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**Origin of dioritic magma and its contribution to porphyry Cu–Au mineralization
at Pulang in the Yidun arc, eastern Tibet**

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Abstract

The giant Pulang porphyry Cu–Au deposit in the Yidun arc, eastern Tibet, formed due to westward subduction of the Garze–Litang oceanic plate in the Late Triassic. The deposit is hosted in an intrusive complex comprising primarily coarse-grained quartz diorite and cored quartz monzonite. Here, we investigate a suite of simultaneous (216.6 ± 1.9 Ma) diorite porphyries within the complex. The diorite porphyries are geochemically similar to mafic magmatic enclaves (MME) hosted in

coarse-grained quartz diorite, and both are characterized by low SiO_2 (59.4–63.0 wt.%) and high total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.0\text{--}9.2$ wt.%), K_2O (3.5–6.4 wt.%), MgO (3.2–5.5 wt.%), and compatible trace element (e.g., $\text{Cr} = 72\text{--}149$ ppm) concentrations. They are enriched in large-ion lithophile and light rare earth elements (LILE and LREE, respectively), but depleted in high field-strength and heavy rare earth elements (HFSE and HREE, respectively), and yield variably high $(\text{La/Yb})_N$ ratios (17–126, average 65) with weak to negligible Eu anomalies. Furthermore, they yield low $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios (0.7054–0.7067), weakly negative $\epsilon_{\text{Nd}}(t)$ (–2.8 to –0.8) values, and variable zircon $\epsilon_{\text{Hf}}(t)$ (–5.4 to +0.8) and $\delta^{18}\text{O}$ (6.0‰–6.7‰) values. These geochemical features indicate that the diorite porphyry and MME formed through crustal assimilation of a magma produced during low-degree partial melting of metasomatized phlogopite-rich subcontinental lithospheric mantle. In contrast, the coarse-grained quartz diorite and quartz monzonite have relatively high concentrations of SiO_2 (61.1–65.3 wt.%), K_2O (4.1–5.4 wt.%), and total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.1\text{--}8.1$ wt.%), and low concentrations of MgO (generally <3.0 wt.%) and compatible trace elements (e.g., $\text{Cr} = 38\text{--}61$ ppm). They yield high Sr/Y ratios (50–63) that indicate an adakitic affinity, and are enriched in LILE, depleted in HFSE, and yield lower $(\text{La/Yb})_N$ values (13–20, average 17) than the diorite porphyry and MME. They yield low $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios (0.7046–0.7066), negative $\epsilon_{\text{Nd}}(t)$ (–3.3 to –1.7) values, and zircon $\epsilon_{\text{Hf}}(t)$ and $\delta^{18}\text{O}$ values of –2.9 to –0.1 and 5.7‰–6.5‰, respectively, suggesting that they represent high-K calc-alkaline to shoshonitic adakitic magmas that were sourced from subduction-modified juvenile lower crust. Observations of the

newly identified diorite porphyry and previously reported MME suggest that input of such dioritic magma into the upper crustal porphyry magma chamber would have contributed not only the necessary metals (e.g., Cu and Au), sulfur, but also H₂O to the system, thus aiding in the generation of the giant Pulang porphyry Cu–Au deposit.

Keywords: dioritic magma; high-K; porphyry Cu–Au mineralization; Pulang; Yidun arc

1. Introduction

Porphyry Cu (–Mo–Au) deposits typically form within volcano–plutonic magma systems in arc settings and are associated with calc-alkaline, intermediate to felsic porphyry intrusions (Seedorff et al., 2005; Sillitoe, 2010), although rare deposits also occur in post-collisional settings, associated with high-K calc-alkaline to shoshonitic porphyry intrusions (Hou et al., 2004, 2015; Yang et al., 2009, 2016). The porphyry intrusions are generally sourced from metasomatized mantle wedge (in arc settings; Richards, 2003) or subduction-modified lower crust (in post-collisional settings; Hou et al., 2004, 2015). However, some other magma types, such as mafic magmas, can also be observed in spatial and temporal linkage with porphyry Cu deposits (Seedorff et al., 2005; Sillitoe, 2010; Yang et al., 2016). These magmas may have diverse origins and genetic relationships with porphyry Cu mineralization. For instance, mafic magma injection and subsequent magma mixing within the upper crustal magma chamber is considered an essential step in the formation of porphyry copper systems

(especially giant deposits), as such processes could transport metals and volatiles into the felsic magma (e.g., Hattori, 1993; Keith et al., 1997; Hattori and Keith, 2001; Maughan et al., 2002; Audétat and Simon, 2012; Blundy et al., 2015). Therefore, to better understand magmatic controls on porphyry Cu genesis, the generation and evolution of such magmas must be constrained.

The southern Yidun arc, located within the Sanjiang Tethyan orogenic belt in eastern Tibet, hosts several porphyry Cu deposits (e.g., Pulang, Xuejiping and Chundu) that are genetically related to, and hosted within, Late Triassic high-K calc-alkaline to shoshonitic porphyry intrusions (Wang et al., 2011; Cao et al., 2016). Among them, Pulang is the sole giant deposit and contains total proved reserves of 446.8 Mt at an average ore grade of 0.52% Cu and 0.18 g/t Au (KPDI, 2014). The primary intrusion within the deposit is a ~216 Ma mineralization-related, high-K calc-alkaline to shoshonitic quartz dioritic to quartz monzonitic intrusive complex (Zeng et al., 2006; Pang et al., 2009; Li et al., 2011; Ren et al., 2011; Wang et al., 2011; Cao et al., 2014, 2016; Chen et al., 2014). In this study, we report on a suite of coeval, relatively mafic diorite porphyries within the intrusive complex to: (1) characterize the mineral chemistry, and whole-rock geochemical and isotopic features of the diorite porphyry; (2) constrain the magma source and petrogenetic processes associated with the diorite suite; and (3) investigate the genetic relationship between the diorite porphyry and porphyry Cu–Au mineralization. In addition, mineral chemistry, and whole-rock geochemical and isotopic data for the quartz dioritic to quartz monzonitic intrusions are presented to allow comparison with data for the diorite porphyry.

2. Geological setting

Eastern Tibet comprises four microcontinental blocks/terrane, which, from east to west, are termed the Songpan–Garze, Yidun, Qiangtang, and Lhasa blocks (Fig. 1; Roger et al., 2010; Yang et al., 2012). The NNW-trending Yidun terrane is bounded by the Garze–Litang suture to the east and Jinshajiang suture to the west. These sutures resulted from the closure of two distinct Paleo-Tethys oceans in the Middle–Late Triassic and Late Paleozoic, respectively (Pan et al., 2003; Reid et al., 2005; Pullen et al., 2008; Yang, et al., 2014). The N-trending Xiangcheng–Geza fault divides the Yidun terrane into the Zhongza Massif (in the west) and the Yidun arc (in the east) (Reid et al., 2005, 2007). The oldest rocks within the Zhongza Massif are Paleozoic metasediments that contain similar fossil assemblages to those observed in equivalent strata of the Longmenshan Thrust Nappe Belt, to the west of the Yangtze block (Chang, 1997). Therefore, the Zhongza Massif is thought to have rifted from the western Yangtze block during opening of the Garze–Litang ocean, which was triggered by the Late Permian Emeishan mantle plume (Song et al., 2004; Leng et al., 2012; Wang et al., 2013).

The Yidun arc formed due to westward subduction of the Garze–Litang oceanic plate beneath the Zhongza Massif in the Middle–Late Triassic (Reid et al., 2005; Yang et al., 2012). The arc is overlain by the Triassic Yidun Group consisting of a flysch–volcanic succession and intrusive rocks (BGS, 1991). The Zhongdian arc, within the southern segment of the Yidun arc, contains numerous Late Triassic quartz

dioritic to quartz monzonitic porphyries, which formed over a short period at ~216 Ma (Cao et al., 2016), at a similar time to many regional volcanic rocks (219–213 Ma) (Huang, 2013; Leng et al., 2014; Chen et al., 2017). The porphyries host several economic porphyry deposits, including the Pulang, Xuejiping, Lannitang and Chundu deposits (Li et al., 2011).

The 36.4 km² Pulang porphyry Cu–Au district is located at 28°02'19"N, 99°59'23"E, ~36 km northeast of the Shangri-La (Zhongdian) County (Fig. 2). The district comprises three deposits: the largest South Pulang deposit (~96% of the total reserves in the district), and the smaller East and North Pulang deposits (Fig. 2) (KPDI, 2014). The detailed geology of the district has been described by Cao et al. (2017). Three lithologic units are observed at Pulang: (1) the Middle Triassic Niru Formation comprising gray to light gray crystalline limestones and dolomitic limestones; (2) the Late Triassic Tumugou Formation consisting of interlayered slates and sandstones, with minor limestones and volcanic rocks; and (3) a Late Triassic intrusive complex including premineral fine-grained quartz diorite (FQD) and coarse-grained quartz diorite (CQD), intermineral quartz monzonite (QM), and late-mineral diorite porphyry (DP) (Fig. 2). The FQD primarily crops out in North Pulang and is moderately altered. The DP is the focus of this study, and is geochemically similar to mafic magmatic enclaves (MME) within the CQD.

3. Petrography of the major intrusions

The premineral CQD is the most widely distributed intrusion at Pulang. It

comprises five stocks and crops out over $\sim 9.0 \text{ km}^2$ (Fig. 2a). The CQD is porphyritic and contains phenocrysts of plagioclase (15–25 vol.%), amphibole (5–10 vol.%) and minor biotite (Fig. 3a–b). Plagioclase (typically 1–8 mm, up to 20 mm) is euhedral to subhedral, commonly displays albite-Carlsbad twinning and zoned texture. Amphibole (typically 1–5 mm, up to 15 mm) occurs as euhedral to subhedral tabular crystals (Fig. 3d). Spherical to ellipsoidal MME are locally present in the CQD (Fig. 3a). The QM occurs in the center of the CQD at surface. Phenocrysts of the QM are dominated by K-feldspar (1–15 mm) and plagioclase (1–10 mm), which account for 25–35% of the whole rock volume (Fig. 3c). The QM also contains minor amphibole (~ 5 vol.%) and biotite phenocrysts. Plagioclase is euhedral to subhedral and displays albite-Carlsbad twinning and zoning. Amphibole (typically 1–5 mm) is commonly euhedral to subhedral and tabular (Fig. 3e).

The DP typically occurs as dikes (mostly < 10 m wide) at surface (Fig. 2), and is also unraveled at depth of all three deposits. Clear contacts are observed between the DP and the CQD and QM (Fig. 3b–c). Phenocrysts within the DP are primarily plagioclase (1–5 vol.%), amphibole (~ 1 vol.%), and biotite (~ 1 vol.%) (Fig. 3b–c). Plagioclase (1–10 mm) is subhedral to anhedral, rounded or embayed (Fig. 3c), and displays clear zoning texture. Amphibole is elongate and smaller (generally < 2 mm; Fig. 3f) than those in the CQD and QM. The groundmass comprises feldspar and quartz, with minor amphibole and biotite. Accessory minerals within the CQD, QM and DP are dominantly apatite, magnetite, titanite and zircon.

4. Sampling and analytical methods

All the samples were collected from the drill holes and surface exposures, and they are unaltered or least altered. Five CQD, five QM and seven DP samples were selected for elemental and/or Sr–Nd isotopic analysis. One DP sample was selected for zircon U–Pb dating and three samples from each porphyry unit were selected for zircon Hf–O isotopic analysis. Sample locations are shown in Fig. 2. Detailed analytical methods and analyses of standards are given in Appendixes 1–3.

5. Results

5.1. Zircon U–Pb ages

Zircon grains from the analyzed DP sample are mostly euhedral to subhedral, colorless or weakly cloudy, 50–200 μm long, and have aspect ratios of 1:1 to 3:1 (Fig. 4). Cathodoluminescence (CL) images reveal that most grains exhibit concentric oscillatory zoning, typical of magmatic growth (Fig. 4). Results of SHRIMP zircon U–Pb analysis are listed in Table 1 and illustrated in Fig. 5. The DP yields a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 216.6 ± 1.9 Ma (1σ , MSWD = 0.45, $n = 17$), which represents the crystallization age of the DP (Fig. 5). Zircon LA–ICP–MS and SIMS U–Pb ages have been previously reported for the CQD and QM, both of which were shown to have ages of ~ 216 Ma (Cao et al., 2016; Kong et al., 2016), indicating that the formation of the CQD, QM and DP were coeval.

5.2. Mineral chemistry

Major element compositions of amphibole from the CQD, QM and DP are provided

in Appendix 4. Amphibole from these rocks are exclusively classified as calcic amphibole, and subdivided into magnesiohornblende based on the nomenclature of Leake et al. (1997) (Fig. 6), with Mg# values $[\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$ of 0.67–0.70, 0.70–0.75 and 0.70–0.93, respectively. We calculated pressures using the empirical Al-in-amphibole geobarometer $[P \text{ (kbar)} = 0.5 + 0.331(8) \times \text{Al}^{\text{tot}} + 0.995(4) \times (\text{Al}^{\text{tot}})^2]$, Al^{tot} is the total Al content of amphibole in atoms per formula unit (apfu) calculated on the basis of 23 oxygen anions] (Mutch et al., 2016), which was developed after experimental calibrations of Johnson and Rutherford (1989), Thomas and Ernst (1990) and Schmidt (1992) under conditions between 0.8–10 kbar. Amphibole within the analyzed samples occurs in equilibrium assemblage amphibole + plagioclase (An_{15-80}) + biotite + quartz + K-feldspar + ilmenite/titanite + magnetite + apatite, suggesting that it can be used to estimate the crystallization pressures. Furthermore, equilibrium between amphibole and plagioclase allows the temperatures and water contents to be estimated using the method of Ridolfi et al. (2010). The estimated crystallization pressures of amphibole from the CQD, QM and DP are 2.1–2.5, 2.1–2.6, and 2.9–4.1 kbar, respectively (Appendix 4).

5.3 Whole-rock geochemistry

Representative whole-rock major and trace element data for samples in this study, as well as previously reported MME samples (Cao et al., 2009) are listed in Table 2 (the complete data are given in Appendix 5). As illustrated in Figs. 7–8, the DP samples are comparable with MME hosted in the CQD (Cao et al., 2009), they are characterized by low SiO_2 contents (59.4–63.0 wt.%) and high total alkali ($\text{Na}_2\text{O} +$

$K_2O = 7.0\text{--}9.2$ wt.%), plotting in the field of alkaline series or subalkaline series that are very close to the boundary between these two rock series (Fig. 7a). The samples yield variably high K_2O ($3.5\text{--}6.4$ wt.%) (Fig. 7b), and high MgO ($3.2\text{--}5.5$ wt.%) and compatible trace element (e.g., $Cr = 72\text{--}149$ ppm) concentrations (Appendix 5). In the chondrite-normalized REE diagram (Fig. 8a), they display highly variable and strongly enriched LREE relative to HREE, with $(La/Yb)_N$ and $(Gd/Yb)_N$ ratios of $17\text{--}126$ (average 65) and $2.7\text{--}10.1$ (average 5.5), respectively, and weak to negligible Eu anomalies ($Eu/Eu^* = 0.7\text{--}1.2$). In the primitive mantle-normalized trace element diagram (Fig. 8b), the samples are enriched in LILE (e.g., $Sr = 627\text{--}2050$ ppm) but depleted in HFSE, with negative Nb, Ta and Ti anomalies.

In contrast, the CQD and QM contain relatively high concentrations of SiO_2 ($61.1\text{--}65.3$ wt.%), K_2O ($4.1\text{--}5.4$ wt.%) and total alkali ($Na_2O + K_2O = 7.1\text{--}8.1$ wt.%) (Fig. 7a–b), but low MgO (mostly <3.0 wt.%), Cr ($37.6\text{--}61.3$ ppm) and Ni contents (Appendix 5). Compared with the DP and MME, the CQD and QM display less fractionated REE patterns (Fig. 8a), with lower $(La/Yb)_N$ and $(Gd/Yb)_N$ ratios of $14\text{--}20$ (average 16) and $2.0\text{--}2.5$ (average 2.2), respectively, and negligible Eu anomalies ($Eu/Eu^* = 0.8\text{--}1.0$). The CQD and QM samples are also enriched in LILE (e.g., Rb, Sr, and Ba) and depleted in HFSE (e.g., Nb, Ta and Ti) (Fig. 8b). Furthermore, most samples display adakitic affinities (Fig. 7c), with high Sr ($634\text{--}854$ ppm), and low Y ($12.3\text{--}15.1$ ppm) and Yb ($1.4\text{--}1.7$ ppm) contents, and high Sr/Y ratios ($50\text{--}63$), similar to those reported from analogous rocks at Pulang and other deposits (e.g., Xuejiping and Chundu; Wang et al., 2011; Chen et al., 2014; Cao et al.,

2016).

5.4. Sr–Nd isotopic systematics

Sr–Nd isotopic compositions for samples from the three porphyries were calculated at 216 Ma, on the basis of zircon U–Pb dates previously reported and presented in this study (Cao et al., 2016; Kong et al., 2016). The data are listed in Table 3 and shown in Fig. 9 together with reported Sr–Nd isotopic data for contemporaneous volcanic rocks and porphyries in the Zhongdian arc (Wang et al., 2011; Chen et al., 2014; Leng et al., 2014). The DP yields relatively homogeneous $(^{87}\text{Sr}/^{86}\text{Sr})_i$ (0.705365–0.706724) and $\epsilon_{\text{Nd}}(t)$ (–2.8 to –0.8) values. The CQD and QM have similar isotopic compositions characterized by relatively high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ (0.704591–0.706608) and weakly negative $\epsilon_{\text{Nd}}(t)$ (–3.3 to –1.7) values. All acquired Sr–Nd isotopic compositions overlap those of coeval porphyries at other deposits in the Zhongdian arc (Fig. 9).

5.5. Zircon O–Hf isotopes

In situ oxygen isotopic compositions of zircons from each porphyry are presented in Appendix 6 and shown in Fig. 10. The zircon grains yield a relatively narrow range of $\delta^{18}\text{O}$ values from 5.5‰ to 6.7‰, with weighted mean values of $6.1 \pm 0.1\text{‰}$ (2σ), $6.3 \pm 0.1\text{‰}$ and $6.3 \pm 0.1\text{‰}$ for the CQD, QM and DP, respectively. Zircon $\epsilon_{\text{Hf}}(t)$ values from the CQD and QM samples were back-calculated to 216.0 Ma, which is the mean age reported in previous studies (Cao et al., 2016; Kong et al., 2016). For the DP sample, we back-calculated to ages acquired using U–Pb dating in this study, which were performed on the same analytical spots. Hf isotopic data are given in Appendix 6 and illustrated in Fig. 10. The CQD and QM yield similar zircon $\epsilon_{\text{Hf}}(t)$

values of -2.9 to -0.1 and -2.5 to -0.1 , respectively. These values are slightly higher than those of zircons from the DP (dominantly -5.4 to -1.3 , average -2.9 ; Appendix 6).

6. Discussion

6.1. Alteration effects

All porphyry samples collected for analysis in this study are relatively fresh or least altered with low loss on ignition (LOI) values of <2.6 wt.% (Appendix 5). The major element (especially K_2O and Na_2O) and LILE (e.g., Rb, Ba) concentrations of above samples show no clear correlations with LOI (Appendix 7), suggesting minimal modification of these elements due to alteration. This is consistent with the petrographic observation that only low-temperature alteration assemblage chlorite + sericite in some samples, which would not significantly affect mobile element concentrations. Mg generally remains immobile and will not be readily affected by hydrothermal alteration in these intermediate to felsic porphyries due to the lack of olivine and pyroxene (Zhou, 1999). Other major elements, such as TiO_2 , Al_2O_3 , P_2O_5 , and MnO , are also typically fluid-immobile (Zhou, 1999), which is supported by their lack of correlation with LOI (Appendix 7). REE, HFSE, and transition elements (e.g., Cr, Ni) are not significantly fluid soluble and thus remain immobile during intensive hydrothermal alteration (Hawkesworth et al., 1997; Wang et al., 2006). Therefore, we infer that major and trace elements within the analyzed samples were isochemical during subsequent geological processes. Additionally, $\epsilon_{Nd}(t)$ and $(^{87}Sr/^{86}Sr)_i$ values are

not correlated with LOI (Appendix 7), indicating that they were also not affected by alteration.

6.2. Two magma sources for the major Pulang intrusions

As mentioned, the DP and MME within the CQD have similar major and trace element concentrations and REE patterns, indicating their derivations from a common source. However, these two lithologies (henceforth referred to as Group I porphyries) have distinct compositions to the contemporaneous CQD and QM (Group II porphyries). For example, Group I porphyries show lower SiO_2 and higher MgO and compatible trace element (e.g., Cr) concentrations than Group II porphyries (Appendix 5; Fig. 11). Therefore, two mechanisms can be invoked to interpret the genetic relationship between the two groups: (1) they are cognate magmas formed through fractional crystallization; or (2) they were derived from distinct magma sources, with Group I porphyry magma being injected into the magma chamber of Group II. The first possibility is considered unlikely, based on the following observations.

(1) Group I and II porphyries yield quite distinct Nb/Ta and Zr/Nb ratios (Fig. 11b), indicating that Group I porphyries are unlikely to represent the less evolved remnants of parental mafic magmas from which Group II porphyries evolved. Because fractional crystallization would not lead to remarkable variations in ratios of these incompatible elements. Group I porphyries yield Nb/Ta ratios of 13.2–21.6 (average 16.1), which are close to that (average 17.7) of enriched mantle (Sun and McDonough, 1989). Whereas Group II porphyries have Nb/Ta ratios of 11.0–12.4 (average 11.8),

close to that (average 8.3) of the lower crust (Rudnick and Gao, 2003).

(2) The relatively mafic Group I porphyries yield higher LILE and/or HFSE contents (e.g., Rb = average 185, Sr = average 1177, Ba = average 2138, and Th = average 26.4 ppm) than the felsic Group II porphyries (Rb = average 159, Sr = average 760, Ba = average 1540, and Th = average 16.0 ppm) (Appendix 5; Fig. 11d–f). These incompatible elements are typically enriched in more evolved magmas during fractional crystallization, and therefore the observed trends are incompatible with derivation from an evolving melt.

(3) Group I porphyries yield higher LREE contents than Group II porphyries (Fig. 8). As LREE are incompatible during melting, they are typically enriched upon fractionations. Therefore, fractional crystallization processes are inconsistent with the observed REE patterns of the two group porphyries.

(4) The DP (Group I porphyry) has variable and lower $\varepsilon_{\text{Hf}}(t)$ values (−5.4 to +0.8) than the Group II porphyries (−2.9 to −0.1) (Fig. 10), which is also inconsistent with fractional crystallization.

Furthermore, given the widespread occurrence of adakitic Group II porphyries at Pulang, as well as their analogues (i.e., quartz dioritic to quartz monzonitic intrusions) throughout the Zhongdian arc (Wang et al., 2011; Chen et al., 2014; Cao et al., 2016; Fig. 1b), a fractionation hypothesis would require a large volume of mafic magma (represented by the Group I porphyries). However, there is a near-absence of such coeval mafic magmas within the Zhongdian arc, except for minor Group I porphyries at Pulang. Meanwhile, no petrological and mineralogical evidence supports the

preferential retention of such mafic magma at depth. Therefore, we infer that the Group I and II porphyries were derived from different sources.

6.3. Origin of the Group I porphyries

6.3.1. Evaluation of crustal contaminations

Group I porphyries are shoshonitic and have high K_2O (3.5–6.4 wt.%, average 4.7 wt.%), total alkali ($Na_2O + K_2O = 7.0–9.2$ wt.%), and LILE (e.g., Rb, Sr, Ba) concentrations (Fig. 7). Their high-K characteristic may be related to crustal contaminations. Furthermore, their $(^{87}Sr/^{86}Sr)_i$ (0.7054–0.7067), $\epsilon_{Nd}(t)$ (–2.8 to –0.8) and $\epsilon_{Hf}(t)$ (–5.4 to +0.8) values reflect additional input of ancient crustal materials. In the Sr–Nd (Fig. 9) and Hf–O (Fig. 10) isotopic diagrams, the DP samples plot along a mixing curve between an inferred depleted mantle component and ancient Yangtze lower crust. From these data we infer that the DP represents 60–80% mantle materials with additions of 20–40% ancient crustal materials. However, Group I porphyries yield higher K_2O , Ba and Sr concentrations than the lower or upper continental crust (Rudnick and Gao, 2003) (Fig. 11). These concentrations do not correlate with MgO (Fig. 11), SiO_2 (not shown), or Al_2O_3 (not shown), as would be expected if contaminations of granitic crust were responsible for the elevated LILE concentrations (Feldstein et al., 1999). Furthermore, the sample with the lowest SiO_2 content has one of the highest Ba contents (2438 ppm) (Appendix 5). Therefore, although contaminations of Group I porphyries by ancient crustal materials likely did occur, we consider their high K_2O and LILE concentrations to be intrinsic.

6.3.2. Source region, and LILE and LREE enrichment

Group I porphyries are characterized by relatively low SiO_2 (59.3–63.0 wt.%), and high MgO (3.2–5.5 wt.%) and compatible trace element (e.g., Cr: 72–149 ppm; Ni: 21–109 ppm) contents, variably high $\text{Mg\#}$ (48–68) (Appendix 5). These characteristics are inconsistent with a crustal source, as experimental results show that partial melting of crustal materials, regardless young or old, produces high-Si, low-Mg liquids (i.e., granitoid magma; Rapp et al., 2003).

Group I porphyries have high concentrations of incompatible trace elements, such as Rb, Ba, Th, U and La (Appendix 5), enriched by up to 100–500 times that of primitive mantle (Sun and McDonough, 1989; Fig. 8b). In addition, samples with low SiO_2 and high MgO concentrations are also enriched in LILE (e.g., Rb, Sr, Ba) and LREE, and depleted in HFSE (Appendix 5; Fig. 8). These characteristics, combined with their negative $\epsilon_{\text{Nd}}(t)$ (–2.8 to –0.8) values (Table 3; Fig. 9), indicate that they were derived from a mantle source that was metasomatized by subduction-related fluids (Tatsumi et al., 1986; Schmidt et al., 2004). Similar geochemical features are commonly reported from ultrapotassic rocks, such as melilitites, nephelinites and meimechites, which are produced during low-degree partial melting of enriched volatile-bearing mantle (e.g., Nelson et al., 1988; Taylor et al., 1994; Mahotkin et al., 2000; Larson et al., 2003).

Furthermore, Group I porphyries display highly fractionated REE patterns with extremely high $(\text{La/Yb})_{\text{N}}$ (17–126, average 65) and $(\text{Gd/Yb})_{\text{N}}$ (2.7–10.1, average 5.5) ratios (Appendix 5), as well as relatively low heavy REE (HREE) abundances (e.g., Y = 12–22 ppm, Yb = 1.1–1.6 ppm), suggesting garnet was present as a residual phase

in their source, which is supported by melting experiments involving garnet and spinel peridotite compositions (Hirose and Kushiro, 1993; Herzberg and Zhang, 1996; Falloon et al., 2001). Therefore, the geochemical and Sr–Nd–Hf–O isotopic compositions of Group I porphyries indicate that they were produced during low-degree partial melting of enriched lithospheric mantle.

Enriched lithospheric mantle typically comprises olivine, orthopyroxene, and clinopyroxene, with minor amphibole, phlogopite, apatite, carbonate, ilmenite, and rutile, as well as exotic oxides (observed in metasomatized mantle xenoliths; e.g., O'Reilly and Griffin, 1988; Yaxley et al., 1998). Group I porphyries show high K₂O contents and K₂O/Na₂O ratios (>1, average 1.6), but lack a negative correlation between K₂O and MgO (Fig. 11c), which is inconsistent with potassium enrichment via fractional crystallization. Mixing with K-rich magma is also unlikely, as Group I porphyries contain higher K₂O contents than Group II (Fig. 11c), although magma mixing between the two groups has been suggested (Cao et al., 2009; Liu et al., 2015). Therefore, the high-K characteristics of Group I porphyries indicate the presence of a K-bearing phase, such as phlogopite or amphibole (e.g., K-richterite), in their source. Melts in equilibrium with phlogopite typically yield higher Rb/Sr (>0.1) and lower Ba/Rb (<20) ratios than those from amphibole-bearing sources (Furman and Graham, 1999). The relatively high Rb/Sr (0.10–0.41, except for two samples yielding 0.06 and 0.09) and low Ba/Rb (6.0–17.8) ratios of Group I porphyries are thus indicative of a phlogopite-bearing source (e.g. Williams et al., 2004; Condamine and Médard, 2014; Fig. 12a). Furthermore, La concentrations of Group I porphyries are correlated with

La/K and La/Ba (Fig. 12b–c), also suggesting the presence of phlogopite, as La is incompatible but K and Ba are compatible in phlogopite (Feldstein and Lange, 1999).

In conclusion, the most possible source for Group I porphyries is metasomatized lithospheric mantle in phlogopite-rich lithologies. Experimental melts from such lithologies (Condamine and Médard, 2014) are similar to the Group I porphyries, and such mantle sources for high-K magmas in similar compositions have also been proposed in other regions (e.g., Tibet, Turner et al., 1996; Miller et al., 1999; Anatolia, Harris et al., 1994; Prelevic et al., 2012). Therefore, we propose that Group I porphyries were produced during small-degree partial melting of metasomatized phlogopite-rich lithospheric mantle, followed by crustal assimilation.

6.4. Origin of Group II porphyries

The petrogenesis of mineralization-related Late Triassic porphyry intrusions at Pulang (Group II porphyries) and other porphyry Cu deposits within the Zhongdian arc (e.g., Xuejiping and Chundu) has been well studied, but remains debated. Leng et al. (2012) and Chen et al. (2014) proposed that such intrusions were produced during partial melting of the wedge mantle. In contrast, Peng et al. (2014) suggested that they were produced during post-collisional remelting of Late Mesoproterozoic (1.2 Ga) juvenile continental lower crust, whereas Cao et al. (2016) proposed a subduction-modified lower crustal source. The Group II porphyries have high SiO₂ (up to 68 wt.%) and Th (9.6–20.5 ppm) concentrations, high Sr/Y (>20), K₂O/Na₂O (>1), and Th/Ce (0.15–0.36) ratios (Ren et al., 2011; Cao et al., 2014; this study), and negative $\varepsilon_{\text{Hf}}(t)$ values (–2.9 to –0.1), suggesting that they were derived from partial

melting of subduction-modified mafic lower crust (Cao et al., 2016), similar to the model proposed by Hou et al. (2004, 2013b, 2015) and Yang et al. (2015, 2016) for porphyries in the Gangdese porphyry Cu belt. Furthermore, Sr–Nd and Hf–O isotopic modeling shows that ~30–50% ancient lower crustal materials were added during their formation (Figs. 9–10).

Compared with the lower crust-derived adakitic rocks in the Gangdese porphyry Cu belt (Hou et al., 2004, 2013b, 2015; Yang et al., 2015, 2016), Cordillera Blanca (Atherton and Petford, 1993; Petford and Atherton, 1996), Separation Point (Muir et al., 1995), and Zhantang (Xiong et al., 2003), the Group II porphyries at Pulang are dominantly shoshonitic and yield higher K_2O contents for a given SiO_2 contents (Figs. 7a, 13). The high-K feature of Group II porphyries may have been: (1) inherited from their source; (2) achieved during fractional crystallization of plagioclase, leaving K-feldspar as a late crystallization mineral in the remaining magmas (Glazner and Johnson, 2013), which would remove Na from the liquids and increase K_2O/Na_2O ; or (3) caused by the input of high-K magma, represented by the Group I porphyries. Given the high K_2O content of the least evolved sample (Figs. 7, 13) and the lack of negative Eu anomalies (suggesting a lack of plagioclase fractionation) (Fig. 8a), we propose that the high-K signatures of the Group II porphyries were inherited mainly from their source. Late Triassic basalts in the Zhongdian arc, considered as the representative compositions of juvenile Zhongdian lower crust (Cao et al., 2016), have high K_2O contents (up to 4.6 wt.%; Leng et al., 2014) and are shoshonitic in composition (Fig. 7b). Therefore, melting of such K-rich basalt underplates would

generate high-K melts, similar to the Group II porphyries. However, the possibility that the input of high-K Group I porphyry magma contributed to an increase in K_2O contents in the Group II porphyries cannot be excluded.

Adakitic signatures (e.g., high Sr/Y and La/Yb ratios, and low HREE concentrations) may: (1) reflect the characteristics of the source, such as the presence of residual garnet but without plagioclase in the residue (Martin, 1999); or (2) have been produced during fractional crystallization within the stability field of garnet and amphibole but outside that of plagioclase (Castillo et al., 1999; Richards and Kerrich, 2007; Chiaradia et al., 2009). The least fractionated (i.e., lowest SiO_2 content) Group II porphyry sample also shows an adakitic affinity (e.g., Sr/Y = 61; Fig. 7d), suggesting that such adakitic signatures relate to the source. In addition, Group II porphyries display a negative correlation between Dy/Yb and SiO_2 , indicating amphibole fractionation in their deep magma chamber, but the adakitic signatures (e.g., high Sr/Y ratios) are consistent (Fig. 14), even without plagioclase fractionation, as indicated by the lack of a significant negative Eu anomalies (Fig. 8a). Hence, the adakitic signatures of the Group II porphyries were inherited mainly from their source rather than obtained during subsequent magma evolution.

6.5. Contribution to porphyry Cu–Au mineralization

Based on the presence of MME within the Group II porphyries at Pulang, Cao et al. (2009) suggested that magma mixing occurred during the generation of mineralization-related porphyries, and that the Group I porphyry magma was injected into the magma chamber comprising Group II porphyries. Such a model is supported

by the following evidence. (1) The observation of repeated oscillatory zoning and core-to-rim variations of anorthite content in plagioclase phenocrysts within Group II porphyries (Liu et al., 2015; Li et al., 2017). (2) The Group I porphyry samples show highly variable LREE contents, with some having higher LREE contents and much more fractionated REE patterns than Group II porphyries but others exactly mimicking REE patterns of Group II porphyries (Fig. 8a). This is consistent with mixing between the two group porphyry magmas. (3) Zircons from the DP (Group I porphyry) yield variable Hf–O isotopic compositions, with some grains having compositions similar to the lower crust, whereas others overlap with the range defined by Group II porphyries.

The source of metals and sulfur for porphyry copper deposits is widely accepted to be the felsic magmas themselves (Hedenquist and Richards, 1998). However, experimental studies indicate that felsic magmas typically exhibit low sulfur and metal solubilities (Wallance and Carmichael 1992; Hattori and Keith 2001; Mungall 2002). Therefore, the generation of giant porphyry Cu deposits, such as Pulang (446.8 Mt at 0.52% Cu and 0.18 g/t Au), which contain large quantities of sulfides (i.e., chalcopyrite and pyrite) and anhydrite, requires an additional source of sulfur and metals (Hattori and Keith 2001; Hou et al., 2013a). Considering the presence of dioritic magma and aforementioned magma mixing at Pulang, the lack of such dioritic magmatism in moderate to small deposits elsewhere in the region (e.g., Xuejiping, Chundu), and the commonly high metal (e.g., Cu and Au) and sulfur concentrations in mafic magmas (Hattori and Keith, 2001; Halter et al., 2005; Zajacz and Halter, 2009),

we propose that the input of dioritic magma into the upper crustal porphyry magma chamber would have contributed mass of metals (e.g., Cu and Au) and sulfur. This process enhanced the formation of the Pulang deposit, allowing it to become the only giant porphyry copper deposit in the Zhongdian arc.

The Al-in-amphibole geobarometer suggests that amphibole phenocrysts in Group II porphyries crystallized at pressures of 2.1–2.6 kbar, which correspond to paleodepths of 8.0–9.8 km (average ~9.1 km) under lithostatic pressure (Appendix 4). In contrast, amphibole in the DP (Group I porphyry) crystallized at much higher pressures of 2.9–4.1 kbar, corresponding to paleodepths of 10.8–15.4 km (average ~13.1 km) (Appendix 4). In this case, although the exposed DP intrusions at Pulang are relatively small, they could have provided sufficient copper and gold through the direct injection of mafic dioritic magma from a larger magmatic reservoir at a depth of ~13.1 km to an upper crustal porphyry magma chamber at a depth of ~9.1 km (Appendix 4; Fig. 15), resulting in the generation of porphyry Cu–Au mineralization at Pulang.

Additionally, H₂O exerts a critical control on the budget of ore-forming metals in porphyry system (Sillitoe, 2010; Audétat and Simon, 2012). Parental magmas of porphyry Cu deposits need to be water-rich (>~4 wt.%) and oxidized so as to maximize the metal abundances of the resultant exsolved hydrothermal fluids (Richards, 2005; Sillitoe, 2010). The dioritic magma at Pulang contains up to ~6.2 wt.% H₂O at a paleodepth of ~14.1 km (3.7 kbar; Appendix 4). When such H₂O-rich magma was injected into the Group II porphyry magma chamber at a depth of ~9.1

km (Appendix 4; Fig. 15), it would also result in abundant water endowment. Therefore, the Group I porphyry magma played a critical role, increasing not only the necessary metals (e.g., Cu and Au), sulfur, but also H₂O contents of the system, which are all favorable for the generation of the giant porphyry Cu–Au deposit at Pulang.

7. Conclusions

- (1) The newly identified diorite porphyry at Pulang formed at 216.6 ± 1.9 Ma, simultaneous with the mineralization-related coarse-grained quartz diorite and quartz monzonite (Group II porphyries).
- (2) The diorite porphyry has similar geochemical characteristics to MME within Group II porphyries, but quite distinct from the Group II porphyries. Group I porphyries (diorite porphyry and MME) were derived from a magma produced during low-degree partial melting of metasomatized phlogopite-rich lithospheric mantle, followed by crustal assimilation. Group II porphyries are adakitic and were produced during partial melting of subduction-modified juvenile lower crust due to underplating of the high-K arc basalt magmas.
- (3) Input of dioritic magma into the upper crustal magma chamber containing the Group II porphyries would have contributed not only the necessary metals (e.g., Cu and Au), sulfur, but also H₂O to the system, which aided the generation of the giant Pulang porphyry Cu–Au deposit.

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Figure and Table captions

Figure 1. (a) Tectonic framework of the Yidun arc (after Wang et al., 2014a), and (b) sketch geological map of the Zhongdian arc (after Leng et al., 2012). Abbreviations: BNS = Bangong–Nujiang Suture, GLS = Garze–Litang Suture, JS = Jinshajiang Suture, LB = Lhasa Block, NCC = North China Craton, QTB = Qiangtang Block, SGT = Songpan–Garze Terrane; TTD = Tibetan Tectonic Domain, YB = Yangtze Block, YC = Yangtze Craton, YDT = Yidun Terrane, ZM = Zhongza Massif.

Figure 2. Geological map of (a) the Pulang porphyry Cu–Au district, (b) East Pulang and (c) cross-section along section A–A' from South Pulang showing lithologies based on core logs of sixteen drill holes (after KPDI, 2014).

Figure 3. Photographs of the various porphyries in the Pulang district. (a) Mafic magmatic enclave (MME) in the CQD; (b) sharp contact between the CQD and DP; (c) sharp contact between the QM and DP. Plagioclase phenocrysts in the DP are rounded and embayed; (d–f) polarized light images showing amphibole in the CQD, QM and DP, respectively. Abbreviations: amp = amphibole, bt = biotite, pl = plagioclase.

Figure 4. Cathodoluminescence (CL) images and U–Pb ages and O–Hf isotopic values for representative zircon grains from the Late Triassic CQD, QM and DP at Pulang. Numbers represent SHRIMP U–Pb ages ($\pm 1\sigma$; solid pink ellipse; the ages of the CQD (4408–537) and QM (0713–713) are not analyzed and all their zircon grains

are given the widely reported ages of 216.0 Ma (Chen et al., 2014; Cao et al., 2016; Kong et al., 2016)) and $\delta^{18}\text{O}$ values (dashed yellow ellipse) and LA-MC-ICP-MS $\epsilon_{\text{Hf}}(t)$ values (underlined; solid white square).

Figure 5. U–Pb reverse concordia diagram for zircons from the DP (sample E601-20) at Pulang.

Figure 6. Classification of amphibole within the CQD, QM and DP in terms of Si vs $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ (Leake et al, 1997).

Figure 7. Plots of (a) $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ vs SiO_2 (after Irvine and Baragar, 1971; Middlemost, 1994); (b) K_2O vs SiO_2 (after Peccerillo and Taylor, 1976); and (c) Y vs Sr/Y (after Drummond and Defant, 1990) for the CQD, QM, DP and MME at Pulang. Data sources: CQD and QM in literature from Ren et al. (2011) and Cao et al. (2014, 2016); MME in literature from Cao et al. (2009); Arc basalts in the Zhongdian arc from Leng et al. (2014); underplated basaltic crust-derived adakitic rocks from Muir et al. (1995), Petford and Atherton (1996) and Xiong et al. (2003).

Figure 8. (a) Chondrite-normalized REE and (b) primitive mantle-normalized trace elemental spider diagrams for the CQD, QM, DP and MME at Pulang. Normalizing values are from Sun and McDonough (1989). MME from Cao et al. (2009).

Figure 9. $\epsilon_{\text{Nd}}(t)$ vs $(^{87}\text{Sr}/^{86}\text{Sr})_i$ for the CQD, QM and DP at Pulang. The orange solid curve represents a magma mixing model between mantle-derived magma (represented by Jinshajiang MORB: Sr = 260 ppm, Nd = 7.2 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7054$, $\epsilon_{\text{Nd}}(t) = +6.1$; Xu and Castillo, 2004) and the Yangtze lower crust (represented by the Kongling amphibolites: Sr = 200 ppm, Nd = 14 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.710$, $\epsilon_{\text{Nd}}(t) = -12$; estimated from Gao et al., 1999; Zhang, 2008). The blue solid curve also represents a magma mixing model between subduction-modified juvenile Zhongdian lower crust (represented by a basalt sample LNT10-1: Sr = 651 ppm, Nd = 41.7 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7058$, $\epsilon_{\text{Nd}}(t) = +0.7$; Leng et al., 2014) and the aforementioned Yangtze lower crust represented by the Kongling amphibolites. Numbers labeled on the binary mixing curves represent the weight percentages of the Yangtze lower crust materials in the mixture. Data sources: Xiaxiaoliu basalts from Chen et al. (2017); Late Triassic porphyries at other porphyry Cu deposits from Wang et al. (2011), Leng et al. (2012) and Chen et al. (2014); volcanic rocks in the Zhongdian arc from Wang et al. (2011), Chen et al. (2014) and Leng et al. (2014); Upper continental crust (UCC) from Jahn et al. (1999).

Figure 10. Plot of $\delta^{18}\text{O}$ vs $\epsilon_{\text{Hf}}(t)$ for zircons from the CQD, QM and DP at Pulang. The dotted curves denote the two-component mixing trends between the depleted mantle ($\epsilon_{\text{Hf}}(t) = 12$, O = 437000 ppm, $\delta^{18}\text{O} = 5.3$; Roberts et al., 2013) and lower crust-derived magmas (represented by zircons from the Kongling amphibolites with estimated $\epsilon_{\text{Hf}}(t) = -12$, O = 502000 ppm, $\delta^{18}\text{O} = 7.5$; Zhang et al., 2006; Roberts et al.,

2013; Wang et al., 2014b). Hf_{pm}/Hf_c ratios show the parental mantle magma (pm) to that in the crustal (c) melts, as indicated for each curve. The small open circles on the curves represent 10% mixing increments. Error bars indicate typical 2σ for the analyzed data.

Figure 11. Variations of (a) Cr vs MgO; (b) Zr/Nb vs Nb/Ta; (c) K_2O vs MgO; (d) Ba vs MgO; (e) Sr vs MgO; and (f) Th vs MgO for the Group I and II porphyries at Pulang. CQD and QM in literature from Ren et al. (2011) and Cao et al. (2014, 2016). LC = lower crust, UC = upper crust, values for both of them are from Rudnick and Gao (2003).

Figure 12. (a) Rb/Sr vs Ba/Rb (Furman and Graham, 1999). CLM = common lithospheric mantle; PM = primitive mantle. (b) La/K and (c) La/Ba vs La for the Group I and II porphyries at Pulang. Data sources are as in Fig. 7.

Figure 13. Variations of K_2O/Na_2O vs (a) MgO and (b) Sr/Y for the Group I and II porphyries at Pulang. Data sources are as in Fig. 7.

Figure 14. Plots of (a) Dy/Yb and (b) Sr/Y vs SiO_2 for the Group II porphyries at Pulang. Fractional crystallization vectors of garnet, ol + pl + cpx, and amphibole are from Davidson et al. (2007); Cpx = clinopyroxene, Ol = olivine, Pl = plagioclase. The evolution trend (pink arrow) of the adakitic Group II porphyries at Pulang suggests a

predominant amphibole fractional crystallization in the adakite-like parental magma. However, Sr/Y signatures of the adakitic rocks have no systematic changes with increasing SiO₂ contents. Data sources are as in Fig. 7.

Figure 15. Schematic illustration showing the geodynamic setting and petrogenesis model for the Group I and II porphyries at Pulang. Primary magma from the metasomatized subcontinental lithospheric mantle rose up to form a magma reservoir at a depth of ~13.1 km. Then injection of dioritic magma from such reservoir into the upper crustal adakitic magma chamber at a depths of ~9.1 km would have contributed mass of metals (e.g., Cu and Au), sulfur and H₂O to generate porphyry Cu–Au mineralization at Pulang.

Table 1. LA–ICP–MS U–Pb isotopic data for zircons from the diorite porphyry (DP; sample E601-20) at Pulang.

Table 2. Representative major (wt.%) and trace element (ppm) data for the coarse-grained quartz diorite (CQD), quartz monzonite (QM), diorite porphyry (DP) and reported MME at Pulang (see Appendix 5 for the complete dataset).

Table 3. Whole-rock Sr–Nd isotopic data for the coarse-grained quartz diorite (CQD), quartz monzonite (QM) and diorite porphyry (DP) at Pulang.

Table 1. LA-ICP-MS U-Pb isotopic data for zircons from the diorite porphyry (DP; sample E601-20) at Pulang.

Sp ot	% ²⁰⁶ Pb c	U (p p m)	Th (p p m)	Pb * (p p m)	²³² T h/ ²³⁸ U	²³⁸ U/ ²⁰⁶ Pb *	± %	²⁰⁷ Pb */ ²⁰⁶ Pb *	± %	²⁰⁷ Pb */ ²³⁵ U	± %	²⁰⁶ Pb / ²³⁸ U (Ma)	± 1 σ	²⁰⁷ Pb / ²⁰⁶ Pb (Ma)	± 1 σ
20 _1	0. 04	60 5	34 3	17. 7	0.59	29.37	0 9	0.050 2	2. 8	0.235	2. 9	215. 8	1. 8	202.0	6 4.
20 _1. 2	0. 18	59 1	36 8	17. 1	0.64	29.51	0 9	0.052 8	2. 1	0.246	2. 3	214. 8	1. 9	318.5	4 7.
20 _2	0. 16	42 8	45 1	12. 4	1.09	29.62	0 9	0.047 9	5. 1	0.223	5. 2	214. 0	2. 0	92.35	1 2
20 _3	0. 08	10 65	11 22	30. 5	1.09	29.92	0 8	0.052 1	2. 1	0.240	2. 3	212. 0	1. 7	290.9	4 8.
20 _4	0. 21	58 5	38 4	16. 8	0.68	29.82	0 9	0.050 6	3. 6	0.234	3. 7	212. 7	1. 9	224.8	8 2.
20 _5	0. 14	65 5	35 3	19. 5	0.56	28.89	0 9	0.051 5	2. 3	0.246	2. 5	219. 3	1. 9	264.6	5 3.
20 _6	0. 22	11 51	11 16	33. 6	1.00	29.41	0 8	0.052 1	1. 6	0.244	1. 8	215. 6	1. 7	290.5	3 7.
20 _7	1. 07	68 9	56 0	20. 1	0.84	29.22	0 9	0.055 3	1 2	0.261	1 3	216. 9	1. 9	423.8	2 7
20 _8	0. 04	12 25	10 14	36. 1	0.86	29.16	0 8	0.049 4	2. 0	0.234	2. 1	217. 4	1. 8	167.6	4 6.
20 _9	0. 25	72 9	48 1	21. 3	0.68	29.24	0 9	0.052 8	2. 0	0.249	2. 2	216. 8	1. 8	318.7	4 5.
20 _1 0	0. 09	90 4	69 3	27. 1	0.79	28.66	0 9	0.051 9	2. 0	0.250	2. 2	221. 1	1. 9	280.8	4 6.
20 _1 1	0. 13	10 01	84 1	29. 4	0.87	29.23	0 9	0.051 1	1. 9	0.241	2. 1	216. 8	1. 8	245.6	4 3.
20 _1 2	0. 01	80 9	59 6	23. 9	0.76	29.04	0 9	0.050 9	2. 2	0.242	2. 4	218. 3	1. 9	235.8	5 1.
20 _1 3	0. 02	73 7	44 4	21. 8	0.62	28.98	0 9	0.051 0	2. 1	0.243	2. 3	218. 7	1. 9	241.8	4 8.
20 _1 4	0. 18	24 0	17 9	7.0	0.77	29.69	1 1	0.048 8	7. 5	0.227	7. 5	213. 6	2. 4	140.5	1 7
20 _1 5	-0. 02	55 7	56 9	16. 6	1.05	28.82	0 9	0.050 2	3. 9	0.240	4. 0	219. 9	2. 0	204.0	9 0.
20	0.	79	99	23.	1.30	28.75	0	0.051	1.	0.247	2.	220.	1.	265.9	4

<u>1</u>	09	3	5	7	.	6	8	0	4	9	1.
6					9						6

Notes: Errors are 1-sigma; Pb_c and Pb* indicate the common and radiogenic portions, respectively. Common Pb and ²⁰⁶Pb* corrected using measured ²⁰⁷Pb; ²³⁸U/²⁰⁶Pb*, ²⁰⁷Pb*/²⁰⁶Pb*, ²⁰⁷Pb*/²³⁵U ratios, ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages corrected using measured ²⁰⁴Pb.

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Table 2. Representative major (wt.%) and trace element (ppm) data for the coarse-grained quartz diorite (CQD), quartz monzonite (QM), diorite porphyry (DP) and reported MME at Pulang (see Appendix 5 for the complete dataset).

Sample no.	6628-44 6	6628-48 7	E002-20 1	0713-65 5	0713-74 9	0713-98 0	2812-49 4	E303-85	E601-20	PB1*	PB4*
Lithology	CQD	CQD	CQD	QM	QM	QM	DP	DP	DP	MME	MME
SiO ₂	62.8	62.8	61.1	64.3	65.2	65.3	59.6	60.7	59.9	59.3	59.4
TiO ₂	0.54	0.60	0.69	0.55	0.52	0.55	0.59	0.75	0.57	0.56	0.69
Al ₂ O ₃	13.66	14.2	14.6	14.2	14.1	14.4	13.9	13.7	15.2	13.4	13.9
Fe ₂ O ₃ ^T	6.81	5.88	5.37	4.04	3.77	4.00	6.13	3.83	5.35	6.15	6.22
MgO	3.07	2.96	3.46	2.48	2.35	2.44	4.66	4.08	3.79	5.21	5.45
MnO	0.04	0.05	0.06	0.06	0.05	0.04	0.06	0.04	0.08	0.06	0.06
CaO	3.49	3.96	4.51	4.16	3.45	3.25	4.08	3.86	5.20	4.63	4.35
Na ₂ O	2.24	2.48	3.22	3.62	2.80	3.54	3.42	2.83	3.27	2.70	2.74
K ₂ O	5.06	4.57	4.37	4.30	4.75	4.60	4.86	6.41	4.01	4.79	4.57
P ₂ O ₅	0.48	0.43	0.39	0.36	0.34	0.35	0.69	0.43	0.42	0.76	0.66
LOI	1.55	1.59	1.10	1.26	2.03	0.63	1.16	2.62	2.50	1.96	1.42
TOTAL	99.76	99.48	98.87	99.38	99.38	99.17	99.14	99.24	100.30	99.48	99.46
K ₂ O/Na ₂ O	2.3	1.8	1.4	1.2	1.7	1.3	1.4	2.3	1.2	1.8	1.7
Mg#	47.4	50.2	56.3	55.1	55.5	55.0	60.3	68.1	58.6	62.9	63.7
Sc	14.4	15.1	16.1	12.6	12.3	12.2	9.0	14.3	12.6	9.6	11.4
V	111.4	120.3	135.1	100.3	89.2	96.8	76.5	106.0	99.0	81.3	96.2
Cr	54.7	50.4	61.3	38.8	40.3	41.9	143.7	114.0	115.0	138.0	115.0
Co	15.2	12.8	9.6	9.5	9.4	10.1	12.6	5.6	18.1	20.0	21.4
Ni	15.8	15.3	21.9	14.9	19.7	15.0	97.8	20.8	32.0	109.0	93.3
Cu	117.3	89.4	72.9	42.1	88.7	35.6	45.9	48.8	56.0	14.8	20.1
Zn	33.9	35.1	36.4	35.8	42.8	29.3	35.4	23.0	38.0	54.5	102.0
Ga	16.2	17.0	16.9	17.2	16.9	17.2	22.3	18.3	19.0	25.1	24.0
Rb	204.7	175.1	147.0	139.2	177.9	172.1	208.7	201.0	122.0	185.0	202.0
Sr	734	854	850	797	634	767	1090	635	2050	1560	1466
Y	13.7	15.1	14.7	12.6	12.6	12.5	15.2	13.4	13.0	22.2	21.6
Zr	180.2	207.2	216.7	178.3	159.4	180.1	336.7	344.0	293.0	664.0	491.0
Nb	12.0	12.9	11.0	11.7	11.7	11.3	11.8	13.5	7.2	13.7	14.6
Cs	8.1	10.6	10.8	3.8	7.6	5.4	12.3	11.1	6.7	16.0	20.1
Ba	1675	1601	2076	1165	1158	1297	2224	2450	2175	2438	2180
La	31.5	37.5	44.3	31.8	30.3	32.1	218.2	33.6	90.0	225.0	147.0
Ce	62.3	73.3	82.9	61.7	59.7	60.1	416.7	74.2	185.0	412.0	245.0
Pr	7.80	8.89	9.62	7.43	7.16	7.19	48.02	8.70	21.30	50.80	32.00
Nd	29.0	32.9	35.0	27.0	26.6	26.5	165.1	33.0	77.1	182.0	117.0
Sm	5.73	6.14	6.47	5.04	4.99	5.03	21.81	6.26	11.50	24.60	16.80
Eu	1.51	1.67	1.82	1.25	1.22	1.26	3.64	2.03	2.66	5.62	3.91
Gd	4.17	4.49	4.90	3.65	3.64	3.67	11.60	4.41	6.13	15.70	11.10
Tb	0.58	0.63	0.64	0.51	0.52	0.50	1.11	0.53	0.62	1.30	1.05
Dy	3.20	3.47	3.53	2.83	2.90	2.78	4.30	2.84	2.90	4.95	4.33
Ho	0.61	0.67	0.66	0.55	0.56	0.53	0.68	0.53	0.49	0.74	0.73
Er	1.67	1.75	1.74	1.53	1.49	1.45	1.51	1.43	1.38	1.87	1.92
Tm	0.24	0.26	0.25	0.22	0.21	0.22	0.19	0.21	0.19	0.21	0.24
Yb	1.59	1.66	1.63	1.45	1.45	1.45	1.25	1.32	1.05	1.28	1.47
Lu	0.24	0.26	0.25	0.22	0.22	0.22	0.18	0.20	0.15	0.18	0.23
Hf	5.17	5.55	5.70	4.88	4.55	4.99	8.28	9.90	7.00	14.30	11.00
Ta	1.03	1.05	0.89	0.94	0.99	0.98	0.78	0.81	0.45	0.77	0.89
Pb	10.3	11.9	13.7	17.4	29.4	13.3	8.8	9.4	9.0	10.6	21.2
Th	17.9	16.9	15.8	17.4	16.6	17.5	40.1	10.1	30.9	40.8	30.6
U	4.98	5.06	3.87	4.88	3.92	4.32	6.26	4.89	4.44	5.39	5.12
Sr/Y	53	57	58	63	50	61	72	47	158	70	68
La/Yb	20	23	27	22	21	22	174	25	86	175.8	100.0
(La/Yb) _N	14.2	16.2	19.5	15.7	15.0	15.9	125.1	18.3	61.5	126.1	71.7
(Gd/Yb) _N	2.2	2.2	2.5	2.1	2.1	2.1	7.7	2.8	4.8	10.1	6.2

Eu/Eu*	0.95	0.97	0.99	0.89	0.88	0.90	0.70	1.18	0.97	0.87	0.88
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$\text{Mg\#} = 100 \times \text{molar Mg}/(\text{Mg} + \text{Fe})$

*MME data from Cao et al. (2009)

Table 3. Whole-rock Sr–Nd isotope data for the coarse-grained quartz diorite (CQD), quartz monzonite (QM) and diorite porphyry (DP) at Pulang.

Sample no.	Lithology	Age (Ma)	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	$\pm 2\sigma$	Sr (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$(^{143}\text{Nd}/^{144}\text{Nd})_i$	$\pm 2\sigma$	ϵ_N	T_{DM} (Ma)
6628-471	CQD	216	256	749	0.989387	0.707630	0.000004	604	320	0.114097	0.512431	0.000008	-1.81	1156
6628-588	CQD	216	179	796	0.646373	0.708594	0.000003	529	272	0.117268	0.512393	0.000001	-2.64	1208
E002-201	CQD	216	147	850	0.500187	0.707765	0.000004	647	350	0.111693	0.512431	0.000008	-1.75	1162
0713-713	QM	216	158	743	0.618527	0.707554	0.000003	480	254	0.114500	0.512384	0.000001	-2.74	1231
0713-897	QM	216	139	734	0.548141	0.708234	0.000002	564	301	0.113212	0.512384	0.000009	-2.71	1235
0713-980	QM	216	172	767	0.649692	0.707563	0.000003	503	265	0.114814	0.512357	0.000005	-3.28	1273
2812-494	DP	216	208	1090	0.553828	0.707066	0.000004	218	161	0.079816	0.512433	0.000007	-0.81	1188
E601-20	DP	216	122	2050	0.172204	0.706868	0.000001	110	770	0.090121	0.512345	0.000000	-2.82	1344
E601-40	DP	216	292	767	1.101605	0.709948	0.000001	751	357	0.127102	0.512476	0.000007	-1.30	1043
E303-85	DP	216	201	635	0.915927	0.709538	0.000004	626	330	0.114615	0.512392	0.000007	-2.59	1218
E101-500	DP	216	167	830	0.582206	0.707452	0.000004	700	331	0.127776	0.512466	0.000007	-1.51	1055

Notes: The Rb, Sr, Sm and Nd contents of sample 6628-588 are from Cao et al. (2016). $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are obtained by calculation of Rb, Sr, Sm, and Nd contents in Table 2: $^{87}\text{Rb}/^{86}\text{Sr} = \text{Rb}/\text{Sr} \times 2.8936$ and $^{147}\text{Sm}/^{144}\text{Nd} = \text{Sm}/\text{Nd} \times 0.6042$. $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $\epsilon_N(t)$ values are calculated at $t=216$ Ma; $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$ and $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$. T_{DM} is calculated using $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.21357$ and $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.51315$.

Highlights:

1. The newly identified diorite porphyry formed at ca. 216 Ma.
2. The diorite porphyry and MME were sourced from metasomatized subcontinental lithospheric mantle.
3. Input of dioritic magma to upper crustal magma chamber has contributed to porphyry Cu–Au mineralization.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

$\text{Ca}_B \geq 1.50$; $(\text{Na} + \text{K})_A < 0.50$; $\text{Ca}_A < 0.50$

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15