

# Crustal Growth Identified by High- $\delta^{18}\text{O}$ Zircon and Olivine: A Perspective from Ultramafic Arc Cumulates in Southern Tibet

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## Abstract

In recent studies of crustal growth using global zircon Hf–O isotopic datasets, high- $\delta^{18}\text{O}$  zircons are typically attributed to intra-crustal reworking during which very little juvenile mantle-derived magmas were added to the crust. Although arc magmas may originate from a high- $\delta^{18}\text{O}$  mantle wedge, it has been difficult to decipher the contribution of high- $\delta^{18}\text{O}$  mantle to zircon-saturated felsic magma due to superimposed intra-crustal processes. We address this issue by combining the data from high- $\delta^{18}\text{O}$  zircon-bearing ultramafic cumulates and coeval lavas from a Cretaceous magmatic arc in southern Tibet. The cumulates mainly consist of different proportions of cumulus olivine and intercumulus amphibole. Amphibole analyses show a transition from increasing to decreasing Zr with increasing  $\text{SiO}_2$  (50–74 wt.%) contents in the intercumulus melts, indicating zircon saturation in late-stage interstitial melts. The  $\epsilon\text{Nd}(t)$  values ( $2.4 \pm 1.4$ ) of the apatite grains crystallized before and after zircon remain almost constant. Interstitial zircons have  $\delta^{18}\text{O}$  (6.1–7.2‰) values similar to the earliest crystallized olivine ( $\delta^{18}\text{O} = 6.3\text{--}7.1\text{‰}$ ) in the cumulates. The coeval lavas may represent the intercumulus melts extracted from amphibole-rich cumulates at different depths. Both the lavas and cumulates were ultimately derived from high- $\delta^{18}\text{O}$  arc mantle modified by small amounts (<12%) of subducted sediments, and crystallized zircon during intra-crustal magma evolution without involving crustal contamination or melting. These high- $\delta^{18}\text{O}$  zircons therefore are not products of crustal reworking, but record crustal growth during their crystallization ( $110 \pm 2$  Ma). Our study shows that the combination of zircon and olivine oxygen isotopes for ultramafic to felsic rocks is more effective than zircon data alone in evaluating the role of crustal growth vs. reworking in an arc system. The implication is that global zircon-based crustal evolution models that attribute all high- $\delta^{18}\text{O}$  zircons to crustal reworking may conceal recent crustal growth.

**Keywords:** crustal growth, zircon, olivine, oxygen isotope, Tibet

## INTRODUCTION

The mechanisms and rates governing the formation of Earth's continental crust are a fundamental topic in Earth sciences (e.g. Armstrong, 1981; Rudnick, 1995; Hawkesworth *et al.*, 2010; Arndt, 2013). Answering this question requires knowledge of the balance between crustal growth and reworking throughout Earth's history (e.g. Kemp *et al.*, 2006; Dhuime *et al.*, 2012; Roberts & Spencer, 2015). Crustal growth involves the addition of mantle-derived magmas to the crust, whereas crustal reworking is the remobilization of pre-existing crust by melting and/or erosion and sedimentation (Hawkesworth *et al.*, 2010). Individual magmatic events may involve crustal growth, reworking, or a combination of the two processes. Due to crustal reworking, the original ages (e.g. before 2.5 Ga) of ancient crustal formation have only rarely been preserved, and as a result present-day surface ages are expected to be biased to younger ages.

Our understanding of the evolution of the continental crust has been enhanced by U–Pb, Hf and O isotopic analyses in zircon. Hafnium isotopes in zircon are used to date the time since the crustal source(s) of the zircon-hosting magma were extracted from a mantle reservoir, commonly referred to as the model or crustal residence age (McCulloch & Wasserburg, 1978; DePaolo, 1981). However, if zircon crystallized from a magma with mixed source rocks, the model age is a meaningless hybrid age that does not represent true periods of crustal growth (Arndt & Goldstein, 1987). The most common mixed sources are sedimentary rocks that have experienced low-temperature water-rock reaction and typically have elevated  $\delta^{18}\text{O}$  (ca. 7–35‰; Bindeman, 2008). Thus, O isotopes in zircon are widely used to distinguish model ages of crust formation from hybrid ages (e.g. Hawkesworth & Kemp, 2006; Dhuime *et al.*, 2012; Iizuka *et al.*, 2013). These studies rely on two assumptions: (1) zircons crystallized from mantle-derived

magmas have a narrow range of  $\delta^{18}\text{O}$  ( $5.3 \pm 0.6\%$ , 2SD; Valley *et al.*, 1998) and record true periods of crustal growth; (2) high- $\delta^{18}\text{O}$  ( $>5.9\%$ ) zircons record periods dominated by the reworking of supracrustal rocks.

These assumptions have recently been questioned (Dan *et al.*, 2015; Roberts & Spencer, 2015; Couzinié *et al.*, 2016; Payne *et al.*, 2016; Cornet *et al.*, 2022). Mass balance calculations indicate that at least 80% of the continental crust was generated at subduction zones (Rudnick, 1995). However, the mantle source of arc magmas can be enriched in  $^{18}\text{O}$  by reaction with high- $\delta^{18}\text{O}$  fluids or melts derived from subducting slabs (including the hydrated oceanic crust and sediments) over millions of years (Dorendorf *et al.*, 2000; Bindeman *et al.*, 2005; Auer *et al.*, 2009; Johnson *et al.*, 2009; Martin *et al.*, 2011). This means that the high- $\delta^{18}\text{O}$  signature of zircons may result from source contamination of the mantle wedge by slab-derived material, crustal contamination of mantle-derived magmas, or simple remelting of supracrustal rocks. High- $\delta^{18}\text{O}$  zircons formed by the first mechanism could be incorrectly attributed to crustal reworking based on the interpretation of Hf–O isotopes in detrital zircons on a global scale (e.g. Couzinié *et al.*, 2016; Cornet *et al.*, 2022). Elucidating the mechanism of high- $\delta^{18}\text{O}$  zircon formation is therefore essential for identifying whether its parent magma contributed to crustal growth during its crystallization.

Felsic magmatic rocks (e.g. granitoids), as the main host rock for zircon, can be produced during crustal reworking (i.e. remelting of older crustal lithologies) or growth (i.e. differentiation of mantle-derived magmas; Moyen *et al.*, 2017). Mantle source compositions can be difficult to identify in crustal magmatic systems that have undergone magma differentiation and so it can be difficult to determine if mantle-derived magmas play a key role in the formation of high- $\delta^{18}\text{O}$  zircons.

In this paper we present detailed geochronological, mineralogical and geochemical data from high- $\delta^{18}\text{O}$  zircon-bearing ultramafic cumulates from a Cretaceous magmatic arc in southern Tibet that have enabled us to see through crustal processes. We combine zircon, olivine and apatite multi-isotope data from cumulates, with data from coeval lavas. These data have enabled us to decipher the contribution of crustal contamination to high- $\delta^{18}\text{O}$  zircon saturation, evaluate the role of crustal growth vs. reworking during this Cretaceous magmatic episode, and tentatively explore the potential biases introduced by zircon Hf–O isotopes in global zircon-based crustal evolution models.

## GEOLOGICAL SETTING AND PETROGRAPHY

The Lhasa Terrane in the southern Tibetan Plateau is separated from the Qiantang Terrane by the Bangong–Nujiang suture to the north and from the Himalaya Terrane by the Indus–Yarlung Zangbo suture to the south. The Lhasa terrane can be divided into southern, central, and northern subterrane by the Luobadui–Milashan fault and Shiquan River–Nam Tso mélangé, respectively (Fig. 1a). Sedimentary cover in the northern Lhasa subterrane consists of Triassic–Cretaceous strata and exposures are dominated by extensive Lower Cretaceous volcano-sedimentary sequences of the Duoni and Qushenla formations, and coeval plutons (Fig. 1b). Zircon Hf isotopic mapping (Zhu *et al.*, 2011; Hou *et al.*, 2015; Lu *et al.*, 2017) has revealed that the western segment (west of E88°) of the northern Lhasa subterrane is a juvenile Phanerozoic crustal block (Fig. 1a) with high  $\epsilon_{\text{Hf}}$  values (up to +15) and young Hf model ages (as young as 200 Ma). The Yanhu area is located at the heart of this juvenile crustal block and magmatism around Yanhu occurred from 131 to 110 Ma. This

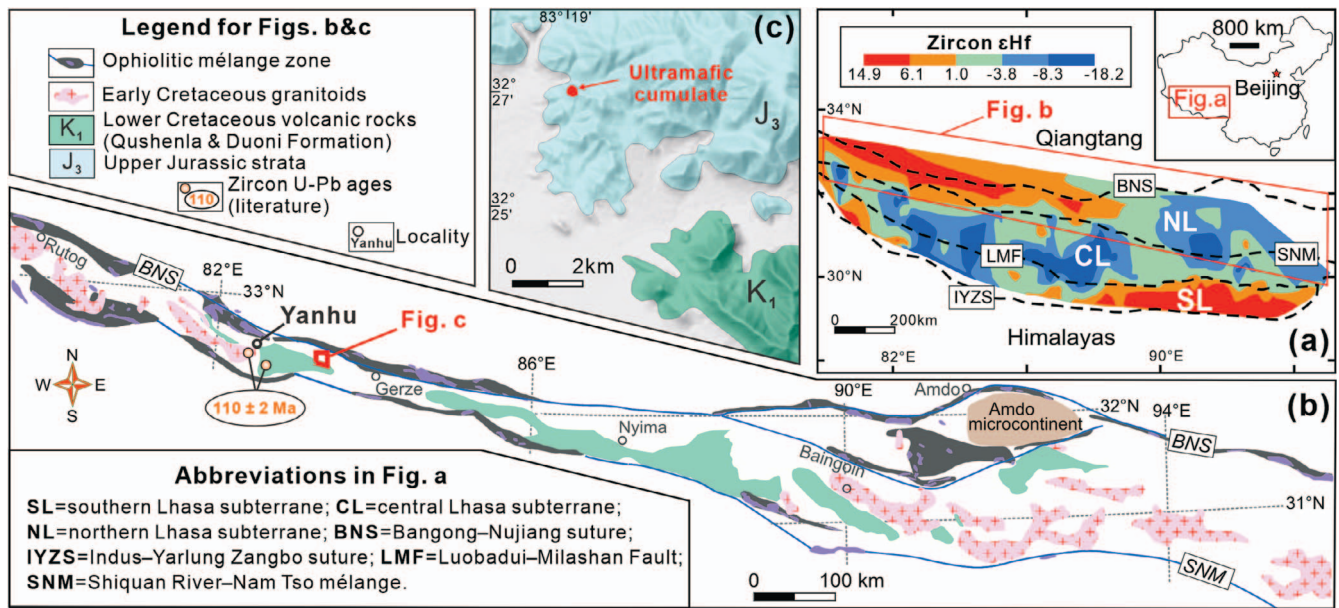
magmatism has been attributed to rollback and breakoff of the south dipping Bangong–Nujiang Tethyan slab (Hao *et al.*, 2016; Li *et al.*, 2018) or northward subduction of the Indus–Yarlung Zangbo Tethyan slab at a low angle (Zeng *et al.*, 2020). Multidisciplinary studies of magmatic rocks, paleomagnetism, and sedimentology show that the western segment of the Bangong–Nujiang Tethyan Ocean closed later ( $<110$  Ma) than its eastern–middle segments (Hu *et al.*, 2022, and references therein). Therefore, it is likely that the Early Cretaceous magmatism around Yanhu was related to oceanic subduction, although questions remain as to which of two opposite-dipping slabs played a dominant role.

The Yanhu ultramafic pluton ( $\sim 0.05$  km<sup>2</sup>; Fig. 1c) intrudes Upper Jurassic strata comprising metamorphosed volcanic rocks intercalated with sandstones (Supplementary Fig. S1). It has an orthocumulate texture, consisting of 35–60 vol.% olivine, 25–55 vol.% amphibole, 5–10 vol.% orthopyroxene,  $<5$  vol.% clinopyroxene (Table S1), and trace amounts of phlogopite, spinel, apatite, and zircon (Fig. 2). Nine samples (Latitude: 32°27′03″N; Longitude: 83°18′59″E) were collected that contained variable proportions of olivine and amphibole. Four samples are olivine hornblende containing more amphibole than olivine; the other samples are hornblende peridotite (Table S1). The main cumulus phase is olivine (Fig. 2a,b), which contains spinel inclusions and is partially altered to serpentine. The intercumulus space is filled with amphibole and orthopyroxene (Fig. 2a,b). Numerous spatially separated, but optically continuous amphibole grains form large oikocrysts that poikilitically enclose smaller grains of olivine and clinopyroxene (Fig. 2a–c). Orthopyroxene also contains olivine inclusions (Fig. 2d), but clinopyroxene inclusions are not observed in orthopyroxene. Olivine and clinopyroxene inclusions are characterized by rounded and irregular shapes or embayed rims (Fig. 2a–d). These disequilibrium textural characteristics indicate that the amphibole and orthopyroxene grew at the expense of olivine and clinopyroxene. Some amphibole crystals have wide, brown cores with narrow, green rims (Fig. 2a,b). Scarce green amphibole ( $<5$  vol.%) can also be found as larger grains between olivine and brown amphibole (Fig. 2c). Two zircon grains are observed in interstitial phlogopite (Fig. 2e). Apatite can coexist with clinopyroxene and can occur both as early-crystallized inclusions within large amphibole oikocrysts (Fig. 2f), and as a late interstitial phase between the intercumulus orthopyroxene and amphibole (Fig. 2g), indicating a wide range of crystallization temperatures.

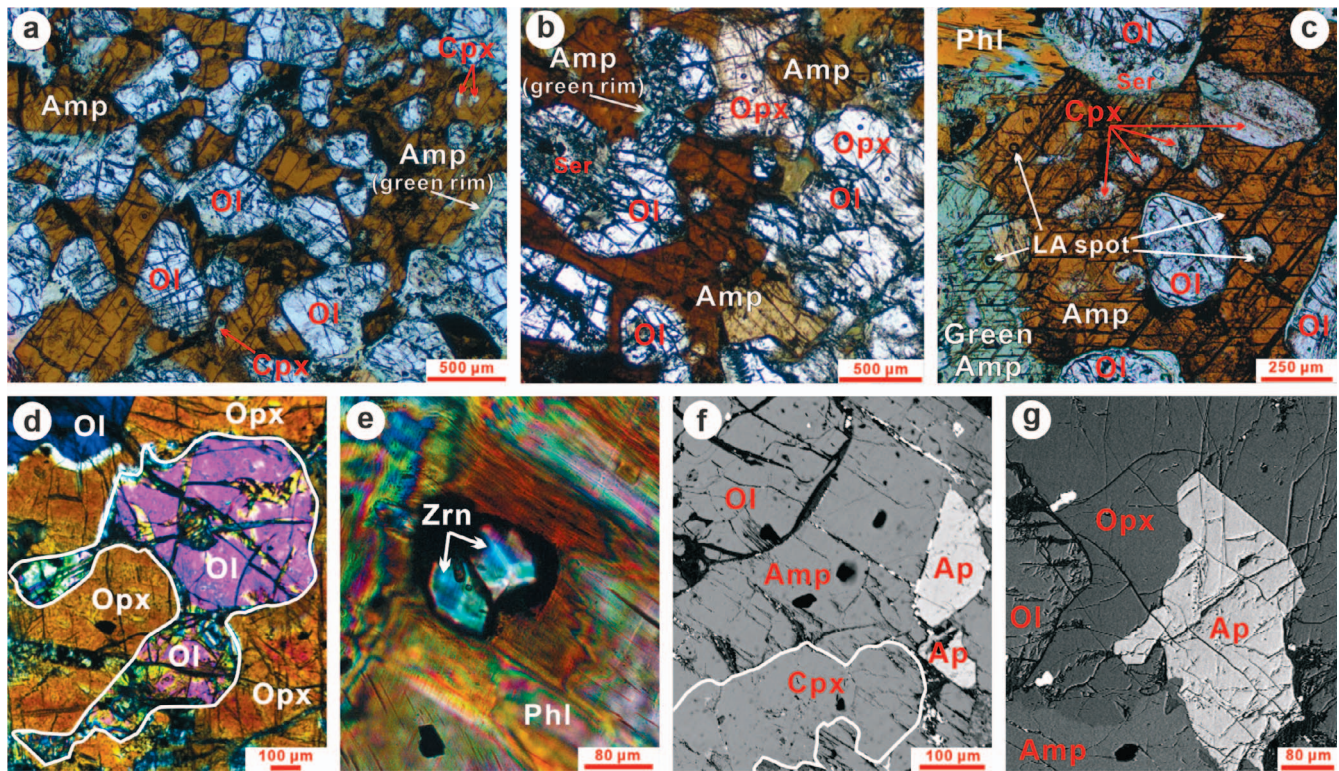
## ANALYTICAL METHODS

### Zircon U–Pb, Hf and O isotopes

Zircons were separated using conventional heavy liquid and magnetic separation techniques (Li & Tan, 1998), and then were mounted in epoxy and polished. To characterize zircon internal structures and choose target sites for isotopic analyses, cathodoluminescence (CL) images were obtained using a Carl Zeiss Field Emission Scanning Electron Microscope + Gatan MonnCL4. U–Th–Pb isotopic analyses were conducted using a Cameca IMS-1280-HR Secondary Ion Mass Spectrometer (SIMS). The analytical procedures were the same as those described by Li *et al.* (2009). The  $\text{O}_2^-$  primary ion beam with an intensity of  $\sim 10$  nA was accelerated at  $-13$  kV, and the ellipsoidal spot was about  $20 \times 30$   $\mu\text{m}$  in size. U–Th–Pb ratios were determined relative to the  $\sim 337$  Ma standard zircon Plešovice (Sláma *et al.*, 2008). A second zircon standard (Qinghu; Li *et al.*, 2013) was alternately analyzed as an unknown together with other unknown zircons. Nine analyses of the Qinghu zircon yielded a concordia age of



**Fig. 1.** (a) Contour map of zircon  $\epsilon Hf$  values for the Mesozoic-Cenozoic granitoid rocks and felsic volcanic rocks in the Lhasa terrane (modified from Lu *et al.* (2017)). (b) Simplified geological map showing the spatial distributions of Early Cretaceous magmatism in the northern Lhasa subterrane (Li *et al.*, 2018). Ages for ca. 110 Ma magmatic rocks in the Yanhu area are from Zhu *et al.* (2011) and Sui *et al.* (2013). (c) Geological map showing the location of Yanhu ultramafic cumulates.



**Fig. 2.** Photomicrographs of the Yanhu cumulates. (a–c) Spatially separated but optically continuous amphibole grains enclosing olivine and clinopyroxene of rounded and irregular shapes. (d) An intercumulus orthopyroxene with olivine inclusions. (e) Two zircon grains in phlogopite. (f) Olivine, clinopyroxene, and apatite as inclusions in a large amphibole oikocryst. (g) Apatite as a late interstitial phase between orthopyroxene and amphibole. The olivine (d) and clinopyroxene (f) inclusions have embayed rims that are outlined by the white line. Note that (a–c) and (d–e) were under plane- and cross-polarized light, respectively, and (f–g) are BSE images. Amp, amphibole; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Phl, phlogopite; Ap, apatite; Zrn, zircon; and Ser, serpentine.

$159.2 \pm 1.6$  Ma, which is within error of the recommended value of  $159.5 \pm 0.2$  Ma (Li *et al.*, 2013). The weighted-mean U–Pb ages and concordia plots were processed using Isoplot v. 3.0 (Ludwig, 2003).

Zircon oxygen isotopes were measured using the same Cameca IMS-1280-HR SIMS. The detailed analytical procedures were similar to those described by Li *et al.* (2010). The  $Cs^+$  primary ion beam was accelerated at 10 kV, with an intensity of ca. 2 nA, and

rastered over a  $10 \times 10 \mu\text{m}$  area. The spot size was about  $20 \mu\text{m}$  in diameter. The measured oxygen isotopes were corrected for instrumental mass fractionation using the Penglai zircon standard ( $\delta^{18}\text{O}_{\text{VSMOW}} = 5.3\text{‰}$ ; Li *et al.*, 2010). The internal precision of all single analyses were better than  $0.28\text{‰}$  ( $2\sigma$ ; Table S3) for the  $^{18}\text{O}/^{16}\text{O}$  ratio. The external precision, measured by the reproducibility of repeated analyses of the Penglai standard, is  $0.22\text{‰}$  ( $1\sigma$ ;  $n = 15$ ). Eight measurements of the Qinghu zircon standard yielded a weighted-mean  $\delta^{18}\text{O}$  of  $5.3 \pm 0.3\text{‰}$  ( $2\sigma$ ), within error of the reported value of  $5.4 \pm 0.2\text{‰}$  (Li *et al.*, 2013).

Zircon Hf isotopic analyses were undertaken using a Neptune Plus MC-ICP-MS equipped with a RESOLUTION M-50193 nm laser ablation system (Resonetics), with a beam diameter of  $45 \mu\text{m}$ . Analytical procedures have been given by Wu *et al.* (2006). Analyses of the Plešovice zircon standard yielded a weighted mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282479 \pm 0.000013$  ( $1\sigma$ ;  $n = 15$ ), consistent with the certified value of  $0.282482 \pm 0.000013$  (2SD; Sláma *et al.*, 2008). Zircon Hf model ages ( $T_{\text{DM}}$ ) were calculated using the reference line for the Hf isotope evolution of the depleted mantle (DM; Griffin *et al.*, 2000) and assuming  $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$  for the source of magmas from which the zircon crystallized. Zircon U-Pb and Hf-O isotopic data are presented in Tables S2 and S3, respectively.

### Whole-rock geochemistry

The samples for whole-rock chemical analyses were crushed to coarse chips in a jaw crusher having corundum jaws and fresh pieces were hand-picked. The rock chips were rinsed twice with deionized water, dried, and then powdered to  $\sim 200$  mesh size in an agate mortar and pestle that was free from metal contamination. Samples were prepared as glass discs using a Rigaku desktop fusion machine, formed by mixing  $0.50 \text{ g}$  of rock powder with  $4.0 \text{ g}$  of lithium tetraborate for  $15 \text{ min}$  at  $1100^\circ\text{C}$  in  $95\% \text{Pt}-5\% \text{Au}$  crucibles. Major-element oxides were analyzed on fused glass beads using a Rigaku RIX 2000 X-ray fluorescence spectrometer following the procedures of Li *et al.* (2006). Interference-corrected spectra were converted to concentrations using a calibration curve consisting of 36 standard samples. Reproducibility, as gauged from the repeated analyses of two USGS reference materials (BHVO-2 and BCR-2), is better than  $4\%$  (RSD, relative standard deviation; Table S1). Trace elements, including rare earth elements (REE), were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), using a Perkin-Elmer ELAN 6000 instrument following the procedures described by Li *et al.* (2006). About  $40 \text{ mg}$  of each powdered sample was dissolved in a high-pressure Teflon bomb for 2 days at  $190^\circ\text{C}$  using  $\text{HF} + \text{HNO}_3 + \text{HClO}_4$  (1:1:0.2) mixtures. Analytical precision, measured by the reproducibility of repeated analyses of two USGS reference materials, is better than  $5\%$  (RSD; Table S1) for most elements. The remaining elements (Pb, Cs, Sc, and Ge) have the RSD values of  $5\text{--}10\%$ .

Neodymium isotopic compositions were determined on a Neptune Plus multicollector (MC) ICP-MS (Thermo Scientific), using the analytical procedures described by Li *et al.* (2006). Neodymium fractions were separated by passing through cation columns followed by HDEHP columns. Measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . Reference standard solutions (Shin Etsu JNdi-1) analyzed along with unknowns yielded  $^{146}\text{Nd}/^{144}\text{Nd}$  values of  $0.512121 \pm 0.000011$  (2SD;  $n = 11$ ). The basaltic standard BHVO-2 was used to monitor ion-exchange chromatographic purification processes, yielding  $^{143}\text{Nd}/^{144}\text{Nd}$  values of  $0.512989 \pm 0.000008$ , consistent within errors with the recommended values of  $0.512983 \pm 0.000010$  (Weis *et al.*, 2005). Whole-rock elemental and isotopic data of the samples and basaltic standard are listed in Table S1.

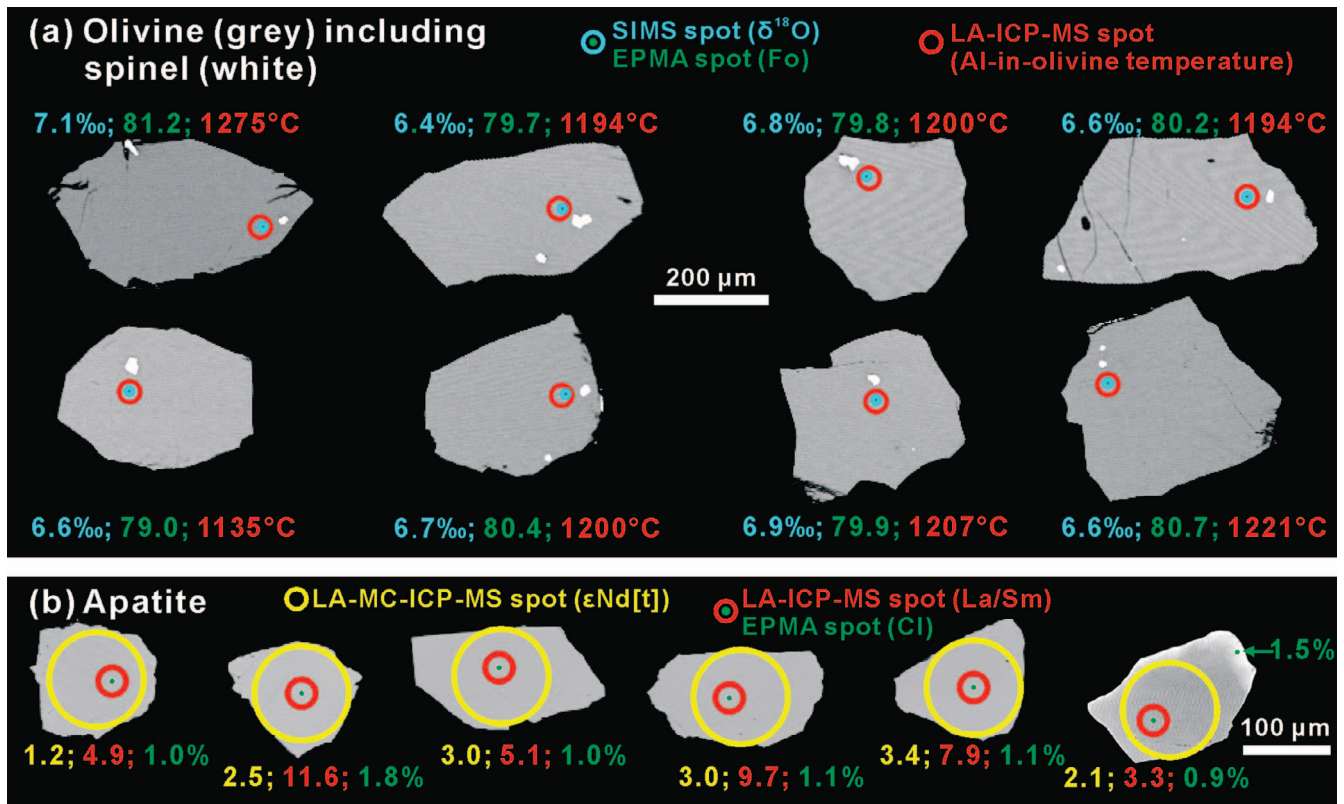
### Mineral major and trace elements

*In situ* major element analyses of apatite and olivine with spinel inclusions in epoxy, and amphibole and pyroxene in thin section were obtained using a JEOL JXA-8100 electron probe microanalyser (EPMA). The operating conditions were a  $15 \text{ kV}$  accelerating voltage, a  $20 \text{ nA}$  beam current, and a beam size of  $1\text{--}2 \mu\text{m}$ . The data reduction was carried out using ZAF correction (Huang *et al.*, 2010). If the analyzed olivine contains spinel, the EPMA spots of olivine are close to spinel inclusions to obtain olivine-spinel Al-exchange crystallization temperatures (Fig. 3a). Given the great uncertainty of the olivine Al content analyzed by EPMA, we only used the Al content of olivine near spinel inclusions measured by LA-ICP-MS to calculate equilibrium temperatures (Fig. 3a).

*In situ* mineral trace-element compositions were determined using an ELEMENT XR ICP-MS coupled with a RESOLUTION M-50193 nm laser ablation system. The laser was set up as follows: beam size,  $33 \mu\text{m}$ ; repetition rate,  $6 \text{ Hz}$ ; energy density,  $\sim 4 \text{ J cm}^{-2}$ . A smoothing device (The Squid, Laurin Technic) was used to smooth the sample signal. More details on the experiment procedure and data reduction strategy are described in detail by Zhang *et al.* (2019). Trace element concentrations were calibrated using multiple reference materials (BCR-2G, BHVO-2G, and GSD-1G) as external standards, and Ca and Si as the internal standard elements for apatite and silicate minerals, respectively. Laser spots were coincident with EPMA spots where possible, so that Ca and Si contents obtained using the EPMA could be used for internal standardization. Contamination from inclusions and fractures was monitored using several elements (e.g. Pb and REE). A reference glass TB-1G was measured as unknown samples. Repeat analyses ( $n = 24$ ; Table S12) of the TB-1G reference glass during this study indicated that precision and accuracy were better than  $10\%$  for the elements of interest. Mineral major- and trace-element compositions are reported in Tables S4–S10.

### Olivine oxygen isotopes

Olivine grains from two samples were mounted in epoxy and polished. The backscattered electron (BSE) images indicate that one (WQ09-1) of the samples contains sufficiently large olivine grains with few serpentinized fractures (Fig. 3a), which can be used for *in situ* analyses. Olivine was first analyzed by EPMA for major elements, then by SIMS for oxygen isotopes, and finally by LA-ICP-MS for Al contents. Laser ablation and SIMS spots were analyzed in the same location as EPMA spots (Fig. 3a). *In situ* oxygen isotopes were determined using a Cameca IMS-1280-HR SIMS. The beam size was about  $10\text{--}15 \mu\text{m}$ . The analytical procedures, instrument conditions, calibration and data reduction are the same as given in Yang *et al.* (2018). Five unknown and two standard (San Carlos and 06JY29)  $\delta^{18}\text{O}$  measurements were run in bracketed mode. Measured  $^{18}\text{O}/^{16}\text{O}$  was normalized using the Vienna Standard Mean Ocean Water composition (VSMOW,  $^{18}\text{O}/^{16}\text{O} = 0.0020052$ ). The measured oxygen isotopic data were corrected for instrumental mass fractionation (IMF) using the San Carlos olivine standard. The experience from the Cameca IMS 1270, 1280 and 1290 labs worldwide indicates that matrix effects resulting from variable Fo (molar  $100 \times \text{Mg}/[\text{Mg} + \text{Fe}]$ ) in olivine on the measured oxygen isotope ratios is not significant, provided that the olivine is characterized by Fo values ranging from 60 to 100 (e.g. Bindeman *et al.*, 2008; Isa *et al.*, 2017; Tang *et al.*, 2019). For example, Bindeman *et al.* (2008) observed a systematic difference of IMF for San Carlos (Fo = 90) and CI114 (Fo = 74) olivine of  $0.12\text{‰}$ , which equates to  $0.0075\text{‰}$  of IMF per each Fo number. Accordingly, a difference of IMF for the Yanhu olivine (Fo = 79–82) is less than  $0.1\text{‰}$ , which is negligible and within error of our



**Fig. 3.** Representative BSE images of olivine with spinel inclusions (a) and apatite (b) in the Yanhu cumulates. The EPMA, LA-ICP-MS, SIMS, and LA-MC-ICP-MS spots for major and trace elements and O and Nd isotopes are marked with circles of different colors, respectively, and representative results are shown near the grains.

measurements. To monitor the external uncertainties, a second olivine standard (06JY29; Fo = 91.2) was alternately analyzed as an unknown together with other unknown olivines. Measurements on 06JY29 olivine yielded a  $\delta^{18}\text{O}$  value of  $5.25 \pm 0.21\text{‰}$  ( $1\sigma$ ;  $n = 11$ ), which is within error of the recommended value of  $5.30 \pm 0.13\text{‰}$  (Tang et al., 2019). Olivine oxygen isotopic data are presented in Table S4.

### Apatite Nd isotopes

Apatite grains from olivine hornblende (WQ09-1) were mounted in epoxy and polished. The BSE images (Fig. 3b) were used to select large grains lacking micro-pores and mineral inclusions for chemical analyses. *In situ* apatite Nd isotope analysis was carried out on a Neptune Plus MC-ICP-MS, coupled with a RESOLUTION M-50193 nm laser ablation system. Apatite was first analyzed by EPMA for major elements, then by LA-ICP-MS for trace elements, and finally by LA-MC-ICP-MS for Nd isotopes. The laser spots were analyzed in the same spots as the EPMA (Fig. 3b). The laser parameters were set as beam diameter of 112  $\mu\text{m}$ , repetition rate of 7 Hz and energy density of  $\sim 4 \text{ J cm}^{-2}$ . The interference of  $^{144}\text{Sm}$  on  $^{144}\text{Nd}$  was calculated with the signal of  $^{147}\text{Sm}$  and the natural  $^{144}\text{Sm}/^{147}\text{Sm}$  ratio of 0.20504 (Wasserburg et al., 1981). The mass bias factor of Sm was calculated from the measured ratio of  $^{147}\text{Sm}/^{149}\text{Sm}$  and its accepted ratio of 1.08507 (Wasserburg et al., 1981). The mass bias of  $^{143}\text{Nd}/^{144}\text{Nd}$  was normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  with an exponential law. The detailed instrumental conditions and data reduction procedure have been reported in Zhang et al. (2021). Every five analyses of our apatite were followed by one analysis of Durango and McClure apatite standards. The nine analyses of Durango and McClure apatite during this study yielded  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of

$0.512485 \pm 0.000022$  ( $2\sigma$ ) and  $0.512262 \pm 0.000042$  ( $2\sigma$ ), which are, respectively, consistent within errors with the reported values of  $0.512493 \pm 0.000021$  and  $0.512282 \pm 0.000011$  (Yang et al., 2014). Apatite Nd isotopic data are given in Table S11.

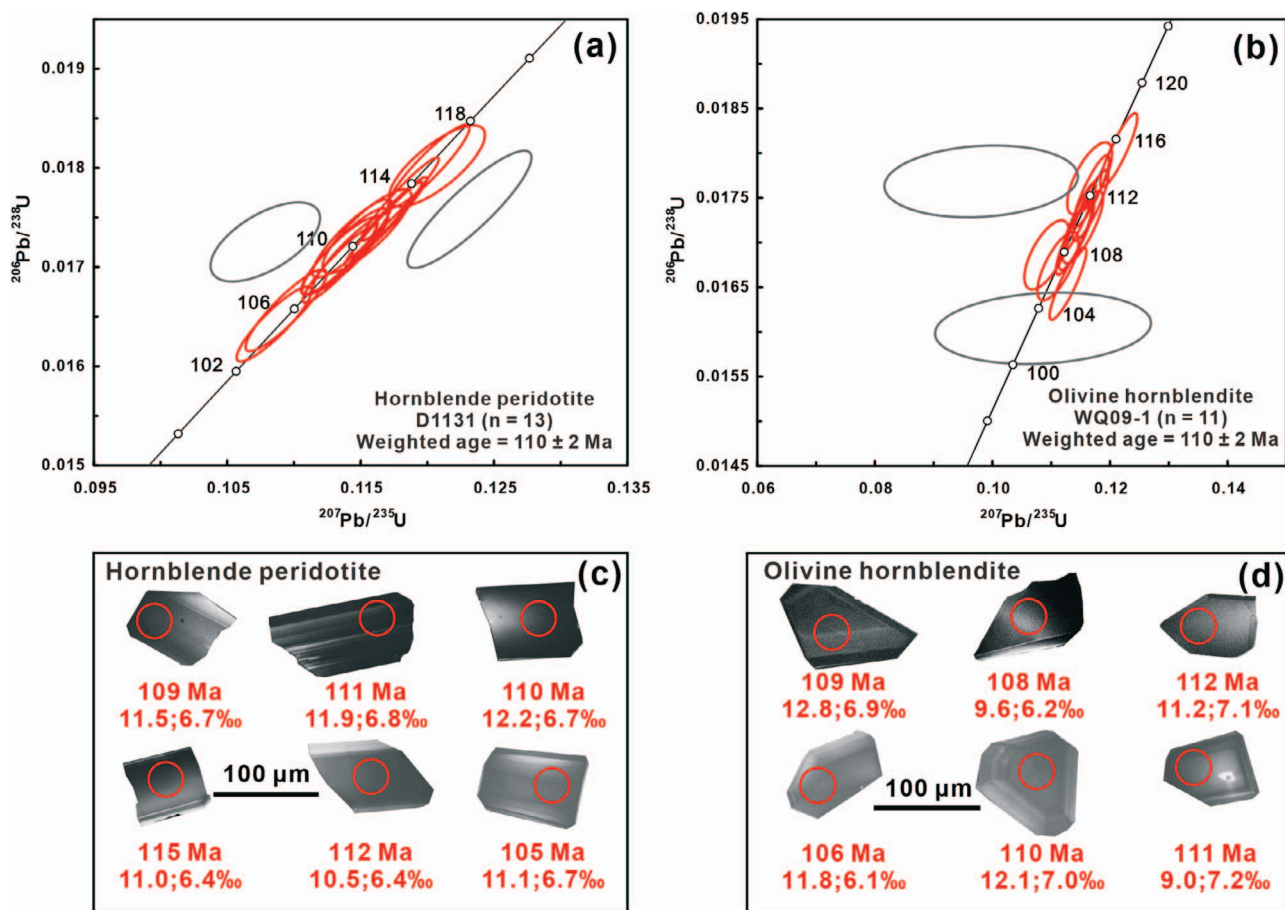
## RESULTS

Whole-rock elemental and Nd isotope, zircon U-Pb-Hf-O isotope, olivine O and apatite Nd isotope, and mineral major- and trace-element data for the Yanhu ultramafic cumulates are presented in the Supplementary Materials (Tables S1-S11). All analyses were carried out at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences in Guangzhou, China.

### Zircon U-Pb, O and Hf isotopic compositions

Zircon U-Pb concordia diagrams and representative CL images for the Yanhu cumulates are given in Fig. 4. Zircon CL images show no or broad-banded zoning in the core, and oscillatory zoning in the rim (Fig. 4c,d), comparable to those reported for zircons from oceanic gabbros (e.g. Grimes et al., 2009). Thirteen of fifteen spot analyses from hornblende peridotite (D1131) and eleven of thirteen spot analyses from olivine hornblende (WQ09-1) yielded weighted-mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $110 \pm 2$  ( $2\sigma$ ) Ma (Fig. 4 a,b), which are interpreted as the crystallization ages of the Yanhu cumulates. The remaining four analyses plot below or above the concordia curve, probably due to radiogenic Pb loss or high common Pb (Table S2), respectively.

Zircon O and Hf isotope analyses were conducted on the same grains that were analyzed for U-Pb dating. Zircon grains from hornblende peridotite (D1131) and olivine hornblende (WQ09-1) have indistinguishable  $\delta^{18}\text{O}$  values of 6.1–6.9‰ and 6.1–7.2‰,



**Fig. 4.** SIMS zircon U–Pb concordia diagram (a–b) with representative zircon CL images (c–d) for the Yanhu cumulates. The spots for chemical analyses are marked on the grains and the numbers below the grains are  $^{206}\text{Pb}/^{238}\text{U}$  ages at the top,  $\epsilon\text{Hf}(t)$  value at the bottom left and  $\delta^{18}\text{O}$  value at the bottom right. The data for spots with gray ellipses are excluded in the calculation of the weighted ages.

respectively (Fig. 5a). Therefore, zircon  $\delta^{18}\text{O}$  values ( $6.7 \pm 0.6\%$  (2SD)) of the Yanhu cumulates are higher than normal mantle zircon values of  $5.3 \pm 0.6\%$  (2SD; Valley *et al.*, 1998). Zircon  $\epsilon\text{Hf}(t)$  values of hornblende peridotite (D1131;  $\epsilon\text{Hf}(t) = 9.9$ – $13.3$ ) and olivine hornblende (WQ09-1;  $\epsilon\text{Hf}(t) = 9.0$ – $13.7$ ) also mostly overlap, with an average of  $11.5 \pm 2.2\%$  (2SD; Fig. 5a). Zircon Hf model ages vary from 291 to 596 Ma (Table S3).

### Whole-rock geochemistry

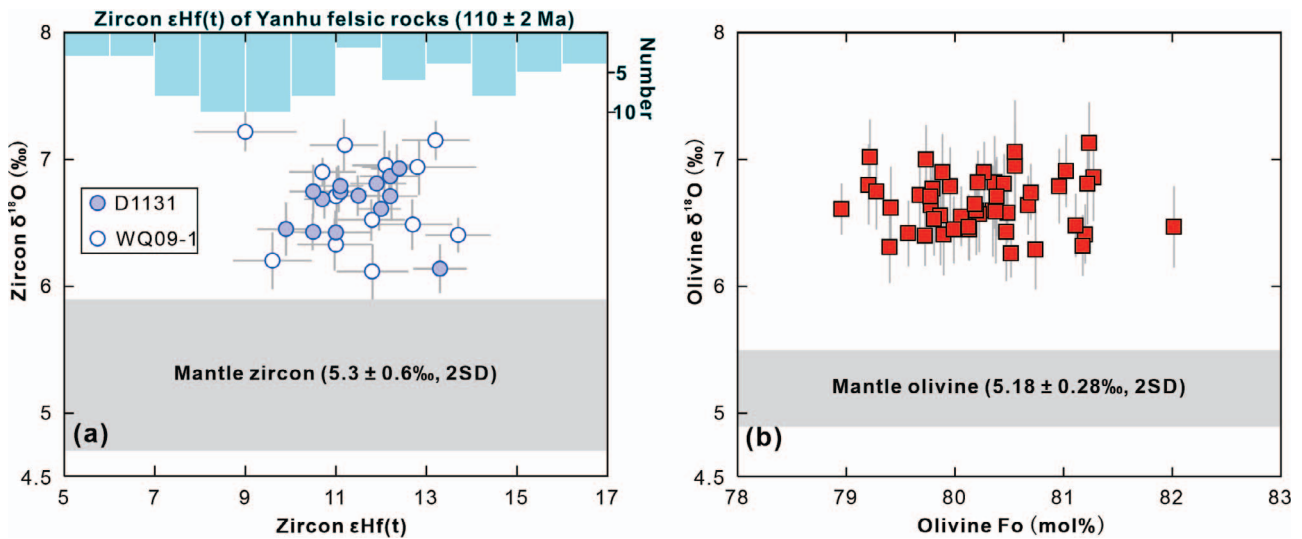
The  $110 \pm 2$  Ma Yanhu magmatic rocks include ultramafic cumulates from this study, and non-cumulate basalts, andesites, rhyolites, and diorites reported by Sui *et al.* (2013) (Fig. 6). The ultramafic cumulates have the highest MgO (27.6–32.8 wt.% on a volatile-free basis) and the lowest  $\text{SiO}_2$  (41.4–43.4 wt.%) contents of the Yanhu rocks (Fig. 6a). Within the ultramafic cumulates, olivine hornblendites have higher CaO (5.3–6.5 wt.%) contents than the hornblende peridotites (CaO = 2.5–3.7 wt.%; Table S1). The REE patterns of all Yanhu rocks show an enrichment in light REE (LREE) over middle REE (MREE) and heavy REE (HREE). The non-cumulate rocks display a gradual decrease in MREE (e.g. Dy) contents from mafic to felsic rocks and a MREE-depleted ‘trough-like’ pattern characterizes the rhyolites (Fig. 6b). All of the Yanhu rocks exhibit decreasing Dy/Yb ratios with increasing  $\text{SiO}_2$  contents (Fig. 6c) and La/Sm ratios (Fig. 6d). These differentiation trends are similar to those of some modern arc lavas, such as those from the Aleutian, Java, and Lesser Antilles arc (Fig. 6c; Davidson *et al.*, 2007). The Yanhu ultramafic cumulates

have homogeneous Nd isotopic compositions ( $\epsilon\text{Nd}(t) = 2.3$ – $3.5$ ; Table S1).

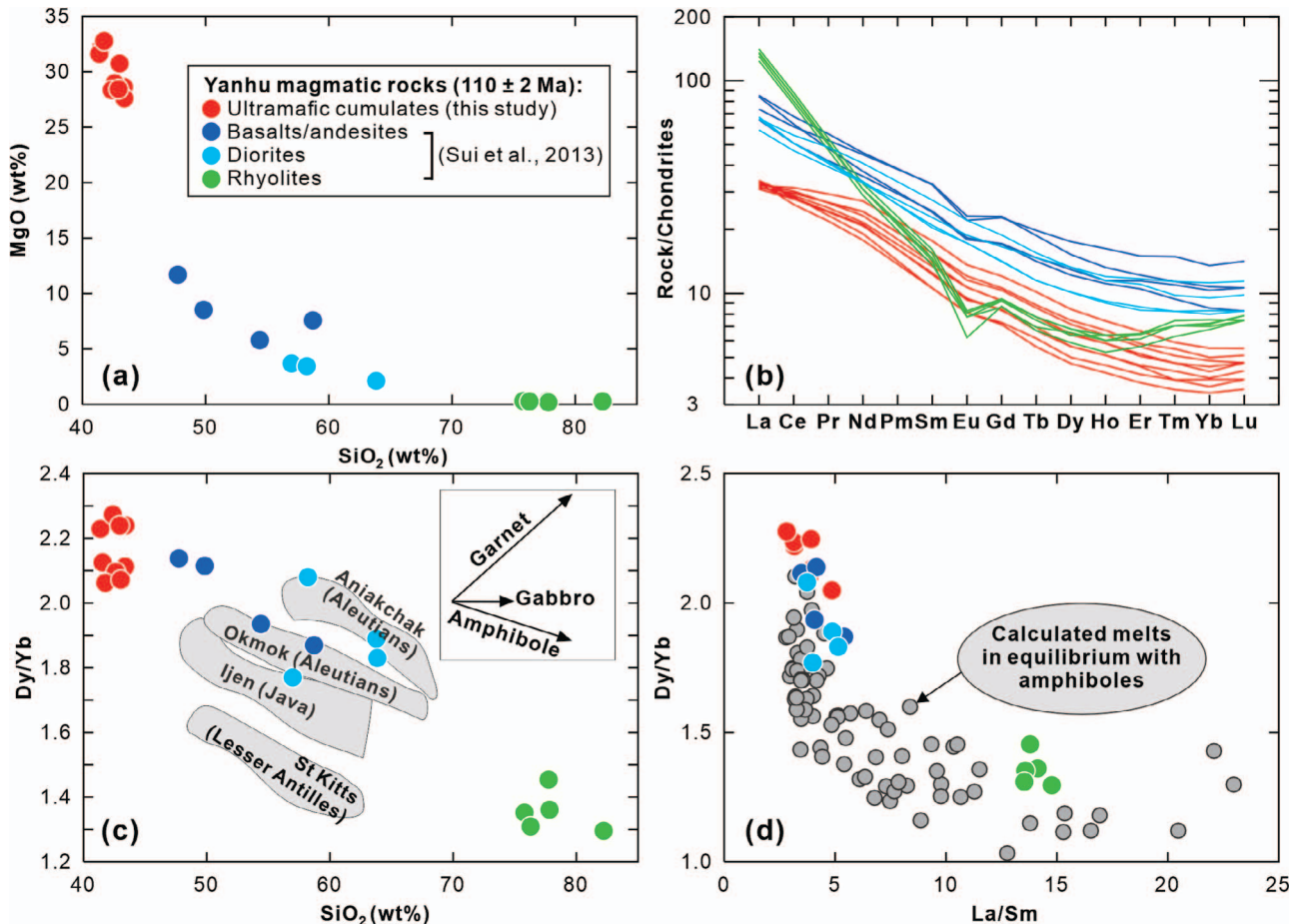
### Mineral geochemistry

Olivine in the ultramafic cumulates contains abundant spinel inclusions. No significant Fe–Mg chemical zoning is observed within individual olivine and spinel inclusions (Fig. 3a). Olivine has Fo values of 79–82 and CaO contents of 0.09–0.19 wt.% (Table S4). The Al content of olivine close to spinel inclusions, measured by LA–ICP–MS (Fig. 3a), ranges from 63 to 101  $\mu\text{g}/\text{g}$  (Table S4). Spinel has a relatively narrow range of Cr# (molar  $\text{Cr}/[\text{Cr} + \text{Al}]$ ) values of 0.60–0.67 (Table S5). Olivine has  $\delta^{18}\text{O}$  values varying from 6.3‰ to 7.1‰, with an average of  $6.7 \pm 0.4\%$  (2SD;  $n = 49$ ), which are higher than typical mantle olivine values of  $5.18 \pm 0.28\%$  (2SD; Matthey *et al.*, 1994; Fig. 5b).

The brown amphibole is pargasite with  $(\text{Na} + \text{K})^{\text{A}} > 0.5$  apfu (atoms per formula unit) and  $(\text{Al} + \text{Fe}^{3+} + 2\text{Ti})^{\text{C}} > 0.5$  apfu. Most of the green amphibole crystals are pargasites, but a small amount of them are edenites with  $(\text{Al} + \text{Fe}^{3+} + 2\text{Ti})^{\text{C}} < 0.5$  apfu (Hawthorne *et al.*, 2012; Table S6). The brown amphibole contains higher  $\text{TiO}_2$  (1.6–4.8 wt.%) and REE contents, but lower  $\text{SiO}_2$  (41.1–44.8 wt.%) contents than green amphibole ( $\text{TiO}_2 = 0.2$ – $1.1$  wt.%,  $\text{SiO}_2 = 47.4$ – $49.5$  wt.%) (Fig. 7a,b). Chondrite-normalized REE patterns of brown amphiboles are hump-shaped, with LREE (e.g. La) and HREE (e.g. Yb) depletion relative to MREE (e.g. Sm) (Fig. 7b). Furthermore, the brown amphiboles show a decrease in Dy/Yb with increasing



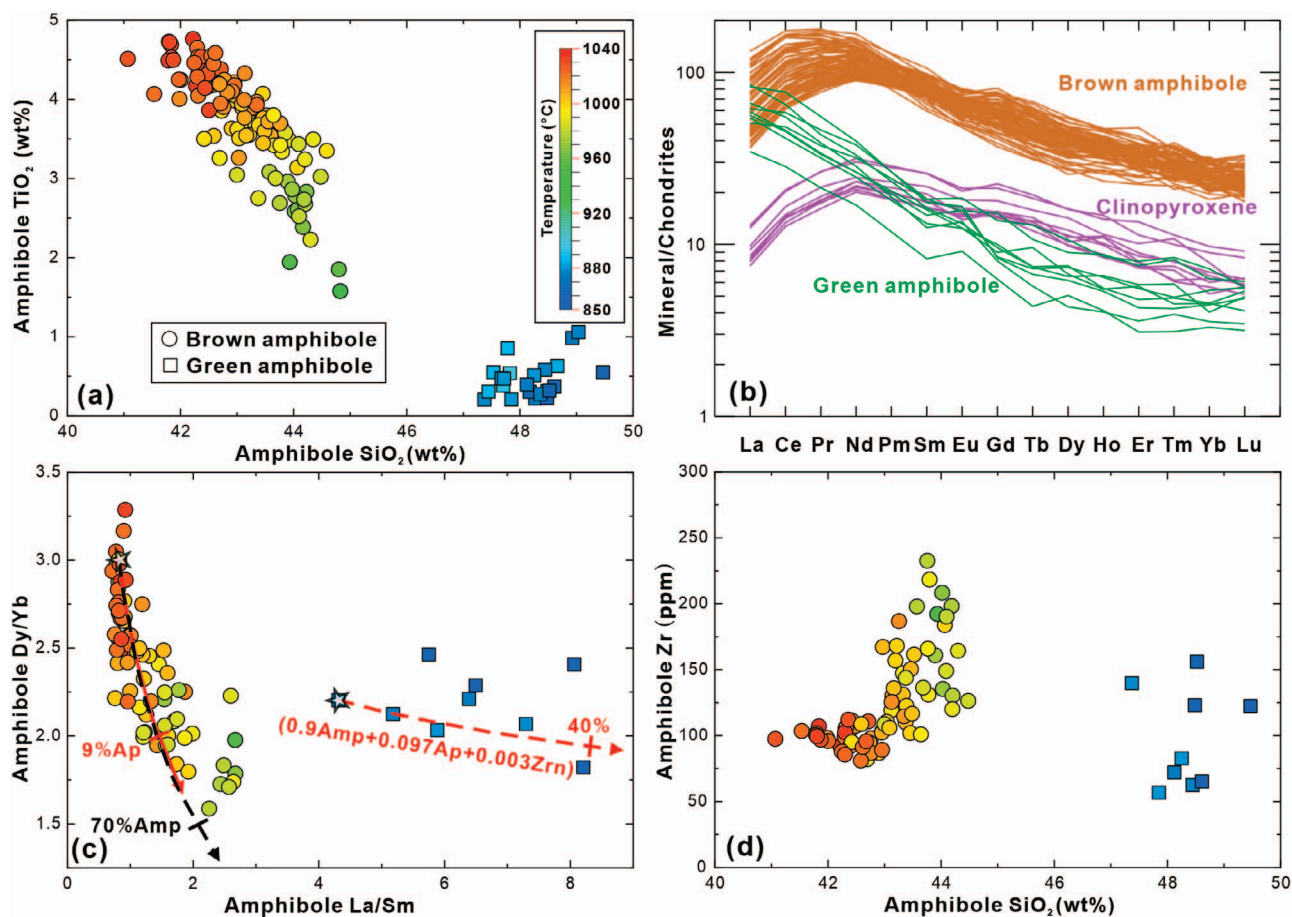
**Fig. 5.** (a) Zircon  $\delta^{18}\text{O}$  vs.  $\epsilon\text{Hf}(t)$ . Also shown for comparison are the histograms of zircon  $\epsilon\text{Hf}(t)$  values for the Yanhu felsic rocks formed at  $110 \pm 2$  Ma (Zhu et al., 2011; Sui et al., 2013). (b) Olivine  $\delta^{18}\text{O}$  vs. Fo. Gray shaded area represents  $\delta^{18}\text{O}$  values of normal mantle zircon and olivine (Mattey et al., 1994; Valley et al., 1998). Error bars are  $2\sigma$  for  $\delta^{18}\text{O}$  values.



**Fig. 6.** Major- and trace-element compositions of ultramafic cumulates in this study and basalts, andesites, rhyolites, and diorites reported by Sui et al. (2013). (a) MgO vs.  $\text{SiO}_2$ . (b) Chondrite-normalized REE patterns. Normalizing values are from Sun & McDonough (1989) (c) Dy/Yb vs.  $\text{SiO}_2$ . The data for several active arc volcanoes are from Davidson et al. (2007), which define differentiation trends indicative of amphibole fractionation. The inset shows the effect of fractionation of garnet, amphibole, and gabbro (pyroxene + plagioclase + olivine) on magma compositions (after Davidson et al. (2007)). (d) Dy/Yb vs. La/Sm. Calculated melts in equilibrium with amphiboles in Yanhu cumulates are shown for comparison.

La/Sm (Fig. 7c) and an increase in Zr (81–233  $\mu\text{g/g}$ ) with increasing  $\text{SiO}_2$  (Fig. 7d). Green amphibole is characterized by marked LREE enrichment over MREE and HREE (Fig. 7b). Therefore,

green amphibole has higher La/Sm than brown amphibole, and its Dy/Yb is similar to that of high-La/Sm brown amphibole (Fig. 7c). However, the Zr (57–156  $\mu\text{g/g}$ ) content of green amphibole is



**Fig. 7.** Major- and trace-element compositions of amphibole in the Yanhu cumulates. (a)  $\text{TiO}_2$  vs.  $\text{SiO}_2$ . (b) Chondrite-normalized REE patterns. Clinopyroxene inclusions in brown amphibole are plotted for comparison. Normalizing values are from Sun & McDonough (1989). (c)  $\text{Dy}/\text{Yb}$  vs.  $\text{La}/\text{Sm}$ . Arrows with scales indicate the compositional variations of amphiboles resulting from the fractionation of different minerals from their equilibrium melts. Numbers along the arrows denote the amount of fractionating minerals. Mineral abbreviations are the same as in Fig. 2. The black stars represent the starting compositions. (d)  $\text{Zr}$  vs.  $\text{SiO}_2$ . All data points in (a), (c) and (d) are color-coded for amphibole crystallization temperatures obtained from Eq. 5 of Putirka (2016), with the scale displayed in (a).

lower than the highest Zr content ( $233 \mu\text{g}/\text{g}$ ) in brown amphibole (Fig. 7d).

Clinopyroxene inclusions (Fig. 2c) in brown amphibole have Mg# (molar  $100 \times \text{Mg}/[\text{Mg} + \text{Fe}]$ ) values of 79.4–83.2 and CaO contents of 22.5–22.8 wt.%. The REE pattern of clinopyroxene is subparallel to that of the host brown amphibole, but the clinopyroxene has lower REE contents (Fig. 7b). Clinopyroxene inclusions have significantly lower Zr contents of 21–40  $\mu\text{g}/\text{g}$  (Table S8) than the host brown amphibole ( $\text{Zr} = 81\text{--}233 \mu\text{g}/\text{g}$ ; Table S7). The intercumulus orthopyroxene crystals have Mg# values of 80.6–82.1 and CaO contents of 0.9–1.3 wt.%, and they have very low REE (e.g.  $\text{La} < 0.11 \mu\text{g}/\text{g}$ ) and Zr (5.1–9.6) contents (Table S9).

Apatite is fluorapatite and hydroxyapatite and has CaO of 53.5–55.9 wt.% and  $\text{P}_2\text{O}_5$  of 40.5–43.3 wt.%. It has variable F (1.3–2.4 wt.%) and Cl contents (0.4–2.1 wt.%) (Table S10), with a positive correlation between  $\Sigma\text{REE}$  and Cl (Fig. 8a). Most of the apatite crystals show a homogeneous texture and lack micropores and mineral inclusions, and some crystals show a narrow, bright rim that has higher Cl than the dark core in BSE images (Fig. 3b). Thus, the variability of lightness on BSE images for apatite reflects a compositional difference, i.e. the bright domains are more enriched in REE and Cl than the dark domains, which are consistent with the detailed research by Krneta et al. (2016). Apatite shows marked LREE enrichment over HREE on chondrite-

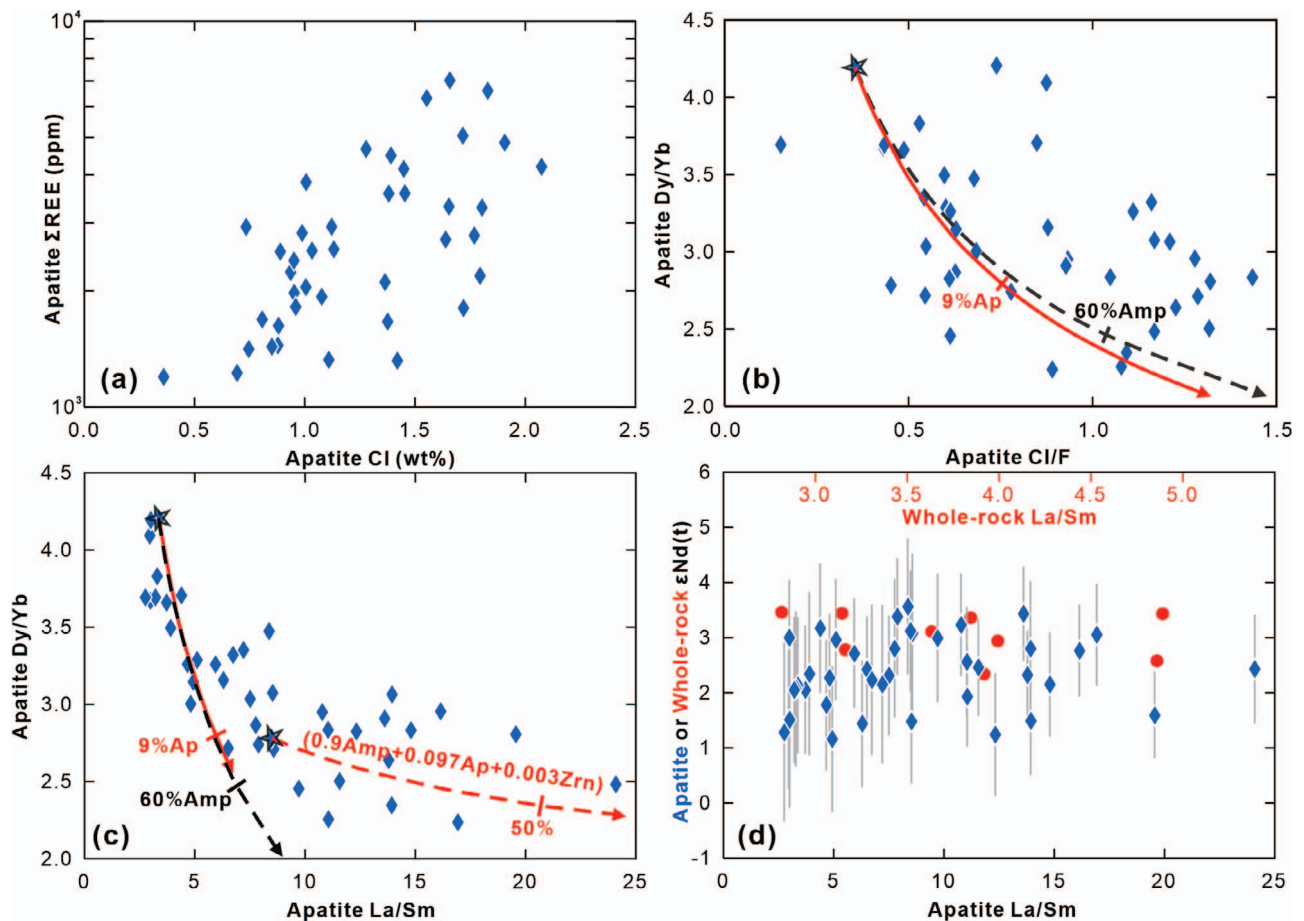
normalized REE diagrams (Supplementary Fig. S2). Its  $\text{Dy}/\text{Yb}$  ratio decreases with increasing  $\text{La}/\text{Sm}$  and  $\text{Cl}/\text{F}$  ratios (Fig. 8b,c). Apatite has  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios ranging from  $0.512619 \pm 0.000068$  to  $0.512753 \pm 0.000063$ , corresponding to  $\epsilon_{\text{Nd}}(t)$  values of 1.2–3.6 (average =  $2.4 \pm 1.4$ ; 2SD;  $n = 41$ ). Apatite  $\epsilon_{\text{Nd}}(t)$  values are relatively invariant over a range of  $\text{La}/\text{Sm}$  (2.8–24.1), which is similar to its host rocks although their  $\text{La}/\text{Sm}$  ranges are different (Fig. 8d).

## DISCUSSION

### Post-magmatic alteration

Before using the mineral compositions to investigate their parent magmas, it is necessary to evaluate the influence of post-magmatic alteration. Interaction between olivine and hydrothermal fluids caused variable serpentinization along micro-fractures and rims of olivine as shown in Fig. 2a–c. Typical temperatures of serpentinization range from  $100^\circ\text{C}$  to  $400^\circ\text{C}$  (Wenner & Taylor, 1971). However, oxygen diffusion rates ( $< 10^{-25} \text{ m}^2/\text{s}$ ) at this temperature range are extremely slow (Chakraborty, 2010). Moreover, as the  $\delta^{18}\text{O}$  values of olivine grains in the samples were determined by an *in situ* method, the analytical targets in the selected olivine grains were always away from micro-fractures (Fig. 3a). Thus, the  $\delta^{18}\text{O}$  values of the Yanhu olivine grains are not





**Fig. 8.** Major- and trace-element compositions of apatite in the Yanhu cumulates. (a)  $\Sigma$ REE vs. Cl. (b) Dy/Yb vs. Cl/F. (c) Dy/Yb vs. La/Sm. Arrows with scales are the same as those in Fig. 7(c), except that the starting compositions (i.e. black stars) are different. (d)  $\epsilon$ Nd(t) vs. La/Sm. Also shown for comparison are the whole-rock  $\epsilon$ Nd(t) values.

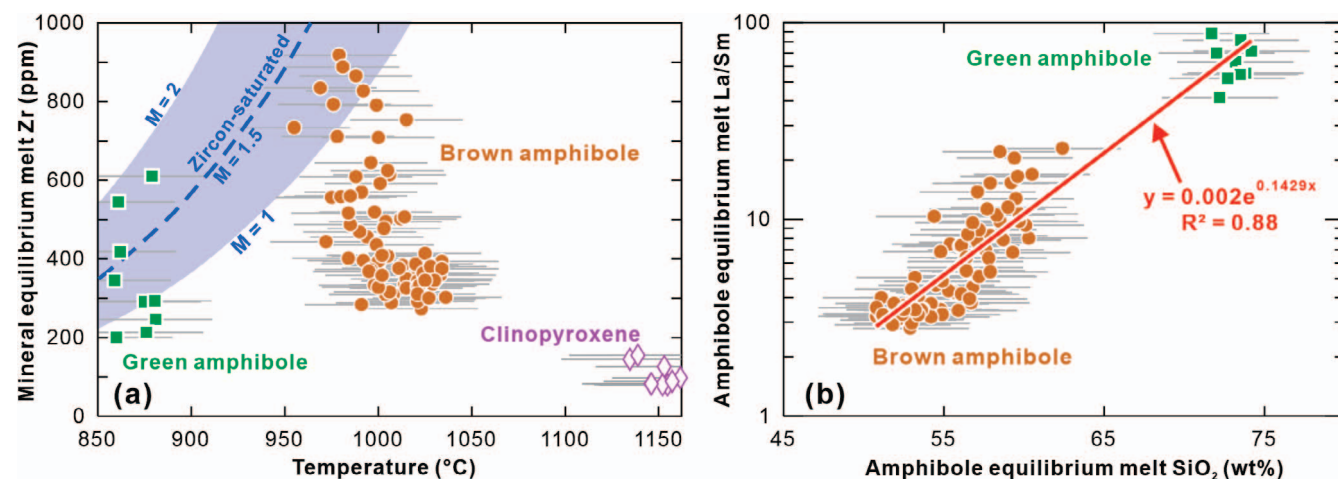
thought to have been affected by post-magmatic hydrothermal alteration.

Hoskin (2005) suggested that hydrothermally-altered or hydrothermal fluid-precipitated zircon usually occurs as rims on magmatic cores and less commonly as individual crystals, and the hydrothermal rims are internally textureless and non-luminescent in CL images whereas magmatic cores are oscillatory zoned. In contrast, the Yanhu zircon CL images show no or broad-banded zoning in the cores, and oscillatory zoning in the rims (Fig. 4c,d). The Th/U ratios of the studied zircons range from 1.0 to 21.3 (average = 4.2; Table S2) as commonly seen in magmatic zircons (Th/U > 0.5; Hoskin & Schaltegger, 2003). However, the zircons interpreted to be hydrothermal from the Boggy Plain Zoned Pluton aplite (Hoskin, 2005) and the Mole Granite (Pettke et al., 2005) have lower Th/U ratios (0.05 to 0.82) due to stronger mobility of U relative to Th in hydrothermal fluids. Hence, the studied zircons are magmatic in origin and their oxygen isotopes were not altered during post-magmatic hydrothermal activity.

Magmatic apatite may experience chemical and textural changes induced by hydrothermal fluids (Harlov, 2015). Compared with HREE and F, LREE and Cl in apatite preferentially partition into hydrothermal fluids. These fluids can then precipitate REE-bearing minerals, such as monazite (Harlov, 2015; Broom-Fendley et al., 2016; Krneta et al., 2016). Previous studies indicate that monazite is commonly found as inclusions in pore-bearing reacted areas that mostly occur along grain rims or cracks of hydrothermally-altered apatite, and these reacted areas are more

depleted in REE and Cl, and so are darker than the unreacted areas in BSE images (Krneta et al., 2016; Zhang et al., 2020). However, most of the Yanhu apatite crystals are homogeneous and lack mineral inclusions, and some crystals have a bright rim in BSE images (Fig. 3b). They contrast markedly with partly altered apatites, which have bright cores and dark rims that represent unreacted and preferentially reacted areas, respectively (e.g. Krneta et al., 2016; Zhang et al., 2020). In addition, the Yanhu apatite has a Dy/Yb versus La/Sm trend similar to coexisting amphibole, that is, its Dy/Yb ratio first decreases rapidly and then remains almost constant with increasing La/Sm (Figs 7c and 8c). Thus, apatite and amphibole simultaneously record compositional changes in the intercumulus melts. Apatite occurs either as inclusions within amphibole or as a late interstitial phase between amphibole and orthopyroxene (Fig. 2f,g), also implying co-crystallization with amphibole. The above chemical and textural evidence suggest that the variation in REE fractionation in apatite was not caused by hydrothermal activity.

The green amphiboles may form during subsolidus hydrothermal alteration given that some of them occur as replacive rims of the brown amphiboles. If green amphibole formed through reaction of brown amphibole with hydrothermal fluids almost devoid of fluid-immobile elements (e.g. Th), it should not contain a higher abundance of Th than its precursor of brown amphibole. However, the Yanhu green amphiboles indeed have a higher Th (1.23–2.08  $\mu$ g/g) content than brown amphiboles (0.06–0.30  $\mu$ g/g) (Table S7), which supports the magmatic nature of green



**Fig. 9.** (a) The crystallization temperatures of amphibole and clinopyroxene vs. their equilibrium melt Zr contents. Solubility of zircon as function of temperature and melt composition ( $M = [\text{Na} + \text{K} + 2\text{Ca}]/[\text{Al-Si}]$ ) is from Watson & Harrison (1983). (b) La/Sm vs. SiO<sub>2</sub> for amphibole equilibrium melts showing the best-fit line. Error bars are  $1\sigma$  for the calculated temperatures and SiO<sub>2</sub> contents.

amphiboles. Thorium will gradually concentrate in the residual melts during magma evolution as it is highly incompatible in olivine, pyroxene, and amphibole (Tiepolo *et al.*, 2007). This is the reason for the difference in Th contents between the green and brown amphiboles. Moreover, green amphibole occurs not only as replacive rims of brown amphibole, but also as large interstitial grains between olivine and brown amphibole (Fig. 2c). The latter is classified as pargasite, suggesting a late-crystallizing igneous phase (e.g. Féménias *et al.*, 2006).

### Intercumulus melt evolution revealed by compositional variations in minerals

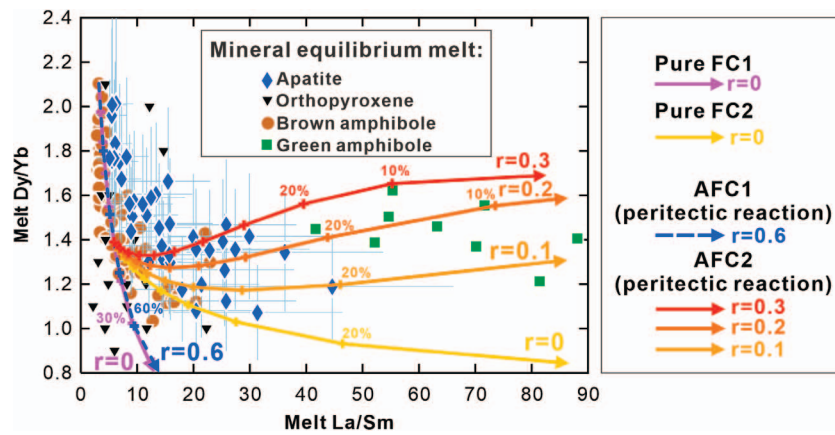
Chemical evolution of intercumulus melt is indicated by the occurrence of: (1) evolved interstitial minerals, such as amphibole, orthopyroxene and zircon, which are not in textural and chemical equilibrium with cumulus olivine and clinopyroxene; (2) a large compositional variation (e.g. Ti and REE) in the intercumulus amphibole. We used thermometric and chemometric equations of different minerals to constrain the variations in the compositions and temperatures of intercumulus melts in the Yanhu cumulates.

Calcic amphibole compositions alone can act as very effective thermometers with a precision of  $\pm 30^\circ\text{C}$  because TiO<sub>2</sub> in amphibole varies considerably with temperature (Fig. 7a; Putirka, 2016). Calcic amphibole compositions can also be used to estimate the major and trace element compositions of its equilibrium melts (Putirka, 2016; Zhang *et al.*, 2017; Humphreys *et al.*, 2019). Recent tests reaffirmed that calculated melt SiO<sub>2</sub> contents and temperatures using different calibrations are consistent and reasonable (Erdmann *et al.*, 2014; Putirka, 2016). We used the empirical equations (Eqs. 5 and 10) of Putirka (2016) to calculate amphibole crystallization temperatures and its equilibrium melt SiO<sub>2</sub> contents. The REE and Zr contents of amphibole equilibrium melts were calculated using partition coefficients from the multiple-regression model of Humphreys *et al.* (2019), which links trace-element partition coefficients to amphibole major-element chemistry. The calculated results indicate that the brown and green amphiboles crystallized from mafic to intermediate melts (SiO<sub>2</sub> = 50–65 wt.%) at 1040°C to 940°C, and from felsic melts (SiO<sub>2</sub> = 70–74 wt.%) at 900°C to 860°C, respectively (Table S6). The calculated La/Sm ratios of amphibole equilibrium melts increase exponentially with increasing SiO<sub>2</sub> (Fig. 9b).

The crystallization temperature of clinopyroxene was calculated using a clinopyroxene-only thermometer of Wang *et al.* (2021). The clinopyroxene equilibrium melt Zr contents were calculated using the partition coefficients compiled by Bedard (2001). The calculated results show that clinopyroxene crystallized from melts with a Zr content of 80–155  $\mu\text{g/g}$  at  $\sim 1150^\circ\text{C}$  (Fig. 9a). The Al-in-olivine thermometer based on the partitioning of Al between coexisting olivine and spinel inclusions (Coogan *et al.*, 2014) was used to estimate olivine crystallization temperatures of 1135–1275°C (Table S4). The spinels in this study have a high Ti (0.04–0.11 apfu; Table S5) that exceeds the thermometer calibration range ( $< 0.025$  apfu), but previous Al-exchange studies noted that Ti contents of  $< 0.32$  apfu do not produce anomalous results (Coogan *et al.*, 2014; Heinson *et al.*, 2015; Jennings *et al.*, 2019).

The melts in equilibrium with clinopyroxene and amphibole display a transition from increasing to decreasing Zr with decreasing temperature (Fig. 9a). The low-temperature felsic melts in equilibrium with green amphibole have sufficiently high Zr content to achieve zircon saturation (Fig. 9a) if felsic melts have  $M$  ( $[\text{Na} + \text{K} + 2\text{Ca}]/[\text{Al-Si}]$ , all in cation fraction) values of 1–2, which characterize most felsic rocks (Miller *et al.*, 2003). This suggests the cotectic crystallization of zircon and green amphibole from the felsic intercumulus melts.

We further explore whether the late-stage saturation of zircon can reproduce a marked inflection in Dy/Yb versus La/Sm trends defined by both amphibole and apatite. We can calculate the variations (i.e. the arrows with scales in Figs 7c and 8c) in these ratios of amphibole/apatite that crystallized from the intercumulus melts variably evolving from more primitive melts in equilibrium with the earlier-crystallized amphibole/apatite. The intercumulus melt evolution was modeled using fractional crystallization (FC) of amphibole, apatite, and zircon, all of which are the REE-rich intercumulus minerals in Yanhu ultramafic rocks. The partition coefficients ( $D$ ) for these minerals are assumed to be constant during the differentiation process and they are given in Table S13. Although many experimental studies (e.g. Prowatke & Klemme, 2006; Tiepolo *et al.*, 2007; Burnham & Berry, 2012) have demonstrated that the absolute  $D_{\text{REE}}$  values vary significantly with temperature and composition of melts, the  $D_{\text{REE}}$  ratios (e.g.  $D_{\text{La/Sm}}$ ) are far less prone to this problem (see below). The MREE (e.g. Sm, Dy) are more compatible than the HREE (e.g. Yb) and LREE (e.g. La) in both amphibole and apatite (Prowatke & Klemme,



**Fig. 10.** Geochemical models reproducing the variations in Dy/Yb and La/Sm ratios of the calculated melts in equilibrium with amphibole, orthopyroxene, and apatite. See text for model details and input parameters are given in Table S13. The AFC1 and AFC2 models are performed assuming the following peritectic reactions: Melt1 + 0.89 Ol + 0.11 Cpx = Melt2 + 0.8 Brown Amp + 0.16 Opx + 0.04 Ap ( $r = 0.6$ ), Melt2 + Brown Amp = Melt3 + 0.9 Green Amp + 0.097 Ap + 0.003 Zrn ( $r = 0.1, 0.2, 0.3$ ), respectively. The proportions of the assimilated (Ol: Cpx = 8:1) and crystallized (Brown Amp: Opx = 5:1) minerals are assumed based on the modal mineral proportions in thin sections (Table S1). The pure FC1 and FC2 models correspond exactly with the AFC1 and AFC2 models with  $r = 0$ , respectively. Errors ( $2\sigma$ ) incorporate the uncertainties of  $D_{\text{REE}}$  values of apatite. Crosses on the modeled curves indicate 10% changes in the fraction of melt remaining.

2006; Tiepolo et al., 2007), but the HREE are more compatible than the MREE and LREE in zircon (Sano et al., 2002; Burnham & Berry, 2012). In addition, F is more compatible than Cl in amphibole (Van den Bleeken & Koga, 2015), fluorapatite, and hydroxyapatite (McCubbin et al., 2015; Li & Costa, 2020). Therefore, the FC of amphibole and/or apatite can produce a negative correlation between Cl/F and Dy/Yb in the residual melts and crystallizing apatite (Fig. 8b).

The involvement of a small amount of zircon, along with amphibole and apatite, in the fractionating mineral assemblages (e.g. amphibole, apatite, and zircon at a 90:9.7:0.3 ratio) can buffer the decrease in Dy/Yb ratios that results from the fractionation of amphibole or apatite alone (Figs 7c and 8c). The proportion of zircon in the fractionating mineral assemblages depends on the difference in absolute  $D_{\text{REE}}$  values of different minerals. The values along the curves with scales in Figs 7c and 8b,c denote the amount of fractionating minerals, but these values and positions of curves are indicative only because they can vary with different choices of the absolute  $D_{\text{REE}}$  values and starting compositions (i.e. black stars in Figs 7c and 8b,c), respectively. However, these parameters do not significantly affect the slope of modeled curves, which were determined by the  $D_{\text{REE}}$  ratios.

Brown amphibole in the Yanhu cumulates usually contains resorbed inclusions of clinopyroxene and olivine, and some of the green amphiboles occur as replacive rims of the brown amphiboles (Fig. 2a–c), suggesting that brown and green amphiboles formed through peritectic reactions consuming the precursors of olivine + clinopyroxene and of brown amphibole, respectively. Amphibole-forming peritectic reactions are different from the pure FC model above (Klaver et al., 2018; Wang et al., 2022). To incorporate the effects of peritectic resorption, we follow the approach of Klaver et al. (2018) and use the two-stage assimilation-fractional crystallization (AFC) processes to model dissolution and precipitation processes. The first stage (AFC1) is the assimilation of olivine + clinopyroxene and the crystallization of brown amphibole + orthopyroxene + apatite, and the second stage (AFC2) is the assimilation of brown amphibole and the crystallization of green amphibole + apatite + zircon. We also show the pure FC1 and FC2 models which correspond exactly with the AFC1 and AFC2 models with the assimilated

to crystallized mass ratio ( $r$ ) of zero, respectively. We calculated the Dy/Yb and La/Sm ratios of melts in equilibrium with the intercumulus amphibole, orthopyroxene, and apatite to compare melt compositions and AFC trends. The  $D_{\text{REE}}$  values of amphibole and orthopyroxene are calculated using the parameterized models developed by Humphreys et al. (2019) and Sun & Liang (2013), respectively. The  $D_{\text{REE}}$  values of apatite are the average values determined in experiments (Watson & Green, 1981; Prowatke & Klemme, 2006), and hence the errors ( $2\sigma$ ), caused by the uncertainties of  $D_{\text{REE}}$  values, are shown for calculated Dy/Yb and La/Sm of apatite equilibrium melts (Fig. 10). The model parameters are described in the caption of Fig. 10 and Table S13.

The modeling results (Fig. 10) show that the AFC1 trends vary insignificantly with  $r$  values. This is because the olivine-clinopyroxene assmilitant in the AFC1 model has low REE contents. In contrast, the assmilitant of brown amphibole in the AFC2 model has high REE contents and Dy/Yb ratios (Table S13). The residual evolving melts show decreasing MREE and HREE contents due to the fractionation of amphibole, apatite, and zircon, and hence they are susceptible to the assimilation of brown amphibole. A low degree of assimilation can even lead to an increase in Dy/Yb of late-stage melts (Fig. 10). Therefore, both the crystallization of zircon and the assimilation of brown amphibole can suppress a decrease in Dy/Yb of late-stage melts.

The peritectic reaction forming amphibole (clinopyroxene + olivine + mafic melt = amphibole + orthopyroxene + felsic melt) observed in our samples has been also reproduced by cooling-driven crystallization experiments on a hydrous basalt (Ulmer et al., 2018). The amphiboles containing resorbed inclusions of clinopyroxene and olivine can be the crystallization products of hydrous basalts in a closed system, which does not necessarily require externally derived evolved melts in an open system. Combined with the calculated temperatures above, the main mineral crystallization sequence is as follows: (1) minerals formed during cumulus processes: olivine + spinel, clinopyroxene; (2) minerals formed during postcumulus processes: brown amphibole + orthopyroxene + apatite, green amphibole + apatite + zircon. The Yanhu apatite crystallized earlier at a lower  $\text{SiO}_2$  content than zircon, consistent with both the solubility models (Watson

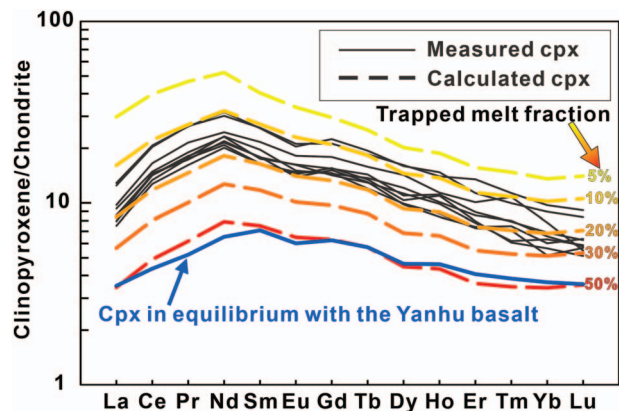
& Harrison, 1983; Harrison & Watson, 1984) and inflections in the Zr- and P-SiO<sub>2</sub> arrays for global arc lavas (Lee & Bachmann, 2014).

### The effect of trapped liquid shift on cumulus olivine Fo values

Postcumulus diffusive re-equilibration between cumulus olivine and intercumulus evolved melts is ubiquitous during solidification of trapped intercumulus liquids in orthocumulates from mafic-ultramafic intrusions (e.g. Barnes, 1986; Yang *et al.*, 2019). The change in composition of a mineral (e.g. olivine) from that of the initially precipitated cumulus crystals to the final composition after complete solidification is termed the 'trapped liquid shift', which can significantly reduce olivine Fo values. The extent of reduction is positively correlated with the initial trapped melt fraction (TMF; Barnes, 1986; Yang *et al.*, 2019). For example, crystallization of 30% trapped liquid can lead to shifts of up to 10 mol.% in Fo values (Barnes, 1986).

The Yanhu whole-rock cumulate compositions are envisaged to be the sum of the composition of cumulus phases (olivine and clinopyroxene) and intercumulus melt (crystallized as amphibole, orthopyroxene and accessory phases) trapped between them in a closed system. Based on this mass balance model, Bedard (1994) proposed an equilibrium distribution method (EDM) to constrain the TMF, assuming that the cumulus minerals are initially in equilibrium with the trapped melt and no significant melt migration has occurred. When the composition of initial trapped melt in equilibrium with cumulus minerals is known, it is possible to estimate the TMF. Modeling results for the Yanhu cumulates are shown in Fig. 11, where we report the REE patterns of clinopyroxene calculated assuming various amounts of TMF (5, 10, 20 and 30%) (see the caption of Fig. 11 for more details). The composition of calculated clinopyroxene is sensitive to the TMF, and REE enrichment in clinopyroxene tends to decrease at increasing amount of trapped melt. If the composition of the melt in equilibrium with the cumulus clinopyroxene included in brown amphibole represents that of the initial trapped melt, the REE pattern of clinopyroxene computed assuming 10–20% of TMF is very similar to that of clinopyroxene. However, TMF should be underestimated because the incompatible REE abundances in the cumulus clinopyroxenes had been elevated by effects of the trapped liquid shift (Barnes, 1986; Yang *et al.*, 2019). If the composition of the coeval basalt at Yanhu reasonably represents the initial composition of potential liquid entrapped in the cumulates, the clinopyroxene computed assuming ~50% of TMF resembles that in equilibrium with the Yanhu basalt. In summary, a high TMF (20–50%) can be expected in the Yanhu cumulates, which is consistent with the high proportions (35–60%) of intercumulus phases (amphibole and orthopyroxene, Table S1). It means a significant postcumulus compositional shift (about 10 mol.%) in the Fo value of cumulus olivine.

The effect of trapped liquid shift on olivine Fo values is further confirmed by the decoupling of Al-in-olivine temperatures and olivine Fo values. We calculated the olivine liquidus of the coeval high-MgO basalt at Yanhu using the Rhyolite-MELTS thermodynamic program (Gualda *et al.*, 2012) to show the real relationship between olivine crystallization temperatures and Fo values (Fig. 12a). Application of the barometric and hygrometric formulations developed by Ridolfi *et al.* (2010) gives pressures of 269 ± 74 MPa and water contents of 4.0 ± 0.6 wt.% for the amphiboles of Yanhu cumulates (Table S6), and hence calculations were performed at 0.1 and 0.3 GPa and assuming initial water contents of 4 wt.%. Aluminum is expected to diffuse much more slowly in olivine than Mg and Fe (Spandler & O'Neill, 2010),

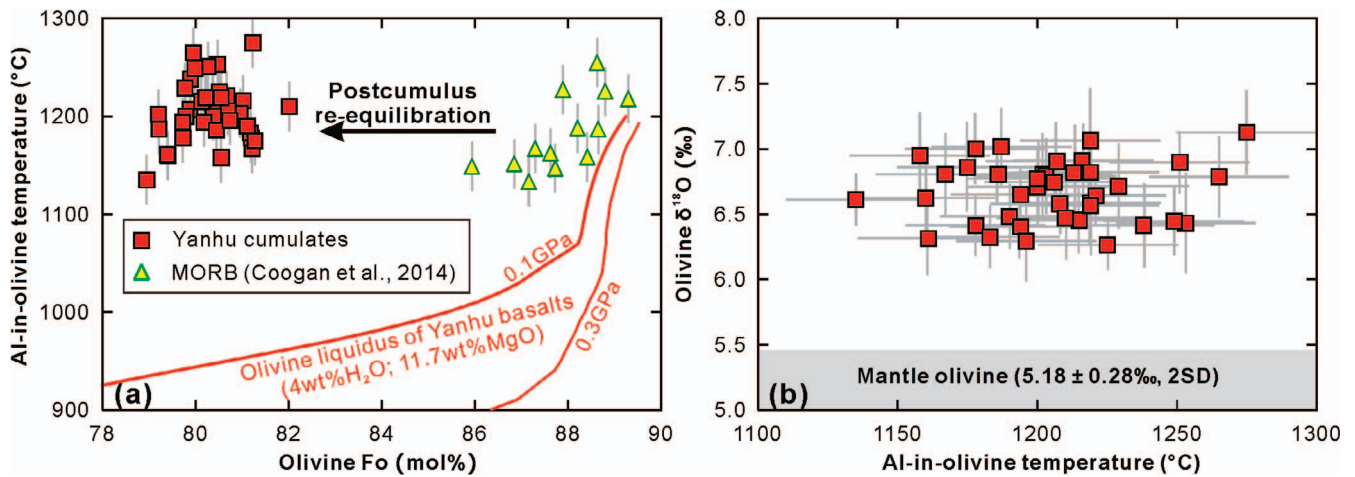


**Fig. 11.** Chondrite-normalized REE abundances of clinopyroxenes calculated with the method of Bedard (1994, 2001) assuming the trapped melt fractions (TMF) of 5, 10, 20, 30 and 50%. The proportion of the initial cumulus phases (olivine: clinopyroxene = 8:1) is assumed for all TMF based on the modal mineral proportions in thin sections (Table S1). We used the average abundances of cumulates and crystal/melt partition coefficients from Bedard (2001). The REE pattern of clinopyroxene in equilibrium with a Yanhu high-MgO basalt (YH22-2; Sui *et al.*, 2013) are also reported for comparison.

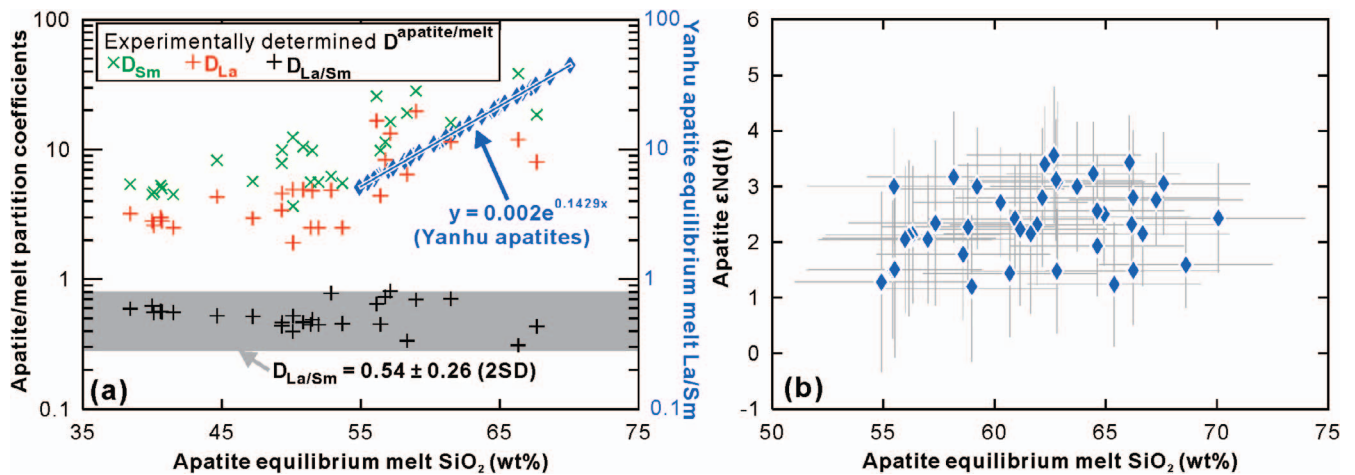
and therefore Al-in-olivine temperature is less susceptible to the trapped liquid shift compared to Fo values. The Al-in-olivine temperatures (1135–1275°C) of Yanhu cumulates overlap with those of mid-ocean ridge basalts (MORB; Coogan *et al.* (2014)) and liquidus temperatures of Yanhu primary basalts, although olivine Fo values of the Yanhu cumulates are significantly lower (Fig. 12a). Thus, the Yanhu olivine grains with crystallization temperatures higher than 1200°C can represent the first crystals (typically Fo = ~90) to crystallize from a primary mantle melt, but their Fo values had decreased by about 10 mol.% after postcumulus diffusive exchange of Mg and Fe with the trapped evolved melts (Fig. 12a). This diffusion process is further supported by the low temperatures (646–754°C; Table S4) of Fe/Mg exchange between olivine and spinel, which were obtained using the thermometer of Ballhaus *et al.* (1991).

### No contribution of crustal contamination to high- $\delta^{18}\text{O}$ zircon saturation

Zircon is a ubiquitous accessory mineral in felsic rocks (e.g. granitoids) because zircon solubility in silicate melts decreases exponentially with decreasing temperature (Watson & Harrison, 1983). Basaltic liquids require an unrealistically high abundance of >5000  $\mu\text{g/g}$  Zr to directly crystallize zircon near the liquidus, and thus zircons found in mafic or ultramafic rocks (including our samples) should crystallize from late-stage, deeply evolved melts, likely of granitic composition, near the solidus (Boehnke *et al.*, 2013; Borisov & Aranovich, 2019). However, the addition of crustal Zr and Si to mafic magmas during the AFC process in an open system may promote zircon saturation (Guo *et al.*, 2013; Wang *et al.*, 2016). This zircon type formed in an open system involves the reworking of preexisting crustal rocks by mantle-derived magmas (Kemp *et al.*, 2007). Crustal contamination may commence before and/or during zircon crystallization, which can explain why late-crystallized zircons have significantly higher  $\delta^{18}\text{O}$  and lower  $\epsilon_{\text{Hf}}$  values than early-crystallized mafic minerals (e.g. olivine and pyroxene) in some mafic-ultramafic rocks (Guo *et al.*, 2013; Wang *et al.*, 2016). Therefore, whether the Yanhu high- $\delta^{18}\text{O}$  zircons record periods dominated by crustal growth or reworking depends on the contribution of crustal contamination to zircon saturation.



**Fig. 12.** Al-in-olivine temperature vs. olivine Fo (a) and olivine  $\delta^{18}\text{O}$  values (b). Two red curves show the olivine liquidus of a Yanhu high-MgO basalt (YH22-2; Sui *et al.*, 2013) at 0.1 and 0.3 GPa, which were obtained using Rhyolite-MELTS (Gualda *et al.*, 2012). The Al-in-olivine temperatures of MORB are from Coogan *et al.* (2014).



**Fig. 13.** (a) Apatite/melt  $D_{\text{REE}}$  and apatite equilibrium melt La/Sm ratios vs. apatite equilibrium melt SiO<sub>2</sub> contents. Experimentally determined  $D_{\text{REE}}$  values are from Prowatke & Klemme (2006) and Watson & Green (1981). (b) Apatite  $\epsilon\text{Nd}(t)$  values vs. its equilibrium melt SiO<sub>2</sub> contents. Errors ( $2\sigma$ ) for calculated SiO<sub>2</sub> contents of apatite equilibrium melts incorporate the uncertainties of apatite/melt  $D_{\text{La/Sm}}$  (Fig. 13a) and predicted melt SiO<sub>2</sub> contents (Fig. 9b) from amphibole chemistry of Putirka (2016).

FC in a closed system will increase the  $\delta^{18}\text{O}$  values of residual melts (M), but the  $\delta^{18}\text{O}$  values of zircon (Zrn) that crystallized from variably evolved melts remains approximately constant because the fractionation,  $\Delta^{18}\text{O}(\text{M-Zrn})$ , increases at nearly the same rate as  $\delta^{18}\text{O}(\text{M})$  (Valley *et al.*, 2005). Zircon ( $\delta^{18}\text{O} = 5.3 \pm 0.6\text{‰}$ ; 2SD) and olivine (Ol;  $\delta^{18}\text{O} = 5.18 \pm 0.28\text{‰}$ ; 2SD) in normal mantle have indistinguishable  $\delta^{18}\text{O}$  values, indicating that  $\Delta^{18}\text{O}(\text{Zrn-Ol})$  is close to zero at magmatic temperatures (Mattey *et al.*, 1994; Valley *et al.*, 1998). Thus, olivine that crystallized from primary mantle melts should have  $\delta^{18}\text{O}$  values similar to zircon that crystallized from evolved melts formed by closed-system FC of primary melts. The Yanhu olivines and zircons have similar  $\delta^{18}\text{O}$  values (Fig. 5), suggesting no crustal contamination during magma evolution from olivine to zircon crystallization.

Oxygen isotopes are less sensitive to crustal contamination compared with radiogenic Nd isotopes owing to the equally high abundance of O in magmas and possible crustal assimilants (James, 1981). Apatite Nd isotopes can further determine whether crustal contamination contributed to zircon saturation in the Yanhu cumulates, considering that the variations in REE composition of apatites record those of intercumulus melts

before and after zircon saturation. The similar trends between Dy/Yb and La/Sm for apatite and amphibole suggest their co-crystallization from the same melt. A clear correlation ( $\text{La/Sm} = 0.002 \times \exp[0.1429 \times \text{SiO}_2]$ ;  $R^2 = 0.88$ ) between La/Sm and SiO<sub>2</sub> for the amphibole equilibrium melts (Figs 9b and 13a) can be used to estimate the SiO<sub>2</sub> contents of apatite equilibrium melts if the La/Sm ratios of apatite equilibrium melts can be calculated using the appropriate  $D_{\text{REE}}$ . Although apatite/melt  $D_{\text{La}}$  and  $D_{\text{Sm}}$  values increase by about an order of magnitude with increasing SiO<sub>2</sub> of the melt, the  $D_{\text{La/Sm}}$  ( $0.54 \pm 0.26$ ; 2SD) ratios do not change significantly (Fig. 13a; Prowatke & Klemme, 2006; Watson & Green, 1981). Hence, the  $D_{\text{La/Sm}}$  ratios are assumed to be constant during the differentiation process. The calculated results indicate that the SiO<sub>2</sub> contents of apatite equilibrium melts increase from ~55 wt.% to ~70 wt.%, but apatite  $\epsilon\text{Nd}(t)$  values remain almost constant (Fig. 13b). Thus, apatite Nd isotopes suggest no contribution of crustal contamination to high- $\delta^{18}\text{O}$  zircon saturation during the closed-system differentiation of mafic to felsic intercumulus melts.

Al-in-olivine temperatures of the ultramafic cumulates record the liquidus temperatures of high-Fo (~90) olivines crystallized

from a primary mantle melt. Considering that diffusion rates of oxygen in olivine are comparable to those of Al (Spandler & O'Neill, 2010), olivine  $\delta^{18}\text{O}$  values are also less susceptible to the trapped liquid shift compared to Fo values. Moreover, a closed-system differentiation of mafic to felsic intercumulus melts implies that postcumulus re-equilibration of olivine with the intercumulus melt, even if present, cannot modify olivine  $\delta^{18}\text{O}$  values. Therefore, the  $\delta^{18}\text{O}$  values of the Yanhu olivines with crystallization temperatures higher than 1200°C can represent those of high-Fo ( $\sim 90$ ) olivines before the trapped liquid shift. The horizontal trend between temperatures (1275–1135°C) and  $\delta^{18}\text{O}$  values (6.3–7.1‰) for the Yanhu olivines (Fig. 12b) precludes the possibility of crustal contamination during the earliest stages of crystallization of primary basalt. It means that parental magmas of the Yanhu cumulates originated a high- $\delta^{18}\text{O}$  mantle.

### Possible connection between the Yanhu volcanic and plutonic rocks

Amphibole-rich mafic-ultramafic rocks are widely found in subduction zones (e.g. Tiepolo *et al.*, 2012; Smith, 2014; Wang *et al.*, 2019; Chang *et al.*, 2021). This is because high  $\text{H}_2\text{O}$  contents in mafic arc magmas can cause the early crystallization of pargasitic amphibole and suppress the crystallization of plagioclase (Sisson & Grove, 1993; Grove *et al.*, 2003; Ulmer *et al.*, 2018). The negative correlations between Dy/Yb and  $\text{SiO}_2$  from erupted lavas in modern subduction zones and Yanhu areas (Fig. 6c) also show that amphibole is an important mineral during differentiation of arc magma (Davidson *et al.*, 2007; Barber *et al.*, 2021). The fractionation of amphibole will more efficiently drive residual melt compositions to higher  $\text{SiO}_2$  and promote calc-alkaline differentiation trends than that of plagioclase and pyroxene. This is because amphibole contains significantly less  $\text{SiO}_2$ . The amphibole-rich ultramafic cumulates are thought to form by the reaction between residual water-rich melts and earlier-formed mushes with a framework of clinopyroxene + olivine crystals during cooling of mafic magmas (Smith, 2014; Wang *et al.*, 2019; Chang *et al.*, 2021). Melt segregation from an amphibole-dominated mush is a manifestation of crustal differentiation, which may be important for the ultimate production of felsic rocks and of  $\text{SiO}_2$ -rich continental crust (Barber *et al.*, 2021).

Calculated melts in equilibrium with the amphiboles in Yanhu cumulates define the ranges of Dy/Yb, La/Sm, and  $\text{SiO}_2$ , overlapping the coeval lavas (Figs 6d and 9b), suggesting that these lavas may represent the intercumulus melts extracted from cumulates with different amounts of residual amphibole. The Yanhu felsic rocks and ultramafic cumulates formed at ca. 110 Ma have similar zircon Hf isotopes (Fig. 5a), indicating a negligible role for crustal contamination or melting in the formation of coeval felsic rocks. However, considering that the Yanhu rhyolites are characterized by significantly negative Eu anomalies and MREE-depleted 'trough-like' patterns (Fig. 6b), we suggest that they were possibly extracted from a shallow mush with a framework of amphibole + plagioclase crystals, rather than directly from the Yanhu ultramafic cumulates. The lack of plagioclase in the Yanhu ultramafic cumulates also excludes a direct connection. The parental magma constructing this shallow mush could be an andesitic melt possibly extracted from a deeper mafic-ultramafic mush (e.g. the Yanhu ultramafic cumulates). This model is consistent with the trans-crustal magma plumbing system described by Cashman *et al.* (2017).

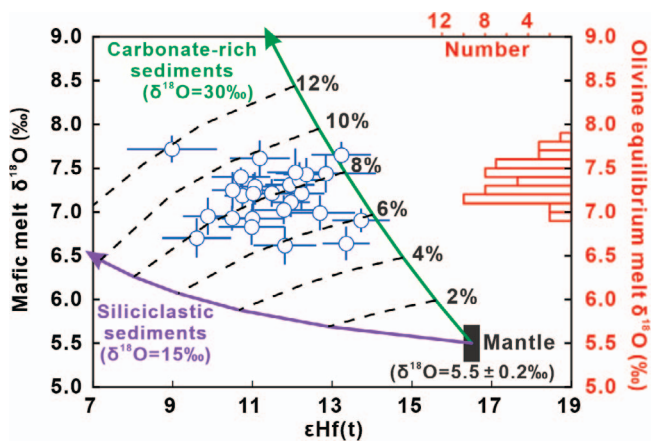
The Dy/Yb variation of the coeval lavas in the extensive Early Cretaceous strata is mainly controlled by amphibole fractionation (Fig. 6c). Thus, many of Early Cretaceous amphibole-rich

cumulates complementary to the extensive lavas are possibly not exposed because the coeval volcanic strata east of Yanhu Town have not been significantly eroded (Fig. 1b). The outcrop of ultramafic cumulates we observed may be a small part of the large intrusion. Many Early Cretaceous batholiths are exposed west of Yanhu Town where the coeval volcanic strata have been eroded (Fig. 1b). In short, the Yanhu ultramafic pluton is only one of the deep amphibole-rich cumulates complementary to the extensive volcanic rocks. These igneous rocks are the products of intra-crustal differentiation of magmas derived from high- $\delta^{18}\text{O}$  arc mantle, and record crustal growth at their zircon crystallization ages.

### Using zircon oxygen isotopes to distinguish between crustal growth and reworking?

Continental crust has been proposed to form predominantly in arc settings (e.g. Rudnick, 1995). As the worldwide dataset for oxygen isotopes of arc samples grows, evidence grows for the presence of high- $\delta^{18}\text{O}$  (5.5–7.6‰) olivine crystals found in mantle-derived magmas (Martin *et al.*, 2011). These examples show that high-Fo ( $\geq 90$ ) olivines have high- $\delta^{18}\text{O}$  values, which cannot result from contamination by high- $\delta^{18}\text{O}$  crustal material, and therefore the mantle source itself must be enriched in  $^{18}\text{O}$  (Martin *et al.*, 2011). Given that oxygen is a major element, the significantly high  $\delta^{18}\text{O}$  values ( $>7\%$ ) observed in some arc olivine crystals from a mass balance standpoint may require unrealistically high amounts of slab-derived components in the mantle source. Therefore, arc olivine crystals with high  $\delta^{18}\text{O}$  ( $>7\%$ ) values are difficult to explain by a single-stage flux-melting process and require a  $^{18}\text{O}$  pre-enriched mantle (e.g. previously fluxed forearc region) with which a high- $\delta^{18}\text{O}$  fluid has isotopically reacted, without melting, during a prolonged subduction history (Dorendorf *et al.*, 2000; Auer *et al.*, 2009; Martin *et al.*, 2011). The Hf isotope ratios of modern island arc magmas worldwide are thought to be more representative of new crust being generated from the mantle than are magmas generated along active continental margins, which are more prone to shallow-level processes of crustal contamination (Dhuime *et al.*, 2011). The  $\epsilon\text{Hf}$  values (5.5–17.7, average = 13.2; Hao *et al.*, 2022) in island arcs are on average lower than the present-day value for the depleted MORB mantle ( $\epsilon\text{Hf} = 16.9$ ; Griffin *et al.*, 2000), primarily because of contributions from subducted sediments (Hao *et al.*, 2022). In short, many arc igneous rocks (e.g. the Yanhu samples), contaminated at their mantle source by subducted sediments, may show 'non-MORB-like' zircon O-Hf signatures. Determining the mass fractions of those high- $\delta^{18}\text{O}$  rocks that derive from the mantle and recycled crust are important to unravel their contribution to crustal growth.

The estimated amount of subducted sediments in the source mantle based on oxygen isotopes of arc magmas is mainly determined by the  $\delta^{18}\text{O}$  values of subducted sediments. The  $\delta^{18}\text{O}$  values of subducted sediments are dominated by the relative proportions of carbonate and siliciclastic sediments ( $\delta^{18}\text{O} = 25\text{--}32\%$  and 10–20‰, respectively; Eiler, 2001). In addition, siliciclastic sediments have higher Hf (generally  $>4 \mu\text{g/g}$ ) contents than carbonate-rich sediments (generally  $<2 \mu\text{g/g}$ ; Plank & Langmuir, 1998). We calculated simple binary mixing between carbonate-rich or siliciclastic sediments and a depleted MORB mantle. We assume the  $\delta^{18}\text{O}$  values of 30‰ and 15‰ and Hf contents of 1  $\mu\text{g/g}$  and 5  $\mu\text{g/g}$  for the subducted carbonate-rich and siliciclastic sediments, respectively. The average  $\epsilon\text{Hf}$  value (+2) for global subducted sediments estimated by Chauvel *et al.* (2008) is used for the sediment end-member. Other parameters used in the mixing calculations are



**Fig. 14.** Calculated  $\delta^{18}\text{O}$  of mafic melts (from the measured  $\delta^{18}\text{O}$  of zircon) vs.  $\epsilon\text{Hf}(t)$ . Also shown for comparison are the histograms of calculated  $\delta^{18}\text{O}$  values for olivine equilibrium melts. The  $\Delta^{18}\text{O}(\text{Melt-Zircon})$  and  $\Delta^{18}\text{O}(\text{Melt-Olivine})$  fractionation factors were assumed to be 0.5‰ for mafic melts (Valley et al., 2005) and 0.7‰ for mafic melts at 1200°C (Eiler, 2001), respectively. Numbers along the green and purple curves of binary mixing denote the amounts of subducted sediments in the source mantle of Yanhu cumulates. The mantle end-member used in the mixing calculation:  $\epsilon\text{Hf}(t = 110 \text{ Ma}) = +16.5$  (Griffin et al., 2000),  $\text{Hf} = 0.309 \mu\text{g/g}$  (Sun & McDonough, 1989),  $\delta^{18}\text{O} = 5.5 \pm 0.2\text{‰}$  (Eiler, 2001).

given in the caption of Fig. 14. The amounts of subducted sediments in the source mantle of Yanhu cumulates are estimated to be 4–12 wt.% (Fig. 14). Other studies (Couzinié et al., 2016; Cornet et al., 2022) also draw the same conclusions that the maximum amount of source contamination to keep the composition of a basalt with  $\delta^{18}\text{O} < 8\text{‰}$  should not exceed 15%. It means that about 88–96% of the bulk mass of our samples are of mantle origin and thus represent new additions to the crust, although their high- $\delta^{18}\text{O}$  signatures come from recycled crustal materials.

The main source rocks from which detrital zircons are derived are felsic magmatic rocks, such as granitoids and their extrusive equivalents. The comparison of experimentally produced melts and cumulates with natural arc rocks shows that FC of mantle-derived magmas is likely to be the dominant process in the formation of arc granitoids, with crustal melting and or assimilation a necessary but secondary contributor (Jagoutz & Klein, 2018; Muntener & Ulmer, 2018). For example, amphibole-rich mafic-ultramafic cumulates and genetically related lavas widely found in subduction zones define Dy/Yb versus  $\text{SiO}_2$  trends indicative of amphibole fractionation (Fig. 6c). The Yanhu felsic rocks and ultramafic cumulates formed at ca. 110 Ma are the products of intra-crustal differentiation of magmas derived from high- $\delta^{18}\text{O}$  arc mantle. Thus, ca. 110 Ma zircons from the Yanhu magmatic rocks record true periods of crustal growth although they have high- $\delta^{18}\text{O}$  values. If these zircon grains are hosted in clastic sedimentary rocks, they should not be simply assigned to crustal reworking in detrital zircon-based crustal evolution models. Our study also shows that the combination of zircon and olivine oxygen isotopes for ultramafic to felsic rocks in a given arc is more effective than zircon data alone in evaluating the role of crustal growth vs. reworking during a magmatic episode.

We stress that our case for source contamination does not preclude other mechanisms, such as crustal contamination and melting, for the generation of high- $\delta^{18}\text{O}$  zircons, particularly for zircons with extremely high  $\delta^{18}\text{O}$  values ( $> 8\text{‰}$ ). For example, pure

sediment-derived granites in the Himalayan orogen have been shown to crystallize zircon with  $\delta^{18}\text{O}$  values of 8–12‰ (Hopkinson et al., 2017). Dhuime et al. (2012) presented a compilation of 1376 detrital zircon  $\delta^{18}\text{O}$  analyses, which is thought to represent the O isotope record available for Earth's continental crust. Twenty-six percent of the zircon analyses in Dhuime et al. (2012) have moderately high  $\delta^{18}\text{O}$  values of 6.1–7.2‰, identical to the Yanhu zircons. However, Spencer et al. (2022) recently recognized the decoupling of oxygen isotopes of zircon in sedimentary and igneous rocks and concluded that the detrital zircon record is strongly biased to upper crustal rocks, especially sediment-derived granites from collisional belts, rather than providing a representative view of the entire crust. A corollary is that the mid-to lower-crustal rocks with moderately high  $\delta^{18}\text{O}$  (e.g. 6.1–7.2‰) zircons are not fully represented in the detrital zircon record. Thus, these moderately high  $\delta^{18}\text{O}$  zircons are not only quantitatively underestimated, but also attributed to crustal reworking in global models, and in turn incorrectly assigned to 'ancient' crust growth (i.e. given by zircon Hf model ages) instead of 'instantaneous' growth (i.e. given by zircon U–Pb ages). Our case study, as well as other regional and global studies (e.g. Cornet et al., 2022), have demonstrated that source contamination of the mantle wedge by slab-derived material plays an important role in imprinting ultramafic to felsic arc rocks with high  $\delta^{18}\text{O}$  compositions. Therefore, distinguishing between crustal growth and reworking simply using zircon oxygen isotopes may be over-simplistic and may underestimate crustal growth over the past 2.5 Ga (Couzinié et al., 2016; Cornet et al., 2022).

## CONCLUSIONS

Geochemical evidence from the Yanhu high- $\delta^{18}\text{O}$  zircon-bearing ultramafic cumulates and coeval lavas from a Cretaceous magmatic arc in southern Tibet offers a unique opportunity to evaluate the role of crustal growth vs. reworking during this Cretaceous (110 ± 2 Ma) magmatic episode. The cumulates mainly comprise olivine and amphibole. Zircon crystallization during differentiation of the intercumulus melts is evidenced by the marked inflections in both Zr versus  $\text{SiO}_2$  trends defined by amphibole and those in Dy/Yb versus La/Sm trends defined by amphibole and apatite. Apatite  $\epsilon\text{Nd}(t)$  values ( $2.4 \pm 1.4$ ) did not change significantly before and after zircon crystallization. Interstitial zircons have  $\delta^{18}\text{O}$  (6.1–7.2‰) values similar to the earliest crystallized olivine ( $\delta^{18}\text{O} = 6.3\text{--}7.1\text{‰}$ ) in the cumulates. The comparison of cumulates and genetically related lavas shows that they were ultimately derived from high- $\delta^{18}\text{O}$  arc mantle, and crystallized zircon during magma evolution controlled by amphibole-dominated fractionation, without involving crustal contamination or melting. Thus, ca. 110 Ma zircons from the Yanhu magmatic rocks are not products of crustal reworking, but crustal growth although they have high- $\delta^{18}\text{O}$  values. Distinguishing between crustal growth and reworking simply using zircon oxygen isotope may be over-simplistic and conceal recent crustal growth in global zircon-based crustal evolution models.

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## DATA AVAILABILITY STATEMENT

The data underlying this article are available in the article and in its online supplementary material.

## SUPPLEMENTARY DATA

Supplementary data are available at *Journal of Petrology* online.

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## References

- Armstrong, R. L. (1981). Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental-growth earth. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **301**, 443–472.
- Arndt, N. T. (2013). The formation and evolution of the continental crust. *Geochemical Perspectives* **2**, 405–533. <https://doi.org/10.7185/geochempersp.2.3>.
- Arndt, N. T. & Goldstein, S. L. (1987). Use and abuse of crust-formation ages. *Geology* **15**, 893–895. [https://doi.org/10.1130/0091-7613\(1987\)15<893:UAAOCA>2.0.CO;2](https://doi.org/10.1130/0091-7613(1987)15<893:UAAOCA>2.0.CO;2).
- Auer, S., Bindeman, I., Wallace, P., Ponomareva, V. & Portnyagin, M. (2009). The origin of hydrous, high-delta O-18 voluminous volcanism: diverse oxygen isotope values and high magmatic water contents within the volcanic record of Klyuchevskoy volcano, Kamchatka, Russia. *Contributions to Mineralogy and Petrology* **157**, 209–230. <https://doi.org/10.1007/s00410-008-0330-0>.
- Ballhaus, C., Berry, R. & Green, D. (1991). High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contributions to Mineralogy and Petrology* **107**, 27–40. <https://doi.org/10.1007/BF00311183>.
- Barber, N. D., Edmonds, M., Jenner, F., Audetat, A. & Williams, H. (2021). Amphibole control on copper systematics in arcs: insights from the analysis of global datasets. *Geochimica et Cosmochimica Acta* **307**, 192–211. <https://doi.org/10.1016/j.gca.2021.05.034>.
- Barnes, S. J. (1986). The effect of trapped liquid crystallization on cumulus mineral compositions in layered intrusions. *Contributions to Mineralogy and Petrology* **93**, 524–531. <https://doi.org/10.1007/BF00371722>.
- Bedard, J. H. (1994). A procedure for calculating the equilibrium distribution of trace-elements among the minerals of cumulate rocks, and the concentration of trace-elements in the coexisting liquids. *Chemical Geology* **118**, 143–153. [https://doi.org/10.1016/0009-2541\(94\)90173-2](https://doi.org/10.1016/0009-2541(94)90173-2).
- Bedard, J. H. (2001). Parental magmas of the Nain plutonic suite anorthosites and mafic cumulates: a trace element modelling approach. *Contributions to Mineralogy and Petrology* **141**, 747–771. <https://doi.org/10.1007/s004100100268>.
- Bindeman, I. (2008). Oxygen isotopes in mantle and crustal magmas as revealed by single crystal analysis. *Reviews in Mineralogy & Geochemistry* **69**, 445–478. <https://doi.org/10.2138/rmg.2008.69.12>.
- Bindeman, I., Gurenko, A., Sigmarsson, O. & Chaussidon, M. (2008). Oxygen isotope heterogeneity and disequilibria of olivine crystals in large volume Holocene basalts from Iceland: evidence for magmatic digestion and erosion of Pleistocene hyaloclastites. *Geochimica et Cosmochimica Acta* **72**, 4397–4420. <https://doi.org/10.1016/j.gca.2008.06.010>.
- Bindeman, I. N., Eiler, J. M., Yogodzinski, G. M., Tatsumi, Y., Stern, C. R., Grove, T. L., Portnyagin, M., Hoernle, K. & Danyushevsky, L. V. (2005). Oxygen isotope evidence for slab melting in modern and ancient subduction zones. *Earth and Planetary Science Letters* **235**, 480–496. <https://doi.org/10.1016/j.epsl.2005.04.014>.
- Boehnke, P., Watson, E. B., Trail, D., Harrison, T. M. & Schmitt, A. K. (2013). Zircon saturation re-visited. *Chemical Geology* **351**, 324–334. <https://doi.org/10.1016/j.chemgeo.2013.05.028>.
- Borisov, A. & Aranovich, L. (2019). Zircon solubility in silicate melts: new experiments and probability of zircon crystallization in deeply evolved basic melts. *Chemical Geology* **510**, 103–112. <https://doi.org/10.1016/j.chemgeo.2019.02.019>.
- Broom-Fendley, S., Styles, M. T., Appleton, J. D., Gunn, G. & Wall, F. (2016). Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *American Mineralogist* **101**, 596–611. <https://doi.org/10.2138/am-2016-5502CCBY>.
- Burnham, A. D. & Berry, A. J. (2012). An experimental study of trace element partitioning between zircon and melt as a function of oxygen fugacity. *Geochimica et Cosmochimica Acta* **95**, 196–212. <https://doi.org/10.1016/j.gca.2012.07.034>.
- Cashman, K. V., Sparks, R. S. J. & Blundy, J. D. (2017). Vertically extensive and unstable magmatic systems: a unified view of igneous processes. *Science* **355**, eaag3055. <https://doi.org/10.1126/science.aag3055>.
- Chakraborty, S. (2010). Diffusion coefficients in olivine, wadsleyite and ringwoodite. *Reviews in Mineralogy and Geochemistry* **72**, 603–639. <https://doi.org/10.2138/rmg.2010.72.13>.
- Chang, J., Audetat, A. & Li, J. W. (2021). In situ reaction-replacement origin of hornblendites in the Early Cretaceous Laiyuan Complex, North China Craton, and implications for its tectono-magmatic evolution. *Journal of Petrology* **62**. <https://doi.org/10.1093/petrology/egab030>.
- Chauvel, C., Lewin, E., Carpentier, M., Arndt, N. T. & Marini, J. C. (2008). Role of recycled oceanic basalt and sediment in generating the Hf-Nd mantle array. *Nature Geoscience* **1**, 64–67. <https://doi.org/10.1038/ngeo.2007.51>.
- Coogan, L. A., Saunders, A. D. & Wilson, R. N. (2014). Aluminum-in-olivine thermometry of primitive basalts: evidence of an anomalously hot mantle source for large igneous provinces. *Chemical Geology* **368**, 1–10. <https://doi.org/10.1016/j.chemgeo.2014.01.004>.
- Cornet, J., Laurent, O., Wotzlaw, J.-F., Antonelli, M. A., Otamendi, J., Bergantz, G. W. & Bachmann, O. (2022). Reworking subducted sediments in arc magmas and the isotopic diversity of the continental crust: the case of the Ordovician Famatinian crustal section, Argentina. *Earth and Planetary Science Letters* **595**, 117706. <https://doi.org/10.1016/j.epsl.2022.117706>.
- Couziñé, S., Laurent, O., Moya, J. F., Zeh, A., Bouilhol, P. & Villaros, A. (2016). Post-collisional magmatism: crustal growth not identified by zircon Hf-O isotopes. *Earth and Planetary Science Letters* **456**, 182–195. <https://doi.org/10.1016/j.epsl.2016.09.033>.
- Dan, W., Wang, Q., Wang, X. C., Liu, Y., Wyman, D. A. & Liu, Y. S. (2015). Overlapping Sr-Nd-Hf-O isotopic compositions in Permian mafic enclaves and host granitoids in Alxa Block, NW China: evidence for crust-mantle interaction and implications for the generation of silicic igneous provinces. *Lithos* **230**, 133–145. <https://doi.org/10.1016/j.lithos.2015.05.016>.
- Davidson, J., Turner, S., Handley, H., Macpherson, C. & Dosseto, A. (2007). Amphibole “sponge” in arc crust? *Geology* **35**, 787–790. <https://doi.org/10.1130/G23637A.1>.



- Depaolo, D. J. (1981). Neodymium isotopes in the Colorado front range and crust-mantle evolution in the Proterozoic. *Nature* **291**, 193–196. <https://doi.org/10.1038/291193a0>.
- Dhuime, B., Hawkesworth, C. & Cawood, P. (2011). When continents formed. *Age (Ga)* **331**, 154–155. <https://doi.org/10.1126/science.1201245>.
- Dhuime, B., Hawkesworth, C. J., Cawood, P. A. & Storey, C. D. (2012). A change in the geodynamics of continental growth 3 billion years ago. *Science* **335**, 1334–1336. <https://doi.org/10.1126/science.1216066>.
- Dorendorf, F., Wiechert, U. & Worner, G. (2000). Hydrated sub-arc mantle: a source for the Kluchevskoy volcano, Kamchatka/Russia. *Earth and Planetary Science Letters* **175**, 69–86. [https://doi.org/10.1016/S0012-821X\(99\)00288-5](https://doi.org/10.1016/S0012-821X(99)00288-5).
- Eiler, J. M. (2001). Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Stable Isotope Geochemistry* **43**, 319–364. <https://doi.org/10.1515/9781501508745-008>.
- Erdmann, S., Martel, C., Pichavant, M. & Kushnir, A. (2014). Amphibole as an archivist of magmatic crystallization conditions: problems, potential, and implications for inferring magma storage prior to the paroxysmal 2010 eruption of Mount Merapi, Indonesia. *Contributions to Mineralogy and Petrology* **167**. <https://doi.org/10.1007/s00410-014-1016-4>.
- Féménias, O., Mercier, J.-C. C., Nkono, C., Diot, H., Berza, T., Tatu, M. & Demaiffe, D. (2006). Calcic amphibole growth and compositions in calc-alkaline magmas: evidence from the Motru Dike Swarm (Southern Carpathians, Romania). *American Mineralogist* **91**, 73–81. <https://doi.org/10.2138/am.2006.1869>.
- Griffin, W. L., Pearson, N. J., Belousova, E., Jackson, S. E., van Achterbergh, E., O'Reilly, S. Y. & Shee, S. R. (2000). The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites. *Geochimica et Cosmochimica Acta* **64**, 133–147. [https://doi.org/10.1016/S0016-7037\(99\)00343-9](https://doi.org/10.1016/S0016-7037(99)00343-9).
- Grimes, C. B., John, B. E., Cheadle, M. J., Mazdab, F. K., Wooden, J. L., Swapp, S. & Schwartz, J. J. (2009). On the occurrence, trace element geochemistry, and crystallization history of zircon from in situ ocean lithosphere. *Contributions to Mineralogy and Petrology* **158**, 757–783. <https://doi.org/10.1007/s00410-009-0409-2>.
- Grove, T. L., Elkins-Tanton, L. T., Parman, S. W., Chatterjee, N., Muntener, O. & Gaetani, G. A. (2003). Fractional crystallization and mantle-melting controls on calc-alkaline differentiation trends. *Contributions to Mineralogy and Petrology* **145**, 515–533. <https://doi.org/10.1007/s00410-003-0448-z>.
- Gualda, G. A. R., Giorso, M. S., Lemons, R. V. & Carley, T. L. (2012). Rhyolite-MELTS: a modified calibration of MELTS optimized for silica-rich, fluid-bearing magmatic systems. *Journal of Petrology* **53**, 875–890. <https://doi.org/10.1093/petrology/egr080>.
- Guo, F., Guo, J. T., Wang, C. Y., Fan, W. M., Li, C. W., Zhao, L., Li, H. X. & Li, J. Y. (2013). Formation of mafic magmas through lower crustal AFC processes: an example from the Jinan gabbroic intrusion in the North China Block. *Lithos* **179**, 157–174. <https://doi.org/10.1016/j.lithos.2013.05.018>.
- Hao, H., Campbell, I. H. & Park, J. W. (2022). Nd-Hf isotopic systematics of the arc mantle and their implication for continental crust growth. *Chemical Geology* **602**, 120897. <https://doi.org/10.1016/j.chemgeo.2022.120897>.
- Hao, L. L., Wang, Q., Wyman, D. A., Ou, Q., Dan, W., Jiang, Z. Q., Wu, F. Y., Yang, J. H., Long, X. P. & Li, J. (2016). Underplating of basaltic magmas and crustal growth in a continental arc: evidence from Late Mesozoic intermediate-felsic intrusive rocks in southern Qiangtang, Central Tibet. *Lithos* **245**, 223–242. <https://doi.org/10.1016/j.lithos.2015.09.015>.
- Harlov, D. E. (2015). Apatite: a fingerprint for Metasomatic processes. *Elements* **11**, 171–176. <https://doi.org/10.2113/gselements.11.3.171>.
- Harrison, T. M. & Watson, E. B. (1984). The behavior of apatite during crustal Anatexis: equilibrium and kinetic considerations. *Geochimica et Cosmochimica Acta* **48**, 1467–1477. [https://doi.org/10.1016/0016-7037\(84\)90403-4](https://doi.org/10.1016/0016-7037(84)90403-4).
- Hawkesworth, C., Dhuime, B., Pietranik, A., Cawood, P., Kemp, A. & Storey, C. (2010). The generation and evolution of the continental crust. *Journal of the Geological Society* **167**, 229–248. <https://doi.org/10.1144/0016-76492009-072>.
- Hawkesworth, C. J. & Kemp, A. I. S. (2006). Using hafnium and oxygen isotopes in zircons to unravel the record of crustal evolution. *Chemical Geology* **226**, 144–162. <https://doi.org/10.1016/j.chemgeo.2005.09.018>.
- Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C. & Welch, M. D. (2012). Nomenclature of the amphibole supergroup. *American Mineralogist* **97**, 2031–2048. <https://doi.org/10.2138/am.2012.4276>.
- Heinonen, J. S., Jennings, E. S. & Riley, T. R. (2015). Crystallisation temperatures of the most Mg-rich magmas of the Karoo LIP on the basis of Al-in-olivine thermometry. *Chemical Geology* **411**, 26–35. <https://doi.org/10.1016/j.chemgeo.2015.06.015>.
- Hopkinson, T. N., Harris, N. B. W., Warren, C. J., Spencer, C. J., Roberts, N. M. W., Horstwood, M. S. A., Parrish, R. R. & EIMF. (2017). The identification and significance of pure sediment-derived granites. *Earth and Planetary Science Letters* **467**, 57–63. <https://doi.org/10.1016/j.epsl.2017.03.018>.
- Hoskin, P. W. O. (2005). Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. *Geochimica et Cosmochimica Acta* **69**, 637–648. <https://doi.org/10.1016/j.gca.2004.07.006>.
- Hoskin, P. W. O. & Schaltegger, U. (2003). The composition of zircon and igneous and metamorphic petrogenesis. *Zircon* **53**, 27–62. <https://doi.org/10.1515/9781501509322-005>.
- Hou, Z. Q., Duan, L. F., Lu, Y. J., Zheng, Y. C., Zhu, D. C., Yang, Z. M., Yang, Z. S., Wang, B. D., Pei, Y. R., Zhao, Z. D. & McCuaig, T. C. (2015). Lithospheric architecture of the Lhasa Terrane and its control on ore deposits in the Himalayan-Tibetan Orogen. *Economic Geology* **110**, 1541–1575. <https://doi.org/10.2113/econgeo.110.6.1541>.
- Hu, W.-L., Wang, Q., Tang, G.-J., Zhang, X.-Z., Qi, Y., Wang, J., Ma, Y.-M., Yang, Z.-Y., Sun, P. & Hao, L.-L. (2022). Late Early Cretaceous magmatic constraints on the timing of closure of the Bangong-Nujiang Tethyan Ocean, Central Tibet. *Lithos* **416–417**, 106648. <https://doi.org/10.1016/j.lithos.2022.106648>.
- Huang, X. L., Niu, Y. L., Xu, Y. G., Chen, L. L. & Yang, Q. J. (2010). Mineralogical and geochemical constraints on the Petrogenesis of post-collisional potassic and ultrapotassic rocks from Western Yunnan, SW China. *Journal of Petrology* **51**, 1617–1654. <https://doi.org/10.1093/petrology/egq032>.
- Humphreys, M. C. S., Cooper, G. F., Zhang, J., Loewen, M., Kent, A. J. R., Macpherson, C. G. & Davidson, J. P. (2019). Unravelling the complexity of magma plumbing at Mount St. Helens: a new trace element partitioning scheme for amphibole. *Contributions to Mineralogy and Petrology* **174**, 1–15.
- Iizuka, T., Campbell, I. H., Allen, C. M., Gill, J. B., Maruyama, S. & Makoka, F. (2013). Evolution of the African continental crust as recorded by U-Pb, Lu-Hf and O isotopes in detrital zircons from modern rivers. *Geochimica et Cosmochimica Acta* **107**, 96–120. <https://doi.org/10.1016/j.gca.2012.12.028>.
- Isa, J., Kohl, I. E., Liu, M. C., Wasson, J. T., Young, E. D. & McKeegan, K. D. (2017). Quantification of oxygen isotope SIMS matrix effects

- in olivine samples: correlation with sputter rate. *Chemical Geology* **458**, 14–21. <https://doi.org/10.1016/j.chemgeo.2017.03.020>.
- Jagoutz, O. & Klein, B. (2018). On the importance of crystallization-differentiation for the generation of SiO<sub>2</sub>-rich melts and the compositional build-up of arc (and continental) crust. *American Journal of Science* **318**, 29–63. <https://doi.org/10.2475/01.2018.03>.
- James, D. E. (1981). The combined use of oxygen and radiogenic isotopes as indicators of crustal contamination. *Annual Review of Earth and Planetary Sciences* **9**, 311–344. <https://doi.org/10.1146/annurev.ea.09.050181.001523>.
- Jennings, E. S., Gibson, S. A. & Maclennan, J. (2019). Hot primary melts and mantle source for the Parana-Etendeka flood basalt province: new constraints from Al-in-olivine thermometry. *Chemical Geology* **529**, 119287. <https://doi.org/10.1016/j.chemgeo.2019.119287>.
- Johnson, E. R., Wallace, P. J., Granados, H. D., Manea, V. C., Kent, A. J. R., Bindeman, I. N. & Donegan, C. S. (2009). Subduction-related volatile recycling and magma generation beneath Central Mexico: insights from melt inclusions, oxygen isotopes and geodynamic models. *Journal of Petrology* **50**, 1729–1764. <https://doi.org/10.1093/petrology/egp051>.
- Kemp, A. I., Hawkesworth, C. J., Foster, G. L., Paterson, B. A., Woodhead, J. D., Hergt, J. M., Gray, C. M. & Whitehouse, M. J. (2007). Magmatic and crustal differentiation history of granitic rocks from Hf-O isotopes in zircon. *Science* **315**, 980–983. <https://doi.org/10.1126/science.1136154>.
- Kemp, A. I. S., Hawkesworth, C. J., Paterson, B. A. & Kinny, P. D. (2006). Episodic growth of the Gondwana supercontinent from hafnium and oxygen isotopes in zircon. *Nature* **439**, 580–583. <https://doi.org/10.1038/nature04505>.
- Klaver, M., Blundy, J. D. & Vroon, P. Z. (2018). Generation of arc rhyodacites through cumulate-melt reactions in a deep crustal hot zone: evidence from Nisyros volcano. *Earth and Planetary Science Letters* **497**, 169–180. <https://doi.org/10.1016/j.epsl.2018.06.019>.
- Krneta, S., Ciobanu, C. L., Cook, N. J., Ehrig, K. & Kontonikas-Charos, A. (2016). Apatite at Olympic Dam, South Australia: a petrogenetic tool. *Lithos* **262**, 470–485. <https://doi.org/10.1016/j.lithos.2016.07.033>.
- Lee, C.-T. A. & Bachmann, O. (2014). How important is the role of crystal fractionation in making intermediate magmas? Insights from Zr and P systematics. *Earth and Planetary Science Letters* **393**, 266–274. <https://doi.org/10.1016/j.epsl.2014.02.044>.
- Li, S. M., Wang, Q., Zhu, D. C., Stern, R. J., Cawood, P. A., Sui, Q. L. & Zhao, Z. D. (2018). One or two Early Cretaceous Arc Systems in the Lhasa Terrane, Southern Tibet. *Journal of Geophysical Research-Solid Earth* **123**, 3391–3413. <https://doi.org/10.1002/2018JB015582>.
- Li, W. & Tan, K. (1998). Signal mineral separate method and its significance in geotectonics: taking apatite and zircon as examples. *Geotectonica et Metallogenia* **22**, 83–86.
- Li, W. R. & Costa, F. (2020). A thermodynamic model for F-Cl-OH partitioning between silicate melts and apatite including non-ideal mixing with application to constraining melt volatile budgets. *Geochimica et Cosmochimica Acta* **269**, 203–222. <https://doi.org/10.1016/j.gca.2019.10.035>.
- Li, X. H., Li, Z. X., Wingate, M. T. D., Chung, S. L., Liu, Y., Lin, G. C. & Li, W. X. (2006). Geochemistry of the 755 Ma Mundine Well dyke swarm, northwestern Australia: part of a Neoproterozoic mantle superplume beneath Rodinia? *Precambrian Research* **146**, 1–15. <https://doi.org/10.1016/j.precamres.2005.12.007>.
- Li, X. H., Liu, Y., Li, Q. L., Guo, C. H. & Chamberlain, K. R. (2009). Precise determination of Phanerozoic zircon Pb/Pb age by multicollector SIMS without external standardization. *Geochemistry, Geophysics, Geosystems* **10**, 1–21.
- Li, X. H., Long, W. G., Li, Q. L., Liu, Y., Zheng, Y. F., Yang, Y. H., Chamberlain, K. R., Wan, D. F., Guo, C. H., Wang, X. C. & Tao, H. (2010). Penglai zircon megacrysts: a potential new working reference material for microbeam determination of Hf-O isotopes and U-Pb age. *Geostandards and Geoanalytical Research* **34**, 117–134. <https://doi.org/10.1111/j.1751-908X.2010.00036.x>.
- Li, X. H., Tang, G. Q., Gong, B., Yang, Y. H., Hou, K. J., Hu, Z. C., Li, Q. L., Liu, Y. & Li, W. X. (2013). Qinghu zircon: a working reference for microbeam analysis of U-Pb age and Hf and O isotopes. *Chinese Science Bulletin* **58**, 4647–4654. <https://doi.org/10.1007/s11434-013-5932-x>.
- Lu, Y.-J., Hou, Z.-Q., Yang, Z.-M., Parra-Avila, L. A., Fiorentini, M., McCuaig, T. C. & Loucks, R. R. (2017). Terrane-scale porphyry Cu fertility in the Lhasa terrane, southern Tibet. *Geological Survey of Western Australia, Record* **6**, 95–100.
- Ludwig, K. R. (2003) *User's manual for Isoplot 3.00: a geochronological toolkit for Microsoft Excel*: Kenneth R. Ludwig. Berkeley: Berkeley Geochronology Center.
- Martin, E., Bindeman, I. & Grove, T. L. (2011). The origin of high-Mg magmas in Mt Shasta and Medicine Lake volcanoes, Cascade Arc (California): higher and lower than mantle oxygen isotope signatures attributed to current and past subduction. *Contributions to Mineralogy and Petrology* **162**, 945–960. <https://doi.org/10.1007/s00410-011-0633-4>.
- Mattey, D., Lowry, D. & Macpherson, C. (1994). Oxygen-isotope composition of mantle peridotite. *Earth and Planetary Science Letters* **128**, 231–241. [https://doi.org/10.1016/0012-821X\(94\)90147-3](https://doi.org/10.1016/0012-821X(94)90147-3).
- McCubbin, F. M., Vander Kaaden, K. E., Tartese, R., Boyce, J. W., Mikhail, S., Whitson, E. S., Bell, A. S., Anand, M., Franchi, I. A., Wang, J. H. & Hauri, E. H. (2015). Experimental investigation of F, Cl, and OH partitioning between apatite and Fe-rich basaltic melt at 1.0–1.2 GPa and 950–1000 degrees C. *American Mineralogist* **100**, 1790–1802. <https://doi.org/10.2138/am-2015-5233>.
- Mcculloch, M. T. & Wasserburg, G. J. (1978). Sm-Nd and Rb-Sr chronology of continental crust formation. *Science* **200**, 1003–1011. <https://doi.org/10.1126/science.200.4345.1003>.
- Miller, C. F., McDowell, S. M. & Mapes, R. W. (2003). Hot and cold granites? Implications of zircon saturation temperatures and preservation of inheritance. *Geology* **31**, 529–532. [https://doi.org/10.1130/0091-7613\(2003\)031<0529:HACGIO>2.0.CO;2](https://doi.org/10.1130/0091-7613(2003)031<0529:HACGIO>2.0.CO;2).
- Moyen, J.-F., Laurent, O., Chelle-Michou, C., Couzinié, S., Vanderhaeghe, O., Zeh, A., Villaros, A. & Gardien, V. (2017). Collision vs. subduction-related magmatism: two contrasting ways of granite formation and implications for crustal growth. *Lithos* **277**, 154–177. <https://doi.org/10.1016/j.lithos.2016.09.018>.
- Muntener, O. & Ulmer, P. (2018). Arc crust formation and differentiation constrained by experimental petrology. *American Journal of Science* **318**, 64–89. <https://doi.org/10.2475/01.2018.04>.
- Payne, J. L., McInerney, D. J., Barovich, K. M., Kirkland, C. L., Pearson, N. J. & Hand, M. (2016). Strengths and limitations of zircon Lu-Hf and O isotopes in modelling crustal growth. *Lithos* **248–251**, 175–192. <https://doi.org/10.1016/j.lithos.2015.12.015>.
- Pettke, T., Audétat, A., Schaltegger, U. & Heinrich, C. A. (2005). Magmatic-to-hydrothermal crystallization in the W-Sn mineralized mole granite (NSW, Australia): part II: evolving zircon and thorite trace element chemistry. *Chemical Geology* **220**, 191–213. <https://doi.org/10.1016/j.chemgeo.2005.02.017>.
- Plank, T. & Langmuir, C. H. (1998). The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chemical Geology* **145**, 325–394. [https://doi.org/10.1016/S0009-2541\(97\)00150-2](https://doi.org/10.1016/S0009-2541(97)00150-2).

- Prowatke, S. & Klemme, S. (2006). Trace element partitioning between apatite and silicate melts. *Geochimica et Cosmochimica Acta* **70**, 4513–4527. <https://doi.org/10.1016/j.gca.2006.06.162>.
- Putirka, K. (2016). Amphibole thermometers and barometers for igneous systems and some implications for eruption mechanisms of felsic magmas at arc volcanoes. *American Mineralogist* **101**, 841–858. <https://doi.org/10.2138/am-2016-5506>.
- Ridolfi, F., Renzulli, A. & Puerini, M. (2010). Stability and chemical equilibrium of amphibole in calc-alkaline magmas: an overview, new thermobarometric formulations and application to subduction-related volcanoes. *Contributions to Mineralogy and Petrology* **160**, 45–66. <https://doi.org/10.1007/s00410-009-0465-7>.
- Roberts, N. M. & Spencer, C. J. (2015). The zircon archive of continent formation through time. *Geological Society, London, Special Publications* **389**, 197–225. <https://doi.org/10.1144/SP389.14>.
- Rudnick, R. L. (1995). Making continental-crust. *Nature* **378**, 571–578. <https://doi.org/10.1038/378571a0>.
- Sano, Y., Terada, K. & Fukuoka, T. (2002). High mass resolution ion microprobe analysis of rare earth elements in silicate glass, apatite and zircon: lack of matrix dependency. *Chemical Geology* **184**, 217–230. [https://doi.org/10.1016/S0009-2541\(01\)00366-7](https://doi.org/10.1016/S0009-2541(01)00366-7).
- Sisson, T. W. & Grove, T. L. (1993). Experimental investigations of the role of H<sub>2</sub>O in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology* **113**, 143–166. <https://doi.org/10.1007/BF00283225>.
- Sláma, J., Kosler, J., Condon, D. J., Crowley, J. L., Gerdes, A., Hanchar, J. M., Horstwood, M. S. A., Morris, G. A., Nasdala, L., Norberg, N., Schaltegger, U., Schoene, B., Tubrett, M. N. & Whitehouse, M. J. (2008). Plesovice zircon - a new natural reference material for U-Pb and Hf isotopic microanalysis. *Chemical Geology* **249**, 1–35. <https://doi.org/10.1016/j.chemgeo.2007.11.005>.
- Smith, D. J. (2014). Clinopyroxene precursors to amphibole sponges in arc crust. *Nature Communications* **5**, 4329. <https://doi.org/10.1038/ncomms5329>.
- Spandler, C. & O'Neill, H. S. (2010). Diffusion and partition coefficients of minor and trace elements in San Carlos olivine at 1,300A degrees C with some geochemical implications. *Contributions to Mineralogy and Petrology* **159**, 791–818. <https://doi.org/10.1007/s00410-009-0456-8>.
- Spencer, C. J., Cavosie, A. J., Morrell, T. R., Lu, G. M., Liebmann, J. & Roberts, N. M. W. (2022). Disparities in oxygen isotopes of detrital and igneous zircon identify erosional bias in crustal rock record. *Earth and Planetary Science Letters* **577**, 117248. <https://doi.org/10.1016/j.epsl.2021.117248>.
- Sui, Q. L., Wang, Q., Zhu, D. C., Zhao, Z. D., Chen, Y., Santosh, M., Hu, Z. C., Yuan, H. L. & Mo, X. X. (2013). Compositional diversity of ca. 110 Ma magmatism in the northern Lhasa Terrane, Tibet: implications for the magmatic origin and crustal growth in a continent-continent collision zone. *Lithos* **168–169**, 144–159. <https://doi.org/10.1016/j.lithos.2013.01.012>.
- Sun, C. G. & Liang, Y. (2013). Distribution of REE and HFSE between low-Ca pyroxene and lunar picritic melts around multiple saturation points. *Geochimica et Cosmochimica Acta* **119**, 340–358. <https://doi.org/10.1016/j.gca.2013.05.036>.
- Sun, S.-S. & McDonough, W. F. (1989). Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society, London, Special Publications* **42**, 313–345. <https://doi.org/10.1144/GSL.SP.1989.042.01.19>.
- Tang, G. Q., Su, B. X., Li, Q. L., Xia, X. P., Jing, J. J., Feng, L. J., Martin, L., Yang, Q. & Li, X. H. (2019). High-mg# olivine, clinopyroxene and orthopyroxene reference materials for in situ oxygen isotope determination. *Geostandards and Geoanalytical Research* **43**, 585–593. <https://doi.org/10.1111/ggr.12288>.
- Tiepolo, M., Langone, A., Morishita, T. & Yuhara, M. (2012). On the recycling of amphibole-rich ultramafic intrusive rocks in the arc crust: evidence from Shikanoshima Island (Kyushu, Japan). *Journal of Petrology* **53**, 1255–1285. <https://doi.org/10.1093/petrology/egs016>.
- Tiepolo, M., Oberti, R., Zanetti, A., Vannucci, R. & Foley, S. F. (2007). Trace-element partitioning between amphibole and silicate melt. *Reviews in Mineralogy and Geochemistry* **67**, 417–452. <https://doi.org/10.2138/rmg.2007.67.11>.
- Ulmer, P., Kaegi, R. & Müntener, O. (2018). Experimentally derived intermediate to silica-rich arc magmas by fractional and equilibrium crystallization at 1.0 GPa: an evaluation of phase relationships, compositions, liquid lines of descent and oxygen fugacity. *Journal of Petrology* **59**, 11–58. <https://doi.org/10.1093/petrology/egy017>.
- Valley, J. W., Kinny, P. D., Schulze, D. J. & Spicuzza, M. J. (1998). Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts. *Contributions to Mineralogy and Petrology* **133**, 1–11. <https://doi.org/10.1007/s004100050432>.
- Valley, J. W., Lackey, J. S., Cavosie, A. J., Clechenko, C. C., Spicuzza, M. J., Basei, M. A. S., Bindeman, I. N., Ferreira, V. P., Sial, A. N., King, E. M., Peck, W. H., Sinha, A. K. & Wei, C. S. (2005). 4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon. *Contributions to Mineralogy and Petrology* **150**, 561–580. <https://doi.org/10.1007/s00410-005-0025-8>.
- Van den Bleeken, G. & Koga, K. T. (2015). Experimentally determined distribution of fluorine and chlorine upon hydrous slab melting, and implications for F-Cl cycling through subduction zones. *Geochimica et Cosmochimica Acta* **171**, 353–373. <https://doi.org/10.1016/j.gca.2015.09.030>.
- Wang, J., Wang, Q., Dan, W., Yang, J.-H., Yang, Z.-Y., Sun, P., Qi, Y. & Hu, W.-L. (2019). The role of clinopyroxene in amphibole fractionation of arc magmas: evidence from mafic intrusive rocks within the Gangdese arc, southern Tibet. *Lithos* **338–339**, 174–188. <https://doi.org/10.1016/j.lithos.2019.04.013>.
- Wang, J., Wang, Q., Zeng, J.-P., Ou, Q., Dan, W., Yang, A., Chen, Y.-W. & Wei, G. (2022). Generation of continental alkalic mafic melts by tholeiitic melt-mush reactions: a new perspective from contrasting mafic cumulates and dikes in Central Tibet. *Journal of Petrology* **63**, 1–21. <https://doi.org/10.1093/petrology/egac039>.
- Wang, M. X., Nebel, O. & Wang, C. Y. (2016). The flaw in the crustal 'Zircon Archive': mixed Hf isotope signatures record progressive contamination of late-stage liquid in mafic-ultramafic layered intrusions. *Journal of Petrology* **57**, 27–52. <https://doi.org/10.1093/petrology/egv072>.
- Wang, X. D., Hou, T., Wang, M., Zhang, C., Zhang, Z. C., Pan, R. H., Marxer, F. & Zhang, H. L. (2021). A new clinopyroxene thermometer for mafic to intermediate magmatic systems. *European Journal of Mineralogy* **33**, 621–637. <https://doi.org/10.5194/ejm-33-621-2021>.
- Wasserburg, G. J., Jacobsen, S. B., Depaolo, D. J., McCulloch, M. T. & Wen, T. (1981). Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta* **45**, 2311–2323. [https://doi.org/10.1016/0016-7037\(81\)90085-5](https://doi.org/10.1016/0016-7037(81)90085-5).
- Watson, E. B. & Green, T. H. (1981). Apatite liquid partition-coefficients for the rare-earth elements and strontium. *Earth and Planetary Science Letters* **56**, 405–421. [https://doi.org/10.1016/0012-821X\(81\)90144-8](https://doi.org/10.1016/0012-821X(81)90144-8).

- Watson, E. B. & Harrison, T. M. (1983). Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth and Planetary Science Letters* **64**, 295–304. [https://doi.org/10.1016/0012-821X\(83\)90211-X](https://doi.org/10.1016/0012-821X(83)90211-X).
- Weis, D., Kieffer, B., Maerschalk, C., Pretorius, W. & Barling, J. (2005). High-precision Pb-Sr-Nd-Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials. *Geochemistry, Geophysics, Geosystems* **6**, Q02002. <https://doi.org/10.1029/2004GC000852>.
- Wenner, D. B. & Taylor, H. P. (1971). Temperatures of serpentinization of ultramafic rocks based on O18/O16 fractionation between coexisting serpentine and magnetite. *Contributions to Mineralogy and Petrology* **32**, 165–185. <https://doi.org/10.1007/BF00643332>.
- Wu, F. Y., Yang, Y. H., Xie, L. W., Yang, J. H. & Xu, P. (2006). Hf isotopic compositions of the standard zircons and baddeleyites used in U-Pb geochronology. *Chemical Geology* **234**, 105–126. <https://doi.org/10.1016/j.chemgeo.2006.05.003>.
- Yang, S. H., Maier, W. D., Godel, B., Barnes, S. J., Hanski, E. & O'Brien, H. (2019). Parental magma composition of the main zone of the Bushveld Complex: Evidence from in situ LA-ICP-MS trace element analysis of silicate minerals in the cumulate rocks. *Journal of Petrology* **60**, 359–392.
- Yang, Q., Xia, X., Zhang, W., Zhang, Y., Xiong, B., Xu, Y., Wang, Q. & Wei, G. (2018). An evaluation of precision and accuracy of SIMS oxygen isotope analysis. *Solid Earth Sciences* **3**, 81–86. <https://doi.org/10.1016/j.sesci.2018.05.001>.
- Yang, Y. H., Wu, F. Y., Yang, J. H., Chew, D. M., Xie, L. W., Chu, Z. Y., Zhang, Y. B. & Huang, C. (2014). Sr and Nd isotopic compositions of apatite reference materials used in U-Th-Pb geochronology. *Chemical Geology* **385**, 35–55. <https://doi.org/10.1016/j.chemgeo.2014.07.012>.
- Zeng, Y. C., Xu, J. F., Huang, F., Li, M. J. & Chen, Q. (2020). Generation of the 105-100 Ma Dagze volcanic rocks in the North Lhasa Terrane by lower crustal melting at different temperature and depth: implications for tectonic transition. *Geological Society of America Bulletin* **132**, 1257–1272. <https://doi.org/10.1130/B35306.1>.
- Zhang, J., Humphreys, M. C. S., Cooper, G. F., Davidson, J. P. & Macpherson, C. G. (2017). Magma mush chemistry at subduction zones, revealed by new melt major element inversion from calcic amphiboles. *American Mineralogist* **102**, 1353–1367. <https://doi.org/10.2138/am-2017-5928>.
- Zhang, L., Ren, Z.-Y., Xia, X.-P., Yang, Q., Hong, L.-B. & Wu, D. (2019). In situ determination of trace elements in melt inclusions using laser ablation inductively coupled plasma sector field mass spectrometry. *Rapid Communications in Mass Spectrometry* **33**, 361–370. <https://doi.org/10.1002/rcm.8359>.
- Zhang, L., Wu, J. L., Zhang, Y. Q., Yang, Y. N., He, P. L., Xia, X. P. & Ren, Z. Y. (2021). Simultaneous determination of Sm-Nd isotopes, trace-element compositions and U-Pb ages of titanite using a laser-ablation split-stream technique with the addition of water vapor. *Journal of Analytical Atomic Spectrometry* **36**, 2312–2321. <https://doi.org/10.1039/D1JA00246E>.
- Zhang, X. B., Guo, F., Zhang, B., Zhao, L., Wu, Y. M., Wang, G. Q. & Ale-mayehu, M. (2020). Magmatic evolution and post-crystallization hydrothermal activity in the Early Cretaceous Pingtan intrusive complex, SE China: records from apatite geochemistry. *Contributions to Mineralogy and Petrology* **175**. <https://doi.org/10.1007/s00410-020-1675-2>.
- Zhu, D.-C., Zhao, Z.-D., Niu, Y., Mo, X.-X., Chung, S.-L., Hou, Z.-Q., Wang, L.-Q. & Wu, F.-Y. (2011). The Lhasa Terrane: record of a microcontinent and its histories of drift and growth. *Earth and Planetary Science Letters* **301**, 241–255. <https://doi.org/10.1016/j.epsl.2010.11.005>.