



Tracing subducted oceanic slabs in the mantle by 1 using molybdenum isotopes: A case study of 2 intraplate basalts from the Northeast China 3 4 Qiugen Zheng^A, Qifang Zheng^{B*}, Yi Zhang^{C*}, Guangyu He ^D, Qian Wang^D, Jane Fitton^E 5 6 A.School of Ocean Sciences, China University of Geosciences (Beijing), Beijing, China,100083 7 B. School of Earth Sciences and Resources, China University of Geosciences (Beijing), Beijing, China, 100083 9 C.School of Earth Sciences, ZheJiang University, Hangzhou, China, 310058 10 D. State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, 11 Chinese Academy of Sciences, Guangzhou, China, 510630 12 E. Dept of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK 13 14 15 16 * Corresponding author: 17 Qifang Zheng and Yi Zhang 18 E-mail: xiaoyi_tu2021@163.com 19 zhangyi920407@163.com 20 21 22





Abstract

23

24

2526

27

28

29

30

31

32 33

34

35

36

37

38 39 Determining subducted processes is very important for understanding lithological heterogeneity because substantial quantities of slabs are recycled into the mantle. Molybdenum isotopes have been used to distinguish sources materials because of the significant Mo isotopic differences between the crust and the mantle. Here, we undertake a systematic Mo isotopic investigation on a suite of well-characterized continental basalts from Keluo and Halaha-Chaoer, located in Northeast China. $\delta^{98}\text{Mo}$ of Keluo varied from -0.41 to -0.23% with an average of -0.34%, and samples from Halaha-Chaoer ranged in δ^{98} Mo from -0.18 to -0.12% with an average of -0.15%. The former is lighter than the mean value of fresh oceanic basalts (-0.21%), while the latter is similar to oceanic basalts. Combined with other geochemical indications (LOI, Ce/Pb, La/Yb and so on), the Mo isotopic variations cannot be interrupted by chemical weathering, continental crust contamination, or magmatic processes. The δ^{98} Mo variation in this study is explained by adding various oceanic crustal materials in magma sources. The relationships of δ⁹⁸Mo with Ba/Th, Th/U, ¹⁴³Nd/¹⁴⁴Nd for the samples indicated that sediment and altered oceanic crust have contributed to the significant variations in these samples. This study indicates the great potential of Mo isotopes to distinguish different types of recycled oceanic crust materials in the mantle.

40 41

Keywords: Molybdenum isotopes; Subducted oceanic slabs; Intraplate basalts; Northeast China





1. Introduction

44

Slab subduction is widely considered to be the primary mechanism for element cycling between 45 the crust and mantle (Hofmann, 1997; Stracke et al., 2003). The recycled materials with slabs 46 subduction are used to either generate the magmas in the subduction zone or form different 47 48 reservoirs, such as enriched mantle component I (EM I) and enriched mantle component II (EM 49 II) (Zindler and Hart, 1986). Previous investigations suggested that the oceanic crust account 50 for ~10% of the total mass of the mantle since the starting of subducted processes (Stracke et al., 2003; Tang et al., 2016). The converted approach took varied materials into mantle and led 51 52 to lithological heterogeneity in the upper mantle (Perfit et al., 1980; Plank and Langmuir, 1998; Castillo et al., 2000). Therefore, distinguishing the contribution of subducted materials was 53 required for understanding the lithological heterogeneity. 54 55 The previous works observed that the mobility of Mo could be negligible in the subduction 56 zones (Noll et al., 1996; Bali et al., 2012), suggesting that Mo isotopic composition of subdued 57 material can be recorded in the mantle (Freymuth et al., 2015). Supposing there are significant 58 differences in δ^{98} Mo and Mo concentration between the upper mantle, fresh oceanic crust, 59 altered oceanic crust, and sediment, the Mo isotope system will be a powerful tool to trace the 60 sources of magma and calculate the contribution proportion of each source. Bezard et al. (2016) 61 measured the Mo isotopic composition of Mid-Ocean Ridges Basalt (MORB) to establish the 62 Mo isotopic composition of the depleted mantle (DM) as -0.21±0.02‰. Freymuth et al. (2015) 63 analyzed the sediment and altered oceanic crust from ODP sites 801 and 802, ranging in δ^{98} Mo from -1.87 to 0.11% with an average value of -0.50% and from -0.88 to 0.86% with an average 64 65 value of -0.03‰, respectively. Moreover, the Mo concentrations of the upper mantle, altered 66 oceanic crust, and sediment are 1.65 µg g⁻¹, 0.35 µg g⁻¹, and 4.03 µg g⁻¹, respectively. The significant differences in Mo isotopic composition and Mo concentrations between mantle and 67 crust indicate that Mo isotope has excellent potential to trace subducted processes. 68 69 Due to the natural advantage of the Mo isotope, many investigations focused on oceanic basalt 70 using Mo isotopic system to trace the subducted processes (König et al., 2016; Willbold and Elliott, 2017; Zhang et al., 2020; Li et al., 2021). However, the current Mo isotope data of 71 72 intraplate basalt is very limited, and it is debated for using Mo isotope to trace recycled





73 materials for intraplate basalt. Here, we measured a systematic Mo isotopic composition of a 74 set of well-characterized basalt samples from Keluo and Halaha-Chaoer of Northeast China. Samples from Keluo display typical EM I characteristics, while samples from Halaha-Chaoer 75 76 have the radiogenic isotopic signatures of the focal zone (FOZO) (Hart et al., 1992; Stracke et 77 al., 2005). Thus, the samples allow us to use the Mo isotope to assess the contributions of 78 recycled crustal materials to the mantle. 79 2 Sample Northeast China was set between the Siberian Craton and the North China Craton, and 80 81 considered as the eastern segment of the Central Asian Orogenic Belt (Chen et al., 2007; Zhang et al., 1995). The plate suffered the closure of the Paleo-Asian Ocean and the amalgamation of 82 many microcontinent (Senger et al., 1993). Intraplate basaltic rocks in North China were formed 83 84 in the Cenozoic (Zhang et al., 1995; Zou et al., 2003). The Halaha-Chaoer and Keluo volcanic 85 fields were set at the Great Xing'an Mountains and the North of Songliao Basin (Zhang, 1992). 86 Fourteen samples were collected from two volcanic fields, including Halaha-Chaoer (2.0 Ma) 87 and Keluo (9.6-0.11 Ma), of Northeast China. These samples come from many works which 88 studied the evolution of volcanoes. Therefore, the geochemical and isotopic compositions of 89 more samples can be found in previous works (Sun et al., 2014, 2017), and particle samples are 90 measured in this study (Table S1). Here, we just provided a brief description of these samples. 91 The Mo concentration and MgO content of Halaha-Chaoer lavas ranged from 0.96 to 1.18 µg 92 g^{-1} with an average value of 1.05 \pm 0.18 μg g^{-1} and from 7.93 to 12.13 wt. %, suggesting significant crystallization. And the Sr-Nd isotopic ratios of Halaha-Chaoer samples is similar 93 to the FOZO component (initial ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.70354 - 0.7037$ and ${}^{143}\text{Nd}/{}^{144}\text{Nd} = 0.51291$ -94 95 0.5193). On the contrary, the Keluo lavas are characterized by a high Mo concentration of 1.21-2.63 µg g⁻¹ and same MgO content (7.67 to 11.28 wt.%) in relation to Halaha-Chaoer lavas. The 96 Sr-Nd isotopic compositions of the group sample are close to the EMI component (${}^{87}\text{Sr}/{}^{86}\text{Sr} =$ 97 0.70503 - 0.70541 and $^{143}Nd/^{144}Nd = 0.51235 - 0.51246)$ (Table 1). The significant chemical 98 99 difference between Keluo and Halaha-Chaoer provided a great opportunity to check the ability

3 Analytical methods

100101

of Mo isotope to trace the contributions of recycled crustal materials to the mantle.





102 3.1 Major and trace element analyses 103 The major and trace elements were conducted following the analytical procedures described by Qi et al. (2000). An Inductively Coupled Plasma-Atomic Emission Spectrometer measured the 104 105 major elemental compositions. The loess on ignition (LOI) was analyzed after the samples were 106 heated for 30 min at 980°C. The samples were digested using a mixture of HF-HNO₃-HF. The 107 clean solutions were diluted to determine the trace element composition on an Inductively 108 Coupled Plasma-Mass Spectrometry (ELEMENT XR, Thermo, Germany). The reproducibility for trace elements is better than 10% (2SD). All uncertainties of the major element are better 109 110 than 2% (2SE). 111 3.3 Mo-Sr-Nd isotopic analyses The Mo isotopic measurement of all samples was carried out at the State Key Laboratory of 112 113 Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. 114 Detailed processes for digestion, chemical purification and isotopic analysis can be found in Li 115 et al. (2014) and Zhao et al. (2017). Sr-Nd isotopes were determined at the China University of 116 Geosciences, Beijing, and a more analyzed method can be found in Xu et al. (2021). 117 The samples were digested using a 7 ml PFA beaker. Approximately 50-100 mg of powdered 118 samples were mixed with 2ml of concentrated HF and 1 ml of concentrated HNO3; the mixtures 119 were heated at 185±5°C for 36 h. The dry residues were dissolved into Aqua regia to digest 120 samples completely. The fully dissolved samples were evaporated to dryness and then 121 redissolved in 5ml 1.5 M HNO3. The digested samples containing 100-200 ng Mo were spiked by the double spikes (100Mo-97Mo) 122 123 in a 15ml PFA beaker to correct the potential Mo isotopic fractionation of chemical purification 124 and measurement. The spiked samples were dried slowly at 90°C to allow the equilibration between the samples and double spike and then redissolved in 4ml mixed acid of 0.1 M HF and 125 1M HCl. The sample solutions were loaded to prepare BPHA resin that was clean with 6 M 126 127 HCl and MQ. The matrix elements were washed out of columns by 0.1M HF-1M HCl. The 128 fraction of Mo was collected by 6 M HF-1M HCl in a 15ml PFA beaker. The eluted solutions were evaporated to dry at 130°C. Concentrated HNO3 and H₂O₂ were used to remove residual 129 130 organic materials from the resin. The total bank of the procedure is 0.5ng which can be





131 neglected in relation to the loaded sample. Sr and Nd were purified from matrix elements using AG50W-X12 (200-400 mesh) resin and LN resin, respectively. 132 133 Molybdenum isotopic measurements were performed with a Multi-collector inductively 134 coupled plasma mass spectrometer (MC-ICP-MS, Neptune Plus, ThermoFisher). Sample 135 solutions were introduced into the plasma by an Aridus II desolvator system. The signal sensitivity of 95 Mo was $\geq 190 \text{ V} \mu\text{g}^{-1} \text{ mL}$, and the bank signal of 95 Mo was less than 4 mV. The 136 137 solutions and samples were dissolved at 0.5 M HHNO₃ and diluted to 30 ng mL⁻¹ for measuring Mo isotopes. All Mo isotope analyses were carried out on the low mass resolution mode 138 139 (\Delta M/M < 3000). The on-peak instrument and acid matrix blank were determined by measuring 1.5M HNO₃ before each sample and standard to subtract from the signal intensities. Every 5 140 samples were bracketed by a spiked SRM 3134 with 30 ng mL⁻¹ to normalize the Mo isotope 141 142 ratio of samples. More detailed parameters for the Mo isotopes measurements have been listed 143 in previous work. The Mo isotopic composition is expressed relative to NIST SRM 3134 as 144 delta (δ) notation: δ^{98} Mo=((98 Mo)/ 95 Mo) sample/(98 Mo)/ 95 Mo)_{NIST SRM 3134}-1) × 1000. Four 145 geological reference materials (NOD-A-1, NOD-P-1, BHVO-2 and BCR-2) from USGS were 146 digested, purified and measured with our samples. The Mo isotopic compositions re -0.79±0.04‰ 147 (2SD, n=5) for NOD-A-1, -0.87±0.05‰ (2SD, n=5) for NOD-P-1, -0.05±0.05‰ (2SD, n=5) 148 for BHVO-2 and -0.06±0.04‰ (2SD, n=5) for BCR-2, similar to previous works (Skierszkan 149 et al., 2015; Li et al., 2016; Willbold et al., 2016). 150 For Sr and Nd isotopic composition, the mass fractionations of chemical purification and instrument were calibrated with 88Sr/86Sr=8.375209 and 146Nd/144Nd=0.7219. The long-term 151 analysis gave 0.710241 ± 24 for $^{87}Sr/^{86}Sr$ of NIST SRM 987 in the lab and 0.512434 ± 29 for 152 153 ¹⁴³Nd/¹⁴⁴Nd of Alfa Aesar Nd. The Sr and Nd isotopic composition of BHVO-2 and BCR-2 determined in this study are consistent with previous values (Li et al., 2012). 154 155 4. Results The δ^{95} Mo values of Northeast China lavas vary from -0.41% to -0.12% (Table 1). The sample 156 from Keluo varied from -0.41 to -0.23\% in δ^{95} Mo with an average of -0.34\pm 0.10\% (2SD), 157 higher than the sediments (-0.50%) and lighter than the altered oceanic basalts (0.03%) 158 159 (Freymuth et al., 2015). The samples from Halaha-chaoer have homogenous Mo isotopic





160 composition, ranging from -0.12 to -0.18‰ with an average of -0.15±0.05‰ (2SD), similar to the fresh MORB (-0.21%, Chen et al., 2022). The Sr-Nd isotopes, major and trace elements 161 162 composition were shown in Table 1 and Table S1. 163 5. Discussion 164 Given Mo isotope can be fractionated during a range of processes, it is necessary to carefully assess the processes that may have modified Mo isotopic composition of these samples, such 165 as chemical weathering, assimilation of shallow continental crust, magmatic differentiation and 166 partial melting. And then, we estimate the effects of recycled crustal materials on the Mo 167 168 isotopic variation of the samples. 5.1 Chemical weathering and Assimilation of crustal materials on Mo isotope 169 Mo isotopes were fractionated during chemical weathering, and lighter isotopes adsorbed onto 170 secondary minerals so that the weathered residual is lighter in δ^{95} Mo than fresh igneous rocks 171 172 (Greaney et al., 2021). However, the samples do not observe secondary minerals (Sun et al., 173 2014). Moreover, the loss on ignition (LOI) ranging from 0.00 to 1.28 does not display a 174 negative correlation (Fig. 1). Both pieces of evidences imply that the observed Mo isotopic 175 variation cannot be attributed to chemical weathering. 176 These basalts erupted through the continental crust, which is about 40km. The Mo content of 177 these basalts varies from 1.28 to 2.82 µg g⁻¹ with an average value of 1.83 µg g⁻¹, higher than 178 the average Mo concentration of continental crust is 0.8 µg g⁻¹ (Rudnick and Gao, 2014). The 179 upper continental crust is significantly different in δ^{95} Mo from the basalt (Yang et al., 2017; 180 Greaney et al., 2020). Hence, we must consider that crustal materials may modify the Mo 181 isotopic composition of these basalts. For the scenario, a negative correlation between Mo 182 content and δ^{95} Mo were expected because of the heavy Mo isotopic composition of the continental crust. However, we do not observe the relationship (Fig. 2). On the other hand, 183 binary mixing calculation implies that the Mo isotopic variation cannot be explain by binary 184 185 mixing between continental crust and mantle melt, because of unrealistic Mo concentration ratio (Fig. 2). Hence, Assimilation of crustal materials is not the main process that leaded to the 186 187 Mo isotopic variation in these basalts.

189

190

191192

193

194

195

196197

198

199200

201

202

203

204205

206

207

208

209

210

211

212213

214

215

216217





5.2 The effect of fractional crystallization on Mo isotope

The Mo isotopic composition of basalts from the Kos Island arc system ranged from 0.3 to 0.6%, indicating that Mo isotopes are fractionated during the fractional crystallization of hornblende and biotite (Voegelin et al., 2014). However, Bezard et al. (2016) measured the Mo isotopic composition of MORB from the Pacific-Antarctic ridge and the Mohns-Knipovich ridge. The δ^{95} Mo did not show correlations with MgO that indicated magma differentiation, suggesting that Mo isotopic fractionation is insignificant during the fractional crystallization of MORB magma. Recently, Chen et al. (2022) analyzed some MORB glass to constrain the Mo isotopic composition of the upper mantle. The correlations between δ^{95} Mo and magmatic differentiation indicators were not observed, inferring that Mo isotopes were not fractionated during magmatic differentiation (Chen et al., 2022). For our samples studied here, the significant variation of MgO contents (from 6.9 to 13.0%) implies that fractional crystallization plays an essential role in changing the chemical composition of basalts. As shown in Fig.3a, Mo concentration in basalt from Northeast China correlates well with MgO; the positive correlation indicates that Mo is a likely incompatible element enriched in solid phases during melt evolution. The unclear correlations between $\delta^{98}\text{Mo}$ and MgO (Fig. 3b) and Mo (Fig. 2) content suggest that the effect of fractional crystallization on the δ^{95} Mo of basalts is likely insignificant. The observation is similar to the previous inference (Bezard et al., 2016 and Chen et al., 2022) but different from the conclusions from Voegelin et al. (2014). Thus, the δ^{98} Mo variation cannot be explained simply to fractional crystallization and may be caused by partial melting.

5.3 The effect of partial melting on Mo isotopic composition of basalts

Since sodium is a moderately incompatible element at melting the with highest concentration at started melting, the Na concentration of melt decreases with the growth of melting degree. Hence, Na_{8.0} indicates the degree of partial melting without the effect of fractional crystallization (Klein and Langmuir, 1987). Bezard et al. (2016) observed the absence of correlation between δ^{95} Mo and Na_{8.0}, explaining the trend that Mo isotopes are not fractionated during mantle melting. Since La is more incompatible than the heavy rare earth element Yb during the partial melting of mantle, (La/Yb)_N ratio is sensitive to the degree of partial melting.





218 Liang et al. (2017) observe broad correlations between δ^{98} Mo and (La/Yb)_N in ocean island 219 basalts (OIB), suggesting a significant effect of melting on the Mo isotopic variations. The conclusion is contrary to Bezard et al. (2016). However, for our samples, we did not observe 220 the clear relationships between δ98Mo and Na_{8.0} (Fig. 4a) as well as (La/Yb)_N (Fig. 4b). In 221 222 addition, McCoy-West et al. (2019) accessed the Mo isotopic behaviors using a non-modal 223 batch melting model and inferred that Mo isotopes were significantly fractionated during 224 mantle partial melting that melt is heavier in δ^{98} Mo than the residue. The fractionation was driven from as that Mo (VI) with heavier isotope is more incompatible than Mo (IV) (Leitzke 225 226 et al., 2017). However, the samples (-0.33±0.10‰) produced by the high degree of partial melting have lighter Mo isotopic composition than the samples with a low degree (-227 0.15±0.05‰), contrary to the prediction trend by the previous model (Fig. 4, McCoy-West et 228 229 al., 2019). Therefore, the evidences suggested that partial melting cannot explain the δ^{98} Mo 230 variation of these basalts. 231 5.4 Molybdenum isotopic variation induced by crustal recycling 232 The above discussions show that the Mo isotopic variation for these basalts cannot be explained 233 by shallow-level processes, fractional crystallization and partial melting. Radiogenic isotopes, 234 such as Nd and Sr, usually are used to reflect heterogeneous sources. The significant variations 235 for 143 Nd/ 144 Nd and δ^{98} Mo imply that there are more than two components at least for the mantle 236 sources of these basalts (Fig. 5). In the following, we will discuss the mechanisms that may be 237 responsible for the processes of mantle enrichment and abnormal Mo isotopic composition. 238 239 Sediments could be recycled into the mantle with subducted slabs (Stracke et al., 2003). The 240 δ^{98} Mo of subducting sediments varied from -1.87 to 0.11% with an average value of -0.50 \pm 0.27‰ (2SE, n=16, Freymuth et al., 2015). Since Mo is a highly incompatible element and 241 lighter isotopes were preserved in the residual produced during metamorphic dehydration 242 243 (König et al., 2016), melts derived from recycled sediments should inherit the light Mo isotopic 244 composition. Hence, the incorporation of recycled sediments into peridotite melting could be responsible the lighter Mo isotopic composition. The δ^{98} Mo of basalt studied here (-0.30%) is 245 lighter than fresh MORB (-0.21‰, Chen et al., 2022), and 143Nd/144Nd is higher than sediment 246

247





suggesting that sediment is one of source for these basalts from Keluo. On the other hand, Th/U 248 ratio is not fractionated significantly during magmatic processes as Th and U are incompatible 249 250 elements. Both elements can be fractionated during fluid processes because of the higher 251 mobility of U than Th (Hawkesworth et al., 1997; Bali et al., 2009; Ling et al., 2011). Thus, 252 there is a significant difference in the Th/U ratio between fresh MORB (3.54, Gale et al., 2013) 253 and sediment (6.64, Vervoort et al., 2011). Reasonability, the ratio is usually used as an indicator of distinguishing the mantle sources (Sun et al., 2020). The Th/U ratio of our basalts (4.94 to 254 255 6.12) falls between sediment and fresh MORB. The observation indicates that sediment may play an essential role in forming these basalts. It is noteworthy that there is not expected positive 256 correlation between δ^{98} Mo and Th/U ratio (Fig. 5b), implying other sources for the basalts. 257 258 Significant Mo isotopic fractionation is observed during seawater alteration (Freymuth et al., 2015), suggesting that altered oceanic crust (-0.02‰) is heavier δ^{98} Mo than fresh ocean crust 259 260 (-0.21\%). Thus, The incorporation of altered oceanic crust during the particle melting of mantle 261 could produce melts with significant various Mo isotopic composition. Due to the mobility 262 difference between Ba and Th (Weaver et al., 1986), the Ba/Th ratio of the altered oceanic crust 263 will be increased with the growing extent of low-temperature hydrothermal alteration (Kelley 264 et al., 2003). Furthermore, the ratio will not be changed during slab dehydration (Kogiso et al., 265 1997; Kessel et al., 2005). Hence, the ratio is used to trace the incorporation of altered oceanic 266 crust in the mantle (Sun et al., 2020). The Ba/Th ratios of these basalts range from 147 to 239, 267 higher than sediment and fresh MORB and similar to altered oceanic crust (Fig. 5c), indicating 268 the incorporation of altered oceanic crust into the source region of these basalts. 269 Therefore, recycled sediment and altered both have contributed to the basalt of Keluo produced in Northeast China. The materials may have come from the westward subduction of the Pacific 270 plate (Tang et al., 2014). The contribution of the fresh oceanic crust is insignificant because of 271 the low Mo concentration. Mixing of melts produced from recycled sediment with the 272 273 contribution of mantle peridotites derived the variation of Mo isotopic composition in the 274 basalts.

(0.51228, Vervoort et al., 2011) and lighter than fresh MORB (0.513074, Gale et al., 2013),

6. Conclusion





276 This work suggests that the basalt from Keluo displays heterogenous Mo isotopic composition 277 and is heavier Mo isotopic compositions than the upper mantle. At the same time, the sample from Halaha-Chaoer is homogenous in δ^{98} Mo, similar to the upper mantle. The isotopic 278 279 variation was explained by adding sediment and altered oceanic basalt with subducted oceanic 280 slabs into mantle sources. Therefore, the Mo isotope is a powerful tool in investigating the 281 effect of crustal recycling on mantle-derived magmas to understand recycling materials' roles 282 in mantle heterogeneity. 283 284 Acknowledgements We are grateful to Jie Li and FanHuang Li for analytical assistance, as well as Yang Sun and 285 Yongwei Zhao for sample collection. The work was supported by the National Key Research 286 287 and Development Program of China (2017YFC0703201), the National Science and Technology 288 Major Project of the Ministry of Science and Technology of China (2016ZX05014001), the 289 Strategic Priority Research Program of the Chinese Academy of Sciences (XDA14010201), the 290 National Natural Science Foundation of China (41530347, 41872225) 291 Reference 292 Bali E., Audetat A. and Keppler H. (2009) Mobility of U and Th in subduction zone fluids-A 293 synthetic fluid inclusion study. Geochim. Cosmochim. Acta 73(13), A80. 294 Bali, E., Keppler, H., Audetat, A., 2012. The mobility of W and Mo in subduction zone fluids and 295 the Mo-W-Th-U systematics of island arc magmas. Earth Planet. Sci. Lett. 351-352, 195-207. 296 Bezard R., Fischer-Godde M., Hamelin C., Brennecka G. A. and Kleine T. (2016) The effects of 297 298 magmatic processes and crustal recycling on the molybdenum stable isotopic composition of 299 Mid-Ocean Ridge Basalts. Earth Planet. Sci. Lett. 453, 171–181. C.J. Hawkesworth, S.P. Turner, F. McDermott, D.W. Peate, P. van Calsteren, U-Th isotopes in arc 300 301 magmas implications for element transfer from the subducted crust, Science 276 (1997) 551-302 555. 303 Castillo P. R. (2015) The recycling of marine carbonates and sources of HIMU and FOZO ocean 304 island basalts. Lithos 216-217, 254-263.





305 Chen, S., Sun, P., Niu, Y., Guo, P., Elliott, T., Hin, R.C., 2022. Molybdenum isotope systematics of 306 lavas from the East Pacific Rise: constraints on the source of enriched mid-ocean ridge basalt. Earth Planet. Sci. Lett. 578, 117283. 307 308 Commun. 12, 6015. 309 Freymuth H., Vils F., Willbold M., Taylor R. N. and Elliott T. (2015) Molybdenum mobility and 310 isotopic fractionation during subduction at the Mariana arc. Earth Planet. Sci. Lett. 432, 176-311 186. Gale A., Dalton C. A., Langmuir C. H., Su Y. and Schilling J.-G. (2013) The mean composition of 312 313 ocean ridge basalts. Geochem. Geophys. Geosyst. 14, 489-518. Greaney, A.T., Rudnick, R.L., Romaniello, S.J., Johnson, A.C., Gaschnig, R.M., Anbar, A.D., 2020. 314 315 Molybdenum isotope fractionation in glacial diamictites tracks the onset of oxidative 316 weathering of the continental crust. Earth Planet. Sci. Lett. 534, 116083. 317 Hart S. R., Hauri E. H., Oschmann L. A. and Whitehead J. A. (1992) Mantle plumes and 318 entrainment-Isotopic evidence. Science 256, 517-520 319 Hofmann A. W. (1997) Mantle geochemistry: The message from oceanic volcanism. Nature 385, 320 219-229. 321 Kelley K. A., Plank T., Ludden J. and Staudigel H. (2003) Composition of altered oceanic crust at 322 ODP Sites 801 and 1149. Geochem. Geophys. Geosyst. 4, 8910. https://doi.org/ 323 10.1029/2002GC000435 324 Kessel R., Schmidt M. W., Ulmer P. and Pettke T. (2005) Trace element signature of subduction-325 zone fluids, melts and supercritical liquids at 120-180 km depth. Nature 437, 724-727. 326 Klein E. and Langmuir C. H. (1987) Global correlations of ocean ridge basalt chemistry with axial 327 depth and crustal thickness. J. Geophys. Res. 92, 8089-8115 328 Kogiso T., Tatsumi Y. and Nakano S. (1997) Trace element transport during dehydration processes 329 in the subducted oceanic crust: 1. Experiments and implications for the origin of ocean island 330 basalts. Earth Planet. Sci. Lett. 148, 193-205. 331 Konig S., Wille M., Voegelin A. and Schoenberg R. (2016) Molybdenum isotope systematics in subduction zones. Earth Planet. Sci. Lett. 447, 95-102. 332 333 Leitzke F. P., Fonsecaa R. O. C., Sprungb P., Mallmannc G., Lagosa M., Michelya L. T. and Mu"nker





334 C. (2017) Redox dependent behaviour of molybdenum during magmatic processes in the 335 terrestrial and lunar mantle: implications for the Mo/W of the bulk silicate Moon. Earth Planet. Sci. Lett. 474, 503-515. 336 337 Li C.-F., Li X.-H., Li Q.-L., Guo J.-H., Li X.-H. and Yang Y.-H. (2012) Rapid and precise 338 determination of Sr and Nd isotopic ratios in geological samples from the same filament 339 loading by thermal ionization mass spectrometry employing a single-step separation scheme. 340 Anal. Chim. Acta 727, 54-60. Li H. Y., Zhao R. P., Li J., Tamura Y., Spencer C., Stern R. J., Ryan J. G. and Xu Y. G. (2021) 341 342 Molybdenum isotopes unmask slab dehydration and melting beneath the Mariana arc. Nat. Arc). Lithos 190-191, 440-448. 343 344 Li J., Liang X.R., Zhong L.F., Wang X.C., Ren Z.Y., Sun S.L., Zhang Z.F. and Xu J.F. (2014). 345 Measurement of the isotopic composition of molybdenum in geological samples by MC-ICP-MS using a novel chromatographic extraction technique. Geostand. Geoanal. Res, 38, 345-346 347 354, Li, J., Liang, X.-R., Zhong, X.-C., Wang, Z.-Y., Ren, S.-L., Sun, Z.-F., Zhang, J.-F., Xu, J.-F., 2014. 348 349 Measurement of the isotopic composition of molybdenum in geological samples by MC-IC-350 MS using a novel chromatographic extraction technique. Geostand. Geoanal. Res. 38 (3), 345-351 354. 352 Liang Y. H., Halliday A. N., Siebert C., Fitton J. G., Burton K. W., Wang K. L. and Harvey J. (2017) 353 Molybdenum isotope fractionation in the mantle. Geochim. Cosmochim. Acta 199, 91–111. 354 Ling M. X., Wang F. Y., Ding X., Zhou J. B. and Sun W. D. (2011) Different origins of adakites 355 from the Dabie Mountains and the Lower Yangtze River Belt, eastern China: geochemical 356 constraints. Int. Geol. Rev. 53(5-6), 727-740. McCoy-West A. J., Chowdhury P., Burton K. W., Sossi P., Nowell G. M., Fitton J. G., Kerr A. C., 357 Cawood P. A. and Williams H. M. (2019) Extensive crustal extraction in Earth's early history 358 inferred from molybdenum isotopes. Nat. Geosci. 12, 946-951 359 360 Noll, P.D., Newsom, H.E., Leeman, W.P., Ryan, J.G., 1996. The role of hydrothermal fluids in the 361 production of subduction zone magmas: evidence from siderophile and chalcophile trace 362 elements and boron. Geochim. Cosmochim. Acta 60, 587-611.





363 Perfit, M., Gust, D., Bence, A., Arculus, R., Taylor, S.R., 1980. Chemical characteristics of island-364 arc basalts – implications for mantle sources. Chem. Geol. 30 (3), 227–256. Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its 365 366 consequences for the crust and mantle. Chem. Geol. 145, 325-394 367 Qi, L., Hu, J., Gregoire, D.C., 2000. Determination of trace elements in granites by inductively 368 coupled plasma-mass spectrometry. Talanta 51, 507-513. Rudnick R. L. and Gao S. (2014) Composition of the continental crust. In Treatise on Geochemistry 369 370 (eds. H. D. Holland and K. K. Turekian), second ed. Elsevier, Oxford, pp. 1–51. 371 Skierszkan EK, Amini M, Weis D (2015) A practical guide for the design and implementation of the double-spike technique for precise determination of molybdenum isotope compositions of 372 373 environmental samples. Anal Bioanal Chem 407:1925–1935 374 Stracke A., Bizimis M. and Salters V. J. M. (2003) Recycling oceanic crust: Quantitative constraints. Geochem. Geophys. Geosyst. 4, 8003. https://doi.org/10.1029/2001GC000223, 3. 375 376 Stracke A., Hofmann A. W. and Hart S. R. (2005) FOZO, HIMU, and the rest of the mantle zoo. Geochem. Geophys. Geosyst. 6, Q05007. https://doi.org/10.1029/2004GC000824. 377 378 Sun Y., Teng F.-Z., Ying J.-F., Su B.-X., Hu Y., Fan Q.-C. and Zhou X.-H. (2017) Magnesium 379 isotopic evidence for ancient subducted oceanic crust in LOMU-like potassium-rich volcanic 380 rocks. J. Geophys. Res. Solid Earth 122, 7562-7572. Sun Y., Ying J., Zhou X., Shao J. A., Chu Z. and Su B. (2014) Geochemistry of ultrapotassic volcanic 381 382 rocks in Xiaogulihe NE China: implications for the role of ancient subducted sediments. Lithos 383 208-209, 53-66. 384 Tang Y., Obayashi M., Niu F., Grand S. P., Chen Y. J., Kawakatsu H., Tanaka S., Ning J. and Ni J. 385 F. (2014) Changbaishan volcanism in northeast China linked to subduction-induced mantle 386 upwelling. Nat. Geosci. 7, 470-475. Vervoort J. D., Plank T. and Prytulak J. (2011) The Hf-Nd isotopic composition of marine sediments. 387 388 Geochim. Cosmochim. Acta 75, 5903-5926 389 Voegelin A. R., Pettke T., Greber N. D., von Niederha"usern B. and Na"gler T. F. (2014) Magma 390 differentiation fractionates Mo isotope ratios: evidence from the Kos Plateau Tuff (Aegean 391 Willbold M. and Elliott T. (2017) Molybdenum isotope variations in magmatic rocks. Chem. Geol.





392	449, 253–268.
393	WillboldM., Hibbert K., Lai Y. J., Freymuth H., HinR. C., Coath C., Vils F. and Elliott T. (2016)
394	High-precision mass-dependent molybdenum isotope variations in magmatic rocks determined
395	by double-spike MC-ICP-MS. Geostand. Geoanal. Res. 40, 389-403.
396	Xu LJ., Liu SA. and Li S. (2021) Zinc isotopic behavior of mafic rocks during continental deep
397	subduction. Geosci. Front. 12(5) 101182.
398	Yang J., Barling J., Siebert C., Fietzke J., Stephens E. and Halliday A. N. (2017) The molybdenum
399	isotopic compositions of I-, S and A-type granitic suites. Geochim. Cosmochim. Acta 205,
400	168–186.
401	Zhang Y., Yuan C., Sun M., Li J., Long X., Jiang Y. and Huang Z. (2020) Molybdenum and boron
402	isotopic evidence for carbonrecycling via carbonate dissolution in subduction zones. Geochim.
403	Cosmochim. Acta 278, 340–352.
404	Zhao, PP., Li J., Zhang L., Wang ZB., Kong DX., Ma J-L., Wei GJ., Xu jF. (2015)
405	Molybdenum mass fractions and isotopic compositions of interna tional geological reference
406	materials. Geostand. Geoanal. Res. 40, 217-226.
407	Zindler A. and Hart S. (1986) Chemical geodynamics. Annu. Rev. Earth Planet. Sci. 14, 493-571.
408	





Table 1 Molybdenum isotopic composition of Northeast China basalt and geological reference materials

Sample	Mo(μg g ⁻¹)	MgO(%)	Na _{8.0}	LOI	Ce/Pb	Th/U	Ba/Th	(La/Yb) _N	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	δ^{98} Mo	2SD
Keluo												
DYS12-01	2.42	7.93	3.61	0.86	10.9	4.94	239	40.6	0.70514	0.51240	-0.38	0.04
DYS12-02	2.45	7.89	3.48	0.75	9.83	5.01	224	43.7	0.70509	0.51241	-0.36	0.04
XYS12-01	2.63	8.02	4.12	0.16	8.53	5.06	147	47.7	0.70541	0.51239	-0.41	0.03
XYS12-04	2.53	8.6	3.98	0.4	17.0	5.15	176	49.1	0.70534	0.51236	-0.38	0.05
JS12-01	1.48	11.28	4.16	1.28	15.4	5.46	227	39.8	0.70511	0.51242	-0.32	0.04
JS12-02	1.52	11.3	4.25	0.9	15.2	5.40	223	36.3	0.70503	0.51243	-0.38	0.03
DZS12-02	1.46	11.43	4.90	0.08	17.6	5.52	202	41.5	0.70514	0.51243	-0.23	0.05
DZS12-03	1.32	11.62	5.09	0.06	17.0	4.93	231	44.3	0.70507	0.51246	-0.34	0.03
XGS12-01	1.73	10.11	4.04	0.68	9.26	4.96	201	42.8	0.70527	0.51238	-0.28	0.04
XGS12-02	1.88	9.93	4.02	0.34	9.99	5.87	198	43.2	0.70531	0.51238	-0.29	0.05
HS12-01	1.21	12.13	4.96	0.12	15.4	6.32	231	35.2	0.70514	0.51244	-0.34	0.04
HS12-03	1.38	12.05	5.02	0.06	20.35	6.12	238	37.2	0.70516	0.51241	-0.32	0.03
Halaha-												
Chaoer												
07CH02	1.04	12.97	4.64	0.10	17.40	4.13	134	10.2	0.70365	0.51293	-0.15	0.03
07AES07	1.01	10.88	4.27	0.30	12.14	4.09	105	10.3	0.70371	0.51291	-0.12	0.03
07AES09	0.96	10.43	4.13	0.12	15.59	3.98	97	9.4	0.70369	0.51293	-0.18	0.04
07AES16	1.18	12.5	4.82	0.11	20.34	4.44	109	9.9	0.70354	0.51293	-0.13	0.05
Geological r	eference n	naterials										
NOD-P-1											-0.79	0.04
NOD-A-1	NOD-A-1							-0.87	0.05			
BCR-2									-0.06	0.04		
BHVO-2											-0.05	0.05





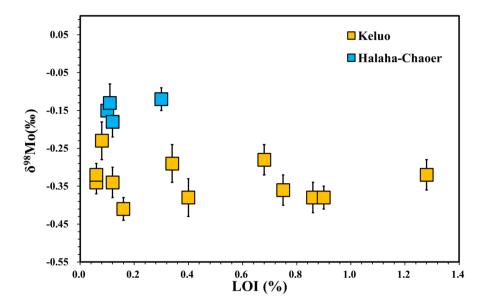


Fig.1 $\delta^{98}\text{Mo}$ versus loss on ignition (LOI) for Northeast China basalts. Data are reported in

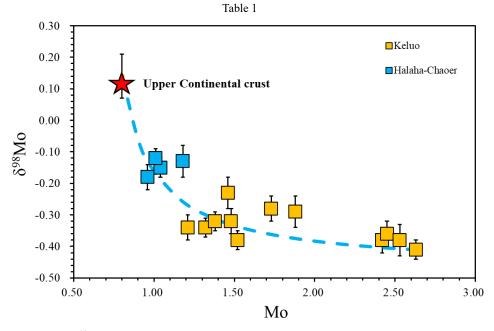


Fig.2 Plots of δ^{98} Mo against Mo concentration for Northeast China basalts. The average Mo isotopic composition of upper continental crust is $0.14\pm0.07\%$ (Yang et al., 2017). Data are reported in Table 1.





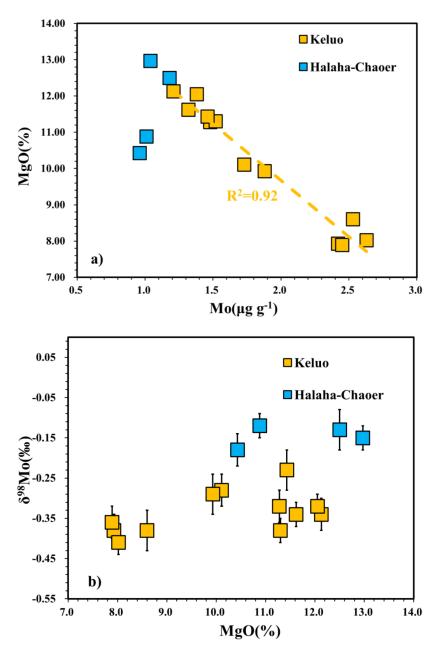


Fig. 3 Plot of δ^{98} Mo against Mo concentration (a) and MgO content (b) for Northeast China basalts.





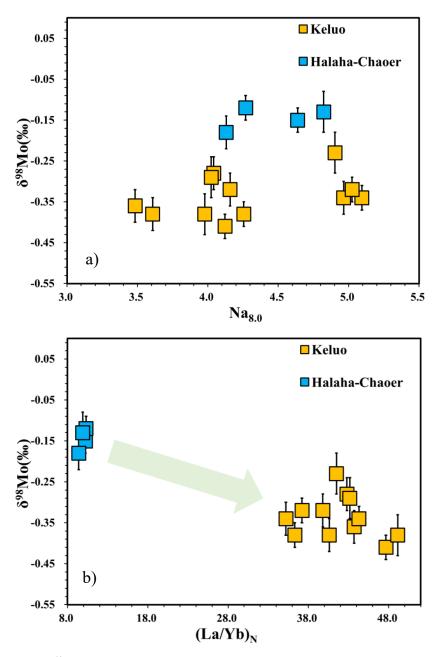
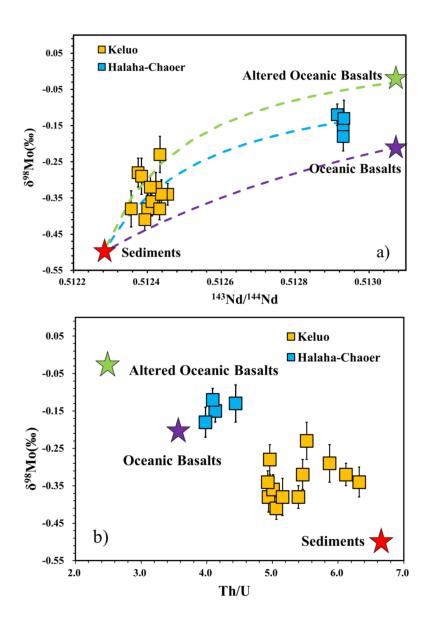


Fig. 4 δ^{98} Mo versus Na_{8.0} (a) and (La/Yb)_N (b) for Northeast China basalts. Na_{8.0} was calculated by Na_{8.0} = Na₂O+(0.373×MgO)-2.98 (Klein and Langmuir, 1987). Data are reported in Table 1











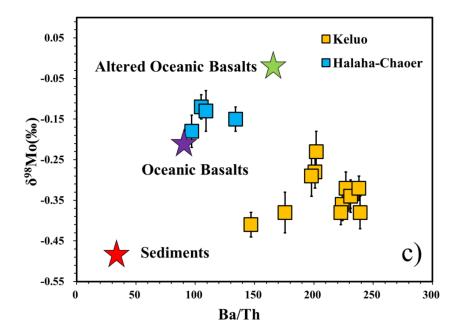


Fig. 5 Plot of δ⁹⁸Mo against ¹⁴³Nd/¹⁴⁴Nd (a), Th/U (b) and Ba/Th (C) for Northeast China basalts. The clay-rich sediments, highly altered oceanic crust, and unaltered oceanic basalts are represented by sediments from DSDP sites 294/295 (Vervoort et al., 2011), samples from the Bay of Islands ophiolite (Parendo et al., 2017), and the average E-MORB (Gale et al., 2013), respectively. The Nd isotopic ratio of clay-rich sediments is 0.512380 (Vervoort et al., 2011), whereas the Nd isotopic compositions of highly altered oceanic crust and unaltered oceanic basalts are assumed to be similar to that of the average E-MORB (0.513074) (Gale et al., 2013). The Th/U and Ba/Th ratios of these components are 6.64 and 35 (Vervoort et al., 2011), 2.5 and 166 (Parendo et al., 2017), and 3.54 and 92 (Gale et al., 2013), respectively.