrations in seawater (~3.3 ng/g), its solubility is sensitive to oxidation conditions 81 82 and it presents isotopic ratios useful for fingerprinting sources and timings of processes (e.g. Andersen et al., 2015; Bacon, 1978). Uranium is, on average, taken up by the ocean crust during 83 exchanges with seawater-derived hydrothermal fluids (e.g. Dunk et al., 2002; Kelley et al., 84 2005; Staudigel et al., 1995). The impact of the most intense, near-axis high-temperature 85 86 hydrothermal alteration is not well quantified, but discharging black smoker-type fluids have low U concentrations, suggesting near-quantitative U removal within the ocean crust (Chen et 87 88 al., 1986; Michard et al., 1983; Mottl et al., 1998). Given the much larger potential for low-89 temperature seawater-basalt exchange during hydrothermal alteration on the ocean ridge 90 flanks, it is likely that this dominates U uptake within the ocean crust (e.g. Alt et al., 2010; 91 Bach et al., 2003; Dunk et al., 2002; Kelley et al., 2005; Staudigel et al., 1995). The low-92 temperature U addition initially occurs under relatively oxidised conditions at high water-torock ratios, leading to U⁺⁶ uptake associated with secondary alteration phases such as iron-93 94 oxyhydroxides and celadonite (e.g. Bach et al., 2003; Mitchell and Aumento, 1977; Türke et al., 2015). However, the formation of secondary minerals and the accumulation of sediments 95 as the crust ages away from the ridge axis can impede the direct recharge of oxygenated 96 97 seawater into the ocean crust leading to lower water-to-rock ratios and more reducing conditions with U⁺⁴ uptake associated with the formation of, for instance, secondary Mg-98

99 saponite, pyrite and carbonates (e.g. Alt and Teagle, 2003; Dunk et al., 2002; Kelley et al., 2005; Staudigel, 2003). The intensity of different alteration processes is linked to the specific 100 lava morphology and thermal evolution of individual ocean crustal sections, leading to 101 102 heterogeneous addition of U to the ocean crust (e.g. Alt and Teagle, 2003; Dunk et al., 2002; Kelley et al., 2003). Estimates to date based on drilled sections of altered upper ocean crust 103 from a range of crustal ages (3 to 167 million years), indicate on average a 5- to 10-fold increase 104 105 in U concentration in the upper ~1000 meters (Fig. 1), compared to unaltered ocean crust (Dunk et al., 2002; Kelley et al., 2005; Staudigel, 2003). 106

107

In addition, U isotope systematics offer further insight into U uptake mechanisms and 108 time scales of seawater-basalt exchanges. The ~245 thousand year half-life of the ²³⁴U daughter 109 compared to its much longer lived parent ²³⁸U (Cheng et al., 2013), means that the preservation 110 of secular disequilibrium in the ${}^{234}U/{}^{238}U$ ratio implies perturbation within the last ~1.5 million 111 years. Here, ${}^{234}U/{}^{238}U$ ratios are expressed as $\delta^{234}U$, where the ${}^{234}U/{}^{238}U$ ratio of the sample is 112 normalized to secular equilibrium and reported in parts per thousand, such that at secular 113 equilibrium $\delta^{234}U = 0$. Low-temperature weathering processes have been shown to cause 114 significant disequilibrium in the ²³⁴U/²³⁸U ratio due to alpha-recoil induced preferential 115 116 redistribution of the ²³⁴U daughter nuclide, generally leading to ²³⁴U excesses in fluids and depletions in leached solid residues (e.g. Andersen et al., 2009; Kigoshi, 1971; Porcelli and 117 Swarzenski, 2003). For instance, modern seawater is characterized by a δ^{234} U of ~+145‰ 118 (Kipp et al., 2022) principally due to the input of high δ^{234} U-bearing waters from rivers (e.g. 119 Dunk et al., 2002). Consequently, $^{234}U/^{238}U$ ratios have the potential to provide chronological 120 121 constraints on the processes of U addition from seawater and hydrothermal fluid leaching 122 processes (e.g. Bacon, 1978; Macdougall et al., 1979).

124	Furthermore, a rapidly growing data-base of ²³⁸ U/ ²³⁵ U ratios from different Earth
125	reservoirs has revealed large natural variability (e.g. Andersen et al., 2017 and references
126	therein). In the following $^{238}U/^{235}U$ ratios are expressed using the $\delta^{238}U$ notation which is the
127	relative difference of the ²³⁸ U/ ²³⁵ U ratio of a sample compared to the standard CRM 145,
128	expressed in parts per thousand. The main driver of $^{238}U/^{235}U$ fractionations are differences in
129	bonding environment between U species in its two common redox states +4 and +6 (Bigeleisen,
130	1996). Uranium uptake or exchange with no redox change, under oxidised conditions (e.g., +6
131	species) generally leads to slightly lower δ^{238} U values in the solid product – for example, the
132	<0.2 ‰ lowering of 238 U/ 235 U ratios by U uptake from seawater to ferro-manganese-oxides
133	(e.g. Brennecka et al., 2011; Goto et al., 2014). In contrast, under more reducing conditions,
134	the isotope fractionation between soluble U^{+6} and immobile U^{+4} may inflict large, per mil level,
135	changes with higher δ^{238} U in the reduced product (e.g. Bigeleisen, 1996; Stirling et al., 2007;
136	Weyer et al., 2008). Measured δ^{238} U values in ~120 to ~170 million year-old ocean crusts from
137	drill Sites 417/418 in the Atlantic and 801 in the Pacific (Fig. 2) illustrate this, showing both
138	isotopically lighter and heavier signatures compared to the compositions of the near-
139	homogenous open-ocean seawater (-0.38±0.02; Kipp et al., 2022), the average continental crust
140	(-0.30±0.03; Tissot and Dauphas, 2015) and average mid-ocean ridge basalts (-0.26±0.03;
141	Andersen et al., 2015). The processes of U uptake in altered ocean crust have been shown to
142	lead to significant δ^{238} U variability, measured in bulk samples (-0.47 to +0.27 ‰), calcium
143	carbonate phases (-0.63 to +0.11 $\%$) and 'composite' samples (-0.49 to +0.23 $\%$), the latter
144	representing average sections of altered ocean crust (Andersen et al., 2015; Noordmann et al.,
145	2016; see also review in Andersen et al., 2017). Such variations in δ^{238} U values indicate that
146	heterogenous and non-quantitative addition of seawater-derived U occurs during the alteration
147	of the ocean crust (Fig. 2).

149 This previous work (Andersen et al., 2015; Noordmann et al., 2016) provides some indication of the overall systematics of δ^{238} U within old (>100 Ma) altered ocean crust. 150 151 However, there is a current lack of information on the temporal evolution of the U isotope systematics as ocean crust ages away from the ridge axis. Additional temporal constraints are 152 153 important to accurately quantify U exchange and isotopic composition estimates for the marine 154 budget and for subducting ocean crust. Although conductive heat flow deficits are present in all ocean basins out to ~65 million years (e.g. Elderfield and Schultz, 1996; Staudigel, 2014; 155 Stein and Stein, 1994), δ^{234} U values can provide additional geochemical evidence for the 156 timing and duration of low-temperature hydrothermal alteration of the ocean crust. Here we 157 perform a comprehensive study of U uptake and isotope systematics $(^{234}U/^{238}U)$ and $^{235}U/^{238}U$ 158 ratios) at depth, for a complete section of intact upper ocean crust from lavas, through the 159 160 sheeted dikes and into the uppermost gabbros from Ocean Drilling Program (ODP) Site 1256, 161 drilled into crust formed 15 million-years ago at the fast spreading East Pacific Rise (Wilson et al., 2006). 162

163

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2. Site 1256 and sample descriptions

165 Holes 1256C and 1256D (Fig. 3) were drilled in the eastern equatorial Pacific (6.736°N, 91.934°W) during four scientific ocean drilling cruises (ODP Leg 206; IODP Expeditions 166 167 309/312, 335; Teagle et al., 2012; Wilson et al., 2006). Site 1256 is in a region of relatively 168 smooth seafloor topography (<10 m relief) although there is a trail of ~500 m-high seamounts 169 15-20 km north-east. Sediment porewater and heat flow measurements at Site 1256 indicate 170 that there is no current evidence for fluid circulation or advective heat transport at the seafloor (Alt et al., 2010; Teagle et al., 2012). From the seafloor, Holes 1256C/D penetrate ~250 m of 171 sediments, (1) ~750 m of extrusive lavas, (2) a ~60 m-thick lava-dike transition zone, 172 173 mineralised in places, $(3) \sim 350$ m of sheeted dikes and $(4) \sim 120$ m into a dike-gabbro transition

zone (Teagle et al., 2012). A thorough description of rock types and estimates of hydrothermal 174 alteration temperatures (from major and trace elements, mineralogy, O isotopes and fluid 175 inclusions in alteration products) can be found in Alt et al. (2010). Subsequent analyses of 176 samples from Site 1256 include Sr, Nd, Pb, Li, Mg and O isotope ratios (Gao et al., 2012; 177 Harris et al., 2015; Höfig et al., 2014; Huang et al., 2015) and trace metal abundances (Höfig 178 et al., 2014; Patten et al., 2016). Furthermore, U concentration and Th/U ratio systematics of 179 180 36 samples were investigated in Höfig et al. (2014) whereas a comprehensive Th/U ratio dataset of 462 samples are available from the Ph.D. thesis of Harris (2011). In this study, 49 181 182 representative samples were selected for U isotope analyses to provide coverage of the four main units and alteration styles at Site 1256. The majority of the samples chosen (41 out of the 183 49) have been analysed previously for other tracers, including radiogenic Sr isotope ratios 184 185 (Harris et al., 2015). The analysed samples are described below, grouped into four main 186 sections of the altered ocean crust, including details on lithology and alteration style.

187

188 *2.1 Extrusive lava section (0-754 meters sub-basement; msb)*

A total of 23 samples (21 and two from the deep Hole 1256D and C, respectively) were 189 190 selected to cover the upper extrusive lava section. The upper ~284 msb of lavas are interpreted to have flowed from the ridge axis, whereas the lower part of the lava sequence have been 191 192 formed at the ridge axis (see Harris et al., 2015; Teagle et al., 2006). The uppermost ocean 193 crust comprises a sequence of lavas dominated by a single ponded lava flow up to 75 meters thick. Below this the extrusive rocks comprise of sheet and massive flows with only minor 194 195 pillow lavas (Alt et al., 2010; Teagle et al., 2012; Tominaga et al., 2009; Wilson et al., 2006). 196 Low-temperature alteration (<150°C) from seawater-derived fluids dominates in the extrusive lava section, with later stages of alteration following existing fluid pathways (Alt et al., 2010; 197 198 Gao et al., 2012). A range of alteration styles is present with a background of moderate 199 alteration to dark grey colour and dark grey patches (mm to cm size) of saponite replacement with secondary sulfides and variable amounts of chlorite (Alt et al., 2010; Teagle et al., 2012). 200 Veins and associated alteration halos up to 3 cm wide, dominated by a brownish (including 201 202 celadonite and iron-oxyhydroxide phases) and darker colours (saponite), are interpreted to have derived from oxidised, hydrothermally heated seawater. Carbonates make up a few percent of 203 the material and some anhydrite is present in the lowest part of the extrusive lava section. A 204 205 general change in alteration style occurs below ~377 msb with more intense saponite and chlorite alteration. At 398 msb there is a ~40 cm band of intense bulk rock alteration to 206 207 celadonite, K-feldspar and iron oxyhydroxide (± quartz and carbonate), known as the 'red brick horizon' (Alt et al., 2010; Harris et al., 2015). The ~750 m extrusive lava sequence is generally 208 less hydrothermally altered than other deep mafic ocean crust sites (e.g. Sites 417/418, and 209 210 Hole 504B; Alt, 1995) and Site 1256 does not show a general systematic change from oxidizing 211 to reducing alteration style with depth, as seen in Hole 504B (Alt et al., 2010). Instead, oxidizing alteration occurs irregularly, commonly near vertically dipping veins, suggesting a 212 213 structural control of alteration, rather than simply decreasing seawater influence downwards 214 (Wilson et al., 2006). The early effective sealing of the basement from ocean waters due to high rates of sedimentation at this site (>30 m/million years; Wilson et al., 2003) and the 215 massive ponded lava that makes up the uppermost crust at Site 1256 could have limited the 216 217 ingress of seawater, thereby leading to the overall lower level of alteration compared to other 218 sites (Alt et al., 2010; Gao et al., 2012; Harris et al., 2015; Höfig et al., 2014). Samples analysed 219 are distributed across the section to cover the different lava (pond, pillows, sheeted and massive 220 flows) and alteration (background, haloes, patchy, 'red brick') styles. Although most were 221 analysed as whole rock samples, samples 26R-2 70-80 and 62R-1 16-21 at ~190 and 437 msb, respectively, were separated into predominantly 'fresh' and 'halo' parts (Supplementary Table 222 223 1).

225

2.2 Lava-dike transition zone (754-811 msb)

The lithological transition zone is marked by subvertical intrusive contacts and 226 227 mineralized hyaloclastic breccias. There is a step-wise increase in alteration temperature from the extrusive lavas above and into the sections below (to $>250^{\circ}$ C), with the transition zone 228 characterized by sub- to greenschist mineral alteration. Hydrothermal alteration halos along 229 230 veins, highly altered patches and localised metal-sulfide mineralization in breccias and veins, occur. Chlorite is a major alteration phase, and some anhydrite is present. The transition zone 231 232 includes a ~3 m thick mineralized hyaloclastite breccia (777-780 msb), where glass shards are replaced by albite, oligoclase, K-feldspar and titanite, cemented by quartz and pyrite ± 233 sphalerite, anhydrite and calcite (Alt et al., 2010). Radiogenic strontium isotope ratio 234 235 measurements from this mineralized breccia indicates it is a mixing zone between seawater-236 derived low-temperature fluids and upwelling high-temperature hydrothermal fluids (Alt et al., 2010; Harris et al., 2015; Höfig et al., 2014). A total of nine samples were analysed from the 237 238 lithological lava-dike transition zone, with samples collected focussed on the mineralized hyaloclastite breccia, including sample 112R-X 96-100 at 778 msb that was divided into 239 240 'breccia' and 'clast' subsamples.

241

242

2.3 Sheeted dike complex (811-1157 msb)

The ~350 m thick sheeted dike complex contains doleritic textures and cross-cutting of subvertical dikes with mineralised chilled margins (Wilson et al., 2006). Similar to the lavadike transition, the upper sheeted dikes are characterized by sub- to greenschist alteration with hydrothermal alteration halos along veins, highly altered patches and local metal-sulfide mineralization. Anhydrite precipitation occurs in the upper section (dominantly between 850– 950 msb) and is interpreted to have been formed from partially reacted heated seawater-derived 249 fluids mixing with hotter magmatic-derived hydrothermal fluids from below (Alt et al., 2010). 250 The general pattern of alteration suggests early stages of high temperature greenschist alteration (>350°C) followed by fracture-controlled alteration with upward migrating 251 252 hydrothermal fluids and leaching of some metals (e.g. Zn, Cu) from the deeper sheeted dikes and gabbro sections, followed by sulfide-precipitation in the upper sheeted dikes and lava-dike 253 transition (Alt et al., 2010; Patten et al., 2016). The lowermost ~60 m of the sheeted dikes 254 255 (1098–1157 msb) are strongly recrystallised to granoblastic textures. Twelve samples were selected from the sheeted dike complex, chosen to cover a range of background rocks and 256 257 alteration patches.

258

259 *2.4 Plutonic dike-gabbro transition (below 1157 msb)*

The crust below 1157 msb comprises a series of gabbro bodies intruded into contact metamorphosed sheeted dikes (Wilson et al., 2006). Early high-temperature alteration (500-1000 °C) is evident in metamorphic assemblages and textures (e.g. metamorphic clinopyroxene and amphibole) and the loss of Cu and Zn to hydrothermal fluids (Alt et al., 2010). Five samples were selected for analyses from this zone covering the gabbroic sections.

265

266 **3.** <u>Methods</u>

267 The U isotope and concentration measurements generally followed Andersen et al. (2015),268 and readers are referred to this for thorough information, with a brief description below.

269

270 *3.1 Sample preparation, U purification and elemental concentrations*

All samples were powdered prior to chemical processing (see Harris et al., 2015).
Chemical processing and analyses were done in the laboratories of the Bristol Isotope Group,
University of Bristol. Sample sizes from 0.1 to 1.5 grams were dissolved in a mixture of

concentrated HF-HNO₃ acid and spiked with the IRMM-3636²³³U-²³⁶U double spike (Richter 274 et al., 2008) aiming for $^{236}U/^{235}U$ ratios of ~5. This sample-spike mixture was heated on a 275 hotplate at 120°C before being dried down. Samples were then twice redissolved in hot 6 N 276 277 HCl before being dried down. Samples were then redissolved in 1.5 N HNO₃. For samples with unknown U and Th concentrations a small (1%) aliquot of the dissolved sample was taken 278 for elemental concentration determination using an Element 2 ICP-MS (following Andersen et 279 280 al., 2013). The U was separated from all other matrices in a two-step procedure consisting of first TRU Resin and then UTEVA chromatographic columns (Andersen et al., 2015). After the 281 282 UTEVA chemistry step, samples were re-dissolved in an appropriate amount of 0.2 N HCl for the desired U concentration for the MC-ICPMS measurements. Near full uranium recoveries 283 (>95%) were obtained for the samples and total full procedural U chemistry blanks were <20 284 285 pg.

286

287

3.2 Uranium isotope measurements

The U isotope measurements were conducted on a Thermo Finnigan Neptune MC-ICP-MS 288 (Serial No. 1002), running in low mass resolution (M/ Δ M ~500), using an Aridus desolvating 289 nebulizer introduction system and a standard and X cones setup (see Andersen et al., 2015). 290 Given the variability in U concentrations of the samples, a range of sample sizes were 291 292 processed to give enough U for analyses (10-200 ng). To optimise precision and accuracy two 293 different measuring protocols were used depending on the amount of U available; a 'high' and 'low' precision set-up (~ 1 nA and ~100 pA for the 238 U beam intensities, respectively). In the 294 'low' precision set-up, Faraday cups were connected to amplifiers with $10^{11} \Omega$ feedback 295 resistors (Andersen et al., 2014), and the minor 234 U beam was either collected in a $10^{11} \Omega$ 296 feedback resistors Faraday cup or, to improve the precision on ²³⁴U/²³⁸U ratios, in a secondary 297 electron multiplier (following previous setup of this method for ²³⁴U collection; Andersen et 298

299 al., 2013). For the 'high' precision set-up, amplifiers with $10^{11} \Omega$ feedback resistors were used 300 apart from the cup collecting the ²³⁸U beam which was connected to an amplifier with a 10^{10} 301 Ω feedback resistor to accommodate a larger ion beam and so facilitate a greater dynamic range 302 (Andersen et al., 2015).

303

Measurements of all unknown samples were bracketed and normalised to measurements of 304 305 the CRM-145 standard, spiked with IRMM-3636 in a similar fashion as the unknown samples. Corrections for mass bias, tailing, hydride interferences, impurities of natural U isotopes in the 306 307 spike, as well as on-peak background subtractions were performed following Andersen et al. (2015). The external reproducibilities of the two different measurement set-ups were tested 308 using the in-house uraninite standard CZ-1. Interspersed measurements of the CZ-1 for the 309 'high' precision set-up gave a δ^{238} U of -0.03±0.03 ‰ and a δ^{234} U of 0±3 ‰ (all ±2 standard 310 deviations), whereas a single measurement of the chemically processed BHVO-2 standard 311 yielded a δ^{238} U of -0.32±0.02 ‰ and a δ^{234} U of 0±1 ‰. The CZ-1 measurements for the 'low' 312 precision set-up gave a δ^{238} U of -0.05±0.11 ‰ and a δ^{234} U of +0.2±0.4 ‰ when using the 313 secondary electron multiplier and -2±4 ‰ using the Faraday cup for ²³⁴U collection (see 314 supplementary table 2 for standard data). These results agree well with previous measurements 315 of CZ-1 and BHVO-2 (Andersen et al., 2015; Li and Tissot, 2023). The associated uncertainties 316 for the Site 1256 samples reported in the following are based on the reproducibility (2SD) for 317 the repeated measurements of CZ-1 in the two different set-ups, scaled to the internal errors 318 (2SE) of the samples. Namely, if internal errors for the unknown were smaller than the average 319 320 internal errors reported for the CZ-1 standard, the external reproducibility for the CZ-1 was 321 used. If internal errors for the unknowns were larger than the average internal error of the CZ-1, the estimated uncertainties of the unknowns were scaled up proportionally compared to the 322 323 external standard reproducibility of the CZ-1 standard.

325 4. <u>Results</u>

326 The data is grouped into the four principal stratigraphical sections of altered ocean crust at Site 1256 as described in section 2 (see supplementary table 1). Each section shows variable U 327 concentrations, Th/U ratios and uranium isotope systematics (Fig. 4). Comparison of U 328 concentrations vs. Th/U ratios of all the data show a general inverse correlation with higher U 329 330 concentrations corresponding to lower Th/U ratios (Fig. 5). The data-set of Harris (2011) is the most comprehensive for U concentrations and Th/U ratios (n=462) and separating these data 331 332 into the four major stratigraphic sections, it shows a pattern of dominantly higher U concentrations in the extrusive lavas (mean U~117 ng/g) and lava-dike transition zone (mean 333 $U \sim 502$ ng/g), here elevated from the samples in the breccia zone, compared to the sheeted 334 335 dikes (mean U ~ 52 ng/g) and plutonic dike-gabbro section (mean U ~ 65 ng/g) (Table 1). The mean Th/U ratios for the stratigraphic sections are lower for the upper extrusive lavas and lava-336 dike transition zone (both ~2.4 g/g) compared to the sheeted dikes and plutonic dike-gabbro 337 section (~3.3 and ~ 4.4 g/g, respectively). The mean Th/U ratios for the stratigraphic sections 338 can also be estimated by weighting the samples by their Th and U concentrations. This 339 340 approach lowers the mean Th/U ratios for all stratigraphic sections based on the Harris et al. 341 (2011) data, most significantly for the lava-dike transition and the plutonic dike-gabbro 342 sections (0.4 and 2.9 g/g, respectively, see Table 1). The overall mean of all the data yields U 343 concentrations of 93 ng/g and mean Th/U ratios of either 3.0 or 2.1 g/g (if Th-U concentrationweighted). Omitting all the data from below the sheeted dikes, only marginally increases the 344 mean U concentration and lowers the mean Th/U ratios (Table 1). Furthermore, if mean U 345 concentrations and Th/U ratios are weighted proportionally to the thickness of each 346 stratigraphic unit (excluding the plutonic dike-gabbro), this also only marginally increases the 347

mean U concentration (~113 ng/g) and lowers the mean Th/U ratios (2.8 or 1.8 g/g for the ThU concentration-weighted; see Table 1).

350

At Site 1256, the δ^{238} U show the largest variability in the extrusive lava section, 351 particularly in the upper 300 meters, with δ^{238} U ranging from -0.18±0.20 ‰ and down to the 352 lowest value of -1.02±0.03 ‰. The lava-dike transition section also shows large variability, 353 with the highest δ^{238} U of -0.03±0.03 ‰ ranging down to -0.60±0.03 ‰. Both the sheeted dike 354 and plutonic dike-gabbro transition sections show less variable δ^{238} U with values from -355 0.16±0.06 to -0.42±0.10 ‰ and -0.18±0.10 to -0.53±0.10 ‰, respectively. A plot of U 356 concentrations versus δ^{238} U shows some overall systematic behaviour in the extrusive lavas 357 and lava-dike transition (Fig. 6). The extrusive lava samples with low δ^{238} U generally 358 correspond to samples with elevated U concentrations compared to mean normal mid-ocean 359 ridge basalts (N-MORB). Samples from the lava-dike transition zone show increasing U 360 concentrations with increasing δ^{238} U (up to -0.03±0.02 ‰) for the samples up to ~1000 ng/g. 361 Samples with U concentrations greater than ~1000 ng/g, show an inverse trend with decreasing 362 δ^{238} U, reaching -0.41±0.02 ‰, at the highest U concentration (Fig. 6). One sample from 363 lowermost part of the lava-dike transition just above the top of the sheeted dikes does not follow 364 this described trend, but has low δ^{238} U value (-0.60±0.03 ‰) with moderately elevated U 365 366 concentration (~210 ng/g) (Fig. 6).

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The 'fresh' and the 'halo' sample pairs show both variable U concentrations and δ^{238} U. At 190 msb, both the 'fresh' and the 'halo' fractions show elevated U concentration (157 and 119 ng/g) compared to the mean Pacific N-MORB. Although the 'halo' sample (-0.26±0.10 %) has a δ^{238} U value overlapping with Pacific N-MORB, the 'fresh' sample has a lower δ^{238} U value (-0.63±0.10 %). The paired samples at 437 msb have lower U concentrations (71 and 83 373 ng/g) than the pair at 190 msb and δ^{238} U that overlap within uncertainty. The 'fresh' sample (-374 0.25±0.10 ‰) is similar to mean Pacific N-MORB whereas the 'halo' is slightly lower (-375 0.43±0.10 ‰). The paired 'clast' and 'breccia' sample from 778 msb in the lava-dike transition 376 zone both have high U concentrations (278 and 780 ng/g, respectively) combined with 377 relatively high, albeit slightly variable δ^{238} U (-0.12±0.03 and -0.03±0.03 ‰).

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The δ^{234} U of the whole data-set show that 34 of 49 samples are out of secular 379 380 equilibrium when taking into account the associated measurement uncertainties, with three below and 31 above secular equilibrium. The extrusive lava samples (with 13 of 25 out of 381 secular equilibrium) show δ^{234} U generally near secular equilibrium, with the highest value of 382 +18±2 ‰ and lowest of -18±10 ‰. The lava-dike transition samples show higher δ^{234} U, up to 383 $+87\pm5$ %, with five of nine samples out of secular equilibrium. The sheeted dike section shows 384 the largest δ^{234} U variability with values up to +326±6 ‰ and ten out of twelve samples out of 385 secular equilibrium. The sheeted dike section also shows a general trend in δ^{234} U with depth, 386 with the highest values in the uppermost dikes (~730-850 msb) that decrease downwards in the 387 section (Fig. 4). The plutonic dike-gabbro transition section shows δ^{234} U both slightly above 388 and below secular equilibrium (from -21 ± 10 to $+11\pm10$ ‰) for the five samples. There are no 389 obvious trends in a plot of δ^{234} U versus δ^{238} U (Fig. 7a). Comparing δ^{234} U with U concentrations 390 391 shows that, although there is no clear overall trend, samples from the lava-dike transition zone and sheeted dike sections each define a rough discrete array (Fig 7b). In the lava-dike transition 392 zone near the mineralised hyaloclastic breccia, samples with the higher δ^{234} U have lower U 393 concentrations. Similarly, samples from the sheeted dike section that yield the highest δ^{234} U 394 (>100 ‰) all have U concentrations below the mean N-MORB. 395

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397 5. Discussion

In the following, the processes and timing of U mobility in altered ocean crust will be discussed, focussing first on the U and Th concentrations and then the U isotope systematics in Site 1256.

5.1 Uranium mobility and source constraints from U concentrations and Th/U

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ratios at Site 1256

404 To investigate the alteration effects on U mobilisation, the protolith of unaltered mid-ocean 405 ridge basalts at Site 1256 is an important reference point for comparison. Based on diagnostic 406 geochemistry and radiogenic isotope ratios, the unaltered protolith material at Site 1256 reflects typical N-MORB (e.g. Höfig et al., 2014). There are a range of methods to estimate the 407 408 unaltered protolith; one option is to use the least altered samples within a sample-set, following 409 past practice (e.g. Staudigel, 2014), while using large data compilations is another option. 410 Establishing a reference within a sample-set may be advantageous for site-specific compositions, but it is problematic at Site 1256 given the evidence for U mobility in all sections 411 of the ocean crust sampled (e.g. variable Th/U and δ^{234} U, Figures 4 and 5). Global compilations 412 413 of MORB samples (Gale et al., 2013; Jenner and O'Neill, 2012) yield mean Th/U ratios (~2.9 g/g) and U concentrations (~70 ng/g, see Table 2) slightly lower and higher, respectively, than 414 the average sheeted dikes and dike-gabbro transition at Site 1256 (Table 1). Refining the 415 416 possible protolith to compiled Pacific N-MORB glasses with ICP-data (best suited for reliable trace metal analyses of Th and U) from the PETDb database yields a mean Th/U ratio of ~2.5 417 g/g and U concentration ~79 ng/g (Table 2). In comparison, a small well-characterised data-set 418 of Pacific N-MORB glasses screened for alteration, with δ^{234} U in secular equilibrium 419 420 (Andersen et al., 2015) gives a mean Th/U ratio of ~2.5 g/g and U concentration of ~49 ng/g (Table 2). There is a significant range in both Th/U and U concentrations depending on the 421 422 data-set chosen; the variation probably reflects the combined effects of sample heterogeneity,

analytical uncertainties and possible minor alteration. Given the variable Th/U ratios and U 423 concentrations from the different compilations (Th/U ratios from 2.5-2.9 g/g and U 424 concentrations from 50-80 ng/g), only relatively large changes from a protolith may be 425 426 confidently identified in Site 1256 samples. Further reasons for caution when using Th/U ratios and/or U concentrations in samples for estimating U gain/loss includes; changing sample mass 427 428 can change the U concentration and the assumption that U is mobile and Th is immobile in the 429 fluid-generating process may not be valid given the potential of significant hydrothermal Th fluid mobility under certain geochemical conditions (e.g. Nisbet et al., 2019). However, general 430 431 inverse correlation between U concentrations and Th/U ratios at Site 1256 (Fig. 5) shows changes which attest to U loss/gain to first order. 432

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434 Both the extrusive lavas sequence and the lava-dike transition zone at Site 1256 show evidence for overall moderate to high U additions from their elevated U concentrations and 435 lowered Th/U ratios (Table 1), although, some extrusive lava samples have high Th/U ratios 436 437 (up to \sim 5) at low [U] which we attribute to U loss (Fig. 5). There are features in the U concentrations in the ~750 m thick extrusive lavas that are consistent with other altered ocean 438 crust sections. The overall significant U enrichments are similar to observations from younger 439 ocean crust, such as from the ~6 Ma Pacific Hole 504B (Bach et al., 2003) and ~8 Ma IODP 440 441 Site U1382/U1383 in the Atlantic (Türke et al., 2015), both of which show significant U 442 enrichment compared to N-MORB in the upper ~500 m (Fig. 1), associated with secondary Feoxyhydroxides, clay minerals and altered glass. The U addition in the upper extrusive lava 443 sections at Site 1256 show a weak overall trend with depth, with the greatest U enrichment in 444 445 samples near the top and decreasing with depth (Fig. 4). Overall, it suggests an irregular 446 addition of U from low-temperature seawater-derived, recharging fluids, with more U addition towards the upper parts of the Site 1256 basement. 447

In the plutonic dike-gabbro transition and deeper sheeted dikes at Site 1256, there is 449 evidence for depletion of a range of elements (e.g. Cu, Zn and Pb), with enrichments of these 450 451 in the upper sheeted dike and lava-dike transition, likely via high-temperature alteration and leaching and hydrothermal fluid transport upwards and precipitation with sulfides (e.g. Alt et 452 al., 2010; Patten et al., 2016). Although there are high U enrichments in the lava-dike transition, 453 454 there are no evidence of U additions in the upper sheeted dikes (Fig. 3). The U concentration and Th/U ratio systematics in the dike-gabbro and sheeted dike sections show clear evidence 455 456 for some U mobility, particular in the deeper plutonic sections with highly variable Th/U ratios from >10 to <1, although the average U concentration (~68 ng/g) and concentration-weighted 457 mean Th/U ratio (~2.9 g/g) for the dike-gabbro section are very close to the compiled fresh N-458 459 MORB range, with no evidence of any overall U loss or gain (Fig. 3 and Table 1). The apparent 460 U mobility and redistribution may be linked to the moderately dipping intrusive margins between the sheeted dikes and gabbros that have guided hydrothermal fluid flow and alteration 461 462 in this section (Alt et al., 2010).

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The sheeted dike section is on average, slightly lower in its mean U concentration (~52 464 ng/g) and higher in the mean concentration-weighted Th/U ratio (~3.2 g/g) than the defined 465 466 fresh N-MORB range, indicating some potential U loss. This U mobility does not seem to 467 follow the redistribution of other elements (e.g. Cu, Zn, Pb) from the dike-gabbro into the upper sheeted dike and lava-dike transition zone. Instead, some U loss in the upper sheeted dikes 468 (from 830-850 msb) may have redistributed into the lava-dike transition zone. At Hole 504B, 469 470 U loss from hydrothermal-fluid leaching processes has been suggested for the low U concentrations and high Th/U ratios in the sheeted dikes, whereas the lava-dike transition zone 471 472 shows moderately elevated U concentrations (up ~150 ng/g; Fig. 1) and only moderately

elevated ⁸⁷Sr/⁸⁶Sr ratios compared to pristine MORB (Bach et al., 2003; Höfig et al., 2014; 473 Teagle et al., 1998) suggesting a dominantly U enrichment from the hydrothermal-fluid 474 leaching of U in the sheeted dikes at Hole 504B. At Site 1256, however, the lava-dike and the 475 476 upper sheeted dike section have been affected by both alteration from upwelling hightemperature and downwelling low-temperature seawater-derived hydrothermal fluids (Alt et 477 al., 2010). The latter is evidenced from ⁸⁷Sr/⁸⁶Sr ratios that are strongly elevated from EPR 478 MORB (although still significantly lower than 15 million year old seawater) and precipitation 479 of both anhydrite and sulfide phases (Alt et al., 2010; Harris et al., 2015). 480

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Strong U enrichment has occurred in the hyaloclastic breccia of the Site 1256 lava-dike 482 transition (Fig. 3). The ultimate source of the U enrichment within the hyaloclastic breccia 483 484 could be either basalt-derived or seawater-derived, or perhaps, a combination of both. The hyaloclastic breccia samples in the lava-dike transition that have ⁸⁷Sr/⁸⁶Sr ratios (0.7052-485 0.7061) above the estimated ratios for black smoker fluids at Site 1256 (0.7050-0.7053: Harris 486 487 et al., 2015) also include the samples with the greatest U additions (210 up to 2599 ng/g). These 488 U concentrations are up to an order of magnitude higher than observed in the transition zone 489 of Hole 504 (Fig. 1). This combination of high U concentrations and seawater-derived, fluiddriven alteration, suggest seawater is the dominant source for the U addition to these samples. 490 491

The transition zone at Site 1256 represents a change to a more reducing environment at depth in the altered crust and includes early, near-axis precipitation of sulfide phases from hightemperature hydrothermal alteration. This may provide the conditions for 'roll-front' U uptake (e.g. Cuney, 2010) with an oxidised seawater-derived recharging fluid transporting U⁺⁶ to the lava-dike transition zone where U precipitate as U⁺⁴. If such a recharging fluid were to migrate further and deeper into the sheeted dikes below, it would be depleted in U from this prior 498 removal. This behaviour could account for the high U addition in the lava-dike transition and the limited U addition observed in the upper sheeted dikes, despite the evidence of seawater-499 500 derived fluid interaction in both areas. The specific form of the U uptake in the lava-dike 501 transition zone is unknown, yet typical phases associated with roll-front U uptake includes precipitation of reduced U oxides species such as uraninite (e.g. Cuney, 2010), whereas 502 carbonates precipitated under reducing conditions may contain high U concentrations (e.g. 503 504 Israelson et al., 1997). It is also worth noting that the mechanisms of U uptake from a seawaterderived fluid into altered ocean crust, may differ from those of other elements such as Rb 505 506 uptake or Sr exchange, and, thus, correlations are not necessarily expected between different elements. Further discussion for the uptake mechanisms and timing of the U mobility at Site 507 1256 based on U isotopes is considered in the next sections. 508

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5.2 Uranium mobility estimates from δ^{238} U at Site 1256

511 Changes in δ^{238} U may be used to further evaluate the U sources and mobility within Site 1256. 512 The protolith δ^{238} U may be estimated from the pristine Pacific N-MORB glasses (with δ^{234} U 513 =0) from Andersen et al. (2015) giving -0.28±0.03 ‰ (2SD, n=7). There are samples deviating 514 from the protolith composition in all the sections within Site 1256.

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5.2.1 $\delta^{238}U$ in the extrusive lavas

517 The extrusive lava section displays an irregular distribution of δ^{238} U values ranging from 518 measurements similar to mean Pacific N-MORB towards lower values (Fig. 4). The δ^{238} U show 519 limited correlation with observed alteration in the samples. For instance, the two sets of paired 520 'halo' and 'fresh' counterparts (190 and 437 msb) show no systematic changes in the δ^{238} U nor 521 U concentrations. At 190 msb, the sample with the lowest δ^{238} U (-0.62 ‰) is in the 522 'background' alteration, whereas at 437 msb it is the 'halo' that shows the lowest δ^{238} U (-0.43

‰) of the sample pairs. Also, the two samples from the highly altered 'red brick horizon' (~398 523 msb) yielded δ^{238} U close to seawater (both -0.43±0.03 ‰) and U concentrations (~50 ng/g) 524 and Th/U ratios (~2.6 g/g) close to mean Pacific N-MORB. It has been suggested that the 'red 525 brick horizon' was likely altered by conductively cooled upwelling hydrothermal fluids (Gao 526 et al., 2012; Harris et al., 2015). If the case, perhaps some U exchange process has occurred 527 with hydrothermal fluids and the δ^{238} U close to seawater is coincidental. Other samples with 528 U enrichments and δ^{238} U near to mean Pacific N-MORB and seawater, may be from near-529 530 quantitative uptake of seawater-derived U or U uptake with limited isotope fractionation. A lower, but muted, δ^{238} U is the expected direction for 238 U/ 235 U fractionation occurring with U 531 exchange in the U⁺⁶ oxidation state, as observed in low-temperature U adsorption experiments 532 and in marine ferro-manganese deposits (e.g. Goto et al., 2014; Jemison et al., 2016). 533

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Another explanation for U addition with low δ^{238} U may be U uptake from an evolving 535 fluid carrying low δ^{238} U, from prior partial U removal with a high δ^{238} U. Correlations between 536 decreasing δ^{238} U and decreasing U concentrations has been observed in evolving fluids and 537 solids downgradient in sandstone-hosted U roll-front redox systems, with prior U⁺⁴ 538 precipitation with high δ^{238} U (Basu et al., 2015; Murphy et al., 2014). In contrast, the samples 539 in the extrusive lava section with the lowest δ^{238} U are characterised by the highest U 540 541 concentrations, showing systematics in the opposite direction. Thus, the more likely scenario is partial U uptake from an oxidised low-temperature recharging seawater-derived fluid and U 542 isotope fractionation towards lighter values. The strong U ppm-level enrichment involving 543 544 secondary Fe-oxyhydroxides in other extrusive sections of altered ocean crust and sediments (Mills and Dunk, 2010; Türke et al., 2015) suggests, this could be a likely secondary phase for 545 significant U addition. Also, marine and terrestrial alteration of serpentinites show strong U 546 enrichments which correlates positively with increasing Fe³⁺ over total Fe (Pavia et al. 2023), 547

suggesting U addition with Fe-oxyhydroxides. The altered serpentinites have $\delta^{238}U \sim 0.2-0.3\%$ lower compared to protolith samples (Pavia et al., 2023) a similar lowering of $\delta^{238}U$ as seen in marine ferro-manganese deposits compared to seawater (e.g. Goto et al., 2014). Lowering of $\delta^{238}U$ on the ~0.2‰ level, is also consistent with experimental result from U adsorption on goethite and birnessite (Brennecka et al., 2011; Jemison et al., 2016).

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A lowering of δ^{238} U on the 0.2-0.3‰ level compared to the protolith or the seawater 554 value is within a range of the δ^{238} U of extrusive lavas with elevated U, however, some samples 555 556 are significantly lower (e.g. sample 16R-1 88-95 at 120 msb at -1.02 ‰). This shows that U 557 uptake in some of the altered oceanic crust samples at Site 1256 is not dominated by the same 558 U equilibrium uptake mechanism as within ferro-manganese deposits. The samples at Site 1256 with the lowest δ^{238} U (<-0.80 ‰) all display 'background' alteration style (Harris et al., 2015). 559 However, some background alteration samples have higher δ^{238} U, and so this alteration style 560 is not definitively diagnostic. The very low δ^{238} U could possibly be linked with multi-stage U 561 562 uptake during adsorption associated with secondary phases or driven by kinetic a/biotic processes within the hydrothermal systems in the upper portion of the altered ocean crust. 563 564 Further work to understand the U uptake mechanisms responsible for these low δ^{238} U in the 565 samples are needed.

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5.2.2 $\mathscr{S}^{38}U$ in the Lava-dike transition zone

The upper, basalt-dominated samples in the lava-dike transition zone show no evidence of significant U uptake, whereas the hyaloclastic breccia samples below show greatest U additions and includes the highest δ^{238} U (-0.03±0.02 to -0.60±0.03 ‰) and most elevated ⁸⁷Sr/⁸⁶Sr ratios of all whole rock samples at Site 1256. As with the U concentrations, there is no clear relationship between the ⁸⁷Sr/⁸⁶Sr ratios and the δ^{238} U (Fig. 8). The high δ^{238} U could be from an evolving seawater-derived fluid which has precipitated U with isotopically light U prior in
the extrusive lava section, however, the very high U concentrations in these samples makes
this scenario unlikely.

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Focussing on the samples in the central hyaloclastic brecciated zone, the two samples 577 with the highest U concentrations have δ^{238} U (-0.41±0.03 and -0.38±0.06 ‰) within the 578 compositional range of modern seawater, whereas the samples with lower U concentrations 579 have higher δ^{238} U (Fig. 6; 777-779 msb). This is consistent with an overall pattern of U isotope 580 fractionation towards higher δ^{238} U moving from partial (lower U concentration samples) to 581 582 near-quantitative (higher U concentration samples) U uptake. The overlap with seawater of δ^{238} U in the highest U concentration samples, again supports seawater-derived U as the 583 dominant source of U added to these samples. As discussed above, the more reducing 584 environment at the lava-dike transition makes a roll-front U removal scenario plausible. This 585 is supported by the elevated δ^{238} U in hyaloclastic samples, as observed in other roll-front U 586 precipitates (e.g. Basu et al. 2015; Murphy et al., 2014). Potential host phases for such U 587 addition could be U oxides or other U⁺⁴-bearing phases and calcite precipitates under reducing 588 environments which generally show elevated δ^{238} U (e.g. Bopp IV et al., 2009; Romaniello et 589 590 al., 2013). A modelled U isotope fractionation evolution for the fluid and precipitates is in principle possible, however, it is limited by the difficulty of estimate the total U fraction from 591 592 the fluid added to each of the samples.

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In contrast, the deepest lava-dike transition sample measured in the hyaloclastic breccia with sheeted dike clasts at 782 msb has a lower (although elevated) U concentration (210 ng/g) and a lower δ^{238} U (-0.60±0.03 ‰) than the hyaloclastite samples above (Fig. 4). This sample also has an elevated ⁸⁷Sr/⁸⁶Sr ratio (0.7054) indicating some seawater-sourced Sr. If this sample is considered in the context of a U roll-front system, where the main area of U uptake is in the hyaloclastic zone above, this sample is below the main U mineralisation zone. The low δ^{238} U in this sample then fits with a scenario of precipitation of U⁺⁴-bearing phases above, making the fluid low in δ^{238} U, in a similar way as measured δ^{238} U in downgradient fluids samples following reductive U removal in sandstone-hosted U roll-front deposits (e.g., Basu et al., 2015; Murphy et al., 2014).

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5.2.3 δ^{238} U in the sheeted dikes and plutonic dike-gabbro sections

In the plutonic dike-gabbro section, the sample with the lowest U concentrations (21 ng/g), 606 shows the highest δ^{238} U (-0.18±0.10 ‰) similar to the mean Pacific N-MORB, whereas the 607 other four samples, also with low U (26-39 ng/g), have δ^{238} U (-0.40±0.10 to -0.53±0.10 ‰) 608 below the mean Pacific N-MORB. This suggests some, but limited, changes in δ^{238} U during 609 the U mobility and redistribution in the dike-gabbro transition section. The sheeted dikes also 610 show limited variation in δ^{238} U, with nine out of twelve samples with δ^{238} U similar to the 611 mean Pacific N-MORB, with two slightly below (-0.42±0.10 and -0.40±0.10 ‰) and one 612 slightly above (-0.16±0.06 ‰) (Fig. 4). If the low U concentrations in the upper part of the 613 sheeted dikes are due to U leaching and loss, it suggests limited U isotope fractionation during 614 this process. The upper sheeted dike section shows precipitation of both anhydrite and sulfide 615 phases (Alt et al., 2010) yet this appears not to be accompanied by significant U uptake. If the 616 anhydrite mineralisation is mainly from a seawater-derived fluid the limited U uptake could be 617 due to the fluid have lost most of the U prior at shallower depth, either via U⁺⁶ adsorption in 618 the extrusive lava section or as U^{+4} across a redox front in the lava-dike transition section. 619 However, despite the low U, the high δ^{234} U values for some samples in the upper sheeted dikes 620 621 are consistent with some U uptake. Thus, it is possible that several different mechanisms for U

622 mobility, with different timings, have contributed to the overall U systematics observed. This 623 will be explored further using the δ^{234} U systematics in section 5.3.

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5.3 Uranium mobility and sources estimated from $\delta^{34}U$ at Site 1256

The measured δ^{234} U at Site 1256 suggest that the timing of the U addition is complex, as 626 samples with evidence of U addition and loss display δ^{234} U within and significantly out of 627 secular equilibrium. There is no trend in δ^{238} U versus δ^{234} U (Fig. 7a), suggesting that U 628 mobility has occurred both prior to, allowing the ²³⁴U/²³⁸U ratios to return to secular 629 equilibrium, and within the last ~1.5 million years. The δ^{234} U values furthest from secular 630 equilibrium are within the lava-dike transition and particularly in the sheeted dikes, with two 631 samples ($+327\pm10$ and $+250\pm10$ ‰) above the modern seawater value of \sim +145 ‰ (Fig. 4). A 632 potential explanation for the excess ²³⁴U is a seawater contaminant during drilling, however, 633 this is an unlikely scenario given the δ^{234} U higher than the seawater value in some samples and 634 that δ^{234} U disequilibrium was measured in samples that were cored during different drilling 635 expeditions (Leg 206, 309 and 312; Fig. 4). Instead, the significant disequilibrium in δ^{234} U is 636 evidence for the 'recent' (here used for the last 1.5 million years) mobility of U at hypabyssal 637 levels of the ocean crust at Site 1256. Previous observations of fresh versus altered pillow lavas 638 and drilled shallower ocean crust have shown δ^{234} U mainly between secular equilibrium (0 ‰) 639 and modern seawater (+145 ‰), but with a few samples falling outside this range, with both 640 higher and lower δ^{234} U values, to the level quantifiable with low precision alphas counting 641 techniques (Bacon, 1978; Macdougall et al., 1979). Also δ^{234} U values higher than the seawater 642 value have been observed from U addition in weathered serpentinites (terrestrial and marine) 643 and altered ocean crust, pointing to U addition from a seawater-derived hydrothermal fluid 644

645 source with further elevation of δ^{234} U from leaching recoiled 234 U along fluid pathways (Pavia 646 et al., 2023; Reyss et al., 1987).

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The very high δ^{234} U values in some samples at Site 1256 are associated with relatively 648 low U concentrations (~ 26 and ~ 31 ng/g) from the uppermost sheeted dikes, while elevated, 649 but lower δ^{234} U occur in samples stratigraphically above and below (Fig. 4). The overall trend 650 in the sheeted dikes with high δ^{234} U in the upper part (~777 to 850 msb) and decreasing with 651 depth, could potentially be explained by upwelling of basalt-derived fluids, rather than 652 downwelling of seawater-derived fluids. However, the ~15 Ma age and progressive cooling of 653 the ocean crust makes recent high-temperature hydrothermal activity unlikely. Also, a positive 654 correlation between δ^{234} U and U concentrations would be expected from this scenario, yet is 655 not observed; samples from the overlying lava-dike transition have higher U concentrations 656 but lower δ^{234} U (up to +87±5 ‰). 657

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Instead, the samples with δ^{234} U above secular equilibrium in Site 1256, are likely to 659 have experienced U uptake via precipitation from a low-temperature seawater-derived fluid, 660 with modified δ^{234} U from 234 U leaching of alpha-recoil damaged sites in the ocean crust rock 661 662 matrix along the fluid pathway (leaving those conduits depleted in ²³⁴U). The downward migration of such a seawater-derived fluid could have precipitated most of the U at the 663 hyaloclastic breccia with the redox transition and leaving a modified fluid, with lower U 664 concentration, to migrate further below into the sheeted dikes. As discussed, some samples in 665 the upper part of the sheeted dikes have very low U concentrations (<30 ng/g) likely from U 666 667 loss during hydrothermal alteration at greenschist facies conditions at an early stage near the ridge axis. Therefore, given the low U concentrations, even minor recent U additions with a 668 high δ^{234} U, will have a large impact on the bulk δ^{234} U value of the sample. Such a scenario is 669

broadly consistent with the pattern of generally higher δ^{234} U with lower U concentrations for samples both in the lava-dike transition and sheeted dike intervals (Fig. 7b).

672

Based on the δ^{234} U data, a sensitivity exercise can be done to estimate the relative 673 674 fraction of recent U uptake compared to the total U in the sample. Assuming the measured δ^{234} U in the samples is a mixture between recent U uptake from a fluid with a high δ^{234} U and 675 older U (>1.5 Ma) with δ^{234} U = 0 ‰, the relative contribution of the recent U uptake can be 676 estimated. This calculation can be done for all samples with $\delta^{234}U > 0$ ‰ if the $\delta^{234}U$ of the 677 fluid is known (all normalised to present-day compositions from the radioactive decay of the 678 U isotopes). In the study of Pavia et al. (2023), the fluid adding excess U during the seawater-679 alteration of marine serpentinites had an estimated δ^{234} U of ~589 ‰. Using a similar δ^{234} U for 680 the U in the fluid (600 ‰), 'recent' U addition from this fluid was estimated for the samples 681 measured at Site 1256 (supplementary table 3). This estimate shows only minor recent U 682 contributions (below 4 ng/g U and below 4% addition) for the shallow extrusive lavas and deep 683 plutonic dike-gabbro transition samples, that show little disequilibrium in δ^{234} U. For some 684 samples in lava-dike transition and sheeted dike section, the changes are more significant. In 685 the high U-containing samples in the hayloclastic breccia, recent U addition contributes up to 686 ~100 ng/g, a maximum 14% recent U addition compared to the total U inventory. In the sheeted 687 dikes, the calculated recent U addition is also significant for the samples with high δ^{234} U, with 688 up to 14 ng/g U addition that contributes up to 52% of the total U. 689

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691 There are some obvious sources of uncertainty with these estimates of recent U 692 addition, including that the fluid δ^{234} U may be variable and/or different from the value used 693 here. Using a higher δ^{234} U in the fluid, the recent U addition estimates would decrease, whereas 694 using a lower δ^{234} U the estimates would increase. However, a significantly lower fluid δ^{234} U 695 would imply some samples were extremely depleted in U prior to recent addition, as the calculated recent U addition already contributes up to 52 % of the total U in some samples with 696 low bulk U (26-39 ng/g) and we consider this unlikely. This simple calculation approach shows 697 that U uptake from recent seawater-derived fluid with a high δ^{234} U may have a significant 698 impact on the δ^{234} U compared more limited effects on the U concentration for most samples. 699 Although the highest δ^{234} U is in the samples from uppermost sheeted dikes, the calculated total 700 amount of recently added U is up to eight times higher in the hyaloclastic breccia than in the 701 702 lava-dike transition samples. These observations point to a seawater-derived fluid active during the last 1.5 my being channelled through and reacting with the deeper parts of the Site 1256, 703 704 with U uptake at the redox change in the lava-dike transition, perhaps via a similar mechanism 705 as the U uptake that occurred prior to the last 1.5 my.

706

The δ^{234} U data also suggest that a range of the sheeted dikes samples experienced recent 707 U addition. However, the overall low bulk U concentration and Th/U ratios point to an overall 708 709 U depletion, suggesting that these samples were previously even more depleted in U. Using the estimated recent U addition, the samples Th/U ratios prior to this addition may be estimated 710 711 by subtracting the recent from the bulk U concentration (supplementary table 3). The estimated Th/U ratios prior to the recent U addition for the two sheeted dike samples with the δ^{234} U above 712 the seawater value, changed significantly to 9.2 and 7.0 (from 4.2 and 4.1, respectively). 713 714 Although these Th/U ratios estimates are lower than any measured bulk samples in the sheeted dike section, they are within the lower Th/U ratios measured in the plutonic dike-gabbro 715 716 transition (Fig. 5), a region with little evidence for recent U addition, making the U losses of 717 these samples within reasonable bounds. Why these upper sheeted dike samples first experienced U loss followed by recent U addition, may be related to the pathways of fluids and 718 719 timing of the U addition (see further discussion in section 5.4).

Lastly, the calculations for recent U addition using the δ^{234} U, can also be extended to 721 include an estimate of the δ^{238} U of the sample prior to recent U addition, if the δ^{238} U of the U-722 carrying fluid is known. Again, there are several complexities here, particularly, whether the 723 U addition from a fluid is invoked with or without an expressed U isotope fractionation (e.g. 724 725 quantitative vs. non-quantitative U addition) and exact U isotope fractionation factors for the U uptake processes. Thus, calculated δ^{238} U in the samples prior to recent U addition, should be 726 727 considered as a measure of sensitivity to the potential impact of the recently added U on the δ^{238} U of the sample. Assuming a δ^{238} U for the U in the fluid of either -0.60 or -0.03 ‰, the 728 highest and lowest δ^{238} U measured in the lava-dike transition and sheeted dike section, and 729 assuming no U isotope fractionation during the U addition process, the δ^{238} U for the samples 730 prior to the recent U addition, can be estimated (supplementary table 3). Using -0.60 or -0.03 731 ‰ as end-members for δ^{238} U in the fluid, only the two samples with the highest δ^{234} U show 732 significant change of >0.1‰ in the δ^{238} U. These two samples show estimated maximum δ^{238} U 733 changes of up to 0.52 ‰ higher and 0.27 ‰ lower than the bulk samples δ^{238} U. For most 734 samples, similar to the U concentrations, the changes in δ^{238} U are generally of little significance 735 despite the changing δ^{234} U, again showing the larger leverage changes in δ^{234} U typically have 736 compared to δ^{238} U and U concentrations. 737

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5.4 General uranium isotope evolution in the altered ocean crust at Site 1256

740 By combining observations of hydrothermal conditions and distribution of alteration products 741 (Alt et al., 2010; Teagle et al., 2006) with the U systematics discussed in the previous sections, 742 it is possible to evaluate the evolution of U mobilisation and uptake in upper ocean crust formed 743 at a fast spreading rate. Thus, we add the U systematics to the stages of alteration suggested by 744 Harris et al. (2015). The first alteration stage is near the ridge axis with high-temperature 745 greenschist facies alteration in the sheeted dikes and dike-gabbro transition (Alt et al., 2010). The magmatic-driven hydrothermal circulation led to metal leaching in the sheeted dikes and 746 gabbro sections with precipitation of metal sulfides (mainly pyrite) near the top of the sheeted 747 748 dikes and in the lava-dike transition (Alt et al., 2010; Patten et al., 2016). These reactions appear to have resulted in only minor localised hydrothermal leaching and re-distribution of U in the 749 sheeted dikes and dike-gabbro transition, possibly with minor addition of U in the lava-dike 750 751 transition (Figs 4 and 5). There is little evidence for net U excess in the sheeted dike and dikegabbro transition, and therefore, little evidence for significant high-temperature near-axis 752 753 quantitative U uptake at depth in this ocean crust, as would be estimated from measurements of low-U fluids at black smoker vents (Chen et al., 1986; Michard et al., 1983; Mottl et al., 754 1998). It may be that U uptake occurs during low temperature processes at shallower depth in 755 756 diffuse, downwellings that feed higher temperature systems at greater depth, or that on-axis U uptake is of less significance from an U uptake mass-balance perspective. The on-axis 757 precipitation of hydrothermal reductive phases (e.g. metal sulfides) would have provided an 758 759 upwards shift in reducing conditions to just below the lavas section.

760

The migration of the ocean crust away from the ridge axis led to more extensive low-761 762 temperature alteration of the lavas by seawater-derived ridge flank hydrothermal fluids (Alt et 763 al., 2010). The uptake of U off-axis is evidenced by the alteration and U uptake in the upper 764 lava pond that cooled and solidified a short distance (~10 km) off-axis (Harris et al., 2015; Teagle et al., 2006). The off-axis low-temperature alteration led to significant U uptake under 765 largely oxidised conditions characterised by low δ^{238} U from U⁺⁶ adsorption or incorporation 766 processes. At depth in the lava-dike transition section, deep channelling of seawater-derived 767 fluids may have provided transport of U to be precipitated as U⁺⁴-bearing phases, including 768 high δ^{238} U across a redox front as an U roll-front type uptake in the lava-dike transition zone. 769

771	The δ^{234} U data shows that the ~15 million old Site 1256 has experienced U mobility
772	within the last ~1.5 years. The slightly positive $\delta^{234}U$ values of some extrusive samples
773	indicates recent channelled flow of seawater-derived fluids in the uppermost basement. While
774	the recent U addition to the extrusive section is minor, there is significant U uptake in the
775	deeper lava-dike transition zone and within the sheeted dikes. The high δ^{234} U values in the
776	lava-dike transition zone and sheeted dikes (with extreme values in the uppermost sheeted
777	dikes) are likely derived from the passage of seawater-derived fluids with additional ²³⁴ U from
778	preferential leaching along the fluid pathways. The U uptake within the sheeted dikes, appears
779	to have mainly been from this recent phase of U uptake and mobility. Although speculative,
780	samples with previous U removal in the sheeted dikes may have mineralogy favouring, this
781	later U uptake, compared to less altered samples within the sheeted dikes, e.g. via adsorption
782	to chlorite, an abundant secondary phase in these samples (Alt et al., 2010).

783

784 The evidence for recent U mobilisation at hypabyssal depths in at Site 1256 is surprising as the hydrologic situation at the site is quite different to some other sites from the eastern 785 Pacific (e.g., Site 504B; EPR; Juan de Fuca Ridge) where the sections show significant faulting 786 787 and basement topography, and/or are only thinly sedimented and show advective heat flow and 788 pore water chemical gradients that provide clear evidence for on-going low-temperature flow 789 of seawater-derived fluids (e.g., Fisher et al., 1994; Kuhn et al., 2017). At Site 1256, the thick 790 sediment cover (>250 m) and smooth basement topography indicates that recharge vertically 791 through the sediment cover is unlikely as evidenced by the diffusive temperature and sediment porewater gradients (Alt et al., 2010; Teagle et al., 2012). However, inflections in wireline 792 793 temperature profiles measured in Hole 1256D indicate zones of elevated porosity and on-going 794 lateral fluid flow in the lower lavas (~670 msb) and the top of the sheeted dikes (805 msb, see

795 Teagle et al., 2006, 2012). Generally low heat flow on the Cocos Plate and the presence of 796 extinct hydrothermal pits in the region of Site 1256 have been interpreted as discharge sites for "hydrothermal siphons" where cold seawater flowed into the ocean crust via seamounts that 797 798 punctured the sediment cover (Villinger et al., 2017). There are seamounts rising to hundreds of meters above the surrounding abyssal plains ~20 km to the north-east of Site 1256 as well 799 as a number of smaller features on the region. Although the hydrothermal pits studied to date 800 801 are not sites of active fluid venting there may still be structures in the region that facilitate the 802 recent ingress of seawater into the ocean crust at Site 1256.

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- 804

5.5. The U isotope signatures of altered ocean crust

The observed U mobility and δ^{238} U variations at Site 1256 are similar to previously 805 investigated profiles of upper ocean crust. In common with Hole 504B (Bach et al., 2003; 806 Höfig et al., 2014), Site 1256 shows only limited U uptake, if any, in the lower sheeted dikes 807 (and gabbros) that may be attributed to high-temperature hydrothermal circulation at the mid-808 ocean ridge axis (Figs 1 and 4). The general U uptake with low δ^{238} U in the upper extrusive 809 lava section at Site 1256 is similar to observations in the upper parts at Site 801 (Andersen et 810 al., 2015; Noordmann et al., 2016). Composite samples representing the upper ~420 meters of 811 812 the ocean crust at Site 801, have U concentrations approximately five times higher than unaltered MORB, although δ^{238} U vary with depth (Fig. 2). The Site 801 composite sample 813 from the uppermost section (0-110 msb) has low δ^{238} U values of ~ -0.44 ‰ whereas composite 814 samples from two deeper sections (110 to 220 and 220 to 420 msb) show significantly higher 815 δ^{238} U values (of ~ +0.16‰ and -0.14‰). The supercomposite sample that integrates the whole 816 drilled section at Site 801 suggests average δ^{238} U of -0.17+0.05‰ (Andersen et al., 2015). The 817 changing δ^{238} U down-hole at Site 801, suggests a change in the dominant U uptake mechanism. 818 819 A typical temporal alteration sequence in altered ocean crust consists of ferric-iron bearing 820 celadonite veins, with later Fe-oxyhydroxides and the then partial overprinting by a reduced assemblage of Mg-saponite and pyrite with interspersed carbonate veins (Alt and Teagle, 821 2003). This change from early oxidised to more reducing conditions later, reflects changing 822 823 fluid flow pathways and more restricted connections to ocean seawater as the crust moves away from the ridge axis due to secondary minerals forming in the basalts and increasing sediment 824 burial. Uranium enrichments are evident in breccia zones including in redox halos moving 825 826 away from alteration veins, displaying roll-front redox U deposition type patterns (Alt and Teagle, 2003; Kelley et al., 2005). The δ^{238} U data implies that in the uppermost levels, the U 827 incorporation from relatively oxidised seawater-derived fluids occurs without any significant 828 redox change, for instance, through the adsorption on to Fe-oxyhydroxides or precipitation of 829 carbonates, with little or isotopically light U uptake. The shift towards higher δ^{238} U in the lower 830 sections of Site 801 suggest change from U^{+6} to U^{+4} - bearing precipitates, as the main process 831 of U removal in the deeper sections. This pattern in the composite samples is consistent with 832 discrete bulk rock and calcite samples at both Site 801 and 417/418 (Fig. 2). 833

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In contrast at Site 1256, the ~750 m of lava section all show δ^{238} U consistent with 835 oxidised U⁺⁶ uptake. We note that oxidation halos are much less strongly developed in the lavas 836 837 at Site 1256 compared with other ocean crust sites, particularly those from slower spreading 838 rates (see Alt et al., 2010). At Site 1256, the strongest U uptake is in the underlying lava-dike 839 transition. As coring in Hole 1256D is only the second in situ sampling of the lava-dike transition (after Hole 504B), it is difficult to evaluate whether such deep U uptake is a common 840 feature of altered ocean crust. The generally higher δ^{238} U in the lava-dike transition section 841 842 compared to the extrusive lava section, likely reflect a change to more reducing character of U^{+4} uptake, as also seen at depth at Site 801. 843

Comparing U concentrations to δ^{238} U for samples from Sites 1256, 801 and 417/418, 845 the combined samples exhibit roughly similar behaviours. Some samples define a trajectory 846 of moderate U uptake under oxidised conditions and yielding rocks with low δ^{238} U (Fig. 9) 847 Some of these samples could in principle also be from the addition of U with low δ^{238} U, 848 although a lower U concentration would then be expected, as previously discussed. A second 849 trend is defined by greater extents of U enrichment with high δ^{238} U indicating U uptake as U⁺⁴ 850 851 under reducing conditions. A third trend is defined by samples with the highest U concentrations with seawater-like $\,\delta^{238}U,\,$ suggesting near-quantitative U uptake from a 852 seawater-derived fluid. A fourth trend to low U concentrations, but with δ^{238} U close to mean 853 Pacific N-MORB, suggest U loss but with only minor isotope fractionation (Fig. 9). These 854 855 combined trends suggest that similar processes for U uptake and U isotope fractionation in the 856 altered ocean crust over the past ~170 million years, although the proportion of oxidised versus 857 reducing U uptake is different at the different sites.

858

859 It is notable that the inferred trends in the mechanisms of U uptake, based on the isotope systematics, are not necessarily directly comparable to the overall observed geology and 860 alteration assemblages in the different drilled sections of ocean crust. For instance, the 861 occurrence of oxidised halos and Fe-oxyhydroxides are more common at Site 801 than at Site 862 1256 (Alt et al., 2010) yet oxidised U uptake is more prevalent at Site 1256 over Site 801. 863 864 However, caution should be taken with broad generalisations between dominant alteration assemblages and U uptake given the very heterogeneous nature and distribution of U in altered 865 ocean crust. Specifically, spatially restrictive reductive areas with high U⁺⁴ uptake may, by 866 mass balance, outweigh large areas of lower levels of U⁺⁶ uptake. A mass balance consideration 867 of the U removal from the dominantly oxidised modern ocean illustrates this, where only <1%868 cover of reducing (sub-oxic to sulfidic-anoxic) sediments on the ocean seafloor are responsible 869

870 for ~55% of the U removal from the ocean (e.g. Dunk et al., 2002). For a high U uptake under reducing conditions, U-rich oxidised hydrothermal fluids are required to transport soluble U 871 to regions of the ocean crust where U removal can occur via U⁺⁴ precipitation, similar to U 872 873 removal in oceanic reducing sediments (e.g. Dunk et al., 2002) or redox sandstone-hosted U roll-front systems (e.g., Cuney, 2010). Thus, evidence of an abundance of oxidised alteration 874 products in an altered ocean crust is not in itself diagnostic of dominantly oxidised U uptake. 875 876 Reductive U uptake in altered ocean crust is likely to occur at different length scales, for example in metre thick zones as in mineralised hyaloclastic breccia in the lava-dike transition 877 878 zone at Site 1256 or, as observed at Site 801, at cm to mm length scales with high U 879 concentrations in redox vein halos and secondary carbonate precipitates (Kelley et al., 2005). Further research on the better characterisation of U uptake and isotope fractionation with 880 881 alteration phases and products is needed.

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5.6. The U budgets and isotope systematics of altered ocean crust

884 By combining the new analyses for Site 1256 with published data, it is possible to make a broad estimate for the typical U uptake for hydrothermally altered upper ocean crust, while 885 acknowledging the caveat of the limited data available to make generalised estimates of a 886 significant portion of Earth's surface (Table 3). Using the average U concentration of an 887 888 estimated pristine rock protolith and subtracting this from the estimated average U 889 concentration obtained from each location of deep-drilled, altered ocean crust, its U excess can 890 be estimated. All the drilled sections of altered ocean crust investigated, show evidence of 891 overall U addition across the age range and geographical cover (Bach et al., 2003; Harris, 2011; 892 Kelley et al., 2005; Kelley et al., 2003; Mitchell and Aumento, 1977; Staudigel et al., 1996; Türke et al., 2015). 893

895 A range of young <20 million years crust (Sites 332/333, 504B, U1392/U1393, 1256) have non-ideal calculated means from averaged, measured U concentrations in discrete 896 897 samples. For Site 1256 the estimate has been taken from the mean using the length-scale of the 898 lithology sections (excluding the plutonic dike-gabbro section) (Table 1). We further note that data from Site 332/333 were not measured using modern techniques (Mitchell and Aumento, 899 1977) and may therefore be less reliable an estimate. However, all locations show a similar 900 901 feature of moderate U enrichments (~50-150 ng/g). In contrast, the estimates for the older Sites 801 (~167 Ma) and 417/418 (~120 Ma), with U excess estimates based on composite samples 902 903 (Kelley et al., 2005; Kelley et al., 2003; Staudigel et al., 1996), show significantly higher U 904 enrichments (346 ng/g and 286 ng/g, respectively) (Fig. 10).

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It is also possible to estimate the mean δ^{238} U for the altered ocean crust sections at 906 Sites 1256, 801, 417/418, where both U concentration and δ^{238} U data is available. The U 907 concentrated-weighted mean of discrete samples from Site 1256 gives a δ^{238} U of -0.37±0.07 908 909 ‰ (standard error of the mean). Taken the U concentrated mean using the length-scale of the lithology sections (excluding the plutonic dike-gabbro section) gives a lower δ^{238} U of -910 0.51±0.15 ‰ (SD), which is likely a more representative value. This estimate is lower than the 911 U concentrated-weighted mean δ^{238} U of the discrete samples at Site 417/418 of -0.20±0.11‰ 912 and Site 801 of -0.23±0.08 ‰ (standard error of the mean) (data; Andersen et al., 2015; 913 Noordmann et al., 2016). The Site 801 U concentration-weighted mean δ^{238} U overlaps with the 914 estimate of the supercomposite at Site 801 of -0.17 \pm 0.03 ‰ (Fig. 10). The lower mean δ^{238} U 915 916 for Site 1256 suggests relatively more oxidised U uptake compared to more reducing U uptake 917 at the older Sites 801 and 417/418. A continuous low-temperature U uptake of more reducing 918 character, beyond the ~15 million year age of Site 1256, could explain the higher U concentration and mean δ^{238} U estimates for the older Sites 417/418 and 801. Another possible 919

920 scenario for the difference could be related to the lava pond at Site 1256, which may have 921 restricted and minimized the seawater-derived circulation and thereby the U uptake during the 922 more reductive U uptake phase compared to the older sites. A combination of the two processes 923 is perhaps the likely explanation to the evolution of the U and its isotope systematics at Site 924 1256 compared to Sites 801 and 417/418.

925

926 6. <u>Concluding remarks</u>

The U concentration and isotope systematics at Site 1256 and other altered ocean crustal 927 928 sites show that the overall U uptake and associated isotope compositions are both spatially and temporally heterogenous. The distribution of δ^{234} U disequilibrium through Site 1256 shows 929 that U uptake from seawater-derived fluids appears active after 15 million years (albeit to a 930 minor extent). This is surprising given little evidence for active seawater recharge into the 931 ocean crust presently at Site 1256. This observation, however, is generally consistent with 932 933 discernible regional conductive heat flow anomalies extending into ocean crust of ~65 Ma 934 suggesting on-going hydrothermal transport of heat and low temperature ocean crust alteration (e.g., Parsons and Sclater, 1977; Stein and Stein, 1994). A change in the mean δ^{238} U for altered 935 ocean crust with increasing age, i.e. between Site 1256 and sites on older crust (801, 417/418), 936 937 is likely driven by the more reductive character of alteration and U uptake over time. This temporal evolution of seawater-derived fluid flow with a change from more oxidised to reduced 938 939 conditions during low temperature alteration, may also play an important role for constraining 940 the overall systematics of other redox-sensitive elements and their isotopes in altered ocean crust such as Tl and Mo (e.g. Coggon et al., 2014; Freymuth et al., 2015; Nielsen et al., 2006). 941 942 Further work should focus on combining detailed studies of alteration assemblages with the U uptake and associated U isotope systematics, as well as community efforts for generating 943 944 quantitatively representative new composite samples at different altered ocean crust sites.

945	Better knowledge on the $\delta^{238} U$ and U concentration of specific alteration assemblages provide
946	improved input values for models of the behaviour and release of U during prograde
947	metamorphism during subduction and its deep cycling beyond the arc front. Furthermore, as
948	shown from the δ^{234} U at Site 1256, U-series disequilibrium systematics may provide important
949	constraints on the timescales of U mobility during low temperature alteration and convective
950	heat fluxes in ageing altered ocean crust.
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	962	Data	availability	
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Contribution 19.

963 Data are available at Mendeley data: DOI: 10.17632/hgnkxhhh2x.1

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- 965 Appendix A. Supplementary material
- 966 Geochemical data obtained during this study is available in supplementary tables.

967

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- 1175

Table 1

	Section thickness (m)	N	Th (ng/g)	SD	U (ng/g)	SD	Th/U	SD	Th/U conc. Weighted	N	δ238U (‰)	SD	δ238U (‰) Weighted	SD
Overall		462	194	112	93	165	3.0	1.3	2.1	49	-0.40	0.21	-0.37	0.21
Overall (excluding Plutonic section)		413	193	101	96	172	2.8	1.0	2.0	44	-0.41	0.22	-0.37	0.22
Lava section	754	218	216	125	117	127	2.4	0.9	1.8	23	-0.50	0.24	-0.63	0.24
Lava-Dike section (Tansition zone)	57	9	189	45	502	913	2.4	1.4	0.4	9	-0.28	0.18	-0.30	0.18
Sheeted dike section	346	186	167	54	52	17	3.4	0.9	3.2	12	-0.32	0.08	-0.32	0.08
Plutonic section*	88	49	198	180	68	80	4.3	2.5	2.9	5	-0.39	0.13	-0.41	0.13
Mean of sections			200	20	113	213	2.8	0.9	1.8		-0.43	0.10	-0.51	0.15
Mean of sections (excl. Plutonic)			200	25	116	243	2.7	0.6	1.7		-0.44	0.12	-0.52	0.18

¹¹⁷⁷

1178

1179 Table 1. Different calculations of mean U, Th concentrations, Th/U ratios and δ^{238} U for Site 1180 1256. The concentration estimates are from the comprehensive data set of Harris (2011), while 1181 δ^{238} U estimates are from this paper. Estimates include overall (with or without plutonic 1182 section), each stratigraphic section, and mean integrating the length scale of each lithology 1183 section scaled proportionally with the thickness of the sections (with or without plutonic 1184 section). The estimated Th/U ratios and δ^{238} U means have been calculated as both averages 1185 and concentrated-weighted averages.

Source	Ν	U (ng/g)	Th/U (g/g)				
I	EPR						
Andersen et al. (2015)	7	49	2.50				
PetDB – Glass	807	79	2.47				
PetDB – Whole rock	479	120	2.37				
Global							
Jenner and O'Neill (2012)	438	66	2.94				
Gale et al. (2013)	1653	73	2.84				

Table 2. The mean U concentrations and Th/U ratios for different MORB compilations from

either East Pacific Rise (EPR) or global coverage.

Table 3

Slow

Fast

Slow

Fast

60

50

35

44

140

113

321

390

U

enrichment

(ng/g) 153ª 39^b

80°

63^d

286e

346^f

δ²³⁸U

(‰)

-0.51g

-0.20^h

-0.17ⁱ

-0.23^j

 $\pm SD/SE$

0.15

0.11

0.03

0.08

		Altered oceanic crust						
Site	Age (Ma)	Region	~DIB (m)	Zone covered	Spreading type	U MORB (ng/g)	U AOC (ng/g)	
332/ 333	3.5	Atlantic	600	Volcanic	Slow	100	253	
504B	5.9	E. Pacific	2000	Volcanic	Intermediate	16	55	
U1382/	0	A 414:	600	V-l	C1	60	140	

Volcanic

Volcanic/SD/

Gabbro

Volcanic

8

15

120

167

1383

1256

417/

418

801

Atlantic

Pacific

Atlantic

W.

Pacific

600

1600

550

400

1194

Table 3: Mean estimated U enrichments for six altered crust sites based on the U 1195 concentration in altered oceanic crust (UAOC) subtracted the estimated protolith (UMORB). 1196 The mean $\delta^{238}U$ estimates for 1256, 417/418 (h) and 801(i) are based on U-weighted averages 1197 of lithology averaged $\delta^{38}U$ values (g) discrete $\delta^{38}U$ values (h,j) and based on supercomposite 1198 measurement (i). 'DIB' is depth in Basement and 'SD' is sheeted dike. Data sources: (a) 1199 Mitchell & Aumento (1979); Average AOC and MORB (MORB estimate from Site 335) / (b) 1200 1201 Bach et al. (2003); Average AOC and MORB / (c) Turke et al. (2015); average AOC, MORB 1202 average for all Th/U > 2 / (d) Harris (2011) average AOC and MORB / (e) Staudigel (1995), Staudigel et al. (1996), Kelley et al. (2005); average AOC from composite and MORB average 1203 from Site / (f) Kelley et al. (2003), Kelley et al., (2005); average AOC from composite and 1204 MORB average from Site / (g) this study; $\delta^{238}U$ data, $\pm 1SD$ / (h) Noordmann et al. (2015); 1205 $\delta^{238}U$ data, $\pm 1SE / (i)$ Andersen et al., (2015); $\delta^{238}U$ supercomposite, $\pm 1SD / (j)$ Andersen et 1206 al. (2015) and Noordmann et al. (2015) $\delta^{238}U$ data, $\pm 1SE$. 1207

1208

Figure Captions

Fig 1 published U concentrations with depth below sub-basement for (a) Site 504B (Pacific ~5.9 Ma: Bach et al., 2003), and Site 1082/1083 (Atlantic, ~8 Ma; Turke et al. 2015). In (a)
reference lines for average East Pacific rise (EPR) N-MORB and estimated unaltered MORB at 504B (Bach et al., 2003) is plotted, while lithological depth sections are separated into lava, transition and sheeted dike. In (b) reference line for average mid-Atlantic ridge (MAR) N-MORB is plotted.

1216

1217 Fig 2. published $\delta^{238}U$ compositions (a,c) and U concentrations (b,d) and vs. depth below sub-1218 basement from (a,b) Pacific Site 801B/C and (c,d) Atlantic Site 417/418, respectively. The top 1219 of both cores is at the sediment to ocean crust transition. Discrete samples and composite samples are shown (see legend). In Site 801, 'composite samples' (mixtures of the different 1220 1221 lithologies and alteration styles, blended as powders in representative proportions (Plank et 1222 al., 2000) from 0-110m, 110-220m and 220-420m are shown as horizontal lines and shaded 1223 area covers the depth range. Composites are marked with the stippled yellow line, with the band around the line representing the variability of the composites within the section ($\delta^{238}U$ 1224 for 801 and U conc. for 801 and 417/418). Reference lines are shown for seawater and 1225 Pacific/Atlantic N-MORB for the $\delta^{238}U$ composition, and average Pacific or Atlantic MORB 1226 1227 for U concentration. Data sources: discrete samples are from Noordmann et al. (2016) and Andersen et al. (2015); $\delta^{238}U$ for composites, seawater and Pacific/Atlantic MORB from 1228 Andersen et al. (2015) and Kipp et al. (2022); Pacific N-MORB U concentration from Andersen 1229 et al. (2015); Atlantic MORB and composite U concentration from Staudigel et al. (1989); 801 1230 1231 composite U concentration Kelley et al. (2003).

1232

- Fig 3. Map showing the locations of Sites 1256 and 504 in the eastern equatorial Pacific with
 crustal ages shown in 5 million year intervals (modified from Wilson et al., 2003).
- 1236

Fig 4. Stratigraphic depth (msb) section of Site 1256 versus Th/U ratios, U concentrations 1237 (logarithmic scale), $\delta^{238}U$ and $\delta^{234}U$ values. Lithologies and stratigraphic sections are labelled 1238 on the left, boundaries between stratigraphic sections are marked with grey horizontal lines, 1239 1240 while the boundaries between sections recovered in different drilling expeditions are marked with red stippled lines (Teagle et al., 2006; Teagle et al., 2012; Wilson et al., 2006). Average 1241 compositions for EPR MORB (in Th/U and U concentrations), seawater (blue dashed in $\delta^{238}U$ 1242 and $\delta^{234}U$), 801 composite (dark dashed with grey \pm uncertainty $\delta^{238}U$) and secular equilibrium 1243 (grey dashed $\delta^{234}U$) are shown as vertical lines (references as in Figure 1). 1244

Fig 5. Th/U ratios versus U concentrations (logarithmic scale) for all samples at Site 1256. Paired samples are linked with tie-lines; coloured and filled = halo and clast; white and hollow = background and breccia, X = 26R; * = 62R; $\bullet = 122R$. In legend; 'transition zone' refers to the lava-dike transition, 'Gabbro' refers to the plutonic gabbro-dike transition. References for superscripts in legend: (a) Harris (2011); (b) Hoefig et al. (2015); (c) this study. EPR N-MORB mean is from PetDb compilation.

1252

1253 Fig 6. $\delta^{238}U$ compositions versus U concentrations (logarithmic scale) at Site 1256. The data 1254 has been subdivided into the four major stratigraphic sections at Site 1256 (see figure 4 for 1255 symbol description). Seawater $\delta^{238}U$ is also plotted as vertical line (reference as in Fig. 2).

1257 Fig 7. (a) $\delta^{234}U$ versus $\delta^{238}U$ compositions of Site 1256 samples. Mean seawater composition 1258 and Pacific N-MORB are plotted as blue and black filled stars, respectively. (b) $\delta^{234}U$

- 1259 composition versus U concentration (logarithmic scale) at Site 1256. The δ^{234} U compositions 1260 of seawater and secular equilibrium are plotted as lines (reference as in Fig. 2) whereas 1261 Pacific N-MORB are plotted as a black star. The data symbols are the same as Figure 4.
- 1262
- Figure 8. ⁸⁷Sr/⁸⁶Sr ratios vs. U concentration (a), δ²³⁸U (b) and δ²³⁴U compositions (c) at Site
 1264 1256 (note U is on a logarithmic scale). The data symbols are the same as Figure 4, but
 1265 additionally include 1256 hydrothermal band (yellow band) and seawater composition (blue
 1266 band or star). The ⁸⁷Sr/⁸⁶Sr ratio data are from Harris et al. (2015).
- 1267

1268 Figure 9. $\delta^{238}U$ versus U concentrations at Sites 1256, 417/418 and 801 (note U is on a 1269 logarithmic scale). The data symbols for 1256 are the same as Figure 4 whereas Sites 801 and 1270 417/418 are described in the legend (see also data sources in Figure 2). Three schematic 1271 pathways of U addition have been added to the figure as arrows of oxic partial U uptake, 1272 reductive partial U uptake and reductive quantitative U uptake. A fourth pathway is plotted 1273 suggesting U loss with little change in $\delta^{38}U$ composition (see text for discussion). Data sources 1274 (a) Noordmann et al. (2016) and (b) Andersen et al. (2015).

1275

1276 Figure 10. Crustal age versus estimated U addition (a) and $\delta^{238}U$ (b) for a range of altered 1277 mafic oceanic crust sites. (a) the U addition is calculated from the measured sample U 1278 concentrations with estimated protolith subtracted (see Table 3 for details). (b) shows the 1279 weighted $\delta^{238}U$ mean composition for Sites 1256, 417/418 and 801. Site 801 also includes the 1280 measured supercomposite (artificially slightly separated in age to allow comparison to the 1281 weighted mean). See Table 3 for data sources and uncertainty estimates. The mean MORB 1282 $\delta^{238}U$ (Andersen et al. 2015) is shown for reference.





Figure 2



Figure 3













Figure 7







Figure 9



