1	Derivation of Jurassic HIMU-like intraplate basalts from mantle transition
2	zone in South China: New geochemical constraints from olivine-
3	hosted melt inclusion
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#### 13 Abstract

The petrogenesis of high- $\mu$  (HIMU,  $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$ ) basalt in a continental setting remains highly 14 controversial. Here we present a comprehensive geochemical (including major and trace 15 elements and isotopic compositions of whole-rock, olivine and melt inclusions) data on Jurassic 16 HIMU-like basalts from the interior (Antang) of South China. This study identified high-H<sub>2</sub>O (up 17 to 5.0 wt%) olivine-hosted melt inclusions in these basalts. After stripping off the effects of 18 19 degassing, post-entrapment crystallization and kinetic diffusion, the primary magma of the 20 Antang basalts was estimated to contain  $\geq 2.65 \text{ wt}\% \text{ H}_2\text{O}$  and the corresponding mantle source contains >1000 ppm H<sub>2</sub>O, which is much higher than the water content of convecting 21 22 asthenosphere and lower mantle. In addition, the relative depletion of fluid-mobile elements and positive Nb-Ta anomalies in bulk rocks and melt inclusions, and the distance far away from the 23 contemporaneous paleo-Pacific subduction zone, preclude an origin from a slab fluid-24 25 metasomatized mantle. The strong depletion of CaO in both olivine phenocrysts and whole-rock compositions further indicates that the basaltic magmas originated from an eclogitic or 26 pyroxenitic mantle source. The combined geochemical data suggest that the Antang basalts were 27 most likely derived from a hydrous source, which was composed mainly of ancient recycled 28 oceanic crust that had stagnated in the mantle transition zone (MTZ) for more than one billion 29 years. Our results therefore provide a new perspective on the MTZ origin of intracontinental 30 basalts and imply that the hydrous MTZ can preserve recycled crustal components for long 31 periods of time and form distinct mantle reservoirs for intraplate basalts. 32

33 Keywords: mantle transition zone; hydrous; melt inclusion; HIMU basalts; South China

#### 34 **1. Introduction**

High- $\mu$  (HIMU,  $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$ ) basalt refers to a group of oceanic island mafic lavas with 35 very high <sup>206</sup>Pb/<sup>204</sup>Pb ratios, coupled with low <sup>87</sup>Sr/<sup>86</sup>Sr and moderate <sup>143</sup>Nd/<sup>144</sup>Nd ratios, 36 suggesting an unusual mantle source characterized by long-term U and Th enrichment relative to 37 Pb without an associated increase in Rb/Sr (Zindler and Hart, 1986). HIMU basalts from 38 different localities have remarkably uniform trace element features, such as Nb and Ta 39 enrichment relative to other incompatible elements and depletion in highly incompatible 40 41 elements (e.g., Cs, Rb, and Ba) and fluid-mobile elements (e.g., K, Pb, and Sr) (e.g., Kogiso et al., 1997a; Thirlwall, 1997). Debate continues regarding the origin of HIMU, with an origin from 42 43 either metasomatized lithospheric mantle (e.g., Pilet et al., 2008; Weiss et al., 2016) or dehydrated altered oceanic crust (e.g., Weaver, 1991; Chauvel et al., 1992), which undergoes 44 long-term isolation from the convective mantle (Thirlwall, 1997; Stracke et al., 2003; Hanyu et 45 46 al., 2011). An origin from partial melting of subducted oceanic slabs that have been buried in the deep mantle has been also proposed to explain the hotspot/plume-related HIMU basalts, such as 47 at St. Helena, Mangaia, and Tubuaii (e.g., Chauvel et al., 1992; Hofmann, 1997; Hanyu et al., 48 2011). In contrast, the lack of evidence for the presence of plume activities (e.g., large-scale 49 doming, linear space-time trends of volcanic centers, and large volumes of erupted magmas) let 50 to argue against a plume origin for many HIMU-type alkaline magmas that erupted in continental 51 settings (e.g., Hoernle et al., 2006; Panter et al., 2006). 52

53 Seismic tomography shows that the intraplate HIMU-like basalts in the Mediterranean area 54 are related to a prominent low-velocity anomaly with a plume-like shape rooted within the 55 mantle transition zone (MTZ) (Vinnik and Farra, 2007). The upwelling of transition zone 56 materials, which have been stagnated for a long period of time, has been proposed to explain the 57 mantle source of lamproites from Gaussberg in the East Antarctic shield (Murphy et al., 2002) and an Enriched Mantle-1 (EM1) feature of Cenozoic potassic basalts from NE China (Kuritani 58 et al., 2011, 2013; Wang et al., 2017). As mixing and petrological homogenization processes are 59 less efficient in the MTZ than in the upper and lower mantle, the MTZ may be heterogeneous 60 and contain discrete lithological domains of former subducted oceanic crust (e.g., Ringwood, 61 1994; Kuritani et al., 2011). The long-term storage of recycled ancient dehydrated oceanic crust 62 in the MTZ thus has the potential to represent a HIMU-like mantle reservoir. HIMU-like basalts 63 can therefore help to identify recycled crustal components in the deep Earth and to understand 64 the mechanism for the long-term preservation of mantle reservoirs. 65

Several petrological and geochemical indexes can be used to determine the mantle source of 66 HIMU-like basalts. For example, experimental studies on mantle melting have demonstrated that 67 68 melt derived from a metasomatized lithospheric mantle (amphibole/phlogopite-bearing 69 peridotite) has a distinct chemical composition from that derived from recycled oceanic crust (eclogite and/or pyroxenite) (e.g., Pilet et al., 2008; Kogiso and Hirschmann, 2006). Moreover, 70 the distinct water distribution in Earth's mantle may provide a new constraint on the mantle 71 source of basalts. The mantle transition zone (MTZ) is proposed to be hydrated and acts as a 72 huge tank in Earth's deep-water cycle (Karato, 2010; Wang et al., 2015, 2016) in accordance 73 with geophysical observations (Meier et al., 2009), electrical-conductivity experiments (Huang et 74 al., 2005), and mineral inclusions in diamonds (Pearson et al., 2014). Whereas, the convecting 75 asthenosphere (Saal et al., 2002) and lower mantle (e.g., Bolfan-Casanova et al., 2002, 2003) are 76 considered to have much lower H<sub>2</sub>O contents than the MTZ. Thus, basalts derived from different 77 mantle layers may contain distinct water contents. In addition, hydrogen isotopes will be 78 fractionated during oceanic slab subduction. Studies on hydrous minerals in subaerial arc rocks, 79

such as amphibole, point to a high δD source for magmatic water (ranging from -45 to -20‰) (Miyagi and Matsubaya, 2003). Thus, lithospheric mantle metasomatized by dehydration of subducting slab will have relatively higher hydrogen isotopes than the pristine mantle, which is contrary to the dehydrated recycled slab (Shaw et al., 2008; Xu et al., 2014). Therefore, the water content and hydrogen isotope of mantle-derived primary melts may be one of the important indexes to identify a HIMU source.

Because olivine is an early crystallizing phase in basalts, olivine-hosted melt inclusions 86 should best represent primary magmas in equilibrium with their mantle sources (e.g., 87 Danyushevsky et al., 2000;). In this paper, we conducted a comprehensive geochemical study of 88 89 the Mesozoic intraplate basalts with HIMU-like features in the interior (Antang) of South China, including in situ element and H-O isotope analyses on olivines and their melt inclusions, together 90 with major, trace element and Sr-Nd-Pb-Hf-Os isotope analyses of whole-rock samples. This 91 92 new dataset enables us to estimate the water content and composition of primary mantle-derived magma and to constrain the source lithology, and provides new perspectives on the origin of 93 intraplate basalts in the light of deep water cycling. 94

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- 96 2. Geological background and sample descriptions

97 The South China Block (SCB) is divided into the Cathaysia Block in the southeast and the 98 Yangtze Craton in the northwest (Fig. 1). The Yangtze Craton consists of an Archean-99 Paleoproterozoic basement, including the 3.3–2.9 Ga Kongling Complex in the Yangtze Gorge 100 area (Gao et al., 2011). Basement outcrops in the Cathaysian Block include the Badu, Chencai 101 and Baoban complexes, with formation ages from Paleoproterozoic to Mesoproterozoic (Yu et 102 al., 2007). The Yangtze and Cathaysia blocks were amalgamated to form the unified SCB during 103 the Neoproterozoic Sibao orogeny (~1.0–0.8 Ga) (Li et al., 2009).

Igneous activity in South China has been voluminous since the Mesozoic (Zhou et al., 104 2006). The intense magmatism, lithospheric deformation, and metal mineralization initiated since 105 middle Permian, possibly related to subduction of the paleo-Pacific Oceanic Plate beneath East 106 Asia (Li et al., 2012). The Mesozoic volcanic lavas in South China are predominantly felsic in 107 composition (95%) with subordinate mafic magmas (<5%) (Zhou et al., 2006). The Jurassic 108 109 basaltic lavas are sporadically distributed across the Cathaysia Block, including the Ningyuan, 110 Antang, Daoxian, Yizhang, Chenlong, Huilongyu, Zhaibei, Fankeng, Baimianshan, and Dongkeng (Fig. 1). 111

Antang village is located along the Chenzhou-Linwu Fault in the Cathaysia Block, south of the Jiangshan-Shaoxing Fault (Fig. 1). The Jurassic Antang basalts (168 Ma) (Wang et al., 2004) are fresh, dark green in colour with euhedral to subhedral olivine (~10%) and lesser clinopyroxene phenocrysts (<4%) up to 1.0 mm in size in a dominantly aphanitic groundmass, composed of microcrystalline olivine, clinopyroxene, plagioclase and Fe-Ti oxides. Melt inclusions are preserved in olivine and occur as droplets <50  $\mu$ m in size, comprising glass, vapour bubbles and microcrystalline clinopyroxene and olivine (Fig. 2).

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## 120 **3. Analytical techniques**

# 121 *3.1.* Whole-rock major and trace element analyses

Seven fresh basalt samples were collected from Antang village (27°0'43.2"N; 123 114°42'38.5"E) for whole-rock geochemical and isotopic analyses. These rock samples were cut 124 into millimeter-scale chips and removed weathered rims. After washed in 3% HCl and cleaned 125 with de-ionized water, these chips were crushed into small fragments (<0.5 cm in diameter) in a

corundum crusher and then reduced to 200 mesh in an agate ring mill. All analyses were 126 undertaken at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of 127 Geochemistry, Chinese Academy of Sciences (GIGCAS). One randomly selected sample (JA16-128 12R) was performed to monitor the data quality and reproducibility. Whole-rock major oxides 129 were determined using a Rigaku RIX 2000 X-ray fluorescence spectrometer (XRF) on fused 130 glass disks, with analytical errors less than 3% for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O and 131 K<sub>2</sub>O, and less than 5% for TiO<sub>2</sub>, MnO and P<sub>2</sub>O<sub>5</sub>. Trace element analyses were carried out using a 132 Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS). The 133 analytical precision is generally better than 5% for element with concentrations > 200 ppm, and 134 5-10% when less than 200 ppm. 135

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# 137 3.2. Whole-rock Sr-Nd-Pb-Hf-Os isotope analyses

138 Whole-rock Sr-Nd-Pb-Hf isotopic compositions were determined using a Neptune multicollector ICP-MS (MC-ICP-MS). The measured <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd ratios were 139 normalized to  ${}^{86}$ Sr/ ${}^{88}$ Sr = 0.1194 and  ${}^{146}$ Nd/ ${}^{144}$ Nd = 0.7219, respectively. Reference standards 140 were analyzed along with samples and gave  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.710297 ± 8 (2 $\sigma$ , n = 7) for NBS987 and 141  $^{143}$ Nd/ $^{144}$ Nd = 0.512101 ± 5 (2 $\sigma$ , n = 7) for JNDi-1 (0.512115 ± 5). For Pb isotopic analyses, 150 142 mg of rock powder was placed into a Teflon vessel and dissolved in an HNO<sub>3</sub> + HF mixture for 143 three days. Pb was separated and purified by conventional anion exchange techniques (AG1X8, 144 200–400 resin) with diluted HBr as eluant. The internal correction performed for the Pb isotopic 145 analyses uesed a thallium solution. Repeated measurements of standard NBS981 yielded 146  $^{206}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 15.4838 \pm 5 \ (2\sigma, n = 8) \ and \ ^{208}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 16.9311 \pm 4 \ (2\sigma, n = 8), \ ^{207}Pb/^{204}Pb = 15.4838 \pm 5 \ (2\sigma, n = 8) \ ^{208}Pb/^{204}Pb = 16.9311 \pm 4 \ ^{208}Pb/^{204}Pb =$ 147  $36.6757 \pm 14$  (2 $\sigma$ , n = 8). For Hf isotope analyses, the <sup>176</sup>Hf/<sup>177</sup>Hf ratios were normalized to 148

 $^{179}$ Hf/ $^{177}$ Hf = 0.7325. The reported  $^{176}$ Hf/ $^{177}$ Hf ratios were adjusted to the standard solution JMC-149 475 of 0.282160. The reference standard gave  ${}^{176}\text{Hf}/{}^{177}\text{Hf} = 0.282184 \pm 4$  (2 $\sigma$ , n = 9). Analyses 150 of the USGS reference material BHVO-2 yielded  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.703511 ± 9 (n = 5),  ${}^{143}$ Nd/ ${}^{144}$ Nd = 151  $0.512972 \pm 5$  (n = 5),  ${}^{206}Pb/{}^{204}Pb = 18.6468 \pm 6$  (n = 5),  ${}^{207}Pb/{}^{204}Pb = 15.5221 \pm 6$  (n = 5), 152  $^{208}$ Pb/ $^{204}$ Pb = 38.1957 ± 17 (n = 5) and  $^{176}$ Hf/ $^{177}$ Hf = 0.283093 ± 4 (n = 5), being in agreement 153 with the recommended values of  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.703481 ± 20,  ${}^{143}$ Nd/ ${}^{144}$ Nd = 0.512983 ± 10, 154  $^{206}Pb/^{204}Pb = 18.6173 \pm 465$ ,  $^{207}Pb/^{204}Pb = 15.5355 \pm 54$  and  $^{208}Pb/^{204}Pb = 38.2108 \pm 384$  and 155  $^{176}$ Hf/ $^{177}$ Hf = 0.283096 ± 20 (Weis et al., 2005). The blanks were generally <100 pg for Sr and 156 <50 pg for Nd, Pb and Hf. 157

158 The basaltic samples chosen for Re-Os isotope analyses were carefully fragmented into chips (<0.5 cm), and then leached and cleaned in 3% HCl for half an hour. The Re concentrations 159 were measured by isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS, 160 161 Thermo-Scientific X2). The isotopic abundance of  $OsO_3^-$  and  $ReO_4^-$  were measured on a thermal ionization mass spectrometer (TIMS, Thermo TRITON). The detailed procedure was described 162 in Li et al. (2014). Total blank levels were  $1.9 \pm 4.2 \text{ pg} (2\sigma)$  and  $0.58 \pm 0.02 \text{ pg} (2\sigma)$  for Re and 163 Os, respectively, with an <sup>187</sup>Os/<sup>188</sup>Os ratio of 0.1109  $\pm$  0.005 (2 $\sigma$ ). The reference basalt BIR-1 was 164 also analyzed in the analytical batch, yielding Re =  $687 \pm 25$  ppt, Os =  $362 \pm 13$  ppt, and  $^{187}$ Os/ $^{188}$ Os 165 =  $0.1338 \pm 2$ , in good agreement with the published data for BIR-1 (Re =  $675 \pm 7$ ; Os =  $355 \pm 20$ , 166  $^{187}$ Os/ $^{188}$ Os = 0.1337 ± 4; Ishikawa et al., 2014). The different Re and Os concentrations and 167 <sup>187</sup>Os/<sup>188</sup>Os for repeated analyses of the same samples are possibly related to the nugget effect 168 (Reisberg and Meisel, 2002). 169

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#### 171 *3.3. In situ chemical and oxygen isotope analyses of olivine*

The chemical composition of olivine was determined by electron probe micro-analyses (EPMA) using a JEOL JXA-8100 at GIGCAS. Olivine analyses followed the procedures of Sobolev et al. (2007). The operating conditions for olivine analyses were an accelerating voltage of 20 kV, a probe current of  $3.0 \times 10^{-7}$ A and a spot size of 3 µm. An internal olivine standard (from mantle xenolith, Hannuoba) was analyzed before and after each batch (every five samples) of analyses. The relative errors for the olivine standard were less than 1% for major elements (SiO<sub>2</sub>, MgO and FeO), and 4.5% for minor elements (CaO, MnO and NiO) (Table S1a).

Oxygen isotopic compositions of olivine were analyzed with a CAMECA HR-IMS-1280 179 ion microprobe at GIGCAS. The Cs<sup>+</sup> primary beam was accelerated at 10 kV with an intensity of 180 ca. 2.0 nA. The spot size was about 20 µm in diameter (10 µm beam diameter + 10 µm raster). 181 An electron gun was used to compensate for sample charging during analyses. Secondary ions 182 were extracted with a -10 kV potential. Oxygen isotopes were measured in multi-collector mode 183 with two off-axis Faraday cups with each analysis consisting of 20 cycles  $\times$  4 counting time. The 184 external reproducibility of the standard (San Carlos) for  $\delta^{18}$ O was 0.4% (2 $\sigma$ ), which was set as 185 the error for individual measurements. Measured <sup>18</sup>O/<sup>16</sup>O ratios were normalized using the 186 Vienna Standard Mean Ocean Water composition (VSMOW, <sup>18</sup>O/<sup>16</sup>O = 0.0020052), and then 187 corrected for instrumental mass fractionation (IMF). Then the  $\delta^{18}$ O for samples were corrected by the 188 equation:  $\delta^{18}O_{\text{sample}} = \delta^{18}O_{\text{measured}} + \text{IMF}$ . Many studies have shown that the impact of mass 189 fractionation (IMF) of SIMS oxygen isotope analysis on olivine could be negligible providing 190 that the olivine has Fo number ranging from 70 to 92 (e.g., Guo et al., 2013; Wang et al., 2015). 191 Thus, the potential IMF effect, especially for olivine with Fo >80, should be negligible. 192

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### 194 *3.4. Major and trace element analyses of homogenized melt inclusion (HMI)*

To obtain the chemical composition of olivine-hosted melt inclusions, it is preferable to 195 analyze a homogenized glass rather than a mixture of various crystalline phases and residual 196 glass (Danyushevsky et al., 2000). Prior to analysis, a 1.0 atm gas-mixing furnace was used to 197 heat the olivine grains to 1250°C at the quartz-fayalite-magnetite buffer. The platinum packet 198 was then rapidly raised back to the top of the furnace tube after being heated for 10 min to 199 achieve homogenization of the glassy inclusions. Then the host olivine was embedded in epoxy 200 resin and polished on one side until the melt inclusions were exposed. Well-preserved melt 201 inclusions with a diameter larger than 30 µm were chosen for analysis. Major element 202 203 compositions of the homogenized melt inclusions were analysed by EPMA with a JEOL JXA-8100 Electron Microprobe following the procedure reported by Wang and Gaetani (2008). The melt 204 inclusions were analyzed using a 15 kV accelerating voltage, 200 nA beam current and 3 µm beam 205 diameter. The volatile elements (Na, K) were analyzed with peak counting time of 10 s and 206 207 background counting time of 5 s. Repeated analyses on the internal glass standard (JB-2) showed that the analytical uncertainty was less than 2% for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO and CaO, and ~5% for TiO<sub>2</sub>, MgO, 208 Na<sub>2</sub>O and K<sub>2</sub>O (Table S1b). 209

The trace element composition of the melt inclusions was analysed by a CAMECA HR-SIMS-1280 ion microprobe at GIGCAS, using a 10 nA, -13kv primary beam of  $O_2^-$  ions and detection of positive secondary ions with a nominal acceleration voltage of + 10 kV. The target area on the sample was pre-sputtered for 100 s using a 25 µm × 25 µm rastering technique to remove the gold coat. During the analysis, the contrast aperture of 400 µm and the field aperture of 5000 µm×5000 µm were used. The magnification of the transfer system was configured as ~100 (equivalent to 80 µm). The entrance slit and the exit slit was set at ~200 µm and 600 µm,

respectively. The energy window was 50 eV and 5 eV energy gap. Energy filter was employed -217 55 V for most elements except for Rb and Pb (-75 V), and Er and Yb (-65 V). Each analysis 218 consisted of a 10-cycle running time and the following isotopes were analysed: <sup>28</sup>Si, <sup>30</sup>Si, <sup>85</sup>Rb, 219 <sup>88</sup>Sr, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>138</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>143</sup>Nd, <sup>149</sup>Sm, <sup>157</sup>Gd, <sup>165</sup>Ho, <sup>167</sup>Er, <sup>172</sup>Yb, <sup>208</sup>Pb, 220 <sup>232</sup>Th, and <sup>238</sup>U. A single analysis normally took 20 minutes. The trace element concentrations of 221 melt inclusions were normalized to <sup>28</sup>Si, which had already been measured by EPMA. Rb, Sr, Y, 222 Zr, Nb, Ba, La, Ce, and Nd calibrations were performed using the values obtained by repeated 223 analyses of standards BHVO-2G, BCR-2G, BIR-1G GSD-1G, and GSC-1G. Pr, Sm, Gd, Ho, Er, 224 Yb, Pb, Th, and U calibrations were performed using those analyzed values of standards BHVO-225 2G, BCR-2G, BIR-1G, and GSC-1G. Repeated analyses of the monitor glass standard (TB-1G) 226 showed that the analytical errors were usually less than 15%, except for Th, U and Pb (~25%) 227 228 (Table S1c).

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# 230 3.5. Major element analyses of glass and mineral in unhomogenized melt inclusion (UMI)

Major elements of glass and mineral in UMI were determined by a Shimadzu Electron Probe Microanalyzer EPMA-1720 at Sun Yat-Sen University. The analytical conditions are 15 kV accelerating voltage, 20 nA beam current and 3  $\mu$ m beam diameter. The JB-2 was used as the internal standard for the glass analysis. Repeated analyses on the internal glass standard showed that the analytical uncertainty was less than 2% for SiO<sub>2</sub>, FeO, CaO and K<sub>2</sub>O, and 5% for TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and Na<sub>2</sub>O.

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## 238 3.6. H<sub>2</sub>O content and H isotope analyses of UMI

239 Previous studies of olivine-hosted melt inclusions showed that loss of hydrogen occurred

during laboratory heating of the host olivine, which could also lead to a decrease of the  $H_2O$ content and an increase in the hydrogen isotope composition of the melt inclusions (Chen et al., 2011; Gaetani et al., 2012). Thus, the  $H_2O$  and H isotope analyses in this study were performed on the original melt inclusion without homogenization.

During sample preparation, the olivine grains were embedded in Crystal-bond resin to avoid 244 the contamination of epoxy in cracks. They were ground and polished on one side until the melt 245 inclusions were exposed. Then the olivine grains were cleaned in acetone in an ultrasonic bath to 246 remove Crystal-bond resin. The resin-free polished olivine grains were set into indium disks. 247 After coating with gold, the samples were loaded and stored in the vessel chamber of a Nano-248 SIMS 50L for three days. The chamber was maintained at high vacuum (<  $5 \times 10^{-10}$  torr) during 249 the analytical session. More detailed descriptions of the sample preparation are reported in Hu et 250 251 al. (2015).

252 The hydrogen isotopic compositions and water content were measured with a Cameca Nano-SIMS 50L at the Institute of Geology and Geophysics, Chinese Academy of Sciences. 253 Each 10  $\mu$ m ×10  $\mu$ m analyses area was rastered by a Cs<sup>+</sup> beam of ~0.5 nA and a diameter of ~5 254 µm. An electron gun was applied for sample surface charge compensation, which maintains an 255 electron cloud over the area of analysis. Each analytical site was pre-sputtered for 2 min by 256 rastering a 10  $\mu$ m ×10  $\mu$ m with a beam current of 2 nA to eliminate surface contamination and 257 achieve stable yield rates of the secondary ions. A mass resolving power (MRP) of 1800-2000 258  $(M/\Delta M, Cameca definition related to the width between 10\% and 90\% intensity of the peak) is$ 259 sufficient to resolve  ${}^{2}D^{-}$  from the interference of  ${}^{1}H_{2}^{-}$  and  ${}^{18}O^{-}$ . Each analysis contained 20 260 blocks of 20 cycles with a total counting time of ~3 min, and the ions were collected with 261 electron multipliers. The detailed analytical procedure is described in Hu et al. (2015, 2019). 262

During the analyses, the instrumental mass fractionation (IMF), matrix effect and water 263 concentration calibration curves were made by analyzing two apatite reference materials, 264 Durango apatite (0.0478 wt% H<sub>2</sub>O) and Kovdor apatite (0.98  $\pm$  0.07 wt% H<sub>2</sub>O and  $\delta D = -66 \pm$ 265 21%), and one MORB glass reference material SWIFT MORB glass (0.258 wt% H<sub>2</sub>O). Previous 266 water and H isotope analyses have showed similar matrix effects for silicates with a range from 267 basaltic to rhyolitic composition, and there were no observable difference of matrix and IMF 268 effects in both apatite and silicate glasses by NanoSIMS (Hu et al., 2015, 2019). The H isotope 269 compositions were calibrated for instrumental mass fractionation (IMF), using  $\alpha_{IMF}$  = 270  $(D/H_{measured})/(D/H_{recommended})$ . The hydrogen isotopes are presented in the form of  $\delta D =$ 271  $((D/H)_{sample}/(D/H)_{SMOW} - 1) \times 1000\%$ , where SMOW is the standard mean ocean water with a 272 D/H ratio of 1.5576×10<sup>-4</sup> (McKeegan et al., 2006). The water content was determined from the 273 <sup>1</sup>H<sup>-</sup> intensities relative to <sup>18</sup>O<sup>-</sup> using the calibration curves of  $[^{1}H/^{18}O] = \alpha \times [H_2O] + \beta$ . Repeated 274 analysis of those standards give  $[{}^{1}H/{}^{18}O] = 1.0039 \times [H_2O]$ ,  $R^2 = 0.9944$ , and  $\alpha_{IMF} = 0.897 \pm$ 275  $0.012 (2\sigma)$  (Table S1d). One of the analytical errors is from the statistical uncertainty of the D/H 276 ratios (most < 30% for  $\delta D$ ) and  $^{1}H/^{18}O$  ratios (<0.3 wt% for H<sub>2</sub>O content). The other analytical 277 error is ascribed to the uncertainties in  $\alpha_{IMF}$  values and the slopes of the calibration curves. Thus, 278 the reproducibility was monitored before and after each batch analysis through repeated 279 measurements of the MORB glass (SWIFT) using the obtained  $\alpha_{IMF}$  and the calibration curves. 280 The measured water contents and H isotopic compositions of standard SWIFT are listed in Table 281 S1e. 282

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#### 284 **4. Results**

#### 285 4.1. Chemical and isotopic composition of the bulk rocks

The Antang basalts have an alkaline affinity and span a narrow whole-rock compositional 286 range (Table S2), with SiO<sub>2</sub> = 46.4-46.8 wt%, MgO = 8.3-8.8 wt%, and CaO = 7.9-8.3 wt%. 287 Their mantle-normalized trace element patterns show enrichments in Nb-Ta, depletion of fluid-288 mobile (e.g., Rb, K and Pb), and heavy rare earth elements (HREEs), analogous to typical HIMU 289 basalts from St. Helena (e.g., Weaver, 1991; Kogiso et al., 1997a; Hanyu et al., 2011) (Fig. 3). 290 These rocks also display unradiogenic Sr ( ${}^{87}$ Sr/ ${}^{86}$ Sr(i) = 0.7032–0.7040), moderately radiogenic 291 Nd ( $^{143}$ Nd/ $^{144}$ Nd(t) ~ 0.5127), Hf ( $^{176}$ Hf/ $^{177}$ Hf(t) ~ 0.2830), and Os ( $^{187}$ Os/ $^{188}$ Os(t) = 0.1653– 292 0.2740), and highly radiogenic Pb isotopic compositions, e.g.,  ${}^{206}Pb/{}^{204}Pb = 19.17-19.44$ , 293  $^{207}$ Pb/ $^{204}$ Pb = 15.55–15.59 and  $^{208}$ Pb/ $^{204}$ Pb = 39.29–39.56 (Table S2; Fig. 5). 294

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# 4.2. *Chemical and O isotopic compositions of olivine*

The olivine phenocrysts span a range of forsterite (Fo) compositions between 77.9 and 85.9. 297 They have lower CaO contents (0.07-0.26 wt%, Table S3) than olivines from MORBs and 298 carbonated peridotite-derived basalts, and most have CaO contents lower than olivine in the 299 plume-related Hawaii basalts (Fig. 6a). The morphologies, textures, and compositions of olivine 300 and the presence of melt inclusions strongly support a magmatic origin for the olivine 301 phenocrysts. Most of olivines yield mantle-like oxygen isotope compositions, with a  $\delta^{18}$ O range 302 of 5.04–5.50%, except for some olivines with F082.0-85.9 showing slightly higher  $\delta^{18}$ O values up 303 to 6.01% (Table S3; Fig. 6b). 304

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# 306 4.3. Composition of HMI and estimated primary magma

Olivine-hosted melt inclusions may re-equilibrate with their host olivine by Fe-Mg 307 exchange reaction (Danyushevsky et al., 2000). This re-equilibrium process is generally called 308 "Fe-loss" and usually results in an increase of MgO and a decrease of FeO<sup>T</sup> (total iron oxides, 309 Danyushevsky et al., 2000). The negative correlation between FeO content of the melt inclusions 310 and Fo of the host olivine indicates that there was Fe-Mg exchange between them (Fig. S1). 311 312 Furthermore, the nearly constant CaO/Al<sub>2</sub>O<sub>3</sub> ratio follows the range of Fo of olivine between 82.2 and 85.9, suggesting only olivine fractionation during magmatic differentiation (Fig. 4). We 313 thus use the PETROLOG software (Danyushevsky and Plechov, 2011) to adjust the measured 314 315 melt inclusion compositions using the "Fe-loss" correction so that we can obtain the composition of the melt in equilibrium with the host olivine. This calculation requires an independent 316 estimation of the initial trapped melt FeO<sup>T</sup> content. According to the FeO<sup>T</sup> fractionation trend, 10 317 wt% is set as the FeO<sup>T</sup> content in the initially trapped melt (Table S4a; Fig. S1). After applying 318 the "Fe-loss" correction, the homogenized melt inclusions in olivine show a range in SiO<sub>2</sub> of 319 44.6–47.3 wt%, in MgO of 6.6–8.3 wt% and in CaO of 8.8–10.7 wt% (Table S4b). The whole-rock 320 chemical composition can be roughly estimated as 93-96% melt inclusion plus 4-7% olivine, 321 consistent with the dominance of olivine phenocrysts in the basalt. 322

In the case of unique olivine fractionation, the primary magma composition of basalts can be calculated through addition of olivine back into the melt until chemical equilibrium between the estimated primary magma and mantle olivine is reached. We therefore selected those melt inclusions within high-Fo (>82.2) olivine to estimate the primary magma composition of the Antang basalts through addition of olivine in 0.1% increments (assuming that 10% of the total iron is Fe<sup>3+</sup> and (Fe<sup>2+</sup>/Mg)<sub>olivine</sub>/ (Fe<sup>2+</sup>/Mg)<sub>melt</sub> = 0.3). The melt compositions are corrected so that

they are in equilibrium with an olivine composition of Fo<sub>90</sub>. The estimated primary magmas span 329 a SiO<sub>2</sub> range of 44.3–46.1 wt%, a MgO range of 13.8–14.4 wt%, and a CaO range of 7.3–8.7 wt% 330 (Table S4c), which can be reconstructed by adding 14–19% olivine back into 81–86% corrected 331 melt inclusion. The magmas also have low CaO contents compared with the experimental melts 332 of peridotite, but show similar CaO contents to melts of eclogitic or pyroxenitic sources (Fig. 7). 333 The melt inclusions also show similar trace element patterns to the bulk rocks, confirming 334 the HIMU-like feature of Antang basalts (Table S5; Fig. 3b). 335 336 4.4. Composition, water content and H isotope ratio of UMI 337 Glasses in UMI show a range in SiO<sub>2</sub> of 56.2–62.9 wt%, in Al<sub>2</sub>O<sub>3</sub> of 17.4–23.6 wt%, in CaO 338

of 1.11–5.04 wt%, and K<sub>2</sub>O of 1.34–4.16 wt% (Table S7). The recrystallized mineral in the UMI belongs to augite, spanning a SiO<sub>2</sub> range of 40.9–42.8 wt%, an Al<sub>2</sub>O<sub>3</sub> range of 13.55–15.59 wt%, a FeO range of 6.70–9.38 wt%, a MgO range of 9.23–12.66 wt%, and a CaO range of 12.11–23.49 wt% (Table S7).

The UMI spans a large range in H<sub>2</sub>O from 0.34 to 4.97 wt% and a  $\delta D$  range between -102 and 141% (Table S6). The H<sub>2</sub>O content shows a broadly negative correlation with  $\delta D$  (Fig. 8a). The melt inclusion hosted in olivine with Fo number less than 82 has a relatively low H<sub>2</sub>O content and  $\delta D$  value (Fig. 8b).

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# 348 5. Discussion

349 5.1. Effects of Alteration, Crustal Assimilation, and Fractional Crystallization

Basaltic rocks can undergo open-system compositional evolution through processes such as crustal contamination or assimilation, magma mixing, and surface weathering or alteration. The absence of secondary minerals (Fig. 2a) suggests an insignificant effect of alteration on the Antang basalts. However, the whole-rock composition may be easily affected by the surface alteration, especially for fluid-mobile elements such as K, Rb, Ba, and Sr. As shown in Fig. 3 and Table S2, except for the sample JA16-14 showing a fluctuating Rb, the other incompatible elements show consistent trace element patterns. This suggests that surface alteration should be negligible for the most of the Antang basalts.

The Mesozoic Antang basalts and their olivine-hosted melt inclusions have high Nb/U and Ce/Pb ratios and show positive Nb-Ta anomalies and prominent Rb, K and Pb depletion (Fig. 3), indicating a negligible role for crustal contamination or assimilation. The relatively homogeneous compositions of the olivine-hosted melt inclusions also preclude any significant magma mixing in their generation.

363 Fractional crystallization of mantle-derived primary melts during magmatic evolution would significantly change the chemical composition of the melts. The Antang basalts show 364 lower Mg# (65.4–66.7) than those of typical mantle-derived primary melts (Mg# = 73-81), 365 implying a role of fractional crystallization. Melt inclusions are small portions of magma trapped 366 by growing crystals and represent snapshots of the crystallization environment (Danyushevsky et 367 al., 2000). The correlation between Fo of the host olivine and CaO/Al<sub>2</sub>O<sub>3</sub> ratios of the melt 368 inclusions indicates that clinopyroxene fractionation took place at Fo < 82.2 (Fig. 4). Moreover, 369 the lack of Sr and Eu anomalies (Fig. 3a) implies that fractional crystallization of plagioclase was 370 negligible during the formation of Antang basalts. In summary, the geochemical features of 371 whole-rock and melt inclusion indicate the Antang basalts mainly experienced a role of olivine + 372 clinopyroxene fractionation, whereas the effect of alteration and crustal assimilation could be 373 negligible. 374

377 inclusion

Since  $H_2O$  is more readily exchanged than most incompatible elements during magmatic evolution and post-entrapment processes, it is important to assess whether the magmatic  $H_2O$ concentrations of the melt inclusions have been compromised by exotic fluid addition, magma degassing, and post-entrapment diffusion and crystallization (e.g., Chen et al., 2011; Gaetani et al., 2012).

Most of olivine phenocrysts have mantle-like  $\delta^{18}$ O values (Fig. 6b), confirming the 383 384 negligible influence of low-temperature alteration. Any addition of meteoric water or seawater with high  $\delta D$  should produce a positive correlation between H<sub>2</sub>O and  $\delta D$ , which is opposite to 385 the negative correlation in the UMI (Fig. 8a). Aqueous fluid addition will significantly change 386 concentrations of fluid-mobile elements of olivine-hosted melt inclusions (Kogiso et al., 1997b). 387 However, the melt inclusions in the Antang basalts show low Rb/Nb, Ba/Nb, and Sr/Nb ratios 388 and positive correlations of Zr with Rb, Ba, Th, and U, precluding the possibility of extra fluid 389 390 addition during olivine crystallization (Fig. 9).

Although we analysed the water content of UMI to avoid water loss during the heating and homogenization processes, the loss of water (or H diffusion) may also have occurred during eruption and cooling of the magma (e.g., Saal et al., 2002; Gaetani et al., 2012). During magma ascent, the solubility of water in magma is mainly controlled by pressure and may reach the critical point at shallow depths. Magmatic degassing will reduce both the water content and  $\delta D$ . The melt inclusion hosted in olivine with Fo number ranging from 82 and 86 exhibits a negative correlation between H<sub>2</sub>O and  $\delta D$ , which is contrary to the effect of magmatic degassing (Fig. 8a). However, the UMIs hosted in olivine with Fo < 82 show a dramatical decrease of H<sub>2</sub>O and  $\delta D$ ratio, which could be affected by degassing (Fig. 8).

After entrapment in the host olivine, the H<sub>2</sub>O content of melt inclusion may decrease via 400 hydrogen diffusion through olivine to keep dynamic equilibrium with the residual magmas (Chen 401 et al., 2011). It is nearly impossible to avoid diffusive loss of hydrogen during magma ascent, 402 because the timescale of magma ascent is close to that of diffusive water exchange as 403 experimentally determined (Hauri, 2002b; Gaetani et al., 2012). Since the diffusion of H is much 404 faster than D, hydrogen diffusion through host olivine will lead to an increase of  $\delta D$  in 405 association with a decrease of H<sub>2</sub>O content in melt inclusion. A large number of UMIs from the 406 407 Antang basalts have fairly positive  $\delta D$  values, which were probably a result of post-entrapment kinetic diffusion (Fig. 8a). By contrast, the UMI with the highest water content (up to 5.0 wt%) 408 409 and mantle-like  $\delta D$  value experienced insignificant hydrogen diffusion.

Crystallization of daughter mineral in melt inclusion will lead to an increase of water content in the residual glass. This process does not reset  $\delta D$  value of the residual glass. The petrographic examination (Fig. 2) shows that the water content of glass in the UMI cannot represent the primary water content of the melt trapped by host olivine, because of the crystallization of daughter mineral. In this respect, it is necessary to reconstruct the water content of primary melt by analysing the relative volume of glass and recrystallizing mineral within the UMI.

The recrystallized mineral in the UMI belongs to augite, which would dramatically decrease the CaO/Al<sub>2</sub>O<sub>3</sub> ratio of residual glass. Because the CaO/Al<sub>2</sub>O<sub>3</sub> ratio of melt inclusion shows a good correlation with Fo number of host olivine (Fig. 4), we calculate the proportion of glass and mineral using the analysed CaO/Al<sub>2</sub>O<sub>3</sub> ratios of glass and mineral in the UMI and the variation

trends of CaO/Al<sub>2</sub>O<sub>3</sub> of HMI at given Fo component of host olivine. With the following equation, 421 we calculate the proportion of glass and mineral within each UMI: 422  $CaO/Al_2O_3$  (HMI) = a × CaO/Al\_2O\_3 (glass in UMI) + b × CaO/Al\_2O\_3 (mineral in UMI) 423 Where a + b = 1424  $CaO/Al_2O_3$  (HMI) = 0.56 (When the host olivine has Fo > 82.2, Fig. 4) 425  $CaO/Al_2O_3$  (HMI) = 0.1167 × Fo – 9.03 (When the host olivine has Fo < 82.2, Fig. 4) 426 The results yield that the proportions of post-entrapment crystallization in these UMIs span a 427 range from 16 to 58% (Table S7). The melt inclusion with the highest water content (4.97 wt%) 428 and low  $\delta D$  experiences ~34% post-entrapment crystallization, yielding 3.28 wt% H<sub>2</sub>O for the 429 bulk UMI, which should represent the minimum of its water content. Considering that the 430 Antang basalts might have experienced about 14–19% olivine fractionation, we finally estimate 431

that the primary magma of Antang basalts was hydrous with at least  $2.65 \text{ wt}\% \text{ H}_2\text{O}$ .

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## 434 5.3. Petrogenesis of the Antang basalts

The HIMU-like whole-rock geochemistry and the H2O-rich compositions indicate 435 derivation of the Antang basalts from a hydrous mantle reservoir. Possible mantle sources for 436 HIMU-like basalts include metasomatized lithospheric mantle (hornblendite, hornblende-bearing 437 mantle and carbonated peridotite) (e.g., Pilet et al., 2008; Weiss et al., 2016) and ancient recycled 438 oceanic crust (e.g., Hofmann, 1997; Hanyu et al., 2011). However, the low TiO<sub>2</sub>, high SiO<sub>2</sub>, 439 MgO and FeO contents and the lack of negative Zr-Hf anomalies distinguish the Antang basalts 440 441 from melts of hornblendite or hornblende peridotite (Fig. 3). In addition, the contemporaneous 442 HIMU-like Ningyuan basalts, which intrude the Cathaysia Block around 300 km to the 443 southwest (Wang et al., 2008) (Fig. 1), contain Mesozoic mantle xenoliths that are characterized by the lack of hydrous minerals, nearly flat REE patterns, and depletion of Ba (Zhang et al., 444

2008). These features of xenoliths imply that the lithospheric mantle beneath South China was 445 nearly anhydrous with little metasomatism from subducted slab-derived fluids. Furthermore, the 446 relatively low Os concentrations and high <sup>187</sup>Os/<sup>188</sup>Os(t) ratios of the Antang basalts (Fig. 10a, b) 447 are inconsistent with melts derived from sub-continental lithospheric mantle (SCLM), which 448 typically has extremely high Os concentrations and low <sup>187</sup>Os/<sup>188</sup>Os ratios. The mantle peridotite 449 xenoliths hosted in Jurassic Ningyuan basalts have higher Sr ( ${}^{87}$ Sr/ ${}^{86}$ Sr(i) = 0.7048–0.7050) and 450 lower Os ( $^{187}$ Os/ $^{188}$ Os(t) = 0.1206–0.1293) isotopic ratios than those of the Antang basalts 451 (Zhang et al., 2008; Liu et al., 2012) (Fig. 10c). If the Antang basalts were derived from the same 452 source as the mantle xenoliths, this could have required a large (>90%) continental crustal input 453 454 to match the Os-isotopic ratios of the primitive Antang magmas (Fig. 10d). This is inconsistent with the HIMU-like trace element features of the Antang basalts that permit negligible crustal 455 contamination. We therefore conclude that the geochemical data from the Antang basalts argue 456 457 against derivation from the SCLM regardless of whether or not it experienced metasomatism.

A systematic study on the primary magmas has revealed that pyroxenite is the principal 458 lithology in the mantle source of Late Mesozoic basalts in SE China (Zeng et al., 2016). 459 Following the method in Thompson et al. (2005), the calculated primary melts were plotted on 460 the CIPW normative Di-Ol-Hy-(Ne+Lc)-Qz projection, along with experimentally determined 461 mantle-derived melts from peridotite, carbonated peridotite, carbonated eclogite, hornblendite, 462 clinopyroxene-hornblendite, silica-deficient pyroxenite and silica-excess pyroxenite (Fig. 11). 463 The Antang basalts plot within the compositional range of silica-deficient garnet-pyroxenite 464 melts. Because clinopyroxene is typically the major CaO-bearing mantle phase, leaving 465 clinopyroxene as a major residual phase is the only effective way of lowering the CaO content of 466 mantle-derived melts (Herzberg, 2011). The low CaO contents (7.3-8.7 wt%) of the primary 467

magmas (Fig. 7) also support a pyroxenitic residue rather than a peridotitic residue in the mantle 468 source. Moreover, the Antang basalts define a negative correlation of Th versus Nb/Ta and Nb/La 469 (Fig. S2), implying a bulk  $D_{Nb/Ta} > 1$  and  $D_{Nb/La} > 1$ . This is a typical characteristic of an eclogitic 470 source because D<sub>Nb/Ta</sub> and D<sub>Nb/La</sub> for eclogitic garnet range from 1.2 to 2.0 and 1.3 to 7.5 (e.g., 471 Klemme et al., 2002; Pertermann et al., 2004), respectively. Partition coefficients show that  $D_{Zr} <$ 472  $D_{Hf}$  in clinopyroxene and  $D_{Zr} > D_{Hf}$  in garnet (Klemme et al., 2002; Pertermann et al., 2004). 473 Thus, low degree melting of a clinopyroxene-rich eclogite can explain the elevated Zr/Hf ratios 474 (43-45) of the Antang basalts. The low CaO content of olivine (Fig. 6a) further indicates a 475 pyroxenitic source (Sobolev et al., 2007). In summary, the residual source region for the Antang 476 basalts was dominated by clinopyroxene and garnet. 477

Recycled upper oceanic mafic crust is known to form eclogitic or pyroxenitic mantle 478 reservoirs (e.g., Sobolev et al., 2007; Kogiso and Hirschmann, 2006). Extremely high <sup>187</sup>Re/<sup>188</sup>Os 479 ratios reported in oceanic crust (80 to 675) would lead to high radiogenic <sup>187</sup>Os/<sup>188</sup>Os ratios over 480 1.0 Ga (Peucker-Ehrenbrink et al., 2012). A major contribution from such a mantle source is also 481 suggested by the relatively high whole-rock <sup>187</sup>Os/<sup>188</sup>Os(t) ratios of the Antang basalts (Fig. 10) 482 and the relatively high  $\delta^{18}$ O values in high-Fo (>82) olivine (Fig. 6b). In order to further 483 determine how the mantle source for the Antang basalts was formed, we compared their isotopic 484 compositions with modelled Sr-Nd-Pb-Hf isotopic evolution paths for both ancient subducted 485 oceanic crust and contemporary subducted sediment (Table S8, Stracke et al., 2003). Compared 486 with typical HIMU basalts, the Antang basalts have lower <sup>206</sup>Pb/<sup>204</sup>Pb and higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios 487 (Fig. 5), and plot in the 1.0–1.5 Ga arrays defined by the mixing curves between contemporary 488 subducted oceanic crust and sediments. These results further suggest that the Antang basalts were 489 490 derived from a HIMU-like mantle reservoir composed principally of 1.0–1.5 Ga recycled oceanic 491 crust plus minor (<1 %) sediment. The involvement of minor sediment may also contribute to the</li>
492 Ba enrichment observed in the Antang basalts (Fig. 3, Weaver, 1991).

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### 494 5.4. Estimation of $H_2O$ in the mantle source

Geochemically, H<sub>2</sub>O behaves incompatibly during partial melting, with a partitioning coefficient similar to that of Ce (Michael, 1995); thus, the H<sub>2</sub>O/Ce ratio of magma has been proven to be a useful geochemical tool to trace the hydrous state of mantle source (Dixon et al., 2002; Xia et al., 2019). Considering the Ce concentrations of the HIMI between 73 and 135 ppm and the primary H<sub>2</sub>O content of melt inclusion is  $\geq$ 3.28 wt%, the calculated H<sub>2</sub>O/Ce ratios (243– 450) of the Antang basalts are higher than MORB (100–200, Michael, 1995; Saal et al., 2002) and EM-type OIB (<150, Dixon et al., 2002), implying a hydrous mantle source.

In addition, the water content of the mantle source can be calculated at a given degree of 502 503 melting and the hydrogen partition coefficient. Using an inferred eclogitic/pyroxenitic source, we then calculate the degree of partial melting based on the relationship between incompatible 504 elemental ratios (e.g., La/Yb versus Sm/Yb). As the La, Sm, and Yb concentrations of the 505 average depleted mantle (0.192 ppm, 0.239 ppm, and 0.365 ppm, respectively) are much less 506 than that of mafic oceanic crust (~3.83 ppm, ~3.11 ppm, and ~3.03 ppm, respectively) (Stracke et 507 al., 2003), some contribution of mantle peridotite could not greatly change the incompatible 508 elemental ratios. To simplify the modelling, we use the elemental ratios of recycled oceanic crust 509 as the starting component to calculate the degree of melting based on the relationship between 510 incompatible elemental ratios (Sm/Yb versus La/La and La/Yb versus La/Sm). The recycled 511 oceanic crust is assumed to consist of 99% mafic oceanic crust (25% N-MORB + 25% altered 512 MORB + 50% gabbro) and 1% subducted sediment represented by global subducted sediment 513

(GLOSS) (Reference can be seen in supplementary A1). Equilibrium non-modal melting
calculation indicates that 4.5–6.0% melting of the assumed source can produce melts with the
Antang basalt compositions (Fig. 12).

Previous SIMS analyses on H in nominally anhydrous minerals have facilitated direct 517 determination of mineral/melt hydrogen partitioning from coexisting mantle minerals and 518 hydrous silicate melts. A compilation of the published data over wide ranges of composition, 519 temperature and pressure yields the range of  $D_H^{Grt/liq}$  from 0.001 to 0.003 and a  $D_H^{Cpx/liq}$  range 520 from 0.01 to 0.03 (Hauri et al., 2006). The calculated bulk  $D_H$  value of eclogite with 80% 521 clinopyroxene plus 20% garnet ranges from 0.008 to 0.024. In combination with the estimated 522 primary magma that has  $H_2O \ge 2.65$  wt%, we finally estimate that the mantle source for the Antang 523 basalts had H<sub>2</sub>O contents between 0.14 and 0.22 wt%. 524

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#### 526 5.5. Origin from a hydrous MTZ

The lines of evidence from geochemical data of the bulk rock, olivine and melt inclusions 527 528 from the Antang basalts suggest that the basaltic magmas were derived from a hydrous mantle source composed principally of eclogite/pyroxenite probably derived from an ancient recycled 529 oceanic slab. The Sr-Nd-Pb-Hf isotopic composition of this hydrous HIMU-like mantle reservoir 530 requires a long (1.0–1.5 Ga) mantle residence time and this requires at least two fundamental 531 conditions: (1) long-term isolation from the convective mantle to avoid chemical and isotopic re-532 homogenization with the surrounding mantle, and (2) a relatively low temperature to avoid large-533 scale partial melting and isotopic disturbance. Considering the asthenosphere is dry (< 200 ppm 534 535  $H_2O$ ) (Saal et al., 2002) and the convection would make the recycled oceanic crust hard to be stagnated for a long time, these factors preclude the possibility that the Antang basalts were 536

derived from the low-viscosity convective asthenosphere. Having already ruled out derivation
from a metasomatized SCLM, the possible alternative sites include the MTZ, the lower mantle or
the D" layer (i.e. the core-mantle boundary).

Cold oceanic slabs can penetrate into the lower mantle and may bring a certain amount of 540 water into the Earth's interior (Poli and Schmidt, 2002). The hydrous aluminosilicate phases, 541 such as  $\delta$ -AlOOH and Al-rich phase D and phase H can be stable under lower mantle conditions 542 543 (Pamato et al., 2015). This suggests the possibility for the existence of locally hydrous sources within the lower mantle. However, the following arguments exclude the possibility that the 544 Antang basalts were derived from the lower mantle: (1) Basalts associated with mantle plumes 545 546 containing recycled subducted slabs are relatively dry (e.g., Dixon et al., 2002; Shaw et al., 2012). The geochemical features such as negative Pb anomalies (high U/Pb ratio or HIMU feature) 547 548 of basalts that originate in the lower mantle also indicate the intense dehydration of such recycled 549 subducted slabs (Kogiso et al., 1997b). The lower mantle is composed predominantly of Mg- and Ca-perovskite and ferropericlase and has low water storage capacity (< 200 ppm) (e.g., Bolfan-550 Casanova et al., 2002, 2003). Thus, the amount of water that can be transported into the lower 551 mantle would be minor; (2) Some OIBs have originated from the lower mantle indeed have low 552 water contents and  $\delta D$  values (Hauri et al., 2002b), indicating that most of the lower mantle is 553 relatively anhydrous; (3) Because the lower mantle is also convective (Chen, 2016), even if the cold 554 subducted slab brings a certain amount of water into this region, any locally hydrous source will be 555 rapidly homogenized. This means that it is difficult to form a long-term isolated hydrous source 556 within the lower mantle. 557

558 Compared with the normal mantle, a deep (e.g., derivation from the D" layer) mantle plume 559 has an extremely high temperature. Based on the estimated primary magma composition and the inferred hydrous eclogitic/pyroxenitic source of the Antang basalts, we calculate that the mantle potential temperature (Tp) spans a range of 1331–1386°C (Table S4d; Supporting Information A2). This Tp is similar to that estimated for the transition-zone derived hydrous mantle plume at Changbaishan (Kuritani et al., 2019). Also, there is no geological evidence to support that a mantle plume was active beneath South China during the Jurassic. Therefore, both the geological records and the estimated lower Tp at that time imply that the D" layer cannot be the source of Antang basalts.

Alternatively, delamination and detachment of oceanic crust from the subducted slabs, with 567 subsequent long-term storage in the MTZ quarantined from the effects of convective stirring, 568 remains a viable option (Ringwood, 1994; Nebel et al., 2013). High-resolution tomographic 569 images in modern subduction zones demonstrate that subducted slabs in some regions do not 570 simply plunge directly through the 660 km discontinuity, deeply into the lower mantle (Kuritani 571 et al., 2011, 2013, 2019). The study of phase transformation in oceanic crust shows that the 572 basaltic crust component would be 0.1-0.2 g/cm<sup>3</sup> lighter than its surrounding mantle pyrolite at 573 the depths of 660-800 km (Irifune and Ringwood, 1993). The buoyancy produced by internal 574 petrological differentiation may prevent basaltic crust entering the lower mantle and segregate it 575 to form a gravitationally stable layer overlying the 660 km discontinuity (Ringwood, 1994). The 576 MTZ thus may contain recycled oceanic crustal components, at least partially shielded from 577 mixing and petrological homogenization typical of the upper mantle. Therefore, the best 578 interpretation is that the source of the Antang basalts was a hydrous MTZ (0.14–0.22 wt% H<sub>2</sub>O) 579 beneath the South China interior. This hydrous MTZ was isolated from mantle convection for 580 over one billion years. 581

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The mechanism for upwelling of hydrous MTZ materials needs to be further discussed. The

estimated mantle potential temperature argues against thermal buoyancy is a primary cause for 583 the Antang basaltic magmatism. South China has been an active continental margin in 584 association with subduction of the paleo-Pacific Ocean beneath the Eurasian Continent during 585 Jurassic. Through 3-D numerical modelling, Faccenna et al. (2010) proposed that the focused 586 mantle upwelling can be generated both ahead of slab in the back-arc region (the disturbing 587 distance could be up to five times as that from trench to magmatic arc) and around the lateral 588 edges of the slab. Moreover, hydrous mantle peridotite is lighter than dry mantle peridotite, so a 589 wet focused mantle upwelling could be generated at the top of the MTZ (Wang et al., 2016; 590 Kuritani et al., 2019). Generation of the Antang basalts might be ascribed to the co-effect of slab 591 592 subduction and hydrous mantle source that led to passive upwelling of hydrous MTZ materials in South China interior. 593

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# 595 5.6. Implications for intraplate magmatism

Subducted slabs in the present-day mantle display a wide variation in behaviour, where 596 some slabs penetrate into the lower mantle, for example beneath Peru, the Marianas and Central 597 America, whereas others seem to stagnate in the transition zone, for example beneath the Izu-598 Bonin region, South-Kurile and Japan (Agrusta et al., 2017). While mantle heterogeneity may be 599 partly ascribed to internal mantle differentiation induced by partial melting and melt transport, 600 the recycled subducted components buried at the core-mantle boundary have been widely 601 accepted to form chemically heterogeneous reservoirs in the Earth (Hofmann, 1997). Regions of 602 buoyant upwelling mantle plume are considered to return some of this ancient oceanic crustal 603 material to the shallow mantle, where it melts to form compositionally variable OIBs (Hofmann, 604 1997). However, many intraplate OIB-type basalts form in splash, edge, or baby plumes, with the 605

lack of features characteristic of plume-related magmatism, and therefore cannot be attributed to 606 upwelling mantle plumes (Conrad et al., 2011). The compositional variation of these basalts may 607 thus need further explanation. Recently, several studies have proposed that the MTZ may be a 608 potential source for the generation of intraplate magmatism. Murphy et al. (2002) proposed that 609 subducted sediment sequestered in the MTZ for 2-3 Ga may be the mantle source of lamproites 610 from Gaussberg, Kuritani et al. (2011) proposed that the MTZ, metasomatized by involvement of 611 ancient (>1 Ga) and recent sediment from a subducted slab, can explain the high Ba/Th and 612 <sup>207</sup>Pb/<sup>206</sup>Pb ratios of the Cenozoic basalts in NE China. Wang et al. (2015) found that 613 contribution of gabbroic components from stagnant slabs in the MTZ significantly affected the 614 615 chemical and oxygen isotopic values of continental flood basalts. Moreover, Wang et al. (2017) proposed that recycled ancient carbonate-bearing sediments, subducted into the mantle transition 616 zone could form the EM1 reservoir of potassic basalts. Therefore, the present work, together with 617 618 previous studies, suggests that the MTZ can sequester subducted components without being admixed into the convecting mantle for long periods of time, and thus form distinct mantle 619 reservoirs for the generation of intraplate basalts. 620

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# 622 6. Conclusions

Our geochemical results from bulk rock, olivine and melt inclusions of Jurassic mafic lavas in South China provide a new perspective on the origin of HIMU-like basalt. The following conclusions can be summarized:

(1) The H<sub>2</sub>O content of melt inclusion was mainly affected by post-entrapment crystallization and
kinetic diffusion through host olivine and can also be influenced by magmatic degassing for lowFo olivine-hosted melt inclusion. Using the least-affected melt inclusion that has the highest

water content (up to 5.0 wt%) and mantle-like  $\delta D$  value, the primary magma of the Antang basalts is estimated to have H<sub>2</sub>O  $\geq$ 2.65 wt% and the corresponding mantle source has H<sub>2</sub>O concentration between 0.14 and 0.22 wt%. The low  $\delta D$  values in the water-rich melt inclusions indicate that water within the source is principally primordial.

(2) The Antang basalts were derived from a hydrous MTZ composed mainly of recycled oceanic
slabs that had stagnated for over 1.0 Ga. The dominant mantle lithology was eclogite or pyroxenite.

(3) The hydrous mantle transition zone is a potential source for generation of compositionally diverseand unusually volatile-rich intraplate basalts.

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## 638 Acknowledgements

We acknowledge H. Smithies for checking the English, suggestions and comments on an 639 earlier version of this paper. We also thank S. Hu., L. Zhang., X.L. Tu., Z.F. Zhang and X.P. Xia 640 641 for analytical assistance and Y.F. Deng for helpful discussions. Comments and suggestions from two anonymous reviewers and the Editor help to greatly improve the manuscript. This study was 642 supported by the National Science Foundation for Outstanding Youth (Grant 41525006) and the 643 Strategic Priority Research Program (B) of the Chinese Academy of Sciences (Grant XDB 644 18000000) to F. Guo., and an Australian Research Council Future Fellowship (FT140100826) to 645 646 X.C. Wang.

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#### 878 Figure captions

Figure 1. A geologic map showing the distributions of Mesozoic magmatic rocks and major faults in Southeast China (Zhou et al. 2006; Wang et al., 2008). Inset figure shows a simplified tectonic map of China with a speculated subduction zone of the Paleo-Pacific slab in the late Mesozoic. The Antang basalt is located ~800 km west of the paleo-Pacific subduction zone.

**Figure 2**. Petrography of the Antang basalts and the melt inclusions in olivine. (a) Photomicrograph of olivine basalt under crossed polarized light. (b) Olivine phenocryst in (a) highlighting melt inclusion under reflected light. (c) A homogenized melt inclusion in olivine. (d) and (e) Original (unhomogenized) melt inclusions in olivine. (f) Enlarged melt inclusion shown in (e). Abbreviations: OI: olivine; Cpx: clinopyroxene; MI: melt inclusion; PI: plagioclase.

**Figure 3**. Primitive mantle-normalized trace element spidergram of bulk rocks (red lines in both a and b) and melt inclusions (yellow lines in b) of the Antang basalts, and the melts derived from carbonated peridotite (Zeng et al., 2010), hornblendite, clinopyroxene-hornblendite, and hornblendite-peridotite (Pilet et al., 2008). HIMU basalts from St. Helena (Kawabata et al., 2011) are also plotted for comparison. Normalized values for primitive mantle are from Sun and McDonough (1989).

**Figure 4**. The CaO/Al<sub>2</sub>O<sub>3</sub> value of melt inclusion versus the Fo number of host olivines.

Figure 5. Sr-Nd-Pb-Hf isotopic comparison between the Antang basalts and typical HIMU basalts, modelling the evolution of recycled oceanic crust plus contemporary sediment (Stracke et al., 2003). The solid blue line with solid circles shows the isotopic growth of recycled oceanic crust. The black lines with crosses connect the recycled oceanic crust and the subducted sediment of various ages (0–2.5 Ga). The numbers on the curves denote the mass fractions of sediment in 900 the mixed source. The isotopic compositions of St. Helena and Cook-Austral HIMU basalts are compiled from the GEOROC Database (http://georoc.mpch-mainz.gwdg.de/georoc/). The typical 901 HIMU basalts with <sup>206</sup>Pb/<sup>204</sup>Pb > 20.5 can be interpreted as melts from 2.0-1.5 Ga recycled 902 oceanic crust, whereas those with  $19.0 < \frac{206}{Pb}/\frac{204}{Pb} < 20.5$  are related to younger recycled 903 oceanic crust (1.0-1.5 Ga) and/or to the addition of minor sediment (0-1%) to the source. The 904 isotopic composition of the Antang basalts indicates their derivation from a mantle source 905 comprising mainly 1.0-1.5 Ga recycled oceanic crust plus minor sediment. The data for other 906 HIMU-like basalts in SE China are from Wang et al. (2008). The detailed calculation process is 907 presented in Table S8. 908

**Figure 6.** (a) Ca (ppm) versus Fo (mol%) of olivine, showing the divisions (blue dashed lines) between carbonated peridotite, peridotite and eclogite/pyroxenite. The purple squares denote olivines of the basalts from Mangaia and Tubuai that were derived from carbonated peridotitic source (Weiss et al., 2016). The olivine data for MORB and Hawaii are compiled from Sobolev et al. (2007). (b) Plot of  $\delta^{18}$ O versus Fo of olivine for the Antang basalts. The shaded band denotes the range of normal mantle olivine with  $\delta^{18}$ O between 4.8 and 5.4% (Mattey et al., 1994).

Figure 7. CaO (wt%) versus MgO (wt%) plot of primary magmas to discriminate between (blue dashed line) the melts from peridotite and eclogite/pyroxenite. The primary magma compositions of the Antang basalts have been corrected for olivine fractionation (Table S4c). Data sources for melts of peridotite, SiO<sub>2</sub>-excess eclogite, SiO<sub>2</sub>-poor eclogite, and eclogite-peridotite hybrid are presented in "Supporting Information A1".

Figure 8. (a)  $\delta D$  versus H<sub>2</sub>O of the melt inclusions. The yellow band denotes the ranges for MORBs (Shaw et al., 2008). The range of Koolau melt inclusions is also shown for comparison (Hauri et al., 2002b). (b)  $\delta D$  versus Fo of the host olivine.

Figure 9. Plots of (a) Rb vs. Zr, (b) Ba vs. Zr, (c) Th vs. Zr, and (d) U vs. Zr for the olivinehosted melt inclusions.

926 Figure 10. Re-Os isotopic systematics of the Antang basalts. (a) Re versus Os compared with typical HIMU basalts from Cook-Austral (Hanyu et al., 2011) and mantle xenoliths (Liu et al., 927 2012; Zhang et al., 2008) from the contemporaneous Ningyuan basalts in South China. (b) The 928 positive correlation between <sup>187</sup>Os/<sup>188</sup>Os and <sup>187</sup>Re/<sup>188</sup>Os indicates a nugget effect or dis-929 equilibrium binary mixing (Meibom et al., 2002). (c) <sup>87</sup>Sr/<sup>86</sup>Sr(i) versus <sup>187</sup>Os/<sup>188</sup>Os(t) for the 930 Antang basalts and the mantle xenoliths. The broad negative correlation between <sup>87</sup>Sr/<sup>86</sup>Sr(i) and 931 <sup>187</sup>Os/<sup>188</sup>Os(t) argues against a role for continental crust contamination. (d) The binary mixing 932 lines (curves 1, 2 and 3) for melts derived from lithospheric mantle and crust. We assume that 933 melts derived from lithospheric mantle have Os = 250 ppt and  ${}^{187}Os/{}^{188}Os$  (168 Ma) = 0.1231, 934 and that the continental crust has  ${}^{187}\text{Os}/{}^{188}\text{Os} = 1.29$  and an Os concentration of 15 ppt in curve 1, 935 5 ppt in curve 2 and 1 ppt in curve 3. 936

**Figure 11.** CIPW normalization plotted in Ne + Lc (nepheline + leucitite), Ol (olivine), Di (diopside), Hy (hypersphene), Q (quartz) space (Thompson et al., 2005). Melt compositions in a range of partial melting experiments on various sources, including: hornblendite, cpxhornblelndite, carbonated peridotite, carbonated eclogite, silica-deficient pyroxenite, silica-rich pyroxenite, and peridotite. All data were calculated using the assumption that 10% of the total iron as Fe<sub>2</sub>O<sub>3</sub>. The related references are listed in "Supporting Information A1". 943 Figure 12. La/Sm vs. Sm/Yb (a) and La/Yb (b) plots of the Antang basalts, modelling the melting degrees (F) of eclogite. During the calculation, the non-modal batch melting equation 944 was used. The initial composition of the mantle source is assumed to comprise 99% basaltic 945 oceanic crust (25% N-MORB + 25% altered MORB + 50% gabbro) and 1% subducted sediment 946 represented by GLOSS, which has La = 3.88 ppm, Sm = 3.03 ppm, and Yb = 3.02 ppm. The 947 residual assemblage of 75% Cpx + 25% Grt, 80% Cpx + 20% Grt and 82% Cpx + 18% Grt is 948 assumed for Curves 1, 2 and 3, respectively. Numbers on the curves denote the degree of 949 950 melting. Mineral abbreviations: Grt = garnet; Cpx = clinopyroxene. Data sources for the related parameters used in the calculation can be seen in "Supporting Information A1". 951





50 µm ⊣ Mag =208 X Signal A = AsB SKLaBIG WD=4.5mm

WD=4.8mm Mag =457 X Signal A = AsB SKLaBIG





















