Geochemistry and zircon U–Pb geochronology of the Pulang complex, Yunnan province, China

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The Pulang complex is located tectonically at the southern margin of the Yidun–Zhongdian island arc belt in Yunnan province, China, and is closely related to formation of the Pulang copper deposit, which is the largest copper deposit in Asia. The Pulang complex can be divided into three intrusion stages based on contact relationships and petrological characteristics: (1) a first stage of quartz dioritic porphyry; (2) a second stage of quartz monzonitic porphyry; and (3) a third stage of granodioritic porphyry. The crystallization ages of these intrusion stages were determined by single-zircon U–Pb dating, yielding ages of 221.0 ± 1.0 , 211.8 ± 0.5 , and 206.3 ± 0.7 Ma for the first, second, and third stages, respectively. These dates, integrated with previous geochronological data and field investigations, indicate that the second-stage quartz monzonitic porphyry has a close spatial and temporal relationship with the large Pulang porphyry copper deposit. These age data, geochemical and Sr–Nd isotopic results suggest that the Pulang complex formed in the Indo-Chinese epoch (257 ~ 205 Ma) by multiphase intrusion of a mixture of mantle- and crust-derived magmas.

1. Introduction

Porphyry ore deposits are widely distributed throughout the world and are the main source of metallic elements such as copper and molybdenum (Harraden *et al.* 2013; Lang *et al.* 2013). These ore deposits have long been a focus of research efforts due to their considerable economic value (Sillitoe 2010; Hollings *et al.* 2011; Li *et al.* 2011a; Ingebritsen 2012; Weis *et al.* 2012; Anderson *et al.* 2013; Gregory *et al.* 2013; Sun *et al.* 2013). The Pulang copper deposit is located tectonically at the southern margin of the Yidun–Zhongdian island arc belt in Yunnan province, China (figure 1a), and is the largest copper deposit in Asia. More than 5×10^6 tons of copper had been identified in the ore deposit by end-2007 in an area of just ca. 6 km²,

highlighting that the deposit is of an extraordinarily large scale. The Pulang complex was formed by multiphase magmatic intrusions that were closely related to formation of the Pulang copper deposit (Fan and Li 2006; Li and Zeng 2007; Li *et al.* 2011a, b; Liu *et al.* 2012). Intrusions with similar emplacement ages and lithological characteristics as the Pulang complex are widely distributed in the Yidun–Zhongdian island arc belt, which are also closely related to ore deposits (Huang *et al.* 2012; Zi *et al.* 2012; Li *et al.* 2013). Therefore, precise dating of the Pulang complex porphyry intrusions is important for furthering our understanding of the Pulang copper deposit and the Yidun–Zhongdian island arc belt.

Previous studies have focused on the petrology, geochemistry, and mineralization of the Pulang

Keywords. Zircon U–Pb age; mantle- and crust-derived magma; multiphase intrusion; Pulang complex; Yunnan province.

Figure 1. (a) Regional setting of Yidun–Zhongdian island arc zone, showing the Indosinian and Himalayan porphyry belts and Pulang porphyry copper deposit (modified after Li *et al.* 2011a). (b) Geological map of the Pulang complex (modified after Zeng *et al.* 2006).

complex (Zeng *et al.* 2003; Wang *et al.* 2007a, b, c, 2008; Cao *et al.* 2009; Li *et al.* 2009, 2011b; Pang *et al.* 2009; Ren *et al.* 2011). These previous studies also determined the mineralization and intrusion ages of the Pulang complex (Zeng *et al.* 2004, 2006; Wang *et al.* 2008; Li *et al.* 2009), although the ages have a relatively large range, including 182 Ma by K–Ar (Zeng *et al.* 2004), and 213–216 Ma by Ar–Ar (Zeng *et al.* 2006). Li *et al.* (2009) obtained several biotite and hornblende ^{40}Ar – ^{39}Ar ages ranging from 209.4 ± 1.7 to 212.3 ± 1.4 Ma. An age range of 182.5 ± 1.8 to 235.4 ± 2.4 Ma of biotite and K-feldspar was also reported by Li *et al.* (2011a) by K–Ar methods. Previous age determinations for the Pulang complex vary widely and are not consistent. Single-zircon U–Pb dating is a favourable method for dating the host rocks of porphyry copper deposits (e.g., Li and Gui 1990; Von *et al.* 2002, 2005; Wilson *et al.* 2007; Wainwright *et al.* 2011; Zhou *et al.* 2012). Herein, in this study, we present single-zircon U–Pb ages of the different intrusion stages of the Pulang complex in order to precisely constrain the formational history of the complex.

2. Geology and petrography of the Pulang complex

The Pulang porphyry copper deposit is situated in Gezan Town, Zhongdian County, Yunnan province. Geological outcrops in this area are Quaternary sediments and the first and second members (including the first and second beds) of the Upper Triassic Tumugou Formation. The Tumugou Formation dominantly comprises epimetamorphic clastic and volcanic rocks. The Pulang complex extends along NW–SE and buried NE–SW trending faults in a horizontal ‘Y’ shape (figure 1b).

The Pulang complex comprises five intermediate–acid, upper- to mid-hypabyssal intrusions (numbered as Intrusion I, II, III, IV, and V; figure 1b). The contact relationships and petrological characteristics of these intrusions allow the Pulang complex to be divided into three stages. Intrusive rocks of the first stage are predominant and constitute the main body of Intrusions I and II, and Intrusions III, IV, and V. Rocks of the first stage are mainly quartz dioritic porphyry that are hosted in epimetamorphic clastic and volcanic rocks of the first and second members of the

Upper Triassic Tumugou Formation. Contact facies of the first stage dip outward from the intrusion at 35°–75°. Roof pendants and xenoliths can be observed at the margins and top of the intrusion. Rocks of the second stage are lithologically dominated by quartz monzonitic porphyry distributed in the core of Intrusions I and II. Intrusive rocks of the second stage are in contact with those of the first stage, along contacts that dip outwards at angles of 56°–78°. Intrusive rocks of the third stage are limited in their extent and are only found to the east of Intrusion I as an elongate band. Third-stage granodioritic porphyry rocks are in intrusive contact with the first- and second-stage rocks. A fine-grained facies that is 0.2–1.5 m wide crops out along the contact zone of the third-stage intrusion. Late-stage quartz diorite porphyry dikes with a nearly E–W strike also cut the Pulang complex.

The quartz dioritic porphyry has a porphyritic texture (figure 2a and b) with twinned and zoned andesine (An_{30–40}) phenocrysts (42–44%) set in a fine-grained (<0.1 mm) microcrystalline matrix. The matrix comprises plagioclase, K-feldspar, amphibole, biotite, and quartz. The quartz monzonitic porphyry has a porphyritic texture (figure 2c and d) with phenocrysts (33–35%) of K-feldspar, oligoclase–andesine (An_{28–33}), and quartz set in a subhedral granular (<0.3 mm) matrix of plagioclase, K-feldspar, quartz, amphibole, and biotite. The granodioritic porphyry has a porphyritic texture (figure 2e and f) with phenocrysts (33–35%) of K-feldspar, oligoclase (An_{28–29}), quartz, and biotite set in a subhedral granular matrix (<0.8 mm) of K-feldspar, plagioclase, quartz, and biotite.

3. Samples and analytical methods

All samples were collected from fresh, unaltered or weakly altered rocks, which had all their weathered surfaces removed. Samples of the first-stage quartz dioritic porphyry were collected from Intrusion I, 160 m west of Drillhole ZK1201 on Exploratory Line 32. Samples of the second-stage quartz monzonitic porphyry were collected from 50 m north of Pithead YD01 in central Intrusion I. Samples of the third-stage granodioritic porphyry were collected from southern Intrusion I at the airport platform of Drillhole ZK0308 on Exploratory Line 3. All samples weighed >15 kg. Zircon separation was performed in the laboratory of the Langfang Research Institute of Regional Geological Survey, Langfang, China. Samples were first coarsely crushed and then zircons were separated by standard magnetic and heavy liquid methods. Finally, the zircons were examined in detail under a microscope to select clean, transparent, and relatively

automorphic crystals without cracks or inclusions for U–Pb dating. U–Pb isotopic dating was carried out on single zircons by the isotope dilution method. All zircon U–Pb preparation (dissolution and U–Pb separation) was carried out in an ultraclean laboratory following Krogh (1973). Zircon grains were dissolved in HF acid in small Teflon beakers with a mixed ²⁰⁵Pb–²³⁵U tracer. The digested zircon (+ spike) was then loaded on a rhenium filament with silica gel and phosphoric acid. U–Pb isotopes were measured with a VG354 thermal ionization mass spectrometer. All U and Pb isotope data were corrected for instrumental mass bias. All work was conducted in an environmentally controlled laboratory at 25°C and 40% humidity.

Major oxides were analysed at the Science Research Institute, China University of Geosciences, Beijing, China. Samples were first crushed and ground to a powder (<200 mesh), and then acid digested and analyzed by ICP–AES. Analyses of standard rocks show that the data are accurate to ±2%. FeO was determined using the traditional wet chemical method. Rare earth elements (REE) abundances were measured at the same institute using inductively coupled plasma mass spectrometers (ICP–MS). The samples were digested by acid (HF + HClO₄) in bombs. Precision for rare earth elements was typically better than 5%.

Sr and Nd isotopic analyses were performed using a Finnigan MAT-261 mass spectrometer at the Tianjin Institute of Geology and Mineral Resources, China Geological Survey, Tianjin, China. Mass fractionation corrections for Sr and Nd isotopic ratios were based on values of ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. Uncertainties in the measured Rb/Sr and Sm/Nd ratios were less than ±2%.

4. Analytical results

4.1 Zircon U–Pb geochronology

Zircon crystal characteristics and U–Pb analytical results are listed in table 1 and U–Pb concordia diagrams are shown in figure 3. ²⁰⁶Pb/²⁰⁴Pb ratios in table 1 have been corrected for laboratory blanks (Pb = 0.050 ng; U = 0.002 ng) and spike contributions. The other Pb isotope ratios are radiogenic values. The three samples are concordant, indicating that these zircon grains have remain closed since their formation and have not experienced obvious U or Pb loss. ²⁰⁶Pb–²³⁸U ages of zircon from the quartz dioritic porphyry range from 220.1 to 221.4 Ma, with a weighted mean age of 221.0 ± 1.0 Ma. ²⁰⁶Pb–²³⁸U ages of zircon from the quartz monzonitic porphyry range from 210.5 to 212.3 Ma, with a weighted mean age of

Figure 2. Photomicrographs of the quartz dioritic porphyry (a, b), quartz monzonitic porphyry (c, d), and granodioritic porphyry (e, f) from the Pulang complex, Yunnan province. Pl: Plagioclase; Kf: K-feldspar; Q: Quartz; Bi: Biotite; Hb: hornblende.

211.8 ± 0.5 Ma. ^{206}Pb – ^{238}U ages of zircon from the granodioritic porphyry range from 205.5 to 208.0 Ma with a weighted mean age of 206.3 ± 0.7 Ma. Therefore, the Pulang complex formed between 206 and 221 Ma, in the Indo-Chinese epoch (257 ~ 205 Ma) of the Late Triassic.

4.2 Whole-rock major element oxides, REE, and Rb–Sr and Sm–Nd isotopic compositions

Whole-rock analyses of major element oxides (table 2) indicate that the quartz dioritic porphyry has average SiO_2 and Al_2O_3 contents of 64.36 wt.% and 15.17 wt.%, respectively. Average total alkali contents ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) are 6.64 wt.%, and the mean $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio is 0.66. On the total alkali *versus* silica diagram (TAS, figure 4) of Irvine and

Baragar (1971), all these samples are plotted in the field of subalkaline rocks. Most of the samples have A/CNK ratios ranging from 0.81 to 1.02 (average of 0.92), showing a metaluminous character (figure 5).

The quartz monzonitic porphyry has average SiO_2 and Al_2O_3 contents of 64.80 wt.% and 14.61 wt.%, respectively. Total alkali contents ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) have an average of 7.69 wt.%, and are relatively K-rich (mean $\text{K}_2\text{O}/\text{Na}_2\text{O} = 1.69$). All these samples are also plotted in the field of subalkaline rocks in the TAS diagram (figure 4). Most of the samples have A/CNK ratios ranging from 0.89 to 1.15 (average of 0.97) and some samples possess normative corundum (Al_2O_3) ranging from 0 to 3.13 wt.%, showing a metaluminous to peraluminous character (figure 5).

The granodioritic porphyry has average SiO_2 and Al_2O_3 contents of 66.49 wt.% and 14.69 wt.%,

Table 1. U–Pb isotopic compositions of zircons from the Pulang complex, Yunnan province.

Sample no.	1	2	3	4	5	6	7	8	9	10	11
Intrusion lithology	Intrusion I Quartz dioritic porphyry			Intrusion I Quartz monzonitic porphyry			Intrusion I Granodioritic porphyry				
Zircon characteristics	Yellow, transparent, columnar, euhedral	Yellowish brown, transparent, columnar, euhedral	Brown, transparent, columnar, euhedral	Yellowish brown, transparent, columnar, euhedral	Yellowish brown, transparent, columnar, euhedral	Brown, transparent, columnar, euhedral	Light yellow, nearly transparent, columnar, euhedral	Light yellow, transparent, columnar, euhedral	Yellow, transparent, columnar, euhedral	Brown, transparent, columnar, euhedral	Yellow, transparent, columnar, euhedral
Mass fraction	21 2007 79 0.057	10 902 41 0.035	18 902 111 0.27	12 1675 64 0.004	12 1788 74 0.034	15 2842 110 0.018	13 3172 131 0.077	20 3154 119 0.057	12 2228 86 0.033	17 2904 108 0.049	12 2146 77 0.006
Isotope atomic ratio	$^{206}\text{Pb}/^{204}\text{Pb}$ $^{208}\text{Pb}/^{206}\text{Pb}$ $^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	3734 0.2413 0.03494 0.2321 0.127 0.04816	232 0.2487 0.03473 0.2428 (323) 0.05017	5615 0.2659 0.03348 0.2184 (170) 0.04731	801 0.2874 0.03347 0.2541 (163) 0.05506	2732 0.2722 0.03342 0.2215 (66) 0.04807	709 0.2892 0.03319 0.2331 (86) 0.05094	1367 0.2303 0.03279 0.2276 (67) 0.05033	1046 0.2476 0.03263 0.2329 (68) 0.05176	1277 0.2245 0.03249 0.2291 (70) 0.05115	4802 0.229 0.03239 0.2134 (122) 0.04777
Surface age (Ma)	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	221.4 211.9 107.2	220.1 220.7 227.5	212.3 200.6 64.7	212.2 229.9 414.7	211.9 203.2 102.7	210.5 212.8 238	208 208.2 210.3	207 212.6 274.9	206.1 209.5 247.6	205.5 196.4 87.7

Figure 3. U–Pb concordia diagram for zircons from the quartz dioritic porphyry (a), quartz monzonitic porphyry (b), and granodioritic porphyry (c) from the Pulang complex, Yunnan province.

respectively. Total alkali contents (K_2O+Na_2O) have an average of 8.75 wt.%, and are relatively K-rich (mean $K_2O/Na_2O = 1.85$). All these samples are also plotted in the field of subalkaline rocks in the TAS diagram (figure 4). Most of the samples have A/CNK ratios ranging from 1.03 to 1.07 (average of 1.05) and possess normative corundum (Al_2O_3) ranging from 1.57 to 1.59 wt.%, showing a peraluminous character (figure 5).

Whole-rock analyses of REE (table 2) reveal that the intrusions from the Pulang complex have total REE concentrations ranging from 99.41 to 147.0 ppm. Chondrite normalized REE patterns for the quartz dioritic porphyry, quartz monzonitic porphyry and granodioritic porphyry (figure 6) from the Pulang complex are enriched in light rare earth elements (LREE) relative to heavy rare earth

elements (HREE), with the $\sum LREE/\sum HREE$ and $(La/Yb)_N$ ratios of 6.99–14.82 and 8.64–24.03, respectively, and by a weak negative Eu anomaly ($\delta Eu = 0.72$ –0.92), showing similar REE patterns.

Rb–Sr and Sm–Nd isotopic data have been obtained from representative samples of the quartz dioritic porphyry, quartz monzonitic porphyry, and granodioritic porphyry from the Pulang complex (table 3). The initial $^{87}Sr/^{86}Sr$ ratios and $\epsilon_{Nd}(t)$ values have been calculated for ages of 221 to 206 Ma on the basis of Zircon U–Pb dating. The quartz dioritic porphyry show low initial $^{87}Sr/^{86}Sr$ ratios ranging from 0.7060 to 0.7065, and $\epsilon_{Nd}(t)$ values from -4.9 to -3.0 . These values are comparable with those of the quartz monzonitic porphyry that have initial $^{87}Sr/^{86}Sr$ ratio of 0.7065, and $\epsilon_{Nd}(t) = -3.0$. The granodioritic porphyry have slightly higher initial $^{87}Sr/^{86}Sr$ ratio (0.7072) and $\epsilon_{Nd}(t)$ values (-3.2).

5. Discussion

5.1 Age of magmatism

The intrusions of the Pulang complex can be divided into three stages based on contact relationships and petrology. The first-stage intrusion is quartz dioritic porphyry. The second-stage intrusion is quartz monzonitic porphyry. Granodioritic porphyry forms the third-stage intrusion. Previous age determinations for the Pulang complex vary widely and are not consistent (Zeng *et al.* 2004, 2006; Li *et al.* 2009, 2011a). This makes it difficult to precisely constrain the emplacement order of the intrusions. This large age range may reflect analytical uncertainties, as well as the wide range of mineral closure temperatures for the isotopic systems used in these dating studied. For example, the K–Ar and $^{40}Ar/^{39}Ar$ biotite dating methods have low closure temperature, which means that they do not yield reliable granite crystallization ages. However, the zircon U–Pb isotopic system has a high closure temperature (Valencia *et al.* 2005; Siddoway and Fanning 2009; Teixeira *et al.* 2011; Wu *et al.* 2012) that is close to the solidus temperature of granite and, hence, generally provides reliable crystallization ages for granites (Chambefort *et al.* 2007; Sato *et al.* 2012; Burda *et al.* 2013; Zhao *et al.* 2013).

Our new zircon U–Pb age data show that the first-stage quartz dioritic porphyry, second-stage quartz monzonitic porphyry, and third-stage granodioritic porphyry crystallized at 221.0 ± 1.0 , 211.8 ± 0.5 , and 206.3 ± 0.7 Ma, respectively. These ages are consistent with the geological relationships and petrology of the intrusions. Regional isotopic ages indicate that granitoids in the Yidun island arc formed between 237 and

Table 2. Major elements (wt.%) and rare earth elements (ppm) composition of intrusions from the Pulang complex, Yunnan province.

Sample ID	D4	D5	D8	D9	DYS21	DYS36	D2	D3	D6	DYS25
Lithology	Quartz dioritic porphyry				Quartz monzonitic porphyry				Granodioritic porphyry	
SiO ₂	64.10	64.42	64.24	64.66	64.32	64.35	64.98	65.53	66.96	66.02
TiO ₂	0.52	0.74	0.85	0.62	0.84	0.79	0.69	0.56	0.51	0.62
Al ₂ O ₃	15.36	14.91	15.27	15.12	15.19	14.02	14.01	15.20	15.09	14.29
Fe ₂ O ₃	2.24	1.65	1.23	1.56	1.82	1.77	2.60	1.57	1.81	1.50
FeO	2.21	1.76	1.24	2.32	1.99	1.76	2.14	1.69	1.53	1.94
MnO	0.03	0.04	0.02	0.06	0.02	0.03	0.04	0.03	0.01	0.02
MgO	2.86	3.23	3.02	2.78	3.75	3.72	2.46	1.98	2.23	2.71
CaO	3.54	3.01	5.36	3.97	2.48	2.69	3.01	2.96	1.58	1.48
Na ₂ O	3.99	3.97	4.19	3.86	3.75	2.43	2.60	2.64	3.39	2.75
K ₂ O	3.01	2.34	2.12	3.05	2.36	5.68	5.49	5.80	5.26	6.09
P ₂ O ₅	0.36	0.50	0.38	0.36	0.45	0.14	0.21	0.12	0.25	0.45
LOI	0.97	2.13	1.26	1.02	1.80	1.43	0.96	1.02	1.01	1.22
H ₂ O ⁺	0.68	1.46	0.89	0.56	1.15	1.17	0.96	0.86	1.06	0.77
Total	99.87	100.16	100.07	99.94	99.92	99.98	100.15	99.96	100.69	99.86
A/NK	1.56	1.64	1.66	1.57	1.74	1.38	1.37	1.43	1.34	1.28
A/CNK	0.94	1.02	0.81	0.90	1.15	0.93	0.89	0.95	1.07	1.03
La	39.30	32.10	21.70	40.90	36.10	27.30	37.06	28.26	36.71	21.31
Ce	68.00	55.90	51.50	68.40	65.22	49.38	66.78	51.73	61.72	40.60
Pr	7.81	6.69	7.07	7.07	7.36	5.36	8.19	5.80	7.09	4.74
Nd	25.30	23.60	26.30	24.20	25.70	18.14	28.47	20.63	23.62	17.90
Sm	4.68	5.39	6.38	4.69	6.24	4.45	5.98	4.37	4.90	4.48
Eu	1.19	1.63	1.47	1.10	1.62	1.26	1.44	1.08	1.29	0.95
Gd	3.73	4.52	5.97	3.43	4.43	3.57	5.49	3.54	3.83	3.08
Tb	0.53	0.70	0.80	0.49	0.58	0.51	0.69	0.53	0.54	0.44
Dy	2.83	3.98	4.33	2.53	3.02	3.03	3.74	2.73	2.97	2.55
Ho	0.57	0.69	0.77	0.47	0.57	0.60	0.69	0.54	0.58	0.46
Er	1.66	2.00	2.11	1.34	1.51	1.62	1.95	1.52	1.70	1.28
Tm	0.24	0.30	0.30	0.20	0.23	0.23	0.30	0.22	0.25	0.19
Yb	1.57	1.92	1.80	1.22	1.59	1.48	1.99	1.39	1.55	1.25
Lu	0.24	0.29	0.28	0.19	0.25	0.23	0.29	0.22	0.25	0.18
∑REE	157.70	139.80	130.80	156.10	154.40	117.20	163.10	122.60	147.00	99.41
LREE/HREE	12.87	8.71	6.99	14.82	11.68	9.40	9.77	10.46	11.60	9.54
(La/Yb) _N	17.97	12.00	8.64	24.03	16.29	13.23	13.36	14.58	16.99	12.23
δEu	0.84	0.98	0.72	0.80	0.90	0.94	0.75	0.81	0.88	0.74

208 Ma, and that the peak of magmatic activity occurred at 215 Ma. The Pulang complex was emplaced between 221 and 206 Ma, and the second-stage quartz monzonitic porphyry that is closely related to copper mineralization was emplaced at 211.8 ± 0.5 Ma, shortly after the peak of regional magmatism.

5.2 Source of the magmatic rocks

The quartz dioritic porphyry have relatively low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7060–0.7065) and striking negative $\varepsilon_{\text{Nd}}(t)$ values (−4.9 to −3.0), showing affinities with enriched lithospheric mantle. The quartz monzonitic porphyry and granodioritic porphyry are geochemically comparable to the quartz dioritic porphyry with respect to its

major element, REE patterns and Sm–Nd isotopic compositions, suggesting the involvement of an enriched lithospheric mantle source in formation of these magma rocks. Plenty of mafic microgranular enclaves that consist mainly of diorite and are of magmatic texture were found in the intrusions of the Pulang complex (Cao *et al.* 2009). Based on petrological and geochemical data of these mafic microgranular enclaves and the host rocks (intrusions from the Pulang complex), Cao *et al.* (2009) proposed that intrusions from the Pulang complex had a mixed source including mantle-derived mafic magma and granitic magma derived from crustal material.

Geochemical data indicate that with time, the rocks of the different stages of the Pulang complex became gradually enriched in Si,

Figure 4. Total alkalis ($K_2O + Na_2O$) versus silica (SiO_2) diagram for the quartz dioritic porphyry, quartz monzonitic porphyry, and granodioritic porphyry from the Pulang complex, Yunnan province. The division between alkaline and subalkaline is after Irvine and Baragar (1971).

Figure 5. A/NK versus A/CNK diagram for the quartz dioritic porphyry, quartz monzonitic porphyry, and granodioritic porphyry from the Pulang complex, Yunnan province. $A/NK = n(Al_2O_3)/[n(Na_2O) + n(K_2O)]$ (molar ratio), $A/CNK = n(Al_2O_3)/[n(CaO) + n(Na_2O) + n(K_2O)]$ (molar ratio).

Al, and alkalis (and K), potentially reflecting the involvement of more crustal material with mantle-derived magmas (Yang *et al.* 2002). An increasing crustal contribution is also consistent with the higher initial Sr isotope ratios of the progressively younger rocks. The difference in the U–Pb zircon ages of the three intrusion stages is 5–10 Ma, and is generally consistent with the multiphase intrusive history of the Pulang complex.

Figure 6. Chondrite-normalized REE diagram for the quartz dioritic porphyry, quartz monzonitic porphyry, and granodioritic porphyry from the Pulang complex, Yunnan Province. Normalization values are from Sun and McDonough (1989).

Thus, in summary, the combined data point to the likely derivation of the parental magma from a mixture of an enriched mantle-derived and crustal material to generate the intrusions of the Pulang complex, and crustal contribution gradually increased with time.

5.3 Relationship between magmatism and mineralization

The relationship between magmatism and mineralization in the Pulang porphyry copper district has been controversial because of the inaccuracy of the geochronological data. Zircon U–Pb age data reported in this paper has revealed the general timing of the magmatism in the Pulang porphyry copper district. Numerous geochronological studies have been carried out on minerals related to the ore stage through different methods and results vary widely (182–216 Ma, Zeng *et al.* 2004, 2006; Li *et al.* 2011a). Taking into consideration the accuracy of the dating method, the molybdenite Re–Os age (213 ± 3.8 Ma, Li *et al.* 2011a) should be the best representative of the mineralization ages. This mineralization age for the Pulang copper deposit is close to the zircon U–Pb age of quartz monzonitic porphyry (211.8 ± 0.5 Ma) from the Pulang complex, suggesting that the mineralization in the Pulang copper district is closely related to the quartz monzonitic porphyry. Field investigations show the orebodies are mainly located within the phyllic and potassium silicate alteration zones in the Pulang porphyry copper deposit, occupying the quartz monzonite porphyry emplaced in quartz-diorite porphyry (Li *et al.* 2011a). In summary, the combined data suggest that the large Pulang

Table 3. Rb–Sr and Sm–Nd isotopic data of intrusions from the Pulang complex, Yunnan province.

Sample ID Lithology	YB07	D8	DYS21	DYS36
	Quartz dioritic porphyry		Quartz monzonitic porphyry	Granodioritic porphyry
Rb/ 10^{-6}	106.47	124.56	140.73	235.05
Sr/ 10^{-6}	1431.09	924.43	824.76	795.49
$^{87}\text{Rb}/^{86}\text{Sr}$	0.2153	0.3903	0.4937	0.855
$^{87}\text{Sr}/^{86}\text{Sr}$	0.7066	0.707	0.7080	0.7097
2σ	0.00001	0.00001	0.00001	0.00001
$(^{87}\text{Sr}/^{86}\text{Sr})_i$	0.7060	0.7065	0.7065	0.7072
Sm/ 10^{-6}	5.17	5.24	5.87	3.78
Nd/ 10^{-6}	37.92	28.55	34.90	19.08
$^{147}\text{Sm}/^{144}\text{Nd}$	0.0824	0.1111	0.1017	0.1198
$^{143}\text{Nd}/^{144}\text{Nd}$	0.5122	0.5124	0.5123	0.5124
2σ	0.00001	0.00001	0.00001	0.00001
$\varepsilon_{\text{Nd}}(t)$	−4.9	−3.0	−3.5	−3.2

porphyry copper deposit has a close spatial and temporal relationship with the second-stage quartz monzonitic porphyry.

6. Conclusions

The Pulang complex was formed by three stages of magmatic intrusion: quartz dioritic porphyry in the first stage at 221.0 ± 1.0 Ma; quartz monzonitic porphyry in the second stage at 211.8 ± 0.5 Ma; and granodioritic porphyry in the third stage at 206.3 ± 0.7 Ma. The second-stage quartz monzonitic porphyry has a close spatial and temporal relationship with the large Pulang porphyry copper deposit.

Our new zircon U–Pb ages and geochemical data indicate that the parental magma was likely derived from a mixture of an enriched mantle-derived and crustal material to generate the intrusions of the Pulang complex, and crustal contribution gradually increased with time.

Single-zircon U–Pb ages coupled with petrological and geochemical information suggest that the Pulang complex intrusions were spatially and temporally related multiphase products of a relatively prolonged (14.7 ± 1.2 Myr) magmatic event, and the results highlight the usefulness of single-zircon U–Pb dating in studying the history of multiphase plutonic complexes.

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