# Magma oxygen fugacity and volatile components control the Miocene high-Sr/Y granitoids forming either Cu or W mineralization in the Gangdese metallogenic region, Xizang, China

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# Abstract

Porphyry copper deposits are usually associated with high-Sr/Y granitoids. The Miocene Gangdese porphyry copper belt in southern Tibet is also associated with high-Sr/Y granitoids, forming wolframite deposits. Why some coeval high-Sr/Y granitoids formed Cu deposits (Cu-granitoids) while others formed W deposits (W-granites) remains unclear. We address this issue by studying magma sources and properties, analyzing magmatic zircons, biotites, and apatites in these granites, and combining this information with previously published bulk-rock and zircon isotopic data. In situ chemical analyses of magmatic zircon, biotite, and apatite show that the properties of the magmas that produced the Cu-granitoids and W-granites were significantly different. Zircon  $\Delta$ FMQ values of the W-granites were much lower than those of the Cu-granitoids, suggesting a more reduced magma for W deposits. Water content of the W-granites (7–9 wt%) seems to be lower than that of the Cu-granitoids (10-12 wt%). This is suggested by the low-zircon Ce/Nd and (Ce/Nd)/Y ratios and high-Dy/Yb ratios in the W-granites. Biotite and apatite from the W-granites generally have lower Cl contents than those from most Cu-granitoids. Moreover, the SO<sub>3</sub> concentration in apatite from the W-granites is also lower than that of the Cu-granitoids. These data agree with the genetic environment suggested by previously published isotopic data. Bulk-rock Sr-Nd and zircon Hf isotopes indicate that the Cu-granitoids were mainly sourced from juvenile lower crust. In contrast, the source of W-granites was contaminated with the old Lhasa terrane basement. Our results highlight the role of magma oxygen fugacity and volatile components in controlling metal variations in high-Sr/Y granitoids. Combinations of magmatic zircon  $\Delta$ FMQ and Ce/Nd, (Ce/Nd)/Y and Dy/Yb ratios, and apatite and biotite SO<sub>3</sub> and Cl contents can be used to discriminate W-granites from Cu-granitoids in the Gangdese metallogenic region, and hence granitoids potentially hosting W vs. Cu ore deposits.

**Keywords:** High-Sr/Y granitoids, porphyry copper deposit, W-related granites, magma oxygen fugacity, volatile components, Gangdese metallogenic region

# INTRODUCTION

Porphyry copper deposits (PCDs) are generally associated with hydrous and oxidized magmas (Richards 2003), which can be generated in both magmatic arcs (Richards 2003; Sillitoe 2010) and collisional orogenic belts (Hou et al. 2015). Studies on PCDs, including cases in magmatic arcs and collisional zones worldwide, have proposed that the magmatic suites associated with PCDs usually have high-Sr/Y ratios (Richards and Kerrich 2007; Chiaradia et al. 2012; Richards et al. 2012; Loucks 2014). High-Sr/Y ratios may reflect garnet and/or hornblende residues in the magma source region during partial melting or fractional crystallization of garnet and/or hornblende at pressures above ~10 kbar (Loucks 2021). In addition, high-Sr/Y ratios can be generated in asthenosphere-derived arc magmas by upper plate crustal interaction and crystal fractionation (Richards and Kerrich 2007). The Gangdese porphyry copper belt (GPCB) in the southern Lhasa terrane (Fig. 1) is a typical collisional metallogenic belt and the PCDs in the GPCB are also associated with high-Sr/Y

during the Miocene (22–12 Ma) (Hou et al. 2015; Yang et al. 2016; Wang et al. 2018b). Recently, several quartz vein- and greisen-type wolframite deposits and mineralization occurrences have been discovered in the northwestern GPCB; these deposits are genetically related to Miocene (14–11 Ma) high-Sr/Y and high-La/Yb biotite monzogranite and two-mica granite (Wang et al. 2018a, 2020, 2022). They typically include the Jiaoxi deposit and the Jiaodong and Anglonggangri mineralization occurrences (Fig. 1b). These discoveries indicate that the Miocene high-Sr/Y granitoids in the Gangdese metallogenic region formed not only Cu but also W deposits. The geological factors controlling the formation of distinct metal deposits by nearly coeval high-Sr/Y granitoids remain unclear. This is an important question that needs to be addressed because of its relationship with regional mineral resource prospecting and exploration.

(>20) and usually high La/Yb (>20) granitoids (Fig. 2) emplaced

The magma source and properties of granitoids (e.g., temperature, oxygen fugacity, sulfur fugacity, water content, and halogen concentration) play key roles in controlling metal associations in magmatic-hydrothermal mineralization systems. Based on the oxygen fugacity ( $f_{O_2}$ ) estimated by bulk-rock

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FIGURE 1. Simplified geological map of the Lhasa terrane showing tectonic units (a) and spatial distributions of the Miocene PCDs and the W mineralized areas (b) modified after Zhu et al. (2013). BNSZ = Bangong-Nujiang suture zone; SNMZ = Shiquan River-Nam Tso mélange zone; LMF = Luobadui-Milashan fault; KF = Karakorum fault; IYZS = Indus-Yarlung Zangbo suture zone; MBT = Main boundary thrust; MCT = Main central thrust; STDS = South Tibet detachment system.

chemical ratios (e.g.,  $Fe^{3+}/Fe^{2+}$ , V/Cr, and  $Eu^{3+}/Eu^{2+}$ ), the amphibole oxybarometer, and the volatile component analysis of melt inclusions from magmatic rocks, the fertile magmas that form PCDs are considered hydrous, oxidized, and enriched in volatiles such as S and Cl (Sillitoe 2010; Richards 2015). A high-magma water (H<sub>2</sub>O) content is crucial for the generation of large volumes of ore-forming fluids in porphyries (Richards et al. 2012; Loucks 2014). The high-oxidation state of a porphyry keeps sulfur mainly in the form of  $SO_4^{2-}$  or  $SO_2$  rather than  $S^{2-}$  in magmas. This facilitates the transport of Cu and prevents the early formation and precipitation of sulfides in magmatichydrothermal systems (Jugo 2009; Richards 2015). The importance of high-magmatic S and Cl concentrations for PCDs lies in

their capacity to make metals form complexing ligands, thereby efficiently promoting metal transport during magmatic-hydrothermal evolution (Chambefort et al. 2008; Chelle-Michou and Chiaradia 2017). Tungsten deposits, however, are usually associated with reduced and F-rich granitic magmas, according to the low bulk-rock Fe<sub>2</sub>O<sub>3</sub>/FeO ratios and high F contents measured in ore-forming granites (Ishihara 1981, 2015; Harlaux et al. 2018; Azadbakht et al. 2020). Experimental studies have shown that W is dominantly present as W<sup>6+</sup> in silicic magma (O'Neill et al. 2008). Although the  $f_{O_2}$  has little influence on the W<sup>6+</sup> ion valence (Che et al. 2013), W is more prone to enter the magmatic-hydrothermal fluids and becoming enriched under low- $f_{O_2}$  conditions (Candela and Bouton 1990). Hence, W



FIGURE 2. Diagrams showing the high-Sr/Y (a) and high-La/Yb (b) features of the Miocene Gangdese Cu- and W-granitoids. The data for the Cu-granitoids are from Zheng et al. (2020) and references therein; the data for the W-granites are from Wang et al. (2020, 2022).

mineralization tends to be associated with reduced granites (Hart et al. 2004). Unlike Cu deposits commonly linked with Cl-rich magma and fluid, W mineralization preferentially occurs in F-rich magmatic-hydrothermal systems (Vigneresse 2009; Ishihara 2015). High F contents may increase the abundance of nonbridging O atoms in melts (Keppler 1993), increasing the proportion of  $WO_4^{2-}$  in the melts (Che et al. 2013). Therefore, high F contents are important for promoting the enrichment of W in residual magmas (Che et al. 2013). Moreover, F can extend the magmatic evolution process and facilitate the migration of W in magmatic-hydrothermal systems (Vigneresse et al. 2011).

Biotite, apatite, and zircon are modally abundant or frequent in felsic intrusions, and many studies have confirmed that the compositions of these minerals can be used to identify the physicochemical properties of their parent magma (Gardiner et al. 2017; Azadbakht et al. 2020). For instance, Ti-in-zircon thermometry has been widely used to calculate magma temperature (Ferry and Watson 2007). In addition, the Ti-Ce-U contents of zircon are useful indicators of the  $f_{0}$ , of their host magmas (Loucks et al. 2020), and (Ce/Nd)/Y and Dy/Yb in zircon can provide H<sub>2</sub>O content information about the magma (Lu et al. 2016; Lee et al. 2021). Moreover, biotite and apatite incorporate volatile components, such as H<sub>2</sub>O, F, Cl, and S (Boomeri et al. 2006; Webster and Piccoli 2015). Accordingly, they are useful for tracking magma's halogen concentrations and sulfur fugacity (Mercer and Reed 2013; Bouzari et al. 2016; Li and Hermann 2017; Moshefi et al. 2018).

In this paper, we present in situ major element analyses of biotite and apatite and trace element analyses of zircon from the W-granites in the Jiaoxi, Jiaodong, and Anglonggangri areas to infer the properties of their associated magmas. These data, together with the published compositions of biotite, apatite, and zircon from the Cu-granitoids and published bulk-rock Sr-Nd and zircon Hf isotopic analyses, provide insights into key factors controlling the formation of either Cu or W mineralization in Miocene high-Sr/Y granitoids in the Gangdese metallogenic region.

#### **GEOLOGICAL SETTING**

The Lhasa terrane (i.e., the Gangdese metallogenic region) is located in the southern Tibetan Plateau south of, and separated from, the Qiangtang terrane by the Bangong-Nujiang suture zone. The Indus-Yarlung Zangbo suture zone to the south separates the Lhasa terrane from the Himalayan orogeny (Fig. 1). The Lhasa terrane can be subdivided into southern, central, and northern subterranes based on the different basement and sedimentary cover rocks (Zhu et al. 2013). The GPCB is located in the eastern part of the southern Lhasa subterrane, whereas the Jiaoxi, Jiaodong, and Anglonggangri wolframite mineralization areas are situated in the western portion of the northern Lhasa subterrane (Fig. 1b).

The southern Lhasa subterrane is bounded by the Indus-Yarlung Zangbo suture zone to the south and by the Luobadui-Milashan fault to the north (Fig. 1). Precambrian crystalline basement may be locally present east of this subterrane (Zhu et al. 2013). The sedimentary cover is mainly composed of early Jurassic to Cretaceous volcano-sedimentary strata with the local late Cambrian Nyningchi Group (Zhu et al. 2013). Magmatism in the southern Lhasa subterrane is dominated by Late Triassic-Cretaceous Gangdese batholiths and the Paleocene-Eocene Linzizong volcanic rocks (Mo et al. 2008; Ji et al. 2009). In addition, post-collisional magmatic rocks (<38 Ma) are widespread. They mainly consist of small-volume Oligocene-Miocene (33-12 Ma) high-Sr/Y intrusions and Miocene (25-8 Ma) potassic-ultrapotassic volcanic rocks (Fig. 1b; Chung et al. 2003; Guo et al. 2007; Liu et al. 2014a). Among these post-collisional intrusions, the Miocene (22-12 Ma) high-Sr/Y granodiorite and monzogranite porphyries are the ore-forming intrusions of PCDs (Hou et al. 2015; Yang et al. 2016; Wang et al. 2018b). The granodiorite porphyry consists of plagioclase, K-feldspar, hornblende, and quartz phenocrysts in a matrix of quartz, plagioclase, and biotite. Accessory minerals include apatite, zircon, titanite, and magnetite (Wang et al. 2015; Yang et al. 2016; Tang et al. 2021). The phenocrysts in the monzogranite porphyry are quartz, plagioclase, K-feldspar, and biotite with accessory apatite, zircon, ilmenite, and magnetite (Wu et al. 2016; Yang et al. 2016; Sun et al. 2018).

The northern Lhasa subterrane is located between the Bangong-Nujiang suture zone and the Shiquanhe-Nam Tso mélange zone (Fig. 1). The oldest sequences in this subterrane are found in the eastern part and contain middle-to-late Triassic sedimentary strata interbedded with volcanic rocks (Zhu et al. 2013). These sequences are unconformably overlain by middle-to-late Jurassic clastic rocks. Cretaceous strata comprising sedimentary and volcanic rocks occur along the strike of this subterrane (Zhu et al. 2013). The northern Lhasa subterrane is characterized by widespread early Cretaceous granitoids, represented by the Anglonggangri, AlongTso, Yanhu, and Baingoin batholiths (Zhu et al. 2016). Furthermore, several late Cretaceous and Paleocene-Eocene granites have been identified as intrusions in the Anglonggangri batholith (Zhu et al. 2016). A previous study reported early Miocene (23 Ma) high-Sr/Y trachytes west of the northern Lhasa subterrane (Guo et al. 2007). In addition to trachytes, studies in the Jiaoxi, Jiaodong, and Anglonggangri areas have shown that Miocene high-Sr/Y granites do exist to the west of this subterrane (Wang et al. 2020, 2022).

The Jiaoxi deposit is composed of quartz vein- and greisentype wolframite ores (Wang et al. 2018a, 2020). The early Cretaceous Shiquanhe ophiolite mélange, containing sandstone, shale, and sheets of ophiolitic rocks, is the main geological body hosting the quartz vein-type wolframite ores (Online Materials<sup>1</sup> Fig. S1). Several Miocene intrusions, including the high-Sr/Y porphyritic biotite monzogranite (14.1 Ma) and the more evolved granite porphyry (13.8 Ma) and muscovite granite (13.7 Ma), have been recognized (Wang et al. 2018a, 2020). The greisen-type wolframite ores are widely developed in the muscovite granite, with minor occurrences in the altered porphyritic biotite monzogranite.

The Jiaodong wolframite mineralization is near the Jiaoxi deposit and shows similar associated geological units (Online Materials<sup>1</sup> Fig. S2). The early Cretaceous Shiquanhe ophiolite mélange was intruded by the high-Sr/Y (porphyritic) biotite monzogranite pluton (14.2 Ma), with numerous pegmatite veins and local two-mica granite and muscovite granite dikes (Wang et al. 2018a). The pegmatite veins cutting through the biotite

monzogranite have muscovite <sup>40</sup>Ar-<sup>39</sup>Ar plateau ages of 10.2 Ma (Wang et al. 2022). The wolframite mineralization exists as veinlets or disseminated styles in the pegmatite and muscovite granite. Geochronology, bulk-rock geochemistry, and Sr-Nd-Hf isotope studies suggest that these intrusions in the Jiaoxi and Jiaodong areas are cogenetic and originated from the same magma source (Wang et al. 2020).

The Anglonggangri wolframite mineralization area is located northeast of the Jiaoxi deposit (Fig. 1). The strata in this area are the middle-late Jurassic Lagongtang Formation and the early Cretaceous Duoni Formation (Online Materials<sup>1</sup> Fig. S3). The Lagongtang Formation consists of sandstones, siltstones, and slates and is unconformably overlain by slates of the Duoni Formation. Intrusions in the area are divided into two episodes, i.e., the late Cretaceous syenogranite and granodiorite and the Miocene high-Sr/Y two-mica granite (11.1-10.7 Ma), garnetmuscovite granite (10.2 Ma) and pegmatite (Wang et al. 2022). The W mineralization is developed in a vein-like style in the two-mica granite. Geochronology, bulk-rock geochemistry, and Sr-Nd-Pb-Hf isotope results of the intrusions indicate that they are cogenetic and that the two-mica granite represents the parent magma of the highly evolved garnet-muscovite granite and pegmatite (Wang et al. 2022).

#### SAMPLING AND ANALYTICAL METHODS

#### Sample description

This study focuses on the biotite monzogranite and two-mica granite, representing the less evolved end-members and parent magmas in their mineralized areas. The biotite monzogranite samples were collected from outcrops in the Jiaoxi and Jiaodong areas and from a drill core in the Jiaoxi deposit. The two-mica granite samples were collected from outcrops in the Jiaodong and Anglonggangri areas. The detailed petrographic features of these rocks and the characteristics of the minerals studied here are provided below, as well as in Wang et al. (2018a, 2021, 2022).

### **Biotite monzogranite**

The biotite monzogranite is porphyritic and consists predominantly of quartz (~25%), K-feldspar (~35%), plagioclase (~30%), and biotite (~10%), with accessory zircon, apatite, monzite, and ilmenite (Online Materials<sup>1</sup> Figs. S4a–S4b). The biotite crystals (0.3–1.0 mm) exhibit a green color (replaced by chlorite due to alteration; Fig. 3a) and contain abundant inclusions of apatite, ilmenite, and monazite (Fig. 3b). Hydrothermal alteration in the biotite monzogranite is extensive and strong. The K-feldspar and plagioclase crystals are commonly altered to sericite, and the biotite crystals are almost completely replaced by chlorite and muscovite (Fig. 3a). Apatite crystals are mainly present as inclusions in biotite; they are subhedral and have sizes of 20–50  $\mu$ m (Figs. 3c–3d). Although apatites appear to develop corrosion edges under the optical microscope, high-magnification backscattered electron (BSE) images show that they are mostly homogeneous and have very few mineral and fluid inclusions (Figs. 3c–3d). These characteristics suggest that these apatites are likely magmatic and crystallized before fluid exsolution.

# Two-mica granite

The two-mica granite is medium- to coarse-grained and mainly comprised of quartz (~30%), plagioclase (~40%), and K-feldspar (~20%), with minor biotite (~5%) and muscovite (~5%) (Online Materials<sup>1</sup> Figs. S4c and S4d). The accessory mineral assemblage is similar to that of the biotite monzogranite and includes zircon, monazite, apatite, and ilmenite. Minerals in most of the granite have not undergone hydrothermal alteration. The euhedral to subhedral biotite crystals are commonly ~0.5 × 2.0 mm and show clear differences from the fine-grained scaly biotite aggregates that re-equilibrate with exsolved fluids. A reddish-brown color (Figs. 3f and 3k) may indicate moderately oxidized to reduced conditions

during growth (Lalonde and Bernard 1993). The biotite crystals often contain zircon, apatite, and ilmenite inclusions (Figs. 3g and 3l), suggesting early crystallization. The zircon crystals in apatite suggest that zircon crystallized earlier than apatite (Figs. 3f–3g). Apatites appear mainly as individual crystals in the matrix (Fig. 3g) or are hosted in biotite (Fig. 3l). They are generally larger and more euhedral compared to those in the biotite monzogranite, typically showing magmatic microstructures such as homogeneous euhedral crystals without fluid inclusions or hydrothermal alteration (Figs. 3h–3i and 3m–3n).

#### Analytical methods

Petrographic studies of 15 biotite and 25 apatite crystals were carried out on 15 polished thin sections using optical microscopy and BSE imaging. Electron microprobe analysis (EMPA) of major elements in biotite and apatite was carried out using a JEOL JXA-8230 electron microprobe at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. To overcome spectral interferences between  $FK\alpha$  of the synthetic W-Si multi-layered pseudocrystals (LDE1) and FeK $\alpha$  of Fe-bearing minerals, the method of Zhang et al. (2016) was adopted to measure F concentration in biotite accurately. The operating conditions were as follows: 15 kV accelerating voltage, 20 nA beam current, and 5 µm beam spot; a ZAF correction procedure for data reduction was used. The following minerals and synthetic oxides were used for calibration: K-feldspar (K), jadeite (Na, Al, Si), apatite (Ca, P), hematite (Fe), pyrope garnet (Mg), MnTiO<sub>3</sub> (Mn), rutile (Ti), topaz (F), barite (S), and halite (Cl). The detection limits for Cl and SO<sub>3</sub> are 90 and 200 ppm, respectively.

The zircon crystals analyzed for trace elements were collected from the Jiaoxi (Fig. 3c) and Jiaodong biotite monzogranites (Fig. 3j) and the Anglonggangri twomica granite (Fig. 3o), with ages of 14–11 Ma. The trace elements in zircons were measured using a Thermo Fisher's X-Series II inductively coupled plasma-mass spectrometry (ICP-MS) instrument attached to a GeoLasPro-193 nm laser system at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geoscience, Beijing. Helium was used as the carrier gas and mixed with argon before entering the ICP-MS torch. All the data were acquired in single post ablation mode at a spot size of 32  $\mu$ m with a frequency of 6 Hz. The standard materials SRM610 glass and <sup>29</sup>Si were used as the external and internal standards, respectively. Standard materials were analyzed once after every 10 analyses on the studied sample. Each analysis included a background acquisition of 20 s (gas blank) followed by 50 s data acquisition from the sample. Quantitative calibration for trace element analyses was performed by ICPMSDataCal.

# Methods for magma temperature and $f_{O_2}$ estimation

The magma temperatures were calculated using the Ti-in-zircon thermometer  $(T_{\text{Ti-Zr}})$  of Ferry and Watson (2007), assuming that  $\alpha_{\text{SiO}_2} = 1.0$  and  $\alpha_{\text{TiO}_2} = 0.7$  based on the presence of quartz and ilmenite in the W-granites. In addition to the mineral geothermometer, bulk-rock geochemistry of the granitoids was also used to constrain the magma temperature. The solubility of zircon in granitic melt is controlled by temperature and M [= (Na + K + 2Ca)/(Al × Si)] (molar contents; Boehnke et al. 2013). When M is <2.1, the bulk-rock zircon concentration can be used to estimate the magma temperature through the zircon saturation thermometry ( $T_{Zr}$ ) of Watson and Harrison (1983). The W-granite oxidation states were assessed using the bulk-rock ferric/ferrous ratios (Fe<sub>2</sub>O<sub>3</sub>/FeO) and zircon oxybarometer of Loucks et al. (2020).

# RESULTS

# **Mineral compositions**

**Biotite composition.** The major elements and halogen contents of the analyzed biotite crystals are presented in Online Materials<sup>1</sup> Table S1. Geochemical data were not obtained for biotite in the Jiaoxi and Jiaodong biotite monzogranites due to the extensive hydrothermal alteration of biotite to chlorite. The chemical composition of biotite was calculated based on 22 atoms of oxygen per formula unit (Online Materials<sup>1</sup> Table S1).

Biotite from the Anglonggangri two-mica granite has relatively uniform SiO<sub>2</sub> (34–39 wt%), Al<sub>2</sub>O<sub>3</sub> (16.4–18.5 wt%), FeO (21.1–22.9 wt%), and MgO (5.1–6.5 wt%) contents, but large variations in TiO<sub>2</sub> (1.4–3.2 wt%) and SO<sub>3</sub> (200–690 ppm) concentrations.



FIGURE 3. Petrographic characteristics of the Miocene Gangdese W-granites. (a) Cross-polarized light (CPL) photomicrograph of the Jiaoxi biotite monzogranite. (b) Backscattered electron (BSE) image of biotite with apatite and ilmenite inclusions from the Jiaoxi biotite monzogranite. (c and d) Subhedral apatite crystals in biotite from biotite monzogranite. (e) Cathodoluminescence (CL) images of zircons in the Jiaoxi biotite monzogranite (Wang et al. 2018a). (f) Plane-polarized light (PPL) photomicrograph of Jiaodong two-mica granite. (g) BSE images of biotite and apatite from the Jiaodong two-mica granite. (h and i) Euhedral crystals and homogeneous textures of apatite in the groundmass (h) and biotite (i) of the Jiaodong twomica granite. (j) CL images of zircons from the Jiaodong biotite monzogranite (Wang et al. 2018a). (k) Photomicrograph of the Anglonggangri twomica granite. (l) BSE images of biotite and apatite from the Anglonggangri two-mica granite. (m and n) Euhedral and homogeneous apatite crystals hosted in the matrix (m) and biotite (n) in Anglonggangri two-mica granite. (o) CL images of zircons from the Anglonggangri two-mica granite (Wang et al. 2022). Hereafter, mineral abbreviations follow Whitney and Evans (2010). Ap = apatite; Bt = biotite; Ms = muscovite; Mnz = monazite; Pl = plagioclase; Qz = quartz; Kfs = K-feldspar; Ilm = ilmenite; Zrn = zircon.

Biotites have F concentrations of 4040–11 430 ppm and Cl concentrations of 90–350 ppm. Compared to that from the Anglonggangri two-mica granite, the biotite from the Jiaodong two-mica granite has higher SiO<sub>2</sub> (39–41 wt%) and Al<sub>2</sub>O<sub>3</sub> (17.6–19.2 wt%) contents, but lower TiO<sub>2</sub> (1.1–1.8 wt%), FeO (16.8–19.5 wt%), and MgO (4.1–5.0 wt%), with similar SO<sub>3</sub> concentrations (200–530 ppm; Fig. 4a). The F (9200–17 140 ppm) and Cl (90–1930 ppm) concentrations are greater than those in the Anglonggangri two-mica granite (Figs. 4b–4c). The higher SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and F contents and lower FeO and MgO contents of biotite from the Jiaodong two-mica granite suggest that this granite is more evolved than the Anglonggangri two-mica granite (Azadbakht et al. 2020). The Fe/(Fe+Mg) ratios and total aluminum content ( $\Sigma$ Al) of biotite increase from the Anglonggangri to Jiaodong two-mica granite (Fig. 4d), further reflecting an

increasing degree of fractionation of their host magmas (Azadbakht et al. 2020). According to the classification diagram of the International Mineralogical Association (Rieder et al. 1998), the Jiaodong and Anglonggangri biotites are categorized as siderophyllite (Fig. 4d).

**Apatite composition.** Online Materials<sup>1</sup> Table S2 presents the geochemical compositions of the apatite crystals. To minimize the F and Cl migration effect during EMPA (Goldoff et al. 2012; Stock et al. 2015), only the data from apatite crystals with elongated hexagonal shapes, indicating that the analytical plane was parallel or oblique to the c-axis of the apatite crystals, were studied. The CaO and  $P_2O_5$  of apatite in the biotite monzogranite account for 52–55 and 38–42 wt%, respectively. The MnO concentration (80–7620 ppm) in apatite from the biotite monzogranite shows significant variations, whereas the F



**FIGURE 4.** Diagrams showing F, Cl, and SO<sub>3</sub> abundances in biotite from the Gangdese W- and Cu-granitoids. (**a**) SO<sub>3</sub> vs. Cl, (**b**) Cl vs. F, and (**c**) F/Cl vs. F diagrams. (**d**) The classification diagram of biotite. The PCD data are from Wu et al. (2016), Tang et al. (2017), Sun et al. (2018), Tian et al. (2021), Zhang (2021), and Yu et al. (2022).

contents (24 770–37 460 ppm) are less variable (Fig. 5). Almost all the apatite crystals have Cl and SO<sub>3</sub> concentrations below the detection limits. The apatite in the two-mica granite has CaO (53–56 wt%) and P<sub>2</sub>O<sub>5</sub> (39–44 wt%) contents similar to those in the biotite monzogranite. In contrast, the MnO (970– 8700 ppm) concentrations increase from the biotite monzogranite to the two-mica granite, whereas the F (14 380–36 490 ppm) concentrations decrease (Fig. 5). Concentrations of SO<sub>3</sub> and Cl in most apatite crystals are below the detection limits, with a few samples containing SO<sub>3</sub> and Cl concentrations of 200–3790 and 90–410 ppm, respectively.

Zircon trace element composition. Only the trace elements for zircons of Miocene U-Pb ages with concordance >90% were selected for this study. The trace element compositions of zircon crystals are provided in Online Materials<sup>1</sup> Table S3. Zircon data with La >0.1 ppm indicating LREE-rich mineral contamination (Zou et al. 2019) and Ti >50 ppm reflecting Ti oxide contamination (Lu et al. 2016) were excluded. Zircons from the W-granites are characterized by total rare earth element ( $\Sigma REE$ ) concentrations of 136–1725 ppm. They are enriched in HREE with positive Ce anomalies (Online Materials<sup>1</sup> Fig. S5), which are typical features of magmatic zircons (Hoskin and Schaltegger 2003). The Ti concentrations in zircons from the W-granites range between 1 and 24 ppm. The crystallization temperatures calculated for zircons from the biotite monzogranite (653–876 °C, average = 777 °C) and two-mica granite (721-840 °C, average = 777 °C) are similar. Zircons from the W-granites have moderate to low ratios of Eu/Eu\* (0.1–0.6, mostly  $\leq$ 0.4), Ce/Nd (0.9–11.5, mostly <5), and Dy/Yb (0.3–0.7, mostly >0.4).

# **Properties of W-granites**

The magma properties and partial key parameters of the W-granites are summarized and presented in Table 1.

**Temperatures of magma.** Using the Ti-in-zircon thermometer, the average crystallization temperature for zircons from the biotite monzogranite and two-mica granite is 777 °C. Based on previously published bulk-rock geochemistry data (Online Materials<sup>1</sup> Table S4) (Wang et al. 2020, 2022), the  $T_{Zr}$  temperatures calculated for the biotite monzogranite (M = 1.0–1.4) and twomica granite (M = 1.3–1.4) are 751–829 °C (average = 784 °C) and 711–768 °C (average = 736 °C), respectively. The average temperatures of these two methods calculated for the W-granites are consistent within error (±50 °C) (Ferry and Watson 2007).

**Magma oxygen fugacity.** Due to the extensive and strong alteration of the Jiaoxi biotite monzogranites,  $f_{O_2}$  estimation using bulk-rock Fe<sub>2</sub>O<sub>3</sub>/FeO ratios was not carried out here. The Jiaodong biotite monzogranite and Anglonggangri two-mica granite have relatively low Fe<sub>2</sub>O<sub>3</sub>/FeO values. They plot below the nickel-nickel (NNO) buffer line in the Fe<sub>2</sub>O<sub>3</sub>/FeO vs. SiO<sub>2</sub> diagram (Fig. 6a), with most data points in the range of Sn-W deposits (Hart et al. 2004). Based on the zircon oxybarometer,  $\log f_{O_2}$  values calculated for the Jiaoxi and Jiaodong biotite monzogranites range from -19.6 to -13.8 (average = -15.5). The



FIGURE 5. Diagrams showing the F, Cl, and SO<sub>3</sub> contents of apatite from the Gangdese W- and Cu-granitoids. (a) Cl vs. F, (b) F/Cl vs. F, (c) SO<sub>3</sub> vs. F, and (d) SO<sub>3</sub> vs. Cl diagrams. Reference lines are given at the estimated break between the W- and Cu-granitoids. The PCD data are from Xiao et al. (2012), Hu (2015), Wu (2016), Wu et al. (2016), Tang et al. (2021), Tian et al. (2021), and Zhang (2021).

Anglonggangri two-mica granite shows slightly lower  $\log f_{O_2}$  values from -21.4 to -14.1 (average = -16.3). In the zircon  $T_{\text{Ti-Zr}}$  vs.  $\log f_{O_2}$  diagram (Fig. 6b), the majority of the W-granites data points plot below the NNO line, indicating that they formed under relatively reducing conditions. Extremely low  $\Delta$ FMQ values for five zircons from the W-granites ( $-4.8 \sim -2.9$ ), associated with high U concentrations, are not included in the following discussion. The calculated zircon  $\Delta$ FMQ values for the biotite monzogranite and two-mica granite vary from -2.1 to 2.4 (average = 0.2) and -2.2 to 0.6 (average = -0.8), respectively. The low-zircon  $\Delta$ FMQ values also suggest that the W-granites formed under reducing conditions (Fig. 6c).

**Magma water content.** Zircons with (Ce/Nd)/Y >0.01 and Dy/Yb <0.3 have been proposed to indicate high water contents (up to 12 wt%) in the magma (Lu et al. 2015, 2016). Although nearly half of the zircon (Ce/Nd)/Y ratios from the biotite monzogranite are >0.01 (Fig. 7a), almost all the Dy/Yb ratios of zircons from the W-granites are higher than 0.3 (Figs. 7b–7c). These trace element compositions of zircon may suggest that the magmas from which the zircon crystallized were relatively low in H<sub>2</sub>O. The discussion of the magma source below, together with a previous study by Wang et al. (2022), shows that the W-granites were likely generated by dehydration melting of garnet amphibolite in the lower crust at high pressure (maybe >12 kbar). Accordingly, a garnet amphibolite sample from the eastern Himalayan syntaxis (LZ06-20-4) (Kang et al. 2020) was selected for phase equilibrium modeling to estimate the magma H<sub>2</sub>O content by using the software GeoPS by Xiang and Connolly (2022). To obtain more complete information on the magma H<sub>2</sub>O content, a relatively large range of pressure (8.2-16.6 kbar) and temperature conditions (720-900 °C), similar to those of the W-granites, were investigated during phase equilibrium modeling. The magma H<sub>2</sub>O content results vary from 8.6 wt% at 720 °C and 8.2 kbar to 6.9 wt% at 900 °C and 16.6 kbar (Fig. 7d), with an average value of 7.7 wt%. The average magma H<sub>2</sub>O content estimated here is consistent with previous experiments  $(6.7 \pm 1.4 \text{ wt\%})$  (Sen and Dunn 1994; Rapp and Watson 1995; Sisson et al. 2005). Hence, we infer that the H<sub>2</sub>O contents in the W-granites magmas at or close to the source region were approximately between 7 and 9 wt%.

Magma halogen fugacity. The average F contents of biotite from the Anglonggangri and Jiaodong two-mica granites are 0.35

and 0.69 atoms per formula unit (apfu), respectively. The average Cl contents are 0.007 and 0.004 apfu for biotite from the Jiaodong and Anglonggangri two-mica granites, respectively. The Mg/Fe ratio of the octahedral site is an important factor affecting F and Cl contents in magmatic biotite (Azadbakht et al. 2020). To normalize this influence, the intercept values IV(F), IV(Cl), and IV(F/Cl) of biotite defined by Munoz (1984) were used to reveal the degree of halogen enrichment in magmas. The Anglonggangri biotite has IV(F) values of 1.49–1.90 with an average of 1.67, whereas the Jiaodong biotite has an average IV(F) value of 1.37. In addition, the Anglonggangri biotite has a slightly higher average IV(Cl) value (-2.55) than the Jiaodong biotite (-2.58). Moreover, the IV(F) and IV(F/Cl) values roughly correlate positively, and most data plot in or close to the Sn-W-Be deposit field in the biotite IV(F/Cl) vs. IV(F) diagram (Fig. 8).

A thermodynamic equation was used to estimate the Cl content of melt in equilibrium with apatite (Li and Hermann 2017). The equation is

$$Cl_{melt}(wt\%) = X_{Cl}^{Ap} / X_{OH}^{Ap} \times (1/Kd_{Cl-OH}^{Ap-melt}) \times 10.79$$

and

 $Kd_{CI-OH}^{Ap-melt} = e^{[25.81+(XCIAp-XOHAp)\times 17.33]\times (1000/8.314/T)},$ 

with the temperature (*T*) in K. According to this equation, the average Cl contents calculated for the magmas of the biotite monzogranite and two-mica granite are 0.01% and 0.03%, respectively. The results suggest that the W-granites are low in Cl. This is in agreement with the low Cl contents measured in apatite (Fig. 5).

#### DISCUSSION

The composition of magmatic biotite, apatite, and zircon have been used to investigate physicochemical information on their associated ore-forming granitoids for PCDs, whereas their application to the W ore-forming granites is relatively rare. The compositions of biotite (Fe<sup>3+</sup>-Fe<sup>2+</sup>-Mg<sup>2+</sup>), apatite (Mn), and zircon (Eu and Ce anomalies and Ce<sup>4+</sup>/Ce<sup>3+</sup>) have been widely analyzed to indicate the high  $f_{O_2}$  conditions or H<sub>2</sub>O contents of granitoids for PCDs (e.g., Ballard et al. 2002; Wang et al. 2014; Gardiner et al. 2017; Azadbakht et al. 2020; Yu et al. 2022). However, recent studies have argued that these mineral indicators are not robust enough to reflect the  $f_{O_2}$  of ore-forming granitoids (Marks et al. 2016; Loucks et al. 2020; Loader et al. 2022); therefore, the zircon oxybarometer from Loucks et al. (2020) is used here. In contrast, it is generally accepted that the high halogen and SO<sub>3</sub> contents of biotite and apatite can reflect the high Cland S-fugacity of fertile granitoids for PCDs (e.g., Chelle-Michou and Chiaradia 2017; Moshefi et al. 2018; Zhu et al. 2018).

### Different properties between W and Cu-granitoids

Based on the Ti-in-zircon thermometer (Ferry and Watson 2007), the crystallization temperatures calculated for zircons from the Cu-granitoids range from 651 to 783 °C (average = 686 °C; Online Materials<sup>1</sup> Table S7). These calculations show that most Cu-granitoids have lower temperatures than the W-granites (Fig. 6b). This is compatible with the interpretation that the Gangdese Cu-granitoids are higher in H<sub>2</sub>O than the W-granites.

TABLE 1. Comparison of key parameters between the Gangdese W granites and Cu granitoids

1 069 29 34 0.04

0	ranitoids	Temperature/°C		f <sub>o2</sub>			H <sub>2</sub> O content			Halogen contents/wt%	
		TTI-Zr	log <b>fo</b> ₂	AFMQ	Bulk-rock Fe <sub>2</sub> O <sub>3</sub> /FeO	wt%	(Ce/Nd)/Y	Dy/Yb	ш	C	SO <sub>3</sub>
W granites	Biotite	653-876	$-19.6 \sim -13.8$	$-2.1 \sim 2.4$	0.14-0.32	7–9	0.001-0.028	>0.3	Ap: 2.48–3.75	Ap: 0.009	Ap: 0.03
	monzogranite	Avg = 777	Avg = -15.5	Avg = 0.2	Avg = 0.22		half <0.01		Avg = 3.05		
	Two-mica granite	721-840	$-21.4 \sim -14.1$	$-2.2 \sim 0.6$	0.13-0.32				Bt: 0.40–1.71	Bt: 0.009–0.193	Bt: 0.020-C
		Avg = 777	Avg = -16.3	Avg = -0.8	Avg = 0.20				Avg = 1.02	Avg = 0.021	Avg = 0.0
									Ap: 1.44–3.65	Ap: 0.009-0.041	Ap: 0.020-0
									Avg = 2.69	Avg = 0.017	most <0.
Cu granitoid	S	651-873	$-18.6 \sim -12.2$	$-0.8 \sim 4.1$	0.08-7.87	10-12	>0.01	most <0.3	Bt: 0.04–1.91	Bt: most >0.03	Ap: most >
		Avg = 686	Avg = -16.1	Avg = 1.6	Avg = 1.34				Avg = 0.62	Ap: most >0.05	
									Ap: 1.37–3.73		
									Avg = 2.68		
Note: Avg = a	verage; Ap = apatite;	Bt = biotite.									



**FIGURE 6.** Diagrams for  $f_{O_2}$  of the Gangdese W- and Cu-granitoids. (a) Bulk-rock Fe<sub>2</sub>O<sub>3</sub>/FeO vs. SiO<sub>2</sub> diagram (modified from Hart et al. 2004). (b) log  $f_{O_2}$  vs. temperature diagram for zircon. (c) Zircon  $\Delta$ FMQ vs.  $T_{\text{Ti-Zr}}$  diagram. QFM = quartz-fayalite-magnetite; NNO = nickel-nickel oxide; Hem-Mag = hematite-magnetite; IW = iron wüsite; QIF = quartz-iron-fayalite. The Fe<sub>2</sub>O<sub>3</sub> and FeO data for the PCDs are the same as those in Figure 2. Data on PCD zircons are from Wang et al. (2014), Hu (2015), Wu et al. (2016), Sun et al. (2018), Zhang et al. (2020), Tang et al. (2021), Li et al. (2021), and Zhang (2021).

The available bulk-rock Fe<sub>2</sub>O<sub>3</sub>/FeO ratios (Zheng et al. 2020 and references therein) show that almost all the Cu-granitoids plot above the NNO line (Fig. 6a), indicating their formation under moderate to strong oxidizing conditions. In contrast, all the W-granites are located below the NNO line, showing more reduced conditions (Fig. 6a). Higher  $f_{O_2}$  values in the Cu-granitoids compared to the W-granites are further supported by the zircon oxybarometer of Loucks et al. (2020). The  $\log f_{O_2}$  values calculated for zircons from the Cu-granitoids range from -18.6 to -12.2 (Online Materials<sup>1</sup> Table S7). As shown in the zircon  $\log f_{O_7}$  vs.  $T_{\text{Ti-Zr}}$  diagram (Fig. 6b), most Cu-granitoids plot above the NNO buffer line. However, the majority of the Wgranite data points plot below the NNO line (Fig. 6b). These differences indicate that the magmas from which the PCDs formed were more oxidized than magmas that formed the W-granites. Moreover, the Cu-granitoids have zircon  $\Delta$ FMQ values of -0.8 to 4.1, which are much higher than those of the W-granites (Fig. 6c). Based on all the above results, it is proposed that the Cu-granitoid magmas were characterized by higher  $f_{O_2}$  than the W-granite magmas.

The H<sub>2</sub>O content in the source area of the W-granite magmas is estimated to be 7–9 wt% (Fig. 7d). Zircons from both the Cu- and W-granitoids have similar Eu/Eu\* ratios, but their Ce/Nd, (Ce/Nd)/Y, and Dy/Yb ratios are significantly different (Figs. 7a–7c). The higher zircon (Ce/Nd)/Y (>0.01) and Ce/Nd (>10) ratios and lower Dy/Yb (<0.3) ratios of the Cu-granitoids suggest higher H<sub>2</sub>O contents in the Cu-granitoid magmas than in the W-granite magmas (Figs. 7a–7c). This is supported by the wt% H<sub>2</sub>O estimates of the Cu-granitoids from Lu et al. (2015). Based on zircon saturation thermometry combined with phase equilibria (Clemens et al. 1986), the minimum magma H<sub>2</sub>O content in the Cu-granitoid magmas is estimated to be 10–12 wt% (Lu et al. 2015). This high H<sub>2</sub>O content has been attributed to the addition of H<sub>2</sub>O from mantle-derived ultrapotassic melts (Yang et al. 2015, 2016).

The F and Cl concentrations of magmatic biotite and apatite crystals were used to compare the magma halogen fugacity of the Cu- and W-granitoid magmas. The biotite from the Cu-granitoids has lower F contents but higher Cl contents (>0.03 wt%) than that from the W-granites (Figs. 4b–4c). The apatite crystals from the Cu-granitoids have F concentrations similar to those from the W-granites (Figs. 5a–5b). However, the Cu-granitoids contain apatites with much higher Cl contents (>0.05 wt%) (Figs. 5a–5b). The halogen compositions show that the fertile magmas for the Gangdese PCDs are enriched in Cl. Compared with the W-granites, the



FIGURE 7. (a–c) Trace element compositions of zircon showing the relative  $H_2O$  content in the W- and Cu-granitoids. (a) Eu/Eu\* vs. (Ce/Nd)/Y, (b) Ce/Nd vs. Dy/Yb, (c) Eu/Eu\* vs. Dy/Yb. The reference lines are from Lu et al. (2016) and Lee et al. (2021) and indicate different  $H_2O$  contents in the W- and Cu-granitoids. The data for the PCDs are the same as those in Figure 6. (d) Diagram showing magma  $H_2O$  content estimated for the W-granites.

Cu-granitoids also exhibit greater sulfur fugacity, as shown by their higher apatite SO<sub>3</sub> contents (>0.04 wt%; Figs. 5c–5d). Although SO<sub>3</sub> contents of some apatites from the W-granites also exceed 0.04 wt%, most have lower SO<sub>3</sub> concentrations (<0.02 wt%) than those of the Cu-granitoids.

# Magma oxygen fugacity and volatile components control the metal variations

The properties of the source and magma generated are important factors in controlling the metal associations in magmatichydrothermal mineralization systems (Hart et al. 2004; Sillitoe 2010; Richards 2015). Constraints on the source regions and magma properties associated with the Gangdese Cu and W granitoids can clarify the critical factors controlling their different metal element associations.

Zircon Hf and bulk-rock Sr-Nd isotope data previously collected (Wang et al. 2020, 2022; Zheng et al. 2020 and references therein) are used to compare the magma sources of the Cu and W granitoids. Both the Cu- and W-granitoids display wide ranges of zircon  $\varepsilon_{\text{Hf}}(t)$  values (Fig. 9a) and Hf isotope two-stage model ages ( $T_{DM}^{C}$ ; Fig. 9b), indicating mixed magma sources. The depleted zircon  $\varepsilon_{\text{Hf}}(t)$  (>5) and young  $T_{DM}^{C}$  (<600 Ma) of the Cu-granitoids were generated from mantle-derived juvenile lower crust (Chung et al. 2003; Hou et al. 2015). However, the non-radiogenic zircon  $\varepsilon_{\rm Hf}(t)$  (<0) and ancient  $T_{DM}^C$  values (>1000 Ma) of the W-granites suggest that their source region was contaminated with the Lhasa terrane basement. The bulk-rock Sr-Nd isotopes also support magma source mixing between a juvenile component and ancient basement material. In the ( $^{87}{\rm Sr}/^{86}{\rm Sr}$ )<sub>i</sub> vs. SiO<sub>2</sub> diagram (Fig. 9c), a crustal assimilation



**FIGURE 8.** IV(F) vs. IV(F/Cl) diagram shows the halogen content of biotite from the W-granites. Fields of porphyry Cu and Mo and Sn-W-Be deposits are from Munoz (1984).



**FIGURE 9.** (a) Zircon  $\varepsilon_{\text{Hf}}(t)$  vs. U-Pb ages; (b) zircon Hf isotope *T* vs. U-Pb ages; (c) ( $^{87}\text{Sr}/^{86}\text{Sr}_i$  vs. SiO<sub>2</sub>; and (d)  $\varepsilon_{\text{Nd}}(t)$  vs. ( $^{87}\text{Sr}/^{86}\text{Sr}_i$ ) i diagrams for the Gangdese Cu and W granitoids. The data for the PCD and W granitoids are the same as those in Figure 2. Other Sr-Nd isotope sources include the Yarlung Zangbo Ophiolite from Mahoney et al. (1998) and Zhang et al. (2005); gabbro 09TB79 from Ma et al. (2013); gneiss G118A and G118D from Harris et al. (1988a, 1988b); Himalayan Eocene two-mica granite from Zeng et al. (2011, 2014) and Hou et al. (2012); and Himalayan Miocene leucogranite and metasediment from Ji et al. (2020) and Liu et al. (2014b) and references within.

(CA) process is suggested. To further clarify the contributions of the basement materials during magma formation, the Cretaceous gabbro in the southern Lhasa subterrane (09TB79) (Ma et al. 2013) was assumed to represent the juvenile lower crust, and the Cambrian Amdo gneiss (G118A and G118D) (Harris et al. 1988a, 1988b) was selected as the basement material for binary mixing during partial melting. All the Cu- and W-granitoids plot along a binary mixing line (Fig. 9d). This diagram shows potentially much greater contributions (30–60%) of the Lhasa terrane basement materials to the W-granites than the Cu-granitoids (mostly <40%; Fig. 9d).

Figure 9 suggests that the combination of partial melting of juvenile lower crust and mixing (0–50%) with gneiss-derived crustal melts formed the oxidized hydrous and S-enriched Cu-granitoids in the Miocene Gangdese metallogenic region (Fig. 10) (Hou et al. 2015; Yang et al. 2016). Compared to the Cu-granitoids, the coeval W-granites were more reduced and S- and Cl-poor, which is compatible with a higher degree of contamination (30–60%) from the Lhasa terrane basement in the magma source (Fig. 10). Although the W-granites were likely hydrous, containing  $\sim$ 7–9 wt% water, the H<sub>2</sub>O contents of the W-granites were likely lower than those of the Cu-granitoids (Figs. 7a–7c). The relatively reduced conditions and lower

H<sub>2</sub>O, Cl, and S contents of the W-granites hindered the sufficient transport of metals to form PCDs. However, the more reduced magma favored the genesis of W deposits. In addition, (garnet) muscovite granite and pegmatite are developed in the W-mineralized areas and are highly evolved phases of the W-granites. The high degrees of magma evolution also promoted W enrichment and mineralization in the late magma stages.

# IMPLICATIONS FOR TUNGSTEN EXPLORATION

There are large volumes of Miocene high-Sr/Y granitoids in the Gangdese region, and they have formed both PCDs and quartz vein and greisen-type wolframite deposits. It is very important to discriminate between granitic suites fertile for either Cu or W mineralization, prospecting and exploration directions in new areas, and to avoid economic losses potentially caused by incorrect exploration.

When comparing the Cu-granitoids and W-granites, the latter are more reduced, less hydrous, and have low magmatic sulfur and chlorine fugacity. Hence, when exploring for tungsten mineralization, this study suggests the importance of determining the reduced character of the related granites by obtaining zircon  $\Delta$ FMQ values (<0) and bulk-rock Fe<sub>2</sub>O<sub>3</sub>/FeO ratios (<0.3) and



**FIGURE 10.** Cartoon illustrating the petrogenetic differences between the Miocene Gangdese Cu and W granitoids.

the less hydrous character of granites by measuring the zircon Ce/Nd/Y (<0.01), Ce/Nd (<10), and Dy/Yb (>0.3) ratios. In addition, the low magmatic sulfur and chlorine features of granites should be determined by measuring SO<sub>3</sub> and Cl contents (<0.04 and <0.05 wt%, respectively) in magmatic apatite and the Cl contents in magmatic biotite (Cl <0.03 wt%).

# FUNDING

This research was financially supported by the National Key R&D Program of China (2021YFC2900100), the National Natural Science Foundation of China (41873046), and the China Geological Survey (DD20240078, DD20230360).

#### ACKNOWLEDGMENTS

We thank the associate editors Antonio Acosta-Vigil and Allen Schaen, the editor Don R. Baker, reviewer Thomas Lamont, and the anonymous reviewers for their thoughtful and constructive comments, which greatly improved this manuscript.

#### **References** Cited

- Azadbakht, Z., Lentz, D.R., McFarlane, C.R.M., and Whalen, J.B. (2020) Using magmatic biotite chemistry to differentiate barren and mineralized Silurian-Devonian granitoids of New Brunswick, Canada. Contributions to Mineralogy and Petrology, 175, 69, https://doi.org/10.1007/s00410-020-01703-2.
- Ballard, J.R., Palin, M.J., and Campbell, I.H. (2002) Relative oxidation states of magma inferred from Ce(IV)/Ce(III) in zircon: Application to porphyry copper deposits of northern Chile. Contributions to Mineralogy and Petrology, 144, 347–364, https://doi.org/10.1007/s00410-002-0402-5.
- Boehnke, P., Watson, E.B., Trail, D., Harrison, T.M., and Schmitt, A.K. (2013) Zircon saturation re-revisited. Chemical Geology, 351, 324–334, https:// doi.org/10.1016/j.chemgeo.2013.05.028.
- Boomeri, M., Mizuta, T., Ishiyama, D., and Nakashima, K. (2006) Fluorine and chlorine in biotite from the Sarnwosar granitic rocks, Northeastern Iran. Indian Journal of Science and Technology, 30, 111–125.
- Bouzari, F., Hart, C.J.R., Bissig, T., and Barker, S. (2016) Hydrothermal alteration revealed by apatite luminescence and chemistry: A potential indicator mineral for exploring covered porphyry copper deposits. Economic Geology and the Bulletin of the Society of Economic Geologists, 111, 1397–1410, https://doi. org/10.2113/econgeo.111.6.1397.
- Candela, P.A. and Bouton, S.L. (1990) The influence of oxygen fugacity on tungsten and molybdenum portioning between silicate melts and ilmenite. Economic Geology and the Bulletin of the Society of Economic Geologists, 85, 633–640, https://doi.org/10.2113/gsecongeo.85.3.633.

- Chambefort, I., Dilles, J.H., and Kent, A.J.R. (2008) Anhydrite-bearing andesite and dacite as a source for sulfur in magmatic-hydrothermal mineral deposit. Geology, 36, 719–722, https://doi.org/10.1130/G24920A.1.
- Che, X.D., Linnen, R.L., Wang, R.C., Aseri, A., and Thibault, Y. (2013) Tungsten solubility in evolved granitic melts: An evaluation of magmatic wolframite. Geochimica et Cosmochimica Acta, 106, 84–98, https://doi.org/10.1016/j. gca.2012.12.007.
- Chelle-Michou, C. and Chiaradia, M. (2017) Amphibole and apatite insights into the evolution and mass balance of Cl and S in magmas associated with porphyry copper deposit. Contributions to Mineralogy and Petrology, 172, 105, https://doi.org/10.1007/s00410-017-1417-2.
- Chiaradia, M., Ulianov, A., Kouzmanov, K., and Beate, B. (2012) Why large porphyry Cu deposits like high Sr/Y magmas? Scientific Reports, 2, 685, https:// doi.org/10.1038/srep00685.
- Chung, S.L., Liu, D., Ji, J., Chu, M.F., Lee, H.Y., Wen, D.J., Lo, C.H., Lee, T.Y., Qian, Q., and Zhang, Q. (2003) Adakites from continental collision zones: Melting of thickened lower crust beneath southern Tibet. Geology, 31, 1021–1024, https://doi.org/10.1130/G19796.1.
- Clemens, J.D., Holloway, J.R., and White, A.J.R. (1986) Origin of an A-type granite: Experimental constraints. American Mineralogist, 71, 317–324.
- Ferry, J.M. and Watson, E.B. (2007) New thermodynamic models and revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers. Contributions to Mineralogy and Petrology, 154, 429–437, https://doi.org/10.1007/s00410-007-0201-0.
- Gardiner, N.J., Hawkesworth, C.J., Robb, L.J., Whitehouse, M.J., Roberts, N.M.W., Kirkland, C.L., and Evans, N.J. (2017) Contrasting granite metallogeny through the zircon record: A case study from Myanmar. Scientific Reports, 7, 748, https://doi.org/10.1038/s41598-017-00832-2.
- Goldoff, B., Webster, J.D., and Harlov, D.E. (2012) Characterization of fluorchlorapatites by electron probe microanalysis with a focus on time-dependent intensity variation of halogens. American Mineralogist, 97, 1103–1115, https://doi.org/10.2138/am.2012.3812.
- Guo, Z.F., Wilson, M., and Liu, J.Q. (2007) Post-collisional adakites in south Tibet: Products of partial melting of subduction-modified lower crust. Lithos, 96, 205–224, https://doi.org/10.1016/j.lithos.2006.09.011.
- Harlaux, M., Romer, R.L., Mercadier, J., Morlot, C., Marignac, C., and Cuney, M. (2018) 40 Ma of hydrothermal W mineralization during the Variscan orogenic evolution of the French Massif Central revealed by U-Pb dating of wolframite. Mineralium Deposita, 53, 21–51, https://doi.org/10.1007/s00126-017-0721-0.
- Harris, N.B.W., Xu, R.H., Lewis, C.L., Hawkesworth, C.J., and Zhang, Y.Q. (1988a) Isotope geochemistry of the 1985 Tibet geotraverse, Lhasa to Golmud. Philosophical Transactions of the Royal Society of London A, Mathematical and Physical Sciences, 327, 263–285, https://doi.org/10.1098/rsta. 1988.0129.
- Harris, N.B.W., Xu, R.H., Lewis, C.L., and Jin, C.W. (1988b) Plutonic rocks of the 1985 Tibet geotraverse, Lhasa to Golmud. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 327, 145–168, https://doi.org/10.1098/rsta.1988.0124.
- Hart, C.J.R., Mair, J.L., Goldfarb, R.J., and Groves, D.I. (2004) Source and redox controls on metallogenic variations in intrusion-related ore systems, Tombstone-Tungsten Belt, Yukon Territory, Canada. Earth and Environmental

Science Transactions of the Royal Society of Edinburgh, 95, 339–356, https://doi.org/10.1017/S0263593300001115.

- Hoskin, P.W. and Schaltegger, U. (2003) The composition of zircon and igneous and metamorphic petrogenesis. Reviews in Mineralogy and Geochemistry, 53, 27–62, https://doi.org/10.2113/0530027.
- Hou, Z.Q., Zheng, Y.C., Zeng, L.S., Gao, L.E., Huang, K.X., Li, W., Li, Q.Y., Fu, Q., Liang, W., and Sun, Q.Z. (2012) Eocene-Oligocene granitoids in southern Tibet: Constraints on crustal anatexis and tectonic evolution of the Himalayan orogen. Earth and Planetary Science Letters, 349-350, 38–52, https://doi.org/10.1016/j.epsl.2012.06.030.Hou, Z.Q., Yang, Z.M., Lu, Y.J., Kemp, A., Zheng, Y.C., Li, Q.Y., Tang, J.X.,
- Hou, Z.Q., Yang, Z.M., Lu, Y.J., Kemp, A., Zheng, Y.C., Li, Q.Y., Tang, J.X., Yang, Z.S., and Duan, L.F. (2015) A genetic linkage between subductionand collision-related porphyry Cu deposits in continental collision zones. Geology, 43, 247–250, https://doi.org/10.1130/G36362.1.
- Hu, Y.B. (2015) Petrogenesis and metallogenetic implications of adakites in the Gangdese porphyry copper belt. A dissertation submitted to University of Chinese Academy of Sciences for the degree of doctor (in Chinese with English abstract).
- Ishihara, S. (1981) The granitoid series and mineralization. Economic Geology, 75th Anniversary volume, 458–484.
- (2015) Comparative studies of the petrochemistry of Sn-W-mineralized granitoids: Continent vs. island arc. Resource Geology, 65, 285–295, https://doi.org/10.1111/rge.12071.
- Ji, W.Q., Wu, F.Y., Chung, S.L., Li, J.X., and Liu, Z.C. (2009) Zircon U-Pb geochronology and Hf isotopic constraints on petrogenesis of the Gangdese batholith, southern Tibet. Chemical Geology, 262, 229–245, https://doi.org/10. 1016/j.chemgeo.2009.01.020.
- Ji, W.Q., Wu, F.Y., Liu, X.C., Liu, Z.C., Zhang, C., Liu, T., Wang, J.G., and Paterson, S.R. (2020) Pervasive Miocene melting of thickened crust from the Lhasa terrane to Himalaya, Southern Tibet and its constraint on generation of Himalayan leucogranite. Geochimica et Cosmochimica Acta, 278, 137–156, https:// doi.org/10.1016/j.gca.2019.07.048.
- Jugo, P.J. (2009) Sulfur content at sulfide saturation in oxidized magmas. Geology, 37, 415–418, https://doi.org/10.1130/G25527A.1.
- Kang, D.Y., Zhang, Z.M., Palin, R.M., Tian, Z.L., and Dong, X. (2020) Prolonged partial melting of garnet amphibolite from the eastern Himalayan syntaxis: Implications for the tectonic evolution of large hot orogens. Journal of Geophysical Research: Solid Earth, 125, e2019JB019119.
- Keppler, H. (1993) Influence of fluorine on the enrichment of high field strength trace elements in granitic rocks. Contributions to Mineralogy and Petrology, 114–479–488.
- Lalonde, A.E. and Bernard, P. (1993) Composition and color of biotite from granites: Two useful properties in characterization of plutonic suites from the Hepburn internal zone of Wopmay Orogen, Northwest Territories. Canadian Mineralogist, 31, 203–217.
- Lee, R.G., Byrne, K., D'Angelo, M., Hart, C.J.R., Hollings, P., Gleeson, S.A., and Alfaro, M. (2021) Using zircon trace element composition to assess porphyry copper potential of the Guichon Creek batholith and Highland Valley Copper deposit, south-central British Columbia. Mineralium Deposita, 56, 215–238, https://doi.org/10.1007/s00126-020-00961-1.
- Li, H.J. and Hermann, J. (2017) Chlorine and fluorine partitioning between apatite and sediment melt at 2.5 GPa, 800 °C: A new experimentally derived thermodynamic model. American Mineralogist, 102, 580–594, https://doi.org/10. 2138/am-2017-5891.
- Li, Q.Y., Yang, Z.M., Wang, R., Sun, M.Y., and Qu, H.C. (2021) Zircon trace elemental and Hf-O isotopic compositions of the Miocene magmatic suite in the giant Qulong porphyry copper deposit, southern Tibet. Acta Petrologica et Mineralogica, 40, 1023–1048 (in Chinese with English abstract). Liu, D., Zhao, Z.D., Zhu, D.C., Niu, Y.L., Depaolo, D.J., Harrison, T.M., Mo,
- Liu, D., Zhao, Z.D., Zhu, D.C., Niu, Y.L., Depaolo, D.J., Harrison, T.M., Mo, X.X., Dong, G.C., Zhou, S., Sun, C.G., and others. (2014a) Postcollisional potassic and ultrapotassic rocks in southern Tibet: Mantle and crustal origins in response to India-Asia collision and convergence. Geochimica et Cosmochimica Acta, 143, 207–231, https://doi.org/10.1016/j.gca.2014. 03.031.
- Liu, Z.C., Wu, F.Y., Ji, W.Q., Wang, J.G., and Liu, C.Z. (2014b) Petrogenesis of the Ramba leucogranite in the Tethyan Himalaya and constraints on the channel flow mode. Lithos, 208–209, 118–136, https://doi.org/10.1016/j.lithos. 2014.08.022.
- Loader, M.A., Nathwani, C.L., Wilkinson, J.J., and Armstrong, R.N. (2022) Controls on the magnitude of Ce anomalies in zircon. Geochimica et Cosmochimica Acta, 328, 242–257, https://doi.org/10.1016/j.gca.2022.03.024.
- Loucks, R.R. (2014) Distinctive composition of copper-ore-forming arc magmas. Australian Journal of Earth Sciences, 61, 5–16, https://doi.org/10.1080/ 08120099.2013.865676.
- (2021) Deep entrapment of buoyant magmas by orogenic tectonic stress: Its role in producing continental crust, adakites, and porphyry copper deposits. Earth-Science Reviews, 220, 103744, https://doi.org/10.1016/j. earscirev.2021.103744.
- Loucks, R.R., Fiorentini, M.L., and Henríquez, G.J. (2020) New magmatic oxybarometer using trace elements in zircon. Journal of Petrology, 61, egaa034, https://doi.org/10.1093/petrology/egaa034.

- Lu, Y.J., Loucks, R.R., Fiorentini, M.L., Yang, Z.M., and Hou, Z.Q. (2015) Fluid flux melting generated postcollisional high-Sr/Y copper ore-forming water-rich magmas in Tibet. Geology, 43, 583–586, https://doi.org/10.1130/G36734.1.
- Lu, Y.J., Loucks, R.R., Fiorentini, M., McCuaig, T.C., Evans, N.J., Yang, Z.M., Hou, Z.Q., Kirkland, C.L., Parra-Avila, L.A., and Kobusee, A. (2016) Zircon composition as a pathfinder for porphyry Cu ± Mo ± Au deposits. Society of Economic Geologists, Special Publication, 19, 329–347.
- Ma, L., Wang, Q., Wyman, D.A., Jiang, Z.Q., Yang, J.H., Li, Q.L., Gou, G.N., and Guo, H.F. (2013) Late Cretaceous crustal growth in the Gangdese area, southern Tibet: Petrological and Sr-Nd-Hf-O isotopic evidence from Zhengga diorite-gabbro. Chemical Geology, 349-350, 54–70, https://doi.org/10. 1016/j.chemgeo.2013.04.005.
- Mahoney, J.J., Frei, R., Tejada, M.L.G., Mo, X.X., Leat, P.T., and Nägler, T.F. (1998) Tracing the India ocean mantle domain though time: Isotopic results from old West Indian, East Tethyan and South Pacific seafloor. Journal of Petrology, 39, 1285–1306, https://doi.org/10.1093/petroj/39.7.1285.
- Marks, M.A.W., Scharrer, M., Ladenburger, S., and Markl, G. (2016) Comment on "Apatite: A new redox proxy for silicic magmas?" Geochimica et Cosmochimica Acta, 183, 267–270, https://doi.org/10.1016/j.gca.2016.02.017.
- Mercer, C.N. and Reed, M.H. (2013) Porphyry Cu-Mo stockwork formation by dynamic, transient hydrothermal pulses: Mineralogic insights from the deposit at Butte, Montana. Economic Geology and the Bulletin of the Society of Economic Geologists, 108, 1347–1377, https://doi.org/10.2113/econgeo.108.6.1347.
- Mo, X.X., Niu, Y.L., Dong, G.C., Zhao, Z.D., Hou, Z.Q., Zhou, S., and Ke, S. (2008) Contribution of syncollisional felsic magmatism to continental crust growth: A case study of the Paleogene Linzizong volcanic succession in southern Tibet. Chemical Geology, 250, 49–67, https://doi.org/10.1016/j.chemgeo. 2008.02.003.
- Moshefi, P., Hosseinzadeh, M.R., Moayyed, M., and Lentz, D.R. (2018) Comparative study of mineral chemistry of four biotite types as geochemical indicators of mineralized and barren intrusions in the Sungun porphyry Cu-Mo deposit, northwestern Iran. Ore Geology Reviews, 97, 1–20, https://doi.org/10.1016/j. oregeorev.2018.05.003.
- Munoz, J.L. (1984) F-OH and Cl-OH exchange in micas with applications to hydrothermal ore deposits. Reviews in Mineralogy and Geochemistry, 13, 469–493.
- O'Neill, H.St.C., Berry, A.J., and Eggins, S.M. (2008) The solubility and oxidation stage of tungsten in silicate melts: Implications for the comparative chemistry of W and Mo in planetary differentiation processes. Chemical Geology, 255, 346–359, https://doi.org/10.1016/j.chemgeo.2008.07.005.
- Rapp, R.P. and Watson, E.B. (1995) Dehydration melting of metabasalt at 8–32 kbar: Implications for continental growth and crust-mantle recycling. Journal of Petrology, 36, 891–931, https://doi.org/10.1093/petrology/36.4.891.
- Richards, J.P. (2003) Tectono-magatic precursors for porphyry Cu-(Mo-Au) deposit formation. Economic Geology and the Bulletin of the Society of Economic Geologists, 98, 1515–1533, https://doi.org/10.2113/gsecongeo. 98.8.1515.
- (2015) The oxidation state, and sulfur and Cu contents of arc magmas: Implications for metallogeny. Lithos, 233, 27–45, https://doi.org/10.1016/j. lithos.2014.12.011.
- Richards, J.P. and Kerrich, R. (2007) Adakite-like rocks: Their diverse origins and questionable role in metallogenesis. Economic Geology and the Bulletin of the Society of Economic Geologists, 102, 537–576, https://doi.org/10.2113/ gsecongeo.102.4.537.
- Richards, J.P., Spell, T., Rameh, E., Razique, A., and Fletcher, T. (2012) High-Sr/ Y magmas reflect arc maturity, high magmatic water content, and porphyry Cu±Mo±Au potential: Examples from the Tethyan arcs of central and eastern Iran and western Pakistan. Economic Geology and the Bulletin of the Society of Economic Geologists, 107, 295–332, https://doi.org/10.2113/ econgco.107.2.295.
- Rieder, M., Cavazzini, G., D'yakonov, Y.S., Frank-Kamenetskii, V.A., Gottardi, G., Guggenheim, S., Koval, P.W., Müller, G., Neiva, A.M.R., Radoslovich, E.W., and others. (1998) Nomenclature of the micas. Clays and Clay Minerals, 46, 586–595, https://doi.org/10.1346/CCMN.1998.0460513.
- Sen, C. and Dunn, T. (1994) Dehydration melting of a basaltic composition amphibolites at 1.5 and 2.0 GPa: Implications for the origin of adakites. Contributions to Mineralogy and Petrology, 117, 394–409, https://doi.org/10.1007/ BF00307273.
- Sillitoe, R.H. (2010) Porphyry copper systems. Economic Geology and the Bulletin of the Society of Economic Geologists, 105, 3–41, https://doi.org/10.2113/ gsecongeo.105.1.3.
- Sisson, T.W., Ratajeski, K., Hankins, W.B., and Glazner, A.F. (2005) Voluminous granitic magmas from common basaltic sources. Contributions to Mineralogy and Petrology, 148, 635–661, https://doi.org/10.1007/s00410-004-0632-9.
- Stock, M.J., Humphreys, M.C.S., Smith, V.C., Johnson, R.D., Pyle, D.M., and EIMF (2015) New constraints on electron-beam induced halogen migration in apatite. American Mineralogist, 100, 281–293, https://doi.org/10.2138/ am-2015-4949.
- Sun, S.S. and McDonough, W.F. (1989) Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and process. Geological Society, London, Special Publication, 42, 313–345.

- Sun, X., Lu, Y.J., McCuaig, T.C., Zheng, Y.Y., Chang, H.F., Guo, F., and Xu, L.J. (2018) Miocene ultrapotassic, high-Mg dioritic, and adakite-like rocks from Zhunuo in southern Tibet: Implications for mantle metasomatism and porphyry copper mineralization in collisional orogens. Journal of Petrology, 59, 341–386, https://doi.org/10.1093/petrology/egy028.
- Tang, P., Tang, J.X., Zheng, W.B., Leng, Q.F., Lin, B., and Tang, X.Q. (2017) Mineral chemistry of hydrothermal biotites from the Lakange porphyry Cu-Mo deposit, Tibet. Earth Science Frontiers, 24, 265–282 (in Chinese with English abstract).
- Tang, P., Tang, J.X., Wang, Y., Lin, B., Leng, Q.F., Zhang, Q.Z., He, L., Zhang, Z.B., Sun, M., Wu, C.N., and others. (2021) Genesis of the Lakang'e porphyry Mo (Cu) deposit, Tibet: Constraints from geochemistry, geochronology, Sr-Nd-Pb-Hf isotopes, zircon and apatite. Lithos, 380–381, 105834, https:// doi.org/10.1016/j.lithos.2020.105834.
- Tian, F., Leng, C.B., Zhang, X.C., Tian, Z.D., and Zhang, W. (2021) The key role of volatile-rich magma replenishment in the formation of porphyry Cu-Mo deposit: A case study of Gangjiang porphyry Cu-Mo deposit, Tibet. Yanshi Xuebao, 37, 2889–2909 (in Chinese with English abstract).
- Vigneresse, J.L. (2009) Evaluation of the chemical reactivity of the fluid phase through hard-soft acid-base concepts in magmatic intrusions with applications to ore generation. Chemical Geology, 263, 69–81, https://doi.org/10.1016/j. chemgeo.2008.11.019.
- Vigneresse, J.L., Duley, S., and Chattaraj, P.K. (2011) Describing the chemical character of a magma. Chemical Geology, 287, 102–113, https://doi.org/10. 1016/j.chemgeo.2011.06.003.
- Wang, R., Richards, J.P., Hou, Z.Q., Yang, Z.M., Gou, Z.B., and Dufrane, S.A. (2014) Increasing magmatic oxidation state from Paleocene to Miocene in the eastern Gangdese belt, Tibet: Implication for collision-related porphyry Cu-Mo±Au mineralization. Economic Geology and the Bulletin of the Society of Economic Geologists, 109, 1943–1965, https://doi.org/10.2113/econgeo. 109.7.1943.
- Wang, R., Richards, J.P., Zhou, L., Hou, Z.Q., Stern, R.A., Creaser, R.A., and Zhu, J.J. (2015) The role of Indian and Tibetan lithosphere in spatial distribution of Cenozoic magmatism and porphyry Cu-Mo deposits in the Gangdese belt, southern Tibet. Earth-Science Reviews, 150, 68–94, https://doi.org/10. 1016/j.earscirev.2015.07.003.
- Wang, L.Q., Wang, Y., Fan, Y., and Danzhen, W.X. (2018a) A Miocene tungsten mineralization and its implications in the western Bangong-Nujiang metallogenic belt: Constraints from U-Pb, Ar-Ar, and Re-Os geochronology of the Jiaoxi tungsten, Tibet, China. Ore Geology Reviews, 97, 74–87, https://doi. org/10.1016/j.oregeorev.2018.05.006.
- Wang, R., Weinberg, R.F., Collins, W.J., Richards, J.P., and Zhu, D.C. (2018b) Origin of postcollisional magmas and formation of porphyry Cu deposit in southern Tibet. Earth-Science Reviews, 181, 122–143, https://doi.org/10. 1016/j.earscirev.2018.02.019.
- Wang, Y., Tang, J.X., Wang, L.Q., Huizenga, J.M., Santosh, M., Zheng, S.L., Hu, Y., and Gao, T. (2020) Geology, geochronology and geochemistry of the Miocene Jiaoxi quartz vein-type W deposit in the western part of the Lhasa Terrane, Tibet: Implications for ore genesis. Ore Geology Reviews, 120, 103433, https://doi.org/10.1016/j.oregeorev.2020.103433.
- Wang, L.Q., Cheng, W.B., Gao, T., and Wang, Y. (2021) A model involving amphibolite lower crust melting and subsequent melt extraction for leucogranite generation. Geological Society of American Bulletin, 134, 1160–1179.
- Wang, L.Q., Cheng, W.B., Gao, T., and Wang, Y. (2022) A model involving amphibolite lower crust melting and subsequent melt extraction for leucogranite generation. Geological Society of America Bulletin, 134, 1160–1179, https://doi.org/10.1130/B36055.1.
- Watson, E.B. and 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.
- Webster, J.D. and Piccoli, P.M. (2015) Magmatic apatite: A powerful, yet deceptive, mineral. Elements, 11, 177–182, https://doi.org/10.2113/gselements.11.3.177.
- Whitney, D.L. and Evans, B.W. (2010) Abbreviations for names of rock-forming minerals. American Mineralogist, 95, 185–187, https://doi.org/10.2138/am. 2010.3371.
- Wu, S. (2016) The super-large Zhunuo porphyry Cu deposit in the Gangdese belt, southern Tibet: magmatism and mineralization. Doctoral dissertation, China University of Geosciences (in Chinese with English abstract).
- Wu, S., Zheng, Y.Y., and Sun, X. (2016) Subduction metasomatism and collisionrelated metamorphic dehydration controls on the fertility of porphyry copper ore-forming high-Sr/Y magma in Tibet. Ore Geology Reviews, 73, 83–103, https://doi.org/10.1016/j.oregeorev.2015.10.023.
- Xiang, H. and Connolly, J.A.D. (2022) GeoPS: An interactive visual computing tool for thermodynamic modelling of phase. Journal of Metamorphic Geology, 40, 243–255, https://doi.org/10.1111/jmg.12626.
- Xiao, B., Qin, K.Z., Li, G.M., Li, J.X., Xia, D.X., Chen, L., and Zhao, J.X. (2012) Highly oxidized magma and fluid evolution of Miocene Qulong giant

porphyry Cu-Mo deposit, southern Tibet, China. Resource Geology, 62, 4–18, https://doi.org/10.1111/j.1751-3928.2011.00177.x.

- Yang, X.M. and Lentz, D.R. (2005) Chemical composition of rock-forming minerals in gold-related granitoid intrusions, southwestern New Brunswick, Canada: Implications for crystallization conditions, volatile exsolution, and fluorine-chlorine activity. Contributions to Mineralogy and Petrology, 150, 287–305.
- Yang, Z.M., Lu, Y.J., Hou, Z.Q., and Chang, Z.S. (2015) High-Mg diorite from Qulong in southern Tibet: Implications for the genesis of Adakite-like intrusions and associated porphyry Cu deposits in collisional orogens. Journal of Petrology, 56, 227–254, https://doi.org/10.1093/petrology/egu076.
- Yang, Z.M., Goldfarb, R., and Chang, Z.S. (2016) Generation of postcollisional porphyry copper deposits in southern Tibet triggered by subduction of the Indian continental plate. Economic Geology and the Bulletin of the Society of Economic Geologists, S19, 279–300.
- Yu, K.L., Li, G.M., Zhao, J.X., Evans, N.J., Li, J.X., Jiang, G.W., Zou, X.Y., Qin, K.Z., and Guo, H. (2022) Biotite compositions as a tracer of fluid evolution and mineralization center: A case study at the Qulong porphyry Cu-Mo deposit, Tibet. Mineralium Deposita, 57, 1047–1069, https://doi.org/10. 1007/s00126-021-01085-w.
- Zeng, L.S., Gao, L.E., Xie, K.J., and Liu-Zeng, J. (2011) Mid-Eocene high-Sr/Y granites in the Northern Himalayan Gneiss Domes: Melting thickened lower continental crust. Earth and Planetary Science Letters, 303, 251–266, https:// doi.org/10.1016/j.epsl.2011.01.005.
- Zeng, L.S., Gao, L.E., Tang, S.H., Hou, K.J., Guo, C.L., and Hu, G.Y. (2014) Eocene magmatism in the Tethyan Himalaya, southern Tibet. In S. Mukherjee, R. Carosi, P.A. van der Beek, B.K. Mukherjee, and D.M. Robinson, Eds., Tectonics of the Himalayan, 412, 287–316. Geological Society Special Publication.
- Zhang, Z.B. (2021) The Jiama copper-polymetallic deposit in Tibet: Magmatism, diagenetic-metallogenic model. Doctoral Dissertation, China University of Geosciences (in Chinese with English abstract).
- Zhang, S.Q., Mahoney, J.J., Mo, X.X., Ghazi, A.M., Milani, L., Crawford, A.J., Guo, T.Y., and Zhao, Z.D. (2005) Evidence for a widespread Tethyan upper mantle with Indian-Ocean-type isotopic characteristics. Journal of Petrology, 46, 829–858, https://doi.org/10.1093/petrology/egi002.
- Zhang, C., Koepke, J., Wang, L.X., Wolff, P.E., Wilke, S., Stechern, A., Almeev, R., and Holtz, F. (2016) A practical method for accurate measurement of trace level fluorine in Mg- and Fe-bearing minerals and glasses using electron probe microanalysis. Geostandards and Geoanalytical Research, 40, 351–363, https://doi.org/10.1111/j.1751-908X.2015.00390.x.
- Zhang, Z.B., Wang, L.Q., Tang, P., Lin, B., Sun, M., Qi, J., Li, Y.X., and Yang, Z.K. (2020) Geochemistry and zircon trace elements composition of the Miocene ore-bearing biotite monzogranite porphyry in the Demingding porphyry Cu-Mo deposit, Tibet: Petrogenesis and implication for magma fertility. Geological Journal, 55, 4525–4542, https://doi.org/10.1002/gi.3693.
- Zheng, Y.C., Wu, C.D., Tian, S.H., Hou, Z.Q., Fu, B., and Zhu, D. (2020) Magmatic and structural controls on the tonnage and metal association of collisionrelated porphyry copper deposits in southern Tibet. Ore Geology Reviews, 122, 103509, https://doi.org/10.1016/j.oregeorev.2020.103509.
- 122, 103509, https://doi.org/10.1016/j.oregeorev.2020.103509.
  Zhu, D.C., Zhao, Z.D., Niu, Y.L., Dilek, Y., Hou, Z.Q., and Mo, X.X. (2013) The origin and pre-Cenozoic evolution of the Tibetan plateau. Gondwana Research, 23, 1429–1454, https://doi.org/10.1016/j.gr.2012.02.002.
- Zhu, D.C., Li, S.M., Cawood, P.A., Wang, Q., Zhao, Z.D., Liu, S.A., and Wang, L.Q. (2016) Assembly of the Lhasa and Qiangtang terranes in central Tibet by divergent double subduction. Lithos, 245, 7–17, https://doi.org/10.1016/j. lithos.2015.06.023.
- Zhu, J.J., Richards, J.P., Rees, C., Creaser, R., DuFrane, A.A., Locock, A., Petrus, J.A., and Lang, J. (2018) Elevated magmatic sulfur and chlorine contents in ore-forming magmas at the Red Chris porphyry Cu-Au deposit, northern British Columbia, Canada. Economic Geology and the Bulletin of the Society of Economic Geologists, 113, 1047–1075, https://doi.org/10.5382/econgeo. 2018.4581.
- Zou, X.Y., Qin, K.Z., Han, X.L., Li, G.M., Evans, N.J., Li, Z.Z., and Yang, W. (2019) Insight into zircon REE oxy-barometers: A lattice strain model perspective. Earth and Planetary Science Letters, 506, 87–96, https://doi. org/10.1016/j.epsl.2018.10.031.

MANUSCRIPT RECEIVED APRIL 11, 2023

MANUSCRIPT ACCEPTED JUNE 10, 2024

Accepted manuscript online June 17, 2024

MANUSCRIPT HANDLED BY ANTONIO ACOSTA-VIGIL

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