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Post-cumulus control on copper isotopic fractionation during oceanic intra-crustal magmatic differentiation

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1 ABSTRACT

2 Unlike their eruptive counterparts, plutonic rocks often experience post-cumulus
3 evolution prior to their final solidification. These processes have the potential to exert
4 significant control on the distributions of elements and their isotopic compositions of
5 plutonic rocks. However, our understanding in these effects remains limited,
6 particularly for metal stable isotopes. Here, we carried out high-precision $\delta^{65}\text{Cu}$
7 measurements for a suite of primitive to evolved cumulates from the Kane area, 23°N
8 of Mid-Atlantic Ridge. Most mid-ocean ridge basalts (MORBs) exhibit uniformly bulk
9 silicate Earth (BSE)-like $\delta^{65}\text{Cu}$ of $+0.09\pm 0.08\text{‰}$, indicating limited Cu isotopic
10 fractionation in crustal magma reservoirs prior to melt extraction. However, our new
11 Cu isotopic data on these cumulates show that large Cu isotopic variations ($\delta^{65}\text{Cu}=-0.6\text{‰}$
12 to $+0.9\text{‰}$) occur in variably evolved cumulates ($\text{MgO}/\text{total FeO}<3.0$), while the most
13 primitive cumulates ($\text{MgO}/\text{total FeO}>3.0$) exhibit BSE-like $\delta^{65}\text{Cu}$ ($+0.06\pm 0.06\text{‰}$).
14 Petrological and geochemical observations indicate limited hydrothermal effects on
15 Kane cumulate Cu isotopes. Modeling results indicate that the variable $\delta^{65}\text{Cu}$ in Kane
16 cumulates are unlikely to result from magmatic processes during the cumulus stage.
17 Instead, the large Cu isotopic variation in Kane cumulates requires post-cumulus melt
18 evolution involving fractionation between sulfide and intercumulus melts at relatively
19 low temperatures. Textures and mineral chemistry indicate pervasive post-cumulus
20 modifications of Kane cumulates by porous melt flow. Thermodynamic calculations
21 indicate that intercumulus melts persist at temperatures even to 200°C lower than the
22 initial liquidus temperatures. Our data indicate that lower temperatures in the post-
23 cumulus melt evolution and lower sulfide Ni contents result in lower sulfide-silicate
24 melt Cu isotope fractionation factor ($\alpha_{\text{sulfide-melt}}$), then causing greater Cu isotopic
25 variations in cumulates. We suggest that post-cumulus melt evolution reconcile both
26 the Cu depletion and large Cu isotope fractionation in oceanic cumulates that are
27 unexpected by a simple process of crystal accumulation from MORBs. This study
28 highlights the essential role of post-cumulus evolution in controlling metal budget and
29 their stable isotope fractionation during intra-crustal differentiation, which might also
30 be applied to island arc and continental settings.

31 **Keywords:** Copper isotopes, Lower oceanic crust, Mid-ocean ridge basalts, Post-
32 cumulus evolution, Intra-crustal differentiation

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1. Introduction

Following crystal accumulation, cumulate rocks frequently experience post-cumulus evolution, including the *in-situ* crystallization of trapped melt (Bédard, 1994; Borghini and Rampone, 1997) and porous melt flow (Boulanger and France, 2023; Lissenberg and Macleod, 2016; Zhang et al., 2020; Zhang and Liu, 2023). Understanding the effect of the evolution of plutonic rocks after initial crystal accumulation is important, because geophysical, petrological, and geochemical observations consistently indicate that magma reservoirs at different tectonic settings are all crystal-rich and mush-dominated (Cashman et al., 2017; Jackson et al., 2018; Lissenberg and Macleod, 2016). Buoyancy forces cause the migration and extraction of intercumulus melts through the porosity-connected zones of the crystal mush (Jackson et al., 2018). During this process, the melt interacts chemically with the cumulus crystals in a process termed porous melt flow (Boulanger and France, 2023; Jackson et al., 2018). This process is now considered as significant process in mush-dominated magma systems (Jackson et al., 2018; Lissenberg and MacLeod, 2016). Geodynamic and petrochemical modeling indicates that porous melt flow through mush-dominated magma reservoirs plays a crucial role in the chemical differentiation of Earth's crust (e.g., Jackson et al., 2018). It is well recognized that the post-cumulus melt evolution significantly modifies the incompatible element compositions of plutonic rocks (Boulanger and France, 2023; Lissenberg and MacLeod, 2016). Recent studies show that post-cumulus processes might also affect metals, especially those chalcophile, in plutonic rocks (e.g., Ciazela et al., 2018; Pieterek et al., 2022; Zhang et al., 2022). However, effects of the post-cumulus melt evolution on the metal budgets and their stable isotopes (e.g., Cu-Zn-Fe) in plutonic rocks remain to be investigated.

Global average oceanic gabbros and troctolites have Cu contents of 71 ± 19 ppm (Coogan, 2014) and 59 ± 43 ppm (Godard et al., 2009), respectively; both are too Cu-depleted to match the global average mid ocean ridge basalts (MORB, 78 ± 26 ppm; Yang et al., 2021) and primitive MORB (80-120 ppm; Ding and Dasgupta, 2017; Jenner and O'Neill, 2012). The reconstructed bulk plutonic crust exposed at Atlantis Massif, Mid-Atlantic Ridge (MAR), has a primitive MORB-like geochemical composition but exhibits Cu abundances (51 ppm; Godard et al., 2009) much lower than primitive MORB. Assuming a ratio of 1:2 between dikes with lavas and lower oceanic crust, simple mass balance calculation suggests 111 ± 19 ppm Cu in the bulk lower oceanic crust (Ciazela et al., 2018; Pieterek et al., 2022). In addition, considering the compatible behavior of Cu during MORB differentiation (Ding and Dasgupta, 2017; Jenner and O'Neill, 2012), oceanic cumulates should exhibit higher Cu abundances than MORBs, whereas global average oceanic gabbros have Cu (71 ± 19 ppm; Coogan, 2014) similar to average MORBs (78 ± 26 ppm; Yang et al., 2021). Utilizing the Cu partition

coefficient of 1.5-1.6 between MORB and cumulates (Sun et al., 2023), the equilibrium cumulates of global average MORBs (Yang et al., 2021) should have 117 ± 36 ppm average Cu. Thus, most oceanic cumulates are too Cu-depleted to be explained by a simple process of crystal accumulation from MORBs (Ciazela et al., 2018; Pieterek et al., 2022). Previous studies have shown that Cu isotope, expressed as $\delta^{65}\text{Cu}$ (relative to NIST SRM 976), can be utilized to trace Cu mobilization during the open-system magmatic processes in plutonic rocks (Huang et al., 2017; Liu et al., 2015; Zou et al., 2019, 2024). Therefore, Cu isotopes may provide new insights into the Cu behavior in lower oceanic crust.

Copper isotope fractionation during mantle melting and fractional crystallization of MORBs and arc lavas is thought to be limited (Sun et al., 2023; Wang et al., 2019, 2021; Zou et al., 2024). In agreement with this idea, most MORBs [$\text{MgO} > 5$ wt.%; $\delta^{65}\text{Cu} = 0.06 \pm 0.03\text{‰}$] and fresh oceanic peridotites [$\delta^{65}\text{Cu} = 0.10 \pm 0.13\text{‰}$] exhibit uniform and comparable $\delta^{65}\text{Cu}$ (Figs. 1 and S1). These are indicative of a similar $\delta^{65}\text{Cu}$ between bulk silicate Earth (BSE; $\delta^{65}\text{Cu} = 0.06 \pm 0.20\text{‰}$) and Earth's mantle ($\delta^{65}\text{Cu}$ of $0.03 \pm 0.24\text{‰}$ for non-metasomatized mantle; Liu et al., 2015). However, MORBs are well-mixed magmas that reflect differentiation of primary mantle melts along the liquidus line of descent (mainly from 1225 to 1139°C ; Rubin et al., 2009; Sugawara et al., 2001) in the short-lived magma chamber (< 10 kyr; Brandl et al., 2016). By contrast, there are growing evidence supporting the magma differentiation in lower oceanic crust extends down to near-solidus condition (*i.e.*, 750 - 1000°C) and lasts more than 0.2 Ma (Grimes et al., 2009; Lissenberg et al., 2023). Therefore, the published MORB data cannot reflect the Cu isotopes of the complete oceanic crustal section (Savage et al., 2015; Sun et al., 2023; Wang et al., 2021). Instead, the lower oceanic crust cumulates reflect both cumulus and post-cumulus evolutions and, thus, record a more complete magmatic differentiation history than MORBs (Boulanger and France, 2023; Lissenberg and MacLeod, 2016; Zhang et al., 2020, 2021).

In this study, we present new data on whole-rock and mineral major and trace elements, whole-rock Pt-Pd contents, and whole-rock Cu isotopes of fourteen well-characterized cumulates from the Kane Megamullion area, MAR (Fig. 2). Additionally, twelve MORBs from Kane Megamullion are analyzed for major elements and Cu abundances. Our new data reveal a BSE-like $\delta^{65}\text{Cu}$ in primary MORB but a significant $\delta^{65}\text{Cu}$ variation in lower oceanic crust that contrasts with the uniform BSE-like $\delta^{65}\text{Cu}$ in MORBs (Fig. 1). We suggest that the magma chamber processes cause limited Cu isotopic fractionation between MORBs ($\text{MgO} > 5$ wt.%) and cumulates during the cumulus stage. The subsequent post-cumulus melt evolution in the long-lived crystal mush involving pervasive porous melt flow is proposed as an essential mechanism causing the large Cu isotopic fractionation and the Cu deficit in oceanic cumulates.

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115 2. Geological settings and sample description

116 The Mid-Atlantic Ridge south of the Kane fracture zone is located at 23°N and is
117 characterized by a slow-spreading rate (Fig. 2a, full spreading rate of ~26 mm yr⁻¹; Xu
118 et al., 2020). The Kane Megamullion is located 30 to 55 km to the west of the ridge axis
119 and south of the Kane Transform (Fig. 2b), which was produced by detachment faulting
120 between 3.3 and 2.1 Ma (Xu et al., 2020), exposing large sections of mantle and lower
121 crust (Dick et al., 2008, 2010). There are several gabbro bodies with different sizes
122 exposed on the seafloor, including two large gabbro bodies at Adam and Babel Domes
123 (Fig. 2b; Dick et al., 2008; Xu et al., 2020). These gabbroic intrusions represent the
124 localized magmatic centers formed by focused mantle melt migration and subsequent
125 intra-crustal magma differentiation (Dick et al., 2008, 2010; Lissenberg and Dick,
126 2008).

127 The cumulates utilized in this study were collected during R/V Knorr Cruise 180,
128 Leg 2 and Jason II ROV dives (Dick et al., 2008). Samples Jason (JAS) 117-48 to
129 JAS117-64 and Knorr (KN)-180-2-25-1 were dredged from Adam Dome, whereas
130 samples KN180-2-9-1 to KN180-2-9-7 were from Babel Dome (Fig. 2b). All the
131 cumulates are relatively fresh, with limited low-temperature (LT; <250°C; Bach et al.,
132 2001) alteration (Fig. 3). No high-temperature (HT; 450-750°C) alteration secondary
133 mineral (e.g., green amphibole, tremolite, chlorite, and talc; Nozaka and Fryer, 2011)
134 is present in our cumulates. In fact, HT alterations are poorly developed in most plutonic
135 rocks exposed at Kane Megamullion (Dick et al., 2008). Kane cumulates range in
136 lithologies from troctolite through olivine gabbro, gabbro, to oxide-bearing gabbro,
137 based on their olivine (Ol), plagioclase (Pl), clinopyroxene (Cpx), and Fe-Ti oxide
138 modal abundances (Table 1).

139 In troctolites (>20% Ol and <5% Cpx) and Cpx-rich troctolite (>20% Ol and 5-
140 15% Cpx, MacLeod et al., 2017), the main cumulus phases are Ol and Pl, with minor
141 subhedral to euhedral spinel (Sp) and interstitial Cpx, which typically exhibits lobate
142 contact against Pl and Ol (Fig. 3a-c). Specifically, Cpx commonly occurs as film-like
143 grains enclosing large, rounded Ol grains (Fig. 3a). Cpx is also present as anhedral to
144 subhedral oikocrysts enclosing small grains of resorbed Ol (Fig. 3a, b). In olivine
145 gabbros, Ol, Pl, and Cpx all occur as subhedral grains, with minor to absent spinel
146 (Table 1). Some oxide-bearing gabbro and olivine gabbro contain various amounts of
147 Fe-Ti oxides (e.g., ilmenite and titanomagnetite), with Ol, Pl, Cpx, and minor
148 orthopyroxene (Opx) as the cumulus phases (Table 1). In Ol gabbros and oxide-bearing
149 gabbro, Pl commonly exhibits core-rim textures, with clean and inclusion-free core but
150 irregularly shaped overgrowth rims enclosing fine-grained anhedral Cpx (Fig. 3d). In
151 all types of Kane cumulates, the grain boundaries between different silicates are

typically irregular and lobate contacts are common (Fig. 3). Sulfides in Kane cumulates are mainly chalcopyrite (Ccp) and pyrrhotite (Po) that occur together in the same grains in interstitial positions (Fig. 3e, f). These sulfides maintain their primary igneous textures, without any visible secondary replacement textures or oxidized rims (Fig. 3e, f).

3. Analytical methods

Measurements of whole-rock and mineral major and trace elements and whole-rock Pt and Pd abundances were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). Measurements of Cu isotopes were carried out at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. The complete datasets are given in Tables S1-S9. Thermodynamic and petrochemical modeling results related to the data interpretations are given in Table S10-S14. A summary of the essential petrological, geochemical and Cu isotopic data of the studied samples is given in Table 1.

3.1. Whole-rock major and trace elements

For whole-rock major elements, loss on ignition (LOI) was analyzed by the weight contrast before and after heating to ~1,000°C. About 0.6 g 200-mesh sample powder was weighed and mixed with 6 g Li₂BO₇ before making glass beads. The generated glass beads were measured on an AXIOS Mineral Spectrometer, with 1-3% total analytical uncertainties. According to the XRF measurements of USGS standard GSR-1, GSR-3, and an ultramafic standard JP-1, the external uncertainties are 0.1-0.2% (RSD) for SiO₂ and <0.02% (RSD) for Fe₂O₃, MgO, Na₂O, K₂O, TiO₂, MnO, CaO, and P₂O₅, respectively. For whole-rock trace elements, around 40 milligrams of powders were weighted and digested in a 1:2 mixture of 50% HNO₃ and 50% HF for >120 h at 240°C in an oven. Rock standards (JP-1, DTS-2B, and BHVO) and total procedural blanks were prepared along with the sample powders. After drying down and subsequent 50% HNO₃ dry-down steps to break-down fluorides, the sample residues were dissolved in 20% HNO₃ at 150°C for >6 hours. The sample solutions were then diluted by a factor of 1250 in ultra-pure water. Solutions were measured utilizing the Thermo Fisher iCAP RQ quadrupole inductively coupled plasma mass spectrometer (ICP-MS). Reproducibility of the reference materials was overall better than 5% (RSD), and element contents were consistent with recommended values (Table S4).

3.2. Mineral major and trace elements

Mineral major elements were analyzed on a JEOL JXA-8100 Electron Probe at IGGCAS, using an accelerating voltage of 15 keV, a beam current of 10 nA and beam size of 3 to 5 μm. Trace element abundances of Cpx and Ol were determined by laser

ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR ICP-MS instrument (*Thermo Fisher Scientific*, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Germany). The approach is similar to that outlined in [Wu et al. \(2018\)](#) with isotopes measured using a peak-hopping mode with a laser diameter of 32 to 60 μm and 5 Hz repetition rate. The laser energy density is $\sim 4.0 \text{ J/cm}^2$. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high-capacity vacuum pump. Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. ARM-3 reference glass was used for external calibration ([Wu et al., 2019](#)) and BIR-1G glass was used for quality control monitoring. Silicon (^{29}Si) was used as an internal standard. The resulting data were reduced based on the GLITTER program ([Griffin et al., 2008](#)). For most trace elements ($>5 \text{ ppb}$), the accuracy is better than $\pm 10 \%$ with analytical precision (1 RSD) of $\pm 10\%$.

3.3. Whole-rock Pt and Pd contents

Whole-rock Pt and Pd contents were analyzed at the IGGCAS utilizing the isotope dilution method ([Chu et al., 2009](#)). Two grams of 200-mesh sample powders and appropriate amounts of a ^{194}Pt - ^{105}Pd mixed spike were weighted into a Carius Tube and digested in 3 ml purified concentrated HCl and 6 ml purified concentrated HNO_3 for 72 hours at 220°C in an oven. After drying down and subsequent 5 ml 6 M HCl dry-down steps, the sample residues were dissolved in 5 ml 1 M HCl_3 at 100°C for >6 hours. Pt and Pd were separated and purified by anion exchange chromatography using 200 meshed AG 1×8 resin ([Walker et al., 2008](#)) into Ir-Pt and Pd fractions. The Ir-Pt and Pd fractions were purified using an Eichrom LN spec resin for complete removal of Zr and Hf. Finally, each fraction of the Ir-Pt and Pd was dried and re-dissolved in 0.8 N HNO_3 before the measurements by a *Thermo Fisher* iCAP RQ ICP-MS. In-run precisions for $^{194}\text{Pt}/^{196}\text{Pt}$ and $^{105}\text{Pd}/^{106}\text{Pd}$ were $<0.3\%$ (2RSD). The Pt and Pd standard solutions were utilized for mass fractionation correction. The 20 ppb Hf, 20 ppb Zr, and 50 ppb Cd standard solutions were utilized for interference corrections, *i.e.*, $^{90}\text{Zr}^{16}\text{O}^+$ on $^{106}\text{Pd}^+$, $^{178}\text{Hf}^{16}\text{O}^+$ on $^{194}\text{Pt}^+$, $^{180}\text{Hf}^{16}\text{O}^+$ on $^{196}\text{Pt}^+$, and $^{106}\text{Cd}^+$ on $^{106}\text{Pd}^+$. UB-N and BHVO-2 were analyzed together with unknown samples as external standards to monitor the accuracy of the procedures, yielding values consistent with the reported results ([Meisel and Moser, 2004](#)). The total analytical uncertainties are 4% for Pt and 0.6% for Pd. The total procedural blanks are $34\pm 12 \text{ pg}$ for Pt and $23\pm 6 \text{ pg}$ for Pd, resulting the method detection limits of 20 ppt for Pt and 8 ppt for Pd ([Table S2](#)).

3.4. Whole-rock Cu isotopes

Measurements of Cu isotopes were carried out following the procedures described in [Zhu et al. \(2019\)](#). About 20 mg of each sample powder was digested in a mixture of

double-distilled concentrated HF+HNO₃ (1ml HNO₃+1ml HF) and then refluxed with a mixture of aqua regia (0.5ml HNO₃ + 1.5ml HCl). The sample solution was dried down, converted to chloride form, and finally dissolved in 1 ml 8 mol L⁻¹ HCl+0.001% H₂O₂ for purification. The sample solution was loaded into columns filled with 2 ml pre-cleaned AG-MP-1M anion resin. The matrix elements were eluted with 8 mL 8 mol L⁻¹ HCl + 0.001% H₂O₂ vol./vol, and 28 mL 8 mol L⁻¹ HCl + 0.001% H₂O₂ was subsequently collected. The Cu fractions were dried down at 80–100°C and dissolved in 2% HNO₃ at a concentration of ~300 ng g⁻¹ for isotope analysis. High recovery (>99%) with 3-5 ng total procedural blank was achieved. Copper isotope ratios were measured on a Nu Plasma 1700 MC-ICP-MS in wet plasma and low-resolution mode utilizing the sample-standard bracketing method. Copper isotope ratios are reported against standard reference material NIST SRM 976 in δ -notation: $\delta^{65}\text{Cu} = [({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{sample}} / ({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{NIST976}} - 1] \times 1000\text{‰}$. Replicate shows reproducible results with an uncertainty of 0.04‰ (2SD, Table S3). The $\delta^{65}\text{Cu}$ values of USGS geological standards of BCR-2, GSP-2 and BHVO-2 agree well with the published results (Table S3 and references therein).

4. Results

4.1. Whole-rock geochemical compositions

Kane cumulates are divided into two groups based on their FeO-MgO relationships and petrological features: the primitive cumulates with a Fe depletion trend and absence of ilmenite and the evolved cumulates with a Fe-enriched trend and presence of ilmenite (Fig. 4a; Table 1). The primitive cumulates exhibit Mg# [=100*Mg/(Mg+Fe_T)] of 80-87 and Cu contents of 37-101 ppm (Fig. 4b). In contrast, the evolved cumulates display Mg# of 55-77 and Cu contents of 53-83 ppm. No correlation exists between whole-rock Cu contents and Mg# for Kane cumulates nor global MOR cumulates (Fig. 4b). Kane MORBs display Mg# of 50-66, with Cu contents (63-77 ppm) comparable to the published data of Kane MORBs [61-86 ppm, except for those affected by melt-mantle interaction; Bryan et al., 1981; Ciazela et al., 2017]. Of note, both Kane MORBs and cumulates exhibit lower Cu abundances than the primitive MORBs (Fig. 4b).

In CI chondrite-normalized rare earth element (REE) patterns, Kane cumulates display depletions in light rare earth elements (LREE) but flat patterns of heavy rare earth elements (HREE), with positive Eu anomalies (Fig. S2a). In the primitive mantle (PM)-normalized trace element patterns, Kane cumulates display depletions in Nb, Zr, Hf, and Ti but positive anomalies in Sr and Eu (Fig. S2b). Primitive cumulates exhibit REE and trace element patterns comparable to evolved cumulates but display lower REE abundances (Fig. S2).

4.2. Mineral major and trace element compositions

Primitive cumulates display Ol forsterite content [$\text{Fo} = 100 \times \text{Mg} / (\text{Mg} + \text{total Fe})$] of 80-87, Cpx Mg# of 82-91, and Pl anorthite content [$\text{An}\% = 100 \times \text{Ca} / (\text{Ca} + \text{Na} + \text{K})$] of 61-80, which are all higher than those in evolved cumulates ($\text{Fo} = 69-74$, Cpx Mg# = 71-81, and Pl $\text{An}\% = 48-67$; [Table 1](#)). Cpx cores in Kane cumulates exhibit TiO_2 -Mg# correlations consistent with the calculated equilibrium Cpx of MORBs ([Fig. 5a](#)). In primitive cumulates, Cpx rims and interstitial Cpx display higher TiO_2 than Cpx cores at a given Mg# ([Fig. 5a](#)), consistent with the experimental melt-troctolite reaction trend ([Yang et al., 2019](#)). Cpx in Kane cumulates exhibit LREE depletion and flat HREE patterns, with variably negative Eu anomalies ([Fig. S3](#)). These Cpx also display variable Zr contents (5-180 ppm; [Fig. 5b](#)) and wide range in La/Sm ratios (0.1-0.4; [Fig. 5c](#)). Olivine cores for Kane cumulates were analyzed for trace elements, exhibiting 1200-3600 ppm Mn, 31-463 ppm Ti, and Ti/Y ratio (a ratio sensitive to post-cumulus melt evolution, [Sanfilippo et al., 2014](#)) ranging between 300 and 4600 (typical 1σ error of $\pm 15\%$; [Fig. 5d](#)).

4.3. Cu isotopic compositions and Pt-Pd concentrations

The primitive cumulates with >3.0 MgO/FeO_T exhibit uniformly BSE-like $\delta^{65}\text{Cu}$ of $+0.06 \pm 0.06\%$ ([Fig. 1b](#)). With the MgO/FeO_T decreasing from 3.0 to 2.2 and Mg# decreasing from 86 to 80, the primitive cumulates display $\delta^{65}\text{Cu}$ decreasing from $+0.05\%$ to -0.53% ([Figs. 1b and 6a](#)). Kane evolved cumulates exhibit variable $\delta^{65}\text{Cu}$ of -0.63 to $+0.87\%$, without clear correlation with Mg# ([Fig. 6a](#)).

Primitive cumulates exhibit Pt contents of 1 to 3142 ppt and Pd contents of 4 to 10138 ppt, and Cu/Pd ratios (an indicator of sulfide segregation, [Barnes et al., 1993](#)) of 5×10^3 to 8.6×10^6 ([Fig. 6b](#)). In contrast, evolved cumulates exhibit lower Pt and Pd contents (Pt = 3-25 ppt, Pd = 4-17 ppt) and higher Cu/Pd ratios ($\text{Cu/Pd} = 2.1 \times 10^6 - 2.2 \times 10^7$). The cumulates with low Cu/Pd ratios ($<10^6$) display uniform $\delta^{65}\text{Cu}$ of $+0.03\%$, whereas those with $>10^6$ Cu/Pd exhibit large $\delta^{65}\text{Cu}$ variations from -0.63 to $+0.87\%$ ([Fig. 6b](#)).

4.4. Calculated liquidus, solidus, and 8% melt-present temperatures

Liquidus temperatures (T_{liquidus}) for Kane cumulates, *i.e.*, the temperatures of the parental magma of cumulus minerals in each cumulate, were calculated based on Cpx-melt Fe-Mg equilibrium ([Bédard, 2010](#)), while solidus (T_{solidus}) and 8% melt-present temperatures ($T_{8\% \text{ melt-present}}$) were estimated by thermodynamic modeling using GeoPS software ([Fig. S4](#); [Xiang and Connolly, 2022](#)). As 8% is a typical trapped melt fraction in oceanic gabbros ([Natland and Dick, 2001](#)), the 8% melt-present temperature is considered as the lowest temperatures for connecting the porosity of crystal mush which is a prerequisite for porous melt flow. The solidus and 8% melt-present temperatures were estimated assuming a pressure of 1 kbar. Detailed descriptions of these calculations are given in [Supplementary Materials](#). Primitive cumulates have higher

calculated liquidus, solidus, and 8% melt-present temperatures ($T_{\text{liquidus}}=1156\text{-}1231^{\circ}\text{C}$, $T_{\text{solidus}}=904\text{-}973^{\circ}\text{C}$, and $T_{8\% \text{ melt-present}}=961\text{-}1060^{\circ}\text{C}$) than evolved cumulates ($T_{\text{liquidus}}=1105\text{-}1138^{\circ}\text{C}$, $T_{\text{solidus}}=831\text{-}908^{\circ}\text{C}$, and $T_{8\% \text{ melt-present}}=868\text{-}949^{\circ}\text{C}$; Fig. 7).

5. Discussion

5.1. Evidence for porous melt flow during post-cumulus evolution

Based on the calculated liquidus temperatures and the thermodynamic modeling (Table S13), the Kane primitive ($T_{\text{liquidus}}=1156\text{-}1231^{\circ}\text{C}$) and evolved cumulates ($T_{\text{liquidus}}=1105\text{-}1138^{\circ}\text{C}$; Fig. 7) were derived from parental magmas after 12-50% and 58-69% fractional crystallization of primary MORB, respectively. All Kane cumulates exhibit cumulate-like whole-rock REE and trace element patterns, *i.e.*, positive Eu and Sr anomalies indicative of Pl accumulation (Fig. S2). However, textural and geochemical features of Kane cumulates reflect their modifications during post-cumulus melt evolution after early crystal accumulation and MORB extraction.

Textural disequilibrium is ubiquitous in Kane cumulates. For instance, Cpx in primitive cumulates occurs as either replacive rims surrounding rounded Ol (Fig. 3a) or as anhedral oikocrysts enclosing small grains of resorbed Ol (Fig. 3a-b). In troctolite, the interstitial Cpx exhibits lobate contacts against the nearby Pl and locally contains brown amphibole rims (Fig. 3c). These features are consistent with the dissolution of early cumulus Ol and Pl crystals and the precipitation of Cpx during the post-cumulus evolution (Boulanger and France, 2023; Lissenberg and Dick, 2008; Lissenberg and MacLeod, 2016; Zhang et al., 2021). In evolved cumulates, Pl typically display core-rim textures, with inclusion-free cores but overgrowth rims containing anhedral Cpx and common lobate contacts between Pl rims and Cpx (Fig. 3d). This feature is compatible with the partial dissolution of early Cpx and Pl and the subsequent overgrowth of Pl rims (Boulanger et al., 2023).

The textures of Kane cumulates (*i.e.*, interstitial occurrence of Cpx; Fig. 3a-c) indicate the crystallization of Cpx after Ol and Pl, consistent with low-pressure (<7 kbar) and water-poor magma fractional crystallization (Elthon et al., 1982; Feig et al., 2010). Experiments merely generated Cpx with Mg# lower than 83 under low-pressure and water-poor condition (Lissenberg and Dick, 2008). This reflects the late appearance of Cpx on liquidus under low-pressure and water-poor condition, when the magma Mg# had been reduced by prior Ol crystallization (Elthon et al., 1982; Feig et al., 2010). However, eight out of thirteen Kane cumulates display Cpx Mg# higher than 83 (*i.e.*, Cpx Mg#=86-91 for most primitive cumulates; Table 1 and Fig. 5a), implying these Cpx cannot be produced by simple fractional crystallization (Lissenberg and Dick, 2008). Porous melt flow was proposed as a mechanism to explain the occurrence of high-Mg# Cpx in MOR cumulates (Lissenberg and Dick, 2008; Liu et al., 2018). This

is consistent with experimental studies (Yang et al., 2019). During the post-cumulus stage, compaction of crystal mush causes the migration of intercumulus melts, during which melts continuously react with the early accumulated crystals of Ol+Pl±Cpx (Boulanger and France, 2023; Lissenberg and MacLeod, 2016). Modeling indicates that porous melt flow enriches the intercumulus melts in Al and Mg but depletes them in Ca and Si, causing the post-cumulus growth of Cpx (Lissenberg and Dick, 2008). Additionally, the Fe-Mg exchange between intercumulus melts and mafic minerals (Ol, Cpx) lowers the FeO contents in the melts, which could facilitate the crystallization of sulfides (Ariskin et al., 2013; Pieterek et al., 2022).

Cpx cores in Kane cumulates exhibit TiO₂-Mg# correlations consistent with the modeled fractional crystallization (FC) trends and the calculated equilibrium Cpx of MORBs (Fig. 5a). By contrast, Cpx rims and interstitial Cpx in primitive cumulates display elevated TiO₂ relative to FC trend, which are consistent with the experimental post-cumulus melt-troctolite reaction trend (Fig. 5a; Yang et al., 2019). Likewise, significant portions of Cpx in Kane cumulate are too Zr-rich to match a FC trend and the calculated equilibrium Cpx of MORBs (Fig. 5b). These post-cumulus trends reflect the Fe-Mg exchange between Ol and intercumulus melts, which buffered the melt Mg# at high levels while enriching the melt in TiO₂, Zr and REEs through prolonged melt differentiation (e.g., Sanfilippo et al., 2014; Yang et al., 2019). Most Ol cores in Kane cumulates exhibit Ti/Y too high to match FC trend, which are, however, consistent with the post-cumulus porous melt flow trends observed in mid-ocean ridge-type ophiolitic plutonic crust (Fig. 5d; Sanfilippo et al., 2014).

To further examine the mechanisms of post-cumulus melt evolution of Kane cumulates, we performed modelings of simple fractional crystallization, *in-situ* crystallization (Langmuir, 1989), and assimilation-fractional crystallization (AFC) processes (DePaolo, 1981) to reproduce the Cpx REE variations (see figure caption and Table S11 for details). The former two processes operate in closed system, whereas the AFC process occurs during porous melt flow in an open system (e.g., Boulanger and France, 2023). Modeling results indicate that neither FC nor *in-situ* crystallization can reproduce the wide range in Cpx La/Sm ratios (Fig. 5c). Only a few Cpx exhibit La/Sm versus Yb trend consistent with FC or *in-situ* crystallization, whereas the Cpx La/Sm-Yb correlations for most Kane cumulates can be reproduced by the AFC processes at ratios of assimilated to crystallized mass (Ma/Mc) varying between 0.8 and 0.9 (Fig. 5c).

To sum up, our data indicate the Kane cumulates have experienced pervasive post-cumulus modification by porous melt flow. This finding is consistent with previous studies on oceanic cumulates from both Kane (Lissenberg and Dick, 2008) and other ocean ridges across the spreading rate spectrum (e.g., Lissenberg et al., 2013; Zhang et

al., 2020) and those from MOR-type ophiolites (Sanfilippo et al., 2015; Liu et al., 2021), implying that porous melt flow is a dominant post-cumulus process modifying global lower oceanic crust.

5.2. Cu isotopic fractionation in residual melts and cumulates in cumulus stage

In-situ analyses indicate that silicates possess <4 ppm Cu, accounting for only 1-3 wt.% of whole-rock Cu (Fig. S5). Fe-Ti oxide and spinel are minor in modal abundances (mostly <1 vol.%) and typically exhibit <1 ppm Cu (Gamal El Dien et al., 2019; Sun et al., 2023), which have negligible contributions to whole-rock Cu budget. Therefore, sulfide accounts for >97 wt.% budget of whole-rock Cu, and the Cu isotopes in cumulates are mainly controlled by sulfide. Several lines of evidence indicate that the seafloor alteration did not affect the Cu isotopes of the studied cumulates. Firstly, sulfides in all samples occur as interstitial grains of fresh chalcopyrite and pyrrhotite, without any oxidized rims (Fig. 3e, f), indicating these sulfides were unaffected by seawater-derived alterations. Secondly, previous study indicates large Cu isotopic variations in altered plutonic complex at East Pacific Rise (Hole 1256D) are caused by HT alterations (450-750°C, Huang et al., 2016), whereas our samples show no evidence for HT alterations, *i.e.*, no HT alteration secondary minerals like green amphibole or tremolite are present (Nozaka and Fryer, 2011; Zhang et al., 2023). Thirdly, $\delta^{65}\text{Cu}$ exhibits no correlation with either loss on ignition (LOI) values (<1.5 wt.%) or other fluid-rock reaction indicators (Fig. S6). Instead, extent of $\delta^{65}\text{Cu}$ variability correlates with the Cu/Pd ratio, with high Cu/Pd indicating sulfide segregation (Barnes et al., 1993); only samples with >10⁶ Cu/Pd exhibit large $\delta^{65}\text{Cu}$ variations, whereas those with low Cu/Pd (<10⁶) have uniformly mantle-like $\delta^{65}\text{Cu}$ (Fig. 6b). Such a $\delta^{65}\text{Cu}$ -Cu/Pd trend reflects that the large $\delta^{65}\text{Cu}$ variations in Kane cumulates occurred only after significant sulfide segregation.

The primitive cumulates with >3.0 MgO/FeO_T display uniform $\delta^{65}\text{Cu}$ of +0.06±0.06‰ (n=5; Fig. 1b), indicating primary MORB has a BSE-like Cu isotopic composition. This implies limited Cu isotopic fractionation between primary MORB and residual mantle (Sun et al., 2023). Though mantle melt migration may cause large melt $\delta^{65}\text{Cu}$ variations of -0.7 to +0.7‰ (Zou et al., 2019), we suggest that the efficient melt aggregation in dunitic channels homogenizes melt $\delta^{65}\text{Cu}$ to a tight mantle value. However, as MgO/FeO_T decreases from 3.0 to 2.2 and T_{liquidus} decreasing from 1190°C to 1156°C (Figs. 1b and 8a), $\delta^{65}\text{Cu}$ shifts to values of +0.05‰ to -0.53‰, indicating large Cu isotopic fractionation after 34-50% fractional crystallization (based on Petrolog3 modeling in Table S14). Below, the possible Cu isotopic fractionation during the cumulus-stage magma evolution is discussed, based on the $\delta^{65}\text{Cu}$ variations in both Kane cumulates and published MORB data.

Except for the most primitive MORB magmas, the cumulus-stage magma

differentiation at mid-ocean ridge reaches sulfide-saturation (Ding and Dasgupta, 2017; Sun et al., 2023). This is consistent with the observed sulfide grains in cumulates (Fig. 3e, f) and the increase in Kane cumulate Cu/Pd ratios, as Pd is much more compatible than Cu during MORB differentiation (e.g., Hao et al., 2021; Fig. 6b). During MORB differentiation, Cu is incorporated into sulfide and progressively removed from the silicate melts, resulting in the modest compatible behavior of Cu during MORB differentiation (Ariskin et al., 2013; Ding and Dasgupta, 2017; Sun et al., 2023).

Sulfide preferentially incorporates ^{63}Cu relative to the coexisting silicate melts (Savage et al., 2015; Xia et al., 2019), but the sulfide-silicate melt Cu isotopic fractionation factor ($\alpha_{\text{sulfide-melt}}$) varies with temperatures, melt Ni contents (Xia et al., 2019; Fig.S7), and oxidation state (Liu et al., 2023). Lower temperatures cause larger mass-dependent Cu isotopic fractionation between sulfide and melts based on both experiments (Savage et al., 2015; Xia et al., 2019) and natural samples (e.g., Huang et al., 2017). Sulfide-melt Cu isotopic fractionation is also driven by the oxidation state change. Cu is multivalent, and Cu^{2+} preferentially incorporates heavy Cu isotopes than Cu^+ (Huang et al., 2017; Liu et al., 2023). With the increasing oxygen fugacity, $\text{Cu}^{2+}/\text{Cu}^+$ increase in melts but the segregated sulfides that preferentially incorporate Cu^+ would be rich in ^{63}Cu , resulting in larger Cu isotopic fractionation between the segregated sulfides and silicate melts (Liu et al., 2023; Zou et al., 2024). In addition, sulfide Ni contents control the extent of Cu isotopic fractionation, *i.e.*, $\alpha_{\text{sulfide-melt}} \approx 1$ for Ni-rich sulfides but $\alpha_{\text{sulfide-melt}} < 1$ for Ni-poor sulfides (Xia et al., 2019; Fig. S8). To date, there is no first-principal calculation of sulfide-silicate melt Cu isotopic fractionation and no sulfide-melt Cu isotopic fractionation experiments were conducted at temperatures of oceanic crustal accretion (1250-850°C; Fig. S8). Thus, $\alpha_{\text{sulfide-melt}}$ for MORBs and oceanic cumulates are not quantitatively constrained.

Here, instead of calculating fractionation factor $\alpha_{\text{sulfide-melt}}$, we model $\alpha_{\text{sulfide-melt}}$ to fit the observed cumulate Cu isotope data. As >95% MORB are oxide-undersaturated and have $T_{\text{liquidus}} > 1160^\circ\text{C}$, only the Kane primitive cumulates ($T_{\text{liquidus}} = 1156\text{--}1231^\circ\text{C}$) reflect Cu isotopic fractionation during MORB genesis (Fig. S7). By contrast, the Kane evolved cumulates exhibit variable Fe enrichments with decreasing MgO (Fig. 4a), implying they were variably affected by late oxide-saturated melts. Therefore, for Cu isotopic modeling in cumulus stage, only Kane primitive cumulates are considered.

We modeled Cu isotopic fractionation in MORBs and cumulates during fractional crystallization by adjusting $\alpha_{\text{sulfide-melt}}$ to fit the Kane cumulate $\delta^{65}\text{Cu}$ - T_{liquidus} correlations (Fig. 8). To fit the Kane cumulate Cu isotopic compositions, $\alpha_{\text{sulfide-melt}}$ is 1.0000 at $>1190^\circ\text{C}$ but progressively decreases from 0.9998 at 1190°C to 0.9988 at 1140°C (Fig. 8a). However, applying such $\alpha_{\text{sulfide-melt}}-T_{\text{liquidus}}$ correlation, the residual melts exhibit progressive increase in $\delta^{65}\text{Cu}$ but decrease in Cu contents with decreasing

temperature: it is the isotopically heavy Cu counterpart to the light cumulates (Fig. 8b). This trend of increasing $\delta^{65}\text{Cu}$ in the melt fails to match the observed uniform BSE-like MORB $\delta^{65}\text{Cu}$ (Fig. 8b, c). Hence, we conclude that fractional crystallization cannot account for the observed Cu isotopic fractionation in the Kane cumulates.

A potential alternative to fractional crystallization is sulfide assimilation and re-precipitation during MORB differentiation and interaction with sulfide-bearing crystal mush (Gleeson et al., 2023; Pieterek et al., 2022). In principle, assimilation of sulfide with light Cu isotopes at an appropriate Ma/Mc ratio can balance the magmas' $\delta^{65}\text{Cu}$ back to a BSE value. To examine this possibility, we performed additional AFC modeling (Fig. 8). Modeling result indicates that, at Ma/Mc of 1, AFC model reconciles the light $\delta^{65}\text{Cu}$ in Kane cumulates but uniform BSE-like $\delta^{65}\text{Cu}$ in residual melts (Fig. 8b). However, at such a Ma/Mc ratio, the residual melts exhibit elevated Cu contents relative to the initial magma, which fails to match the observed MORB $\delta^{65}\text{Cu}$ -Cu content correlation (Fig. 8c).

Overall, the variable $\delta^{65}\text{Cu}$ in Kane cumulates cannot be explained by neither fractional crystallization nor AFC along the same liquid line of descent as MORBs. Instead, the discrepancy in Cu isotopes between MORBs and oceanic cumulates likely reflect their different stages of evolution. MORB evolution involves the complex open processes in the short-lived magma chamber, *i.e.*, the repeated replenishment, mixing, and crystallization (Coogan and O'Hara, 2015; Hao et al., 2021; O'Neill and Jenner). These processes might result in limited Cu isotopic fractionation between MORBs and cumulates during cumulus stage (Fig. 1a). By contrast, the chemical heterogeneity preserved in lower oceanic crust ranges from crystal scale (<1 cm) to crustal scale (~1 km, Lissenberg et al., 2013), reflecting the post-cumulus evolution of the long-lived crystal mush after MORB extraction. Geochronological studies suggest that the post-cumulus evolution of lower oceanic crust operates in a much longer timescale (~0.2 Ma, Lissenberg et al., 2023) than MORBs (1-10,000 years; Brandl et al., 2016), which might cause protracted Cu isotopic fractionation in cumulates at relatively lower temperatures.

5.3. Post-cumulus control on Cu isotopic fractionation in Kane cumulates

Post-cumulus melt crystallization includes *in-situ* crystallization of trapped melts (Bédard, 1994) and reactive crystallization driven by porous melt flow (*e.g.*, Lissenberg and MacLeod, 2016). *In-situ* crystallization does not cause the segregation of intercumulus melts from the cumulates, thus, failing to explain the variable whole-rock $\delta^{65}\text{Cu}$ for Kane cumulates. Given the robust evidence of post-cumulus porous melt flow (see section 5.1) and the interstitial occurrence of sulfide (Fig. 3e, f), we postulate the large Cu isotopic variations in Kane cumulates were caused by the reactive crystallization driven by porous melt flow. All sulfides in Kane cumulates are fresh and are present as interstitial crystals along the grain boundaries of cumulus minerals (Fig.

3e, f). Therefore, protracted Cu isotopic fractionation in cumulates might occur during the permeable migration of intercumulus melts through the grain boundaries with sulfides.

Reactive porous melt flow induces sulfide resorption, remobilization and reprecipitation through a complex interplay of i) the changes in melt FeO (Pieterrek et al., 2022), ii) melt H₂O enrichments (Fortin et al., 2015), iii) oxidation state (Huang et al., 2017; Liu et al., 2023; Sun et al., 2023), and iv) decompression (e.g., Lee et al., 2014). The post-cumulus fractionation of Ol and Cpx enriches melts in FeO but Fe-Mg exchange with mafic minerals (Ol, Cpx) or saturation of Fe-Ti oxides depletes FeO in residual melts (Pieterrek et al., 2022). These FeO fluctuations alter S solubility in intercumulus melts, triggering sulfide dissolution and precipitation accordingly (Ariskin et al., 2013; Pieterrek et al., 2022). Reactive porous melt flow also enriches H₂O in intercumulus melts (e.g., Zhang and Liu, 2023), as evidenced by the presence of brown amphibole rims in our samples (Fig. 3c). H₂O enrichments increase S solubility in intercumulus melts, promoting sulfide dissolution (Fortin et al., 2015). The other scenario is the oxidation of melts by fractionation of low-Fe³⁺/ΣFe phases, including ilmenite, Ol, and Cpx (Sun et al., 2023). The oxidation changes melts from S-saturated to S-undersaturated, facilitating dissolving sulfides from cumulates into the melts (e.g., Mavrogenes et al., 1999). Moreover, decompression due to either detachment faulting at slow-spreading ridges (e.g., Dick et al., 2008) or the upward melt transport (e.g., Zhang and Liu, 2023) raises S solubility in intercumulus melts (Lee et al., 2014). These integrated effects induce oscillations of S saturation or S undersaturation in intercumulus melts as they reactively flow through crystal mush, resulting in sulfide dissolution, remobilization and reprecipitation (Pieterrek et al., 2022). Consequently, prolonged Cu isotopic fractionation between sulfide-bearing cumulates and migrating melts could occur during the post-cumulus porous melt flow (Liu et al., 2023; Pieterrek et al., 2022; Zou et al., 2024).

Thermodynamic modeling indicates that intercumulus melts in Kane cumulates persisted until their cooling to a considerably low temperature, *i.e.*, T_{solidus} are 962-970°C, 878-973°C, 873-896°C, and 831°C for troctolites, Ol gabbros, gabbros, and oxide-bearing gabbro, respectively (Figs. 7 and S4). Modeling also indicates that >8% intercumulus melts remain in Kane cumulates at relative low temperatures, *i.e.*, at 980-1020°C for troctolites, 905-1060°C for Ol gabbros, 896-917°C for gabbros, and 868°C for oxide-bearing gabbro (Fig. 7). Interpolating between the liquidus (T_{liquidus}) and 8% melt-present temperatures [T_{8% melt-present}, the lowest temperatures for the operation of porous melt flow, based on the typical trapped melt fraction in oceanic gabbros (Natland and Dick, 2001)] and a cooling rate of 3.1°C/kyr (Coogan et al., 2007), the timescale of post-cumulus porous melt flow is up to 40-80 kyr, consistent with the chronological

constraints on the timescale of slow-spreading crustal accretion (Lissenberg et al., 2023). Thus, there was sufficient time for protracted Cu isotopic fractionation in Kane cumulates during their post-cumulus melt evolution.

Porous melt flow allows Cu isotopic fractionation in cumulates at a temperature lower than their liquidus line (as low as 831°C; Fig. 7). A lower temperature causes greater sulfide-silicate melt Cu isotopic fractionation, *i.e.*, $\alpha_{\text{sulfide-melt}} \approx 1$ at high temperatures but $\alpha_{\text{sulfide-melt}} < 1$ at relatively low temperatures, based on experimental results (Fig. S8; Liu et al., 2023; Xia et al., 2019). Consistent with this idea, except for the two heavy- $\delta^{65}\text{Cu}$ cumulates (the origin of which would be interpreted later), other Kane cumulates display positive $\delta^{65}\text{Cu}$ - T_{solidus} correlation ($R^2=0.55$; Fig. 9a). This trend could reflect either a decrease in $\alpha_{\text{sulfide-melt}}$ with decreasing temperature, or an addition of light- $\delta^{65}\text{Cu}$ late melts. As sulfide preferentially incorporates ^{63}Cu relative to silicate melts (Savage et al., 2015; Xia et al., 2019), segregation of light- $\delta^{65}\text{Cu}$ sulfides leads to a heavy $\delta^{65}\text{Cu}$ rather than light $\delta^{65}\text{Cu}$ in residual melts. Therefore, we suggest the positive $\delta^{65}\text{Cu}$ - T_{solidus} correlation ($R^2=0.55$; Fig. 9a) is best explained by the decreasing $\alpha_{\text{sulfide-melt}}$ with declining temperatures for sulfide and melt segregation.

In addition, the extent of $\delta^{65}\text{Cu}$ variation in Kane cumulates is associated with cumulate Ni contents, *i.e.*, Ni-poor cumulates display greater $\delta^{65}\text{Cu}$ variations than Ni-rich cumulates (Fig. 9b). This reflects the sulfide Ni content control $\alpha_{\text{sulfide-melt}}$, *i.e.*, $\alpha_{\text{sulfide-melt}} \approx 1$ for Ni-rich sulfides (sulfide Ni=21-29 wt.%) but $\alpha_{\text{sulfide-melt}} < 1$ for Ni-poor sulfides (sulfide Ni=0.1-1.2 wt.%; Xia et al., 2019; Fig. S7). Due to the low melt fraction in crystal mush (1-15%, *e.g.*, Lissenberg and MacLeod, 2016), intercumulus melt and the equilibrium sulfide Ni contents are buffered by the cumulus phases (*e.g.*, Ol), *i.e.*, intercumulus melts of primitive cumulates would maintain high Ni contents during their post-cumulus differentiation. Thus, the post-cumulus evolution of the Ni-rich cumulates were accompanied by Ni-rich sulfide fractionation, leading to limited Cu isotopic fractionation. By contrast, a prominent Cu isotopic fractionation may occur in the Ni-poor cumulates, due to Ni-poor sulfide fractionation. Assuming a sulfide-melt Ni partition coefficient of 776 (Patten et al., 2013), the estimated sulfide Ni contents of Kane cumulates are intermediate between the experimental Ni-rich and Ni-poor sulfides (Xia et al., 2019; Fig. S9). Based on the experimental empirical equation, $\alpha_{\text{sulfide-melt}}$ for the evolved cumulates could be as low as 0.9987 ($\Delta^{65}\text{Cu}_{\text{sulfide-melt}} \approx -1.3\text{‰}$) at 1000°C and 0.9980 ($\Delta^{65}\text{Cu}_{\text{sulfide-melt}} \approx -2.0\text{‰}$) at 900°C (Xia et al., 2019).

An additional effect on the $\alpha_{\text{sulfide-melt}}$ values is the fractionation of Fe-Ti oxides, which affects the redox conditions of magmas (Sun et al., 2023; Zhao et al., 2022). However, except for one oxide-bearing gabbro (4% oxides in KN180-2-9-1), Kane cumulates contain relatively low modal Fe-Ti oxides (<1%), indicating the effect of Fe-Ti oxide saturation on cumulate redox condition is not expected to be significant.

Moreover, the oxide-free primitive cumulates also display significant $\delta^{65}\text{Cu}$ variations ($\delta^{65}\text{Cu}=-0.53$ to $+0.13\text{‰}$; Fig. 1b). Therefore, the $\delta^{65}\text{Cu}$ variations in Kane cumulates cannot be explained by the changing redox conditions driven by Fe-Ti oxide precipitation alone.

Overall, we speculate that the relatively low temperature (as low as 830°C) during post-cumulus evolution and the variable cumulate Ni contents can explain the large Cu isotopic fractionation in Kane cumulates (Fig. 9). Because the cumulate solidus temperatures are positively correlated with their Ni contents (Fig. 9b), these integrated factors resulted in a larger Cu isotopic fractionation (*i.e.*, lower $\alpha_{\text{sulfide-melt}}$) in the more evolved cumulates (Fig. 6a).

If our model of Cu isotope fractionation during the cumulus and post-cumulus stages is correct, $\delta^{65}\text{Cu}$ value of the bulk lower oceanic crust should retain BSE-like, as the Cu isotopic fractionation between cumulates and MORBs is limited along the same liquid line of descent (see section 5.2). In a mass balance consideration, to maintain a BSE-like bulk lower oceanic crust, the light- $\delta^{65}\text{Cu}$ cumulates should be counterbalanced by heavy- $\delta^{65}\text{Cu}$ cumulates. Our data show two evolved Kane cumulates with such heavy $\delta^{65}\text{Cu}$ signatures (Fig. 1b). Leaving light- $\delta^{65}\text{Cu}$ sulfides residual in cumulates, the migrating melts would progressively enrich in ^{65}Cu . The Cu contents of these reactive melts are difficult to be determined for our samples, due to the lack of high-precision Cu data for silicates and the poorly constrained silicate-melt partition coefficients. IODP Hole U1473A gabbros (SWIR) contain abundant magmatic amphiboles which crystallized from intercumulus melts and exhibit Cu abundances high enough to be precisely measured (Zhang and Liu, 2023). Applying the amphibole-melt Cu partition coefficient of 0.07 (Hsu et al., 2017), the intercumulus melts of magmatic amphiboles in U1473A gabbros (Zhang and Liu, 2023) have 76 ± 15 ppm and 83 ± 14 ppm Cu for olivine gabbros and oxide gabbros, respectively. Either local entrapment and *in-situ* crystallization of these heavy- $\delta^{65}\text{Cu}$ melts in cumulates or direct crystallization of such melts in veins can explain the heavy Cu isotopes ($\delta^{65}\text{Cu}=+0.6$ - $+0.8\text{‰}$) in the two Kane evolved cumulates (Fig. 9).

Based on our new data and earlier studies (Huang et al., 2017; Liu et al., 2015; Sun et al., 2023; Zou et al., 2019), Cu isotopic compositions of the complete section of oceanic lithosphere are summarized in Fig. 10a, b. MORB and oceanic mantle lithosphere both exhibit uniform BSE-like $\delta^{65}\text{Cu}$ ($\sim +0.1\text{‰}$). Though the bulk lower oceanic crust has BSE-like $\delta^{65}\text{Cu}$, large Cu isotopic fractionation occurs during intra-crustal differentiation ($\delta^{65}\text{Cu}=-0.6$ to $+0.9\text{‰}$). The high-temperature magmatic processes ($>1160^\circ\text{C}$ for most MORBs; Fig. S7) in the short-lived magma chamber (<10 kyr; Brandl et al., 2016) causes a uniform BSE-like $\delta^{65}\text{Cu}$ in both MORBs and cumulates (Fig. 10c). The subsequent post-cumulus melt evolution occurs in a longer-

lived crystal mush zone (50-80 kyr). In this stage, reactive porous melt flow through the crystal mush causes the resorption, remobilization and reprecipitation of sulfides (Fig. 10a), leading the way for the large Cu isotopic variations in lower oceanic crust (Fig. 10d). The resulting intercumulus melts during the post-cumulus stage are expected to have heavy- $\delta^{65}\text{Cu}$ through the segregation of light- $\delta^{65}\text{Cu}$ sulfides (Zou et al., 2024).

5.4. Implications for the Cu budget in lower oceanic crust

As shown in Fig. 11a, MORBs and global oceanic cumulates exhibit indistinguishable Cu abundances at a given calculated liquidus temperature, failing to match the compatible behavior of Cu during MORB differentiation (e.g., Ding and Dasgupta, 2017; Sun et al., 2023). Moreover, MORBs and oceanic cumulates both show overall lower Cu than primitive MORBs, failing to match a mass balance in the bulk oceanic crust (Fig. 11a). In a mass balance consideration, the bulk lower oceanic crust should have 111 ± 19 ppm average Cu (see Introduction; Ciazela et al., 2018; Pieterek et al., 2022). Thus, the reported global oceanic cumulates are too Cu-depleted (71 ± 19 ppm for gabbros and 59 ± 43 ppm for troctolites; Coogan, 2014; Godard et al., 2009) to balance the bulk oceanic crust Cu abundance back to a primitive MORB value (80-120 ppm; Ding and Dasgupta, 2017; Jenner and O'Neill, 2012). Such a Cu depletion in oceanic cumulates can be explained if a significant portion of sulfides in primitive MORBs are consumed through the reactive crystallization in shallow mantle (Ciazela et al., 2017, 2018). MORB reactive crystallization mainly occur at slow-spreading ridges (Collier and Kelemen, 2010) but is not profound at fast-spreading ridges due to a shallow thermal boundary for the latter (close to Moho depth, e.g., Liu and Buck, 2023). However, the fast- and slow-spreading ridge cumulates show comparable and low Cu abundances of 69 ± 24 ppm ($n=60$) and 58 ± 38 ppm ($n=231$), respectively (based on the same data sources of Fig. 4b). This indicates that shallow mantle reactive crystallization alone cannot fully explain the observed extent of Cu depletion in oceanic cumulates.

Alternatively, the Cu mobilization during post-cumulus porous melt flow in lower oceanic crust might explain the observed Cu depletion in oceanic cumulates (Pieterek et al., 2022). Our new whole-rock and mineral data on Kane cumulates (see section 5.1) as well as numerous studies on other ocean ridges suggest that porous melt flow through the lower oceanic crust is globally ubiquitous and is independent of spreading rate (e.g., Boulanger and France, 2023; Lissenberg and MacLeod, 2016). As outlined in section 5.3, reactive porous melt flow induces oscillations of S saturation or S undersaturation in intercumulus melts, driven by either the fluctuation in FeO and H₂O contents in melts (Ariskin et al., 2013; Fortin et al., 2015; Pieterek et al., 2022), changes in melt oxidation state (Mavrogenes et al., 1999; Sun et al., 2023), or the decompression (Lee et al., 2014). The variations of melt S solubility result in the resorption, remobilization, and

644 reprecipitation of sulfides during reactive melt flow (Fig. 10a; Pieterek et al., 2022; Zou
 645 et al., 2024). This idea is consistent with the large Cu isotope fractionation in Kane
 646 cumulates, suggesting that the sulfides in crystal mush were not isolated but extensively
 647 interacted with intercumulus melts (see section 5.3; Zou et al., 2019; Zou et al., 2024).
 648 The sulfide mobility in Kane cumulates is also supported by their unexpectedly low Cu
 649 contents (37-101 ppm; Fig. 11a). Five out of fourteen Kane cumulates exhibit Cu
 650 contents even lower than the Kane MORBs at a given liquidus temperature (Fig. 11a).
 651 Applying the cumulate-MORB Cu partition coefficient of 1.5-1.6 (Sun et al., 2023), the
 652 equilibrium cumulates of Kane MORBs should have 95-123 ppm Cu (Fig. 11b). Thus,
 653 most Kane cumulates are too depleted in Cu (37-101 ppm) to match their expected Cu
 654 contents during their initial cumulus conditions, implying that variable amounts of
 655 sulfides were lost from the original crystal mush due to the higher rates of sulfide
 656 dissolution than sulfide segregation during the post-cumulus melt flow (Fig. 10a). In
 657 this scenario, the preserved sulfide grains in Kane cumulates are unlikely the original
 658 ones in cumulus stage but are the residues after extensive reactions.

659 To better address this process, we modeled Cu isotopic and elemental variations
 660 in Kane cumulates driven by porous melt flow. Porous melt flow in lower oceanic crust
 661 behaves in mechanism akin to melt-rock reaction with progressive Cu loss from the
 662 original cumulates (e.g., Pieterek et al., 2022), which can be modeled using a simple
 663 Rayleigh distillation equation with different fractionation factors between migrating
 664 melt and sulfide ($\alpha_{\text{sulfide-melt}}=0.9998, 0.9994, \text{ and } 0.9990$; Fig. 11b):
 665 $\delta^{65}\text{Cu}_{\text{cumulate}}=(\delta^{65}\text{Cu}_{\text{initial}}+1000)\times f\text{Cu}^{(\alpha-1)}-1000$, where $\delta^{65}\text{Cu}_{\text{initial}}$ is the initial isotopic
 666 compositions of cumulates and $f\text{Cu}$ reflects the net consumption of Cu in original
 667 cumulates due to post-cumulus reaction. The uniform BSE-like $\delta^{65}\text{Cu}$ in MORBs
 668 indicate limited Cu isotopic fractionation between MORB and cumulates along the
 669 liquidus line of descent (see section 5.2). Therefore, the initial $\delta^{65}\text{Cu}$ of cumulates and
 670 the initial intercumulus melts are both assumed to be BSE-like at +0.05‰ prior to
 671 reaction. Considering the possible uncertainty in sulfide distributions during initial
 672 accumulation, a wide range of Cu contents (140, 100, and 60 ppm) were examined to
 673 represent the initial cumulate compositions prior to the modification by porous melt
 674 flow. However, we note the initial Cu contents of 100 ppm best fit the estimated
 675 equilibrium cumulates of Kane MORBs along the same liquidus line of descent (Fig.
 676 11b). As the Kane evolved cumulates were derived from a ferrobaltic magma that was
 677 more evolved than Kane MORBs, we only compare the modeling results with the Kane
 678 primitive cumulate data. The model shows that Cu contents and $\delta^{65}\text{Cu}$ of most Kane
 679 primitive cumulates can be reproduced by a Rayleigh distillation with $\alpha_{\text{sulfide-melt}}$
 680 between 0.9990 and 1.0000 (Fig. 11b). Such a $\alpha_{\text{sulfide-melt}}$ range lies between the
 681 experimental $\alpha_{\text{sulfide-melt}}$ for Ni-rich and Ni-poor sulfides in the temperature spectrum of

1200-850°C (Fig. S8).

To date, most investigated oceanic cumulates are coarse- to medium-grained, representing the solidified crystal mush (e.g., Godard et al., 2009; Pieterek et al., 2022). We suggest that variable amounts of sulfides were removed from the original crystal mush driven by post-cumulus porous melt flow, resulting in the observed Cu depletion and Cu isotope fractionation in these cumulates (Pieterek et al., 2022). The removed sulfides from the original crystal mush were likely concentrated into the late segregated intercumulus melts, e.g., the SWIR microgabbro layers with high Cu contents [Cu of 135 ± 80 ppm ($n=12$) in average and up to 361 ppm; Ferrando et al., 2021; Pieterek et al., 2022]. Later melt-rock reaction might further concentrate these sulfides into narrow zones near the boundaries of the segregated melts (Pieterek et al., 2022). These fine-grained microgabbros and their boundaries are rarely investigated for whole-rock compositions (Pieterek et al., 2022), thus, not considered for bulk lower oceanic crust composition calculation. Future studies on these late veins from different sections might provide further insight into the Cu budgets in lower oceanic crust.

5.5. Broader implications

Our results indicate that post-cumulus melt evolution causes significant Cu isotopic fractionation in oceanic cumulates ($\delta^{65}\text{Cu} = -0.6$ to $+0.9\%$), except for the most primitive cumulates ($\delta^{65}\text{Cu} = -0.01$ to $+0.13\%$ for cumulates with $\text{MgO}/\text{FeO}_T > 3.0$; Fig. 1b). Therefore, only the very primitive cumulates display Cu isotopes of source characteristics. The use of plutonic rock Cu isotopes to trace the source heterogeneity should thus be approached with caution.

In addition to mid-ocean ridge, magma plumbing systems at other tectonic settings (e.g., island arc) are increasingly viewed as being mush-dominated (e.g., Cashman et al., 2017). Arc lavas exhibit $\delta^{65}\text{Cu}$ of $+0.2 \pm 0.3\%$, with no correlation with magmatic differentiation indicators, contrasting with the highly variable $\delta^{65}\text{Cu}$ in arc cumulates ($\delta^{65}\text{Cu} = -2.0$ to $+1.4\%$; Fig. S1c, d). The relatively homogenous $\delta^{65}\text{Cu}$ in arc lavas reflect limited Cu isotopic fractionation during cumulus-stage magma chamber processes (e.g., Lee et al., 2014). Considering porous melt flow is the dominant post-cumulus process in any mush-dominated magma reservoir (Boulanger and France, 2023; Jackson et al., 2018; Lissenberg and MacLeod, 2016), the dramatic Cu isotopic fractionation in arc lower crusts might also reflect such post-cumulus melt evolution (Liu et al., 2023).

This study highlights the essential role of post-cumulus control on the Cu isotopic variability in lower oceanic crust. Considering temperature also affects the fractionation of other metal stable isotopes (e.g., Fe-Zn; Chen et al., 2021; Stow et al., 2022), post-cumulus control on these metal stable isotopic compositions of plutonic rocks should also be evaluated.

6. Conclusions

The main conclusions are summarized as follows:

1. The most primitive Kane cumulates ($\text{MgO}/\text{FeO}_{\text{T}} > 3$) display uniform $\delta^{65}\text{Cu}$ of $+0.06 \pm 0.06\text{‰}$, indicating a BSE-like $\delta^{65}\text{Cu}$ for primary MORB magma.
2. The $\delta^{65}\text{Cu}$ variations in Kane cumulates reflect magmatic processes rather than secondary hydrothermal processes. However, such cumulate $\delta^{65}\text{Cu}$ variations cannot be explained by cumulus-stage magma evolution in a short-lived magma chamber.
3. Kane cumulates were pervasively modified by post-cumulus porous melt flow, which causes significant Cu isotopic fractionation at temperatures up to 200°C lower than the initial liquidus temperature of the cumulate.
4. The large Cu isotope fractionation in Kane cumulates suggest sulfides were mobile and reactive during post-cumulus processes, which might explain the Cu depletion in these cumulates as well as that observed in the published global oceanic cumulates.
5. Upper oceanic crust and mantle lithosphere exhibit uniformly BSE-like $\delta^{65}\text{Cu}$ ($\sim +0.1\text{‰}$), whereas the lower oceanic crust displays highly variable $\delta^{65}\text{Cu}$ (-0.6 – $+0.9\text{‰}$), with bulk lower oceanic crust retaining a BSE-like $\delta^{65}\text{Cu}$.
6. In addition to mid-ocean ridges, post-cumulus melt evolution might also affect Cu isotopes in plutonic rocks from other tectonic settings. Future studies on other metal stable isotopes in plutonic rocks should also take the post-cumulus melt evolution into account.

Data availability

Data are available through figshare at <https://doi.org/10.6084/m9.figshare.24969015.v1>.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary Material includes the supplementary text, Figs. S1-S9, and Tables S1-S14. Provided in the supplementary text are descriptions of liquidus and solidus temperature calculations, and numerical modelings of Cu isotopic fractionations during liquidus line evolution and post-cumulus melt evolution. Supplementary Tables S1-S10 are the complete dataset utilized in this study and supplementary Tables S11-S14 are the results of numerical modelings.

Figure captions

Fig. 1 $\delta^{65}\text{Cu}$ values for MORB (a), abyssal cumulates (b), and oceanic mantle (c). Literature data sources: $\delta^{65}\text{Cu}$ in MORBs (Liu et al., 2015; Savage et al., 2015; Sun et al., 2023; Wang et al., 2021; Zou et al., 2024), $\delta^{65}\text{Cu}$ in Southwest Indian Ridge (SWIR) gabbro *in-situ* sulfides (Pieterek et al., 2022), $\delta^{65}\text{Cu}$ in SWIR gabbros (Zou et al., 2024), and $\delta^{65}\text{Cu}$ in fresh oceanic and ophiolitic peridotites (Liu et al., 2019; only those with <1.0 wt.% LOI are plotted).

Fig. 2 Bathymetric map of Mid-Atlantic Ridge [MAR, (a)] and Kane area (b) from GeoMap app (<https://www.geomapapp.org/>). Samples were collected from Kane oceanic core complex (OCC), 30-55 km off-axis at 23°N of MAR. The two large gabbro bodies where samples were collected are labeled in panel (b). Distributions of gabbro bodies are from Dick et al. (2008) and Xu et al. (2020).

Fig. 3 Representative textures indicative of post-cumulus melt evolution. (a) Large, rounded olivine (Ol) enclosed by interstitial clinopyroxene (Cpx) and fine-grained, irregularly shaped Ol chadacrysts enclosed in Cpx oikocryst. (b) Rounded or irregularly shaped Ol chadacrysts enclosed in a large Cpx oikocryst. (c) Interstitial Cpx with local tiny brown amphibole (Amp) films with lobate contacts against subhedral plagioclase (Pl). (d) Overgrowth rims of Pl enclosing the fine-grained Cpx. (e-f) Plane-polarized reflected light images showing the occurrence of sulfides in the studied Kane cumulates. Cpx=clinopyroxene, Pl=plagioclase, Ol=olivine, Sp=spinel, Ccp=chalcopyrite,

Po=pyrrhotite.

Fig. 4 Whole-rock total FeO (FeO_T)-MgO (a) and Cu-Mg# plot (b) for Kane cumulates. Literature data sources: Global mid-ocean ridge (MOR) cumulates (Basch et al., 2022; Chin et al., 2018; Drouin et al., 2009; Gillis et al., 2014; Godard et al., 2009; Zhang et al., 2020), published Kane MORBs (Bryan et al., 1981; Ciazela et al., 2017; The Sundersaturated MORBs are excluded due to melt-mantle interaction) and primitive MORBs (Ding and Dasgupta, 2017; Jenner and O'Neill, 2012).

Fig. 5 Representative mineral major and trace element plots. (a) Cpx TiO₂ versus Mg#, (b) Cpx Zr versus Mg#, (c) Cpx La/Sm versus Yb, and (d) olivine Ti/Y versus Mn. The fractional crystallization (FC) and post-cumulus trends in panels (a), (b), and (c) are from Yang et al. (2019), Lissenberg et al. (2013), and Sanfilippo et al. (2014), respectively. Calculated Cpx in equilibrium with MORB (Yang et al., 2021) in panels (a) and (b) were calculated using Cpx-melt Fe-Mg exchange coefficient from Bédard (2010) and Ti and Zr partition coefficients from Laubier et al. (2014). Trends of FC, *in-situ* crystallization (Langmuir, 1989), and assimilation-fractional crystallization (AFC; DePaolo, 1981) were simulated in panel (c) to examine the mechanisms causing Cpx REE variations, with input parameters given in Table S11.

Fig. 6 Plots of $\delta^{65}\text{Cu}$ against whole-rock Mg# (a) and Cu/Pd (b). $\delta^{65}\text{Cu}$ in MORBs are from Liu et al. (2015), Savage et al. (2015), Sun et al. (2023), and Wang et al. (2021).

Fig. 7 Plots of calculated liquidus temperatures, solidus temperatures, and the 8% melt-present temperatures against whole-rock Mg# for Kane cumulates. Detailed descriptions on the calculations and results are given in Supplementary Materials and Tables S10 and S12, respectively.

Fig. 8 Modeling the Cu isotopic and elemental variations in MORB and Kane cumulates assuming their differentiation along the same liquid line of descent and by adjusting α to fit the cumulate $\delta^{65}\text{Cu}$ -liquidus temperature trend. Both fractional crystallization (FC) and assimilation-fractional crystallization (AFC) processes were modeled, with detailed input parameters and modeled results given in Tables S13 and S14.

Fig. 9 $\delta^{65}\text{Cu}$ versus cumulate solidus temperature (a) and $\delta^{65}\text{Cu}$ versus cumulate Ni contents (b). Inset in panel (b) shows the correlation between cumulate solidus temperature and Ni contents.

Fig. 10 Cu isotopic variations and fractionations in oceanic lithosphere. (a) Cartoon illustrating the Cu isotopic fractionation in a typical slow-spreading oceanic lithosphere with the development of detachment fault. The inset shows the schematic illustration of the resorption, remobilization and reprecipitation of sulfides driven by reactive porous melt flow [modified after Zou et al. (2024)]. (b) Cu isotopic variations in upper

and lower oceanic crust, and oceanic mantle lithosphere. (c) Cu isotopic compositions of cumulates during cumulus stage are inferred to be uniform and BSE-like. (d) Large Cu isotope fractionation in cumulates were driven by the sulfide dissolution, remobilization, and reprecipitation during the post-cumulus stage. Equilibrium melt MgO/FeO_T in panels (c-d) were calculated based on Cpx-melt Fe-Mg equilibration (Bédard, 2010). In panel (c), the original $\delta^{65}\text{Cu}$ in Kane cumulates during their cumulus stage are assumed to be BSE-like. See Fig. 1 for the literature data sources.

Fig. 11 (a) Whole-rock Cu contents versus the calculated liquidus temperatures for MORBs and Kane cumulates. Liquidus temperatures for Kane cumulates were calculated based on Cpx-melt Fe-Mg equilibration (Bédard, 2010). For global MOR cumulates, liquidus temperatures for the samples with Mg# of 80-90, 75-80, and 70-75 was calculated assuming cumulate-melt Fe-Mg exchange coefficient of 0.30 (Ol-dominant), 0.24 (high-Mg# Cpx-dominant), and 0.20 (low-Mg# Cpx-dominant), respectively (Bédard, 2010; Roeder and Emslie, 1970). For global cumulates, those with Mg#<70 are excluded, due to the variable accumulation of Fe-Ti oxides that might cause underestimation of liquidus temperatures. (b) $\delta^{65}\text{Cu}$ versus Cu contents in Kane cumulates compared with modeling results of post-cumulus melt-rock interactions with variable $\alpha_{\text{sulfide-melt}}$ (0.9998, 0.9994, and 0.9990) and initial cumulate Cu contents (60, 100, 140 ppm). The equilibrium cumulates of Kane MORBs along the same liquidus line are calculated assuming Cu partition coefficient of 1.5 (Sun et al., 2023) and limited Cu isotopic fractionation during the cumulus stage (i.e., $\Delta^{65}\text{Cu}_{\text{sulfide-melt}} \approx 0$). Global MORBs are from the new compiled dataset of Yang et al. (2021). See Fig. 4 for the data sources of the MORB cumulates and primitive MORB.

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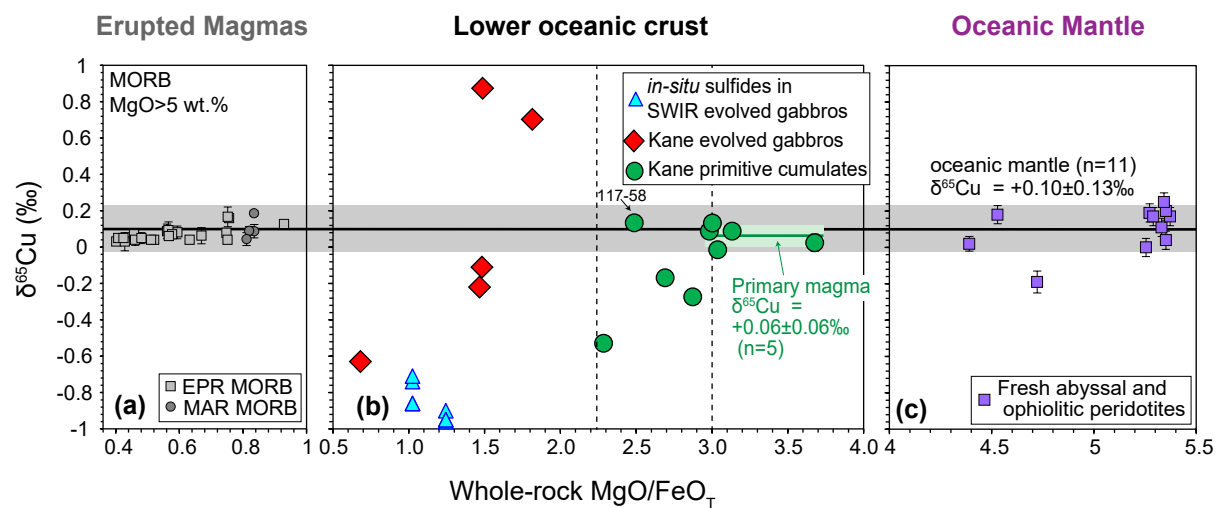


Figure. 1 Zhang et al. 2024

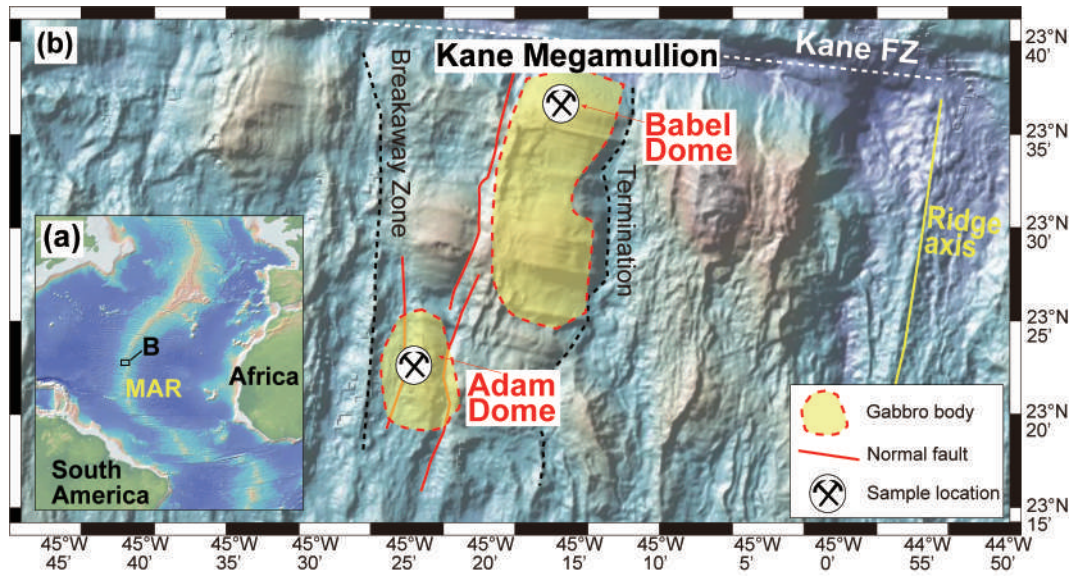


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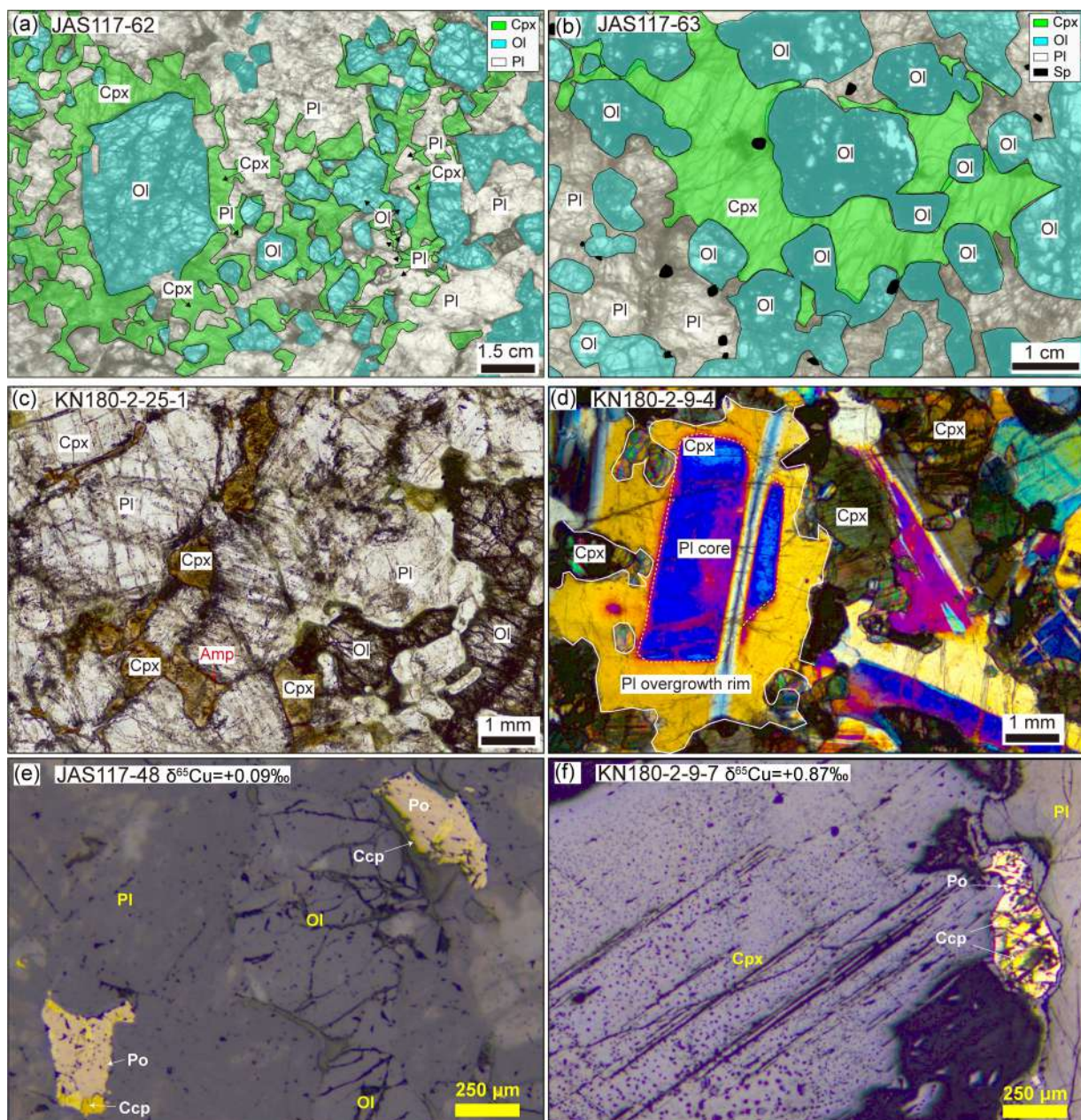


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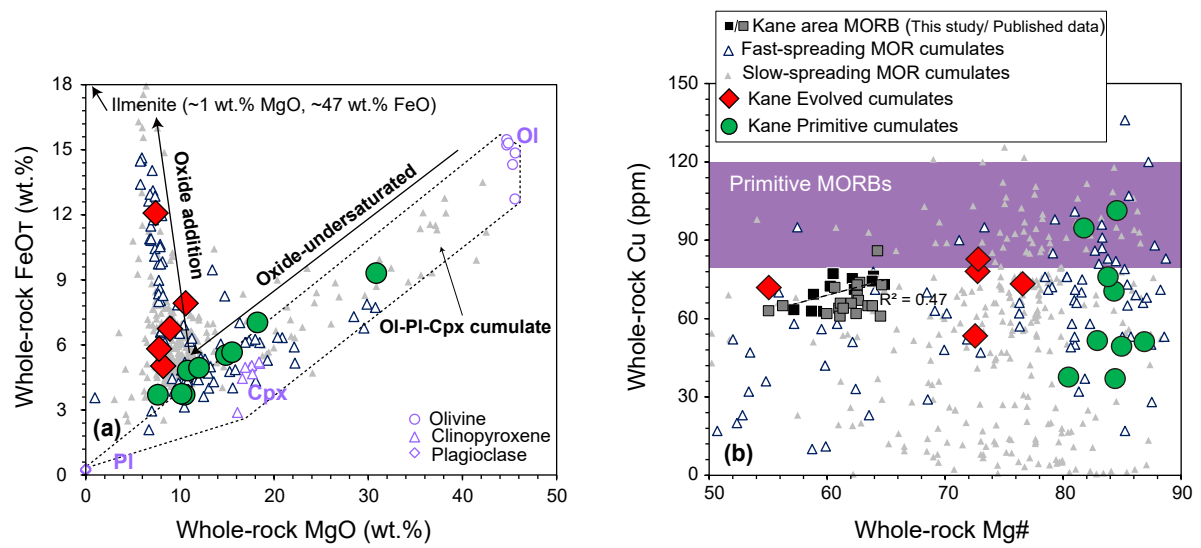


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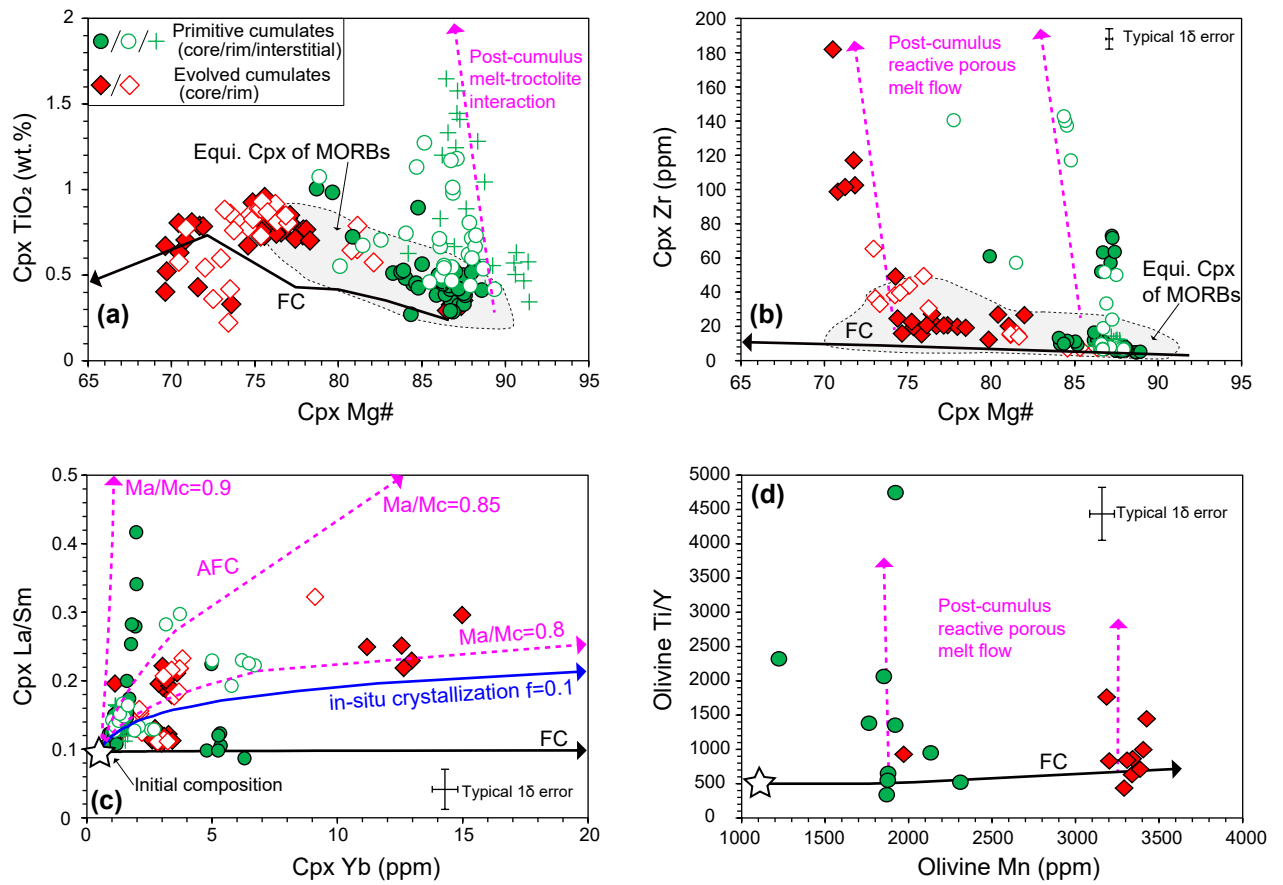


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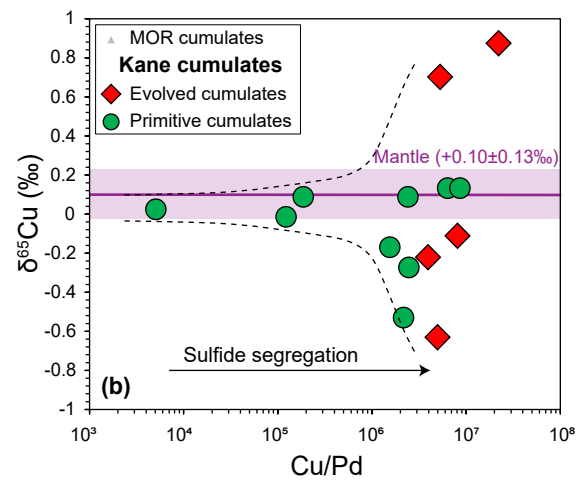
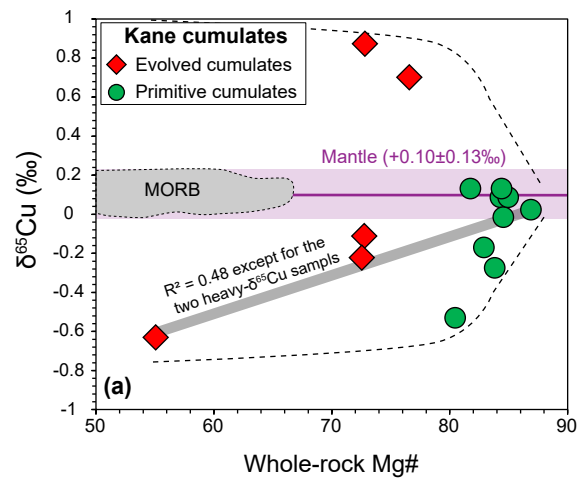


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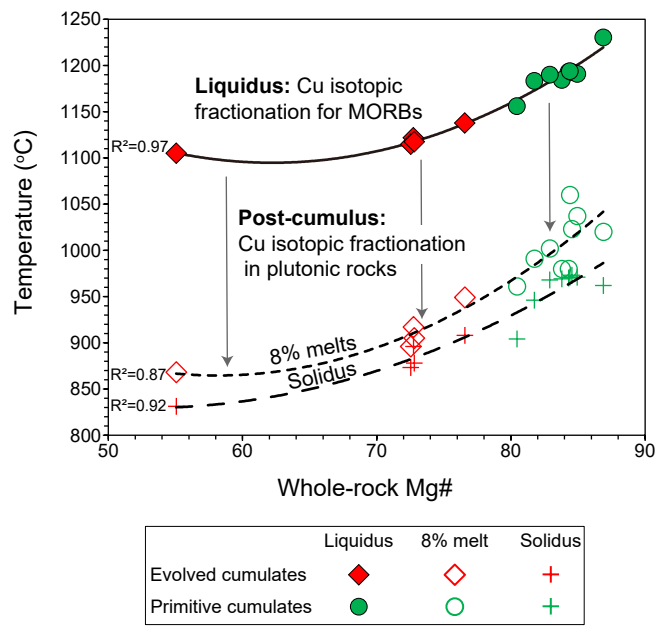


Figure. 7 Zhang et al. 2024

Cu isotopic fractionation along MORB liquidus line (adjust $\alpha_{\text{sulfide-melt}}$ to fit the cumulate trend)

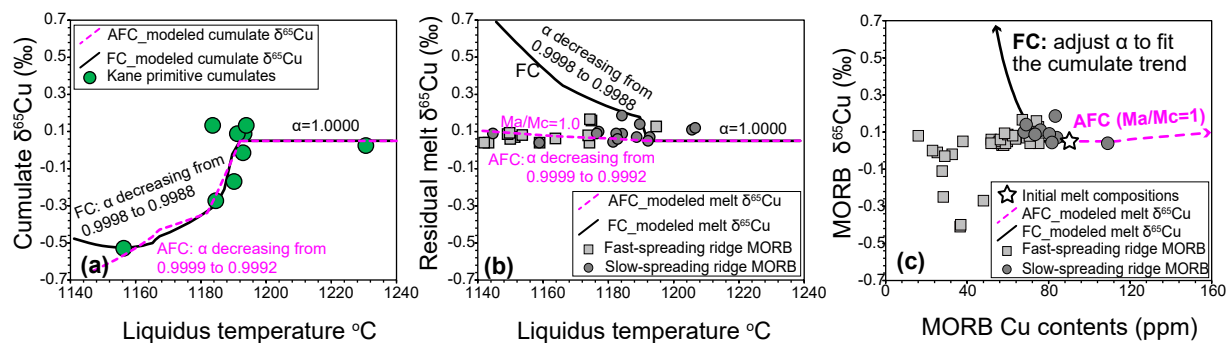


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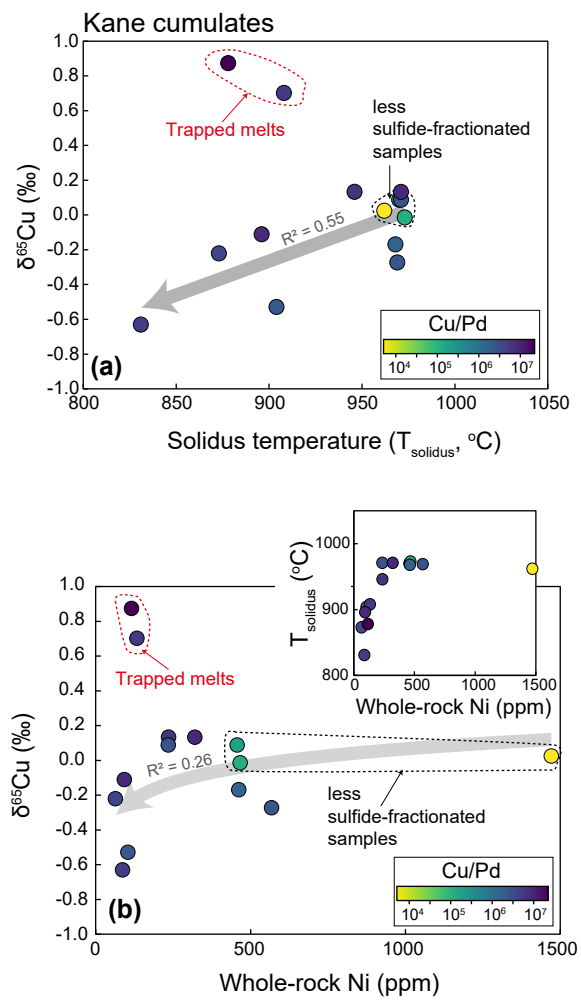


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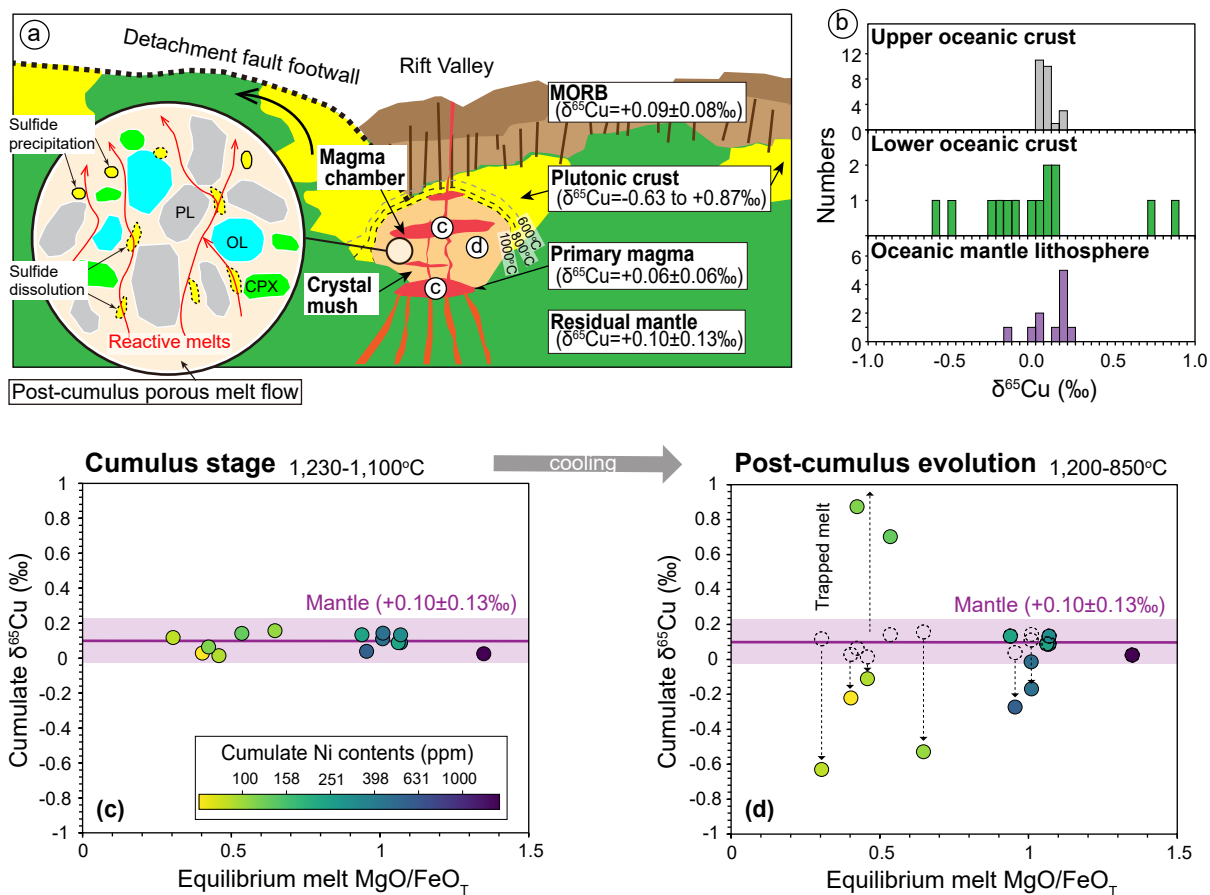


Figure. 10 Zhang et al. 2024

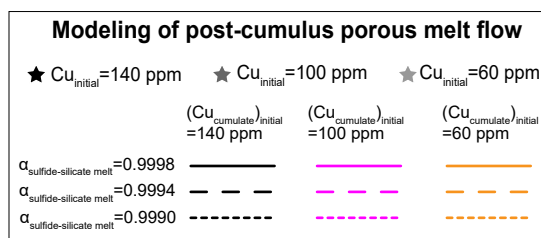
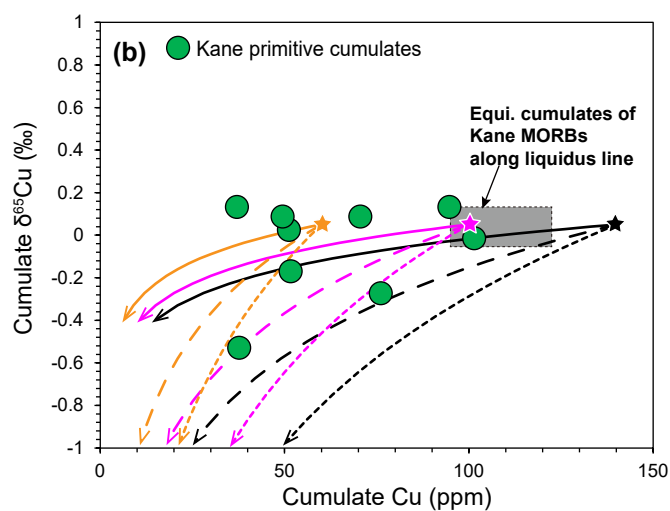
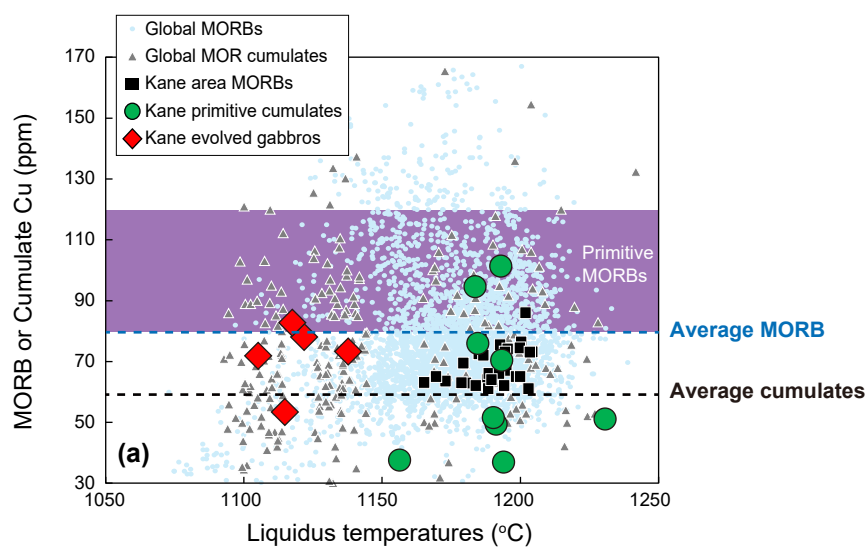


Figure. 11 Zhang et al. 2024

Table 1 Summary of the essential petrological, geochemical, Cu isotopic, and thermodynamic data for Kane cumulates, 23°N Mid-Atlantic Ridge.

Sample	Rock Type	Group ^a	Mineral modes vol.%				Mg# mol%	Cu ppm	Cu/Pd×10 ³	$\delta^{65}\text{Cu}^b$ ‰	2SD	$T_{\text{liquidus}}(^{\circ}\text{C})^c$	GeoPS model at 1 kbar ^d		Ol ^e Fo	Pl ^e An%	Cpx ^e Mg#
			Ol	Pl	Cpx	Ox							$T_{\text{solidus}}(^{\circ}\text{C})$	$T_{8\% \text{ melt}}(^{\circ}\text{C})$			
JAS117-48	Cpx-rich troctolite	primitive	24	66	10	0.0	84	70	185	0.09	0.02	1193	970	980	85	73	87
JAS117-58	Ol gabbro	primitive	10	60	30	0.0	82	95	6355	0.13	0.02	1184	946	991	80	65	86
JAS117-59	Troctolite	primitive	31	60	9	0.0	84	76	2454	-0.27	0.03	1185	969	980	84	75	86
JAS117-60	Troctolite	primitive	58	33	9	0.0	87	51	5	0.02	0.05	1231	962	1020	87	76	91
JAS117-62	Ol gabbro	primitive	20	54	26	0.0	85	101	122	-0.01	0.02	1193	973	1023	84	70	86
JAS117-63	Ol gabbro	primitive	10	64	27	0.0	85	49	2404	0.09	0.01	1191	971	1037	84	72	87
JAS117-64	Ol gabbro	primitive	12	73	15	0.0	84	37	8597	0.13	0.02	1194	971	1060	85	77	86
KN180-2-25-1	Troctolite	primitive	21	75	4	0.0	83	52	1545	-0.17	0.03	1190	968	1002	85	80	87
KN180-2-9-3	Ol gabbro	primitive	6	67	26	0.0	80	38	2156	-0.53	0.01	1156	904	961		61	82
JAS117-47	Ol gabbro	evolved	6	65	29	0.1	77	73	5297	0.70	0.03	1138	908	949	74	67	81
KN180-2-9-1	Ox-bearing gabbro	evolved	0	66	30	4.0	55	72	4977	-0.63	0.00	1105	831	868		48	71
KN180-2-9-4	Gabbro	evolved	2	73	24	0.5	73	78	8111	-0.11	0.03	1122	896	917	70	55	77
KN180-2-9-6	Gabbro	evolved	0	60	39	1.0	73	53	3931	-0.22	0.02	1115	873	896		53	75
KN180-2-9-7	Ol gabbro	evolved	9	53	37	0.8	73	83	22127	0.87	0.03	1118	878	905	69	54	76

^a: The two groups of Kane cumulates are divided based on their whole-rock $\text{Fe}_2\text{O}_3^{\text{T}}\text{-MgO}$ correlations. ^b: $\delta^{65}\text{Cu}=[(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}/(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST SRM 976-1}}] \times 1000\text{‰}$.

^c: Liquidus temperatures for the parental magmas of Kane cumulates were calculated based on clinopyroxene-melt Fe-Mg equilibrium. ^d: Solidus temperatures and the temperatures at which 8 vol.% intercumulus melts are present were calculated based on the thermodynamic calculations using GeoPS software and assuming a pressure of 1 kbar. ^e: All mineral data are shown in the sample-averaged values. Ol=olivine, Pl=plagioclase, Cpx=clinopyroxene, and Ox=Fe-Ti oxide.