

Article

Using Whole Rock and Zircon Geochemistry to Assess Porphyry Copper Potential of the Tonggou Copper Deposit, Eastern Tianshan

Xue-bing Zhang^{1,2*}, Feng-mei Chai¹, Chuan chen¹, Hong-yan Quan³, Ke-yong Wang^{1,4}, Shun-da Li¹ and Shi-shan Wu¹

¹ College of Geology and Mining Engineering, Xinjiang University, Urumqi 830047, China;

² Xinjiang Key Laboratory for Geodynamic Processes and Metallogenic Prognosis of the Central Asian Orogenic Belt;

³ School of Biological, Earth and Environmental Sciences, University of New South Wales, Kensington, New South Wales 2052, Australia

⁴ College of Earth Sciences, Jilin University, Changchun, 130061, China

chaifengmei@163.com (F.-M. Chai); xjzycc2017@163.com (C.Chen); hongyan.quan@student.unsw.edu.au (H.-Y. Quan); wangky@mails.jlu.edu.cn (K.-Y. Wang); sdli16@mails.jlu.edu.cn (S.-D. Li); xjuwss@163.com (S.-S. Wu)

* Correspondence: Corresponding author: zxbvszidane@163.com; Tel: 86-18097603465

Abstract: The Eastern Tianshan hosts a number of porphyry Cu deposits; however, these mainly formed in the Jueluotage Belt, in the middle part of the Eastern Tianshan. ~~In recent times, we discovered the~~ Tonggou porphyry Cu mineralization in the Bogda Orogenic Belt, north of Eastern Tianshan. We obtained new zircon U–Pb ages, whole-rock geochemical, zircon Hf isotope, and zircon trace element data. LA-ICP-MS zircon U–Pb dating indicates an age of 302.2 ± 2.5 Ma for the Tonggou granodiorite, which suggests that the Tonggou porphyry Cu mineralization formed in the Late Carboniferous. According to its Hf isotope composition, the Tonggou granodiorite was sourced from juvenile crustal melts, mixed with some mantle materials. Whole rock and zircon geochemical characteristics show that the Tonggou mineralized granodiorite was formed by fractional crystallization to a greater extent than the Daheyan barren granodiorite in the Bogda Orogenic Belt. Tonggou granodiorite displays low Σ REE, compatible elements (Ba, Sr, Zr, and Hf), Zr/Hf and Nb/Ta ratios, as well as clearly negative Eu anomalies in whole rocks analyses. However, it is enriched in P, Hf values and Th/U ratios in zircon. Moreover, zircon grains of the Tonggou granodiorite show high Ce^{4+}/Ce^{3+} ratios, which are consistent with related values from large porphyry deposits at the CAOB. Based on the relatively high degree of fractional crystallization and the high oxidation state, Tonggou deposit has potential host a large porphyry Cu deposit.

Keywords: porphyry Cu mineralization; fractional crystallization; Ce^{4+}/Ce^{3+} ratio in zircon; Tonggou deposit; Eastern Tianshan

1. Introduction

Porphyry Cu systems provide ~75% of global copper production and a set amount of co- or by-product Mo, Au, Pb and Zn [1–2]. Porphyry Cu is one of the most important metallogenic systems, and has attracted the attention of many economic geologists [3–6]. These systems always form in association with magmatism at subduction and collision setting [6–8]. The high water content and oxidation state of magmas is sufficient to mobilize metals such as Cu partitioned into exsolved hydrothermal fluids and reprecipitated upon cooling to form porphyry Cu deposits [9–10].

The higher oxygen fugacity is favors the transport of metals and S from the mantle to shallow crustal levels, which is an important factor that restricts the formation of porphyry deposits [1, 4, 6, 10]. In addition, the fertility of magmas is always connected with their high water content, since it determines whether a magmatic-hydrothermal system forms or not [11].

Zircon is one of the most common accessory minerals and the most abundant in the majority of intermediate to felsic intrusions [12]. It is an exceptionally robust mineral that retains its primary chemical characteristics and provides information on oxygen fugacity of parental magmas. Recent studies of porphyry copper deposits include trace element analyses of zircon to constrain the oxidation conditions of magmas, especially since an elevated Ce^{4+}/Ce^{3+} ratio is an indicator of oxidizing magmatic conditions [13-16]. Consequently, zircon geochemistry has been proposed as a potential tool to identify redox conditions, which may be useful for exploration vectoring of porphyry Cu deposits [17-18].

On the other hand, estimates for initial water content in primary arc magmas typically range from 1 to 3. % wt H₂O [19]. However, fractional crystallization can increase water content by ~4 wt.% H₂O [9]. Intrusions associated with porphyry Cu deposits worldwide have a typically highly fractionated feature [20]. Evidence for fractional crystallization can be recognized by Zr/Hf, Nb/Ta, and REE values in whole rock [21-22], as well as high P, Hf values and high Th/U ratios in zircon [23-25]. Thus, fractional crystallization can also be an indicator of the potential of any given intrusion for porphyry deposit formation [9, 26].

The Eastern Tianshan has a number of porphyry Cu deposits, mainly located in the Jueluotage Belt [27-29]. However, porphyry Cu mineralization has been discovered in the Tonggou deposit, which is the first porphyry Cu mineralization found in the Bogda Orogenic Belt. Thus, this study presents zircon U-Pb, whole-rock geochemical, zircon Hf isotope and trace element data for the Tonggou mineralized and Daheyan barren intrusions of the Bogda Orogenic Belt. We use the U-Pb age of the mineralized intrusion to define the timing of porphyry Cu mineralization at Tonggou. In addition, we examine the Ce^{4+}/Ce^{3+} ratio in zircon and compare fractionation with geochemistry data from the Tonggou mineralized and Daheyan barren intrusions. This allows us to assess the effectiveness of whole rock and zircon geochemistry as a pathfinder for porphyry copper deposits.

2. Geological setting

The Eastern Tianshan is located in the eastern part of the Chinese Tianshan Belt, bordered by the Junggar Block to the north and the Precambrian Tarim Block to the south (Figure 1a, [30]). In Paleozoic to Triassic times, this belt witnessed the evolution and closure of the Paleo-Asian Ocean [31-34], and experienced multiple subduction, collision, and mineralization events [35]. The Eastern Tianshan can be divided from north to south into the Bogda-Harlik Orogenic Belt, the Jueluotage Belt, and the Central Tianshan Massif [36]. The Jueluotage Belt, located between the Bogda-Harlik Orogenic Belt and the Central Tianshan massif, is comprised of Paleozoic marine sedimentary rocks and felsic to mafic volcanic rocks, as well as late Paleozoic felsic and mafic-ultramafic intrusions [37]. The Central Tianshan massif, located south of the Jueluotage Belt, mainly consists of basement Precambrian gneiss [38].

The Bogda-Harlik Orogenic Belt, situated north of the Turpan-Hami basin, consists of Devonian-Permian volcanic rocks, sedimentary rocks, granitoids, and mafic-ultramafic complexes [39]. Compared to the Harlik Belt in the east or the Jueluotage Belt in the south, the intermediate to felsic intrusions occur sporadically in the Bogda Orogenic Belt (Figure 1a). Based on their zircon U-Pb ages, intermediate to felsic intrusions in the Bogda Orogenic Belt mostly formed in the Late Carboniferous [40-43] and Early Permian [44-45]. Late Carboniferous intermediate to felsic intrusions consist of diorite, syenogranite, granodiorite and granite [42-43]. Early Permian intermediate to felsic intrusions include diorite, monzogranite and granite [45].

Several epithermal gold deposits are hosted in the Harlik Belt [46]. However, mineralization in the Bogda Orogenic Belt is characterized by a series of Cu polymetallic vein deposits, such as the Tonggou, Weicaogou, and Miao'ergou deposits (Figure 1b, [47]). In addition, porphyry Cu mineralization has been discovered at the Tonggou deposit [48]. Re-Os and U-Pb isotopic ages

indicate that the Tonggou porphyry and vein Cu polymetallic mineralizations both formed in the Late Carboniferous (302-303Ma, [47], this study), associated with Late Carboniferous magmatism.

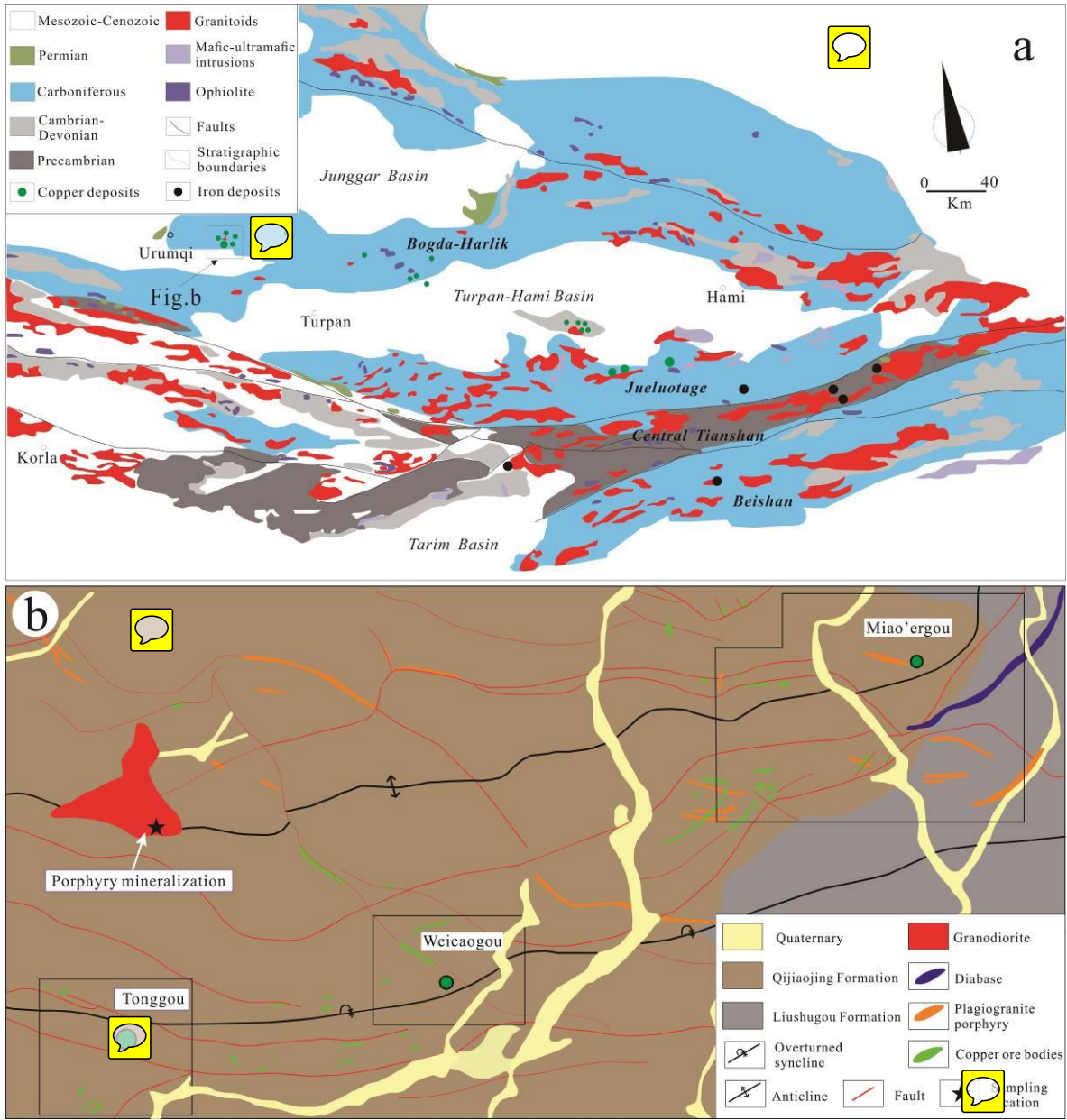


Figure 1. (a) Geological map of Eastern Tianshan [30]; (b) Geological map of the mineralized district in the Tonggou-Miao'ergou area [49].

3. Ore deposit

The Tonggou deposit is located 44 km southeast of Urumqi, and belongs to the Bogda Orogenic Belt (Figure 1). Both porphyry Cu and vein Cu-Zn mineralization occurs at the Tonggou deposit. **Porphyry Cu mineralization is associated with granodiorite** that was emplaced into the Early Carboniferous Qijiaoing Formation. The disseminated and stockwork veins of Cu mineralization occur at the top or contact zone of granodiorite (Figure 2a, b). The porphyry Cu mineralization is accompanied by potassic and propylitic alteration (Figure 2c). The mineral assemblages of the ore bodies mainly include pyrite, magnetite, hematite, and chalcopyrite (Figure 2d-f). Hematite-magnetite intergrowths were found in Tonggou porphyry mineralization, which suggests that Tonggou deposit **form** in oxidized condition. The aforementioned granodiorite was sampled for the present study.

Vein Cu-Zn mineralization occurs in the Qijiaoing Formation as **disseminated**, stratiform, lenticular, and vein-shaped ore bodies, the shape and size are fault-controlled (Figure 2g-h; [47]). **Vein Cu-Zn ore is associated with argillic alteration** (Figure 2i). The mineral assemblages of the ore bodies mainly include pyrite, magnetite, chalcopyrite, and sphalerite (Figure 2j-l), with minor amounts of hematite, galena, and bornite [47].

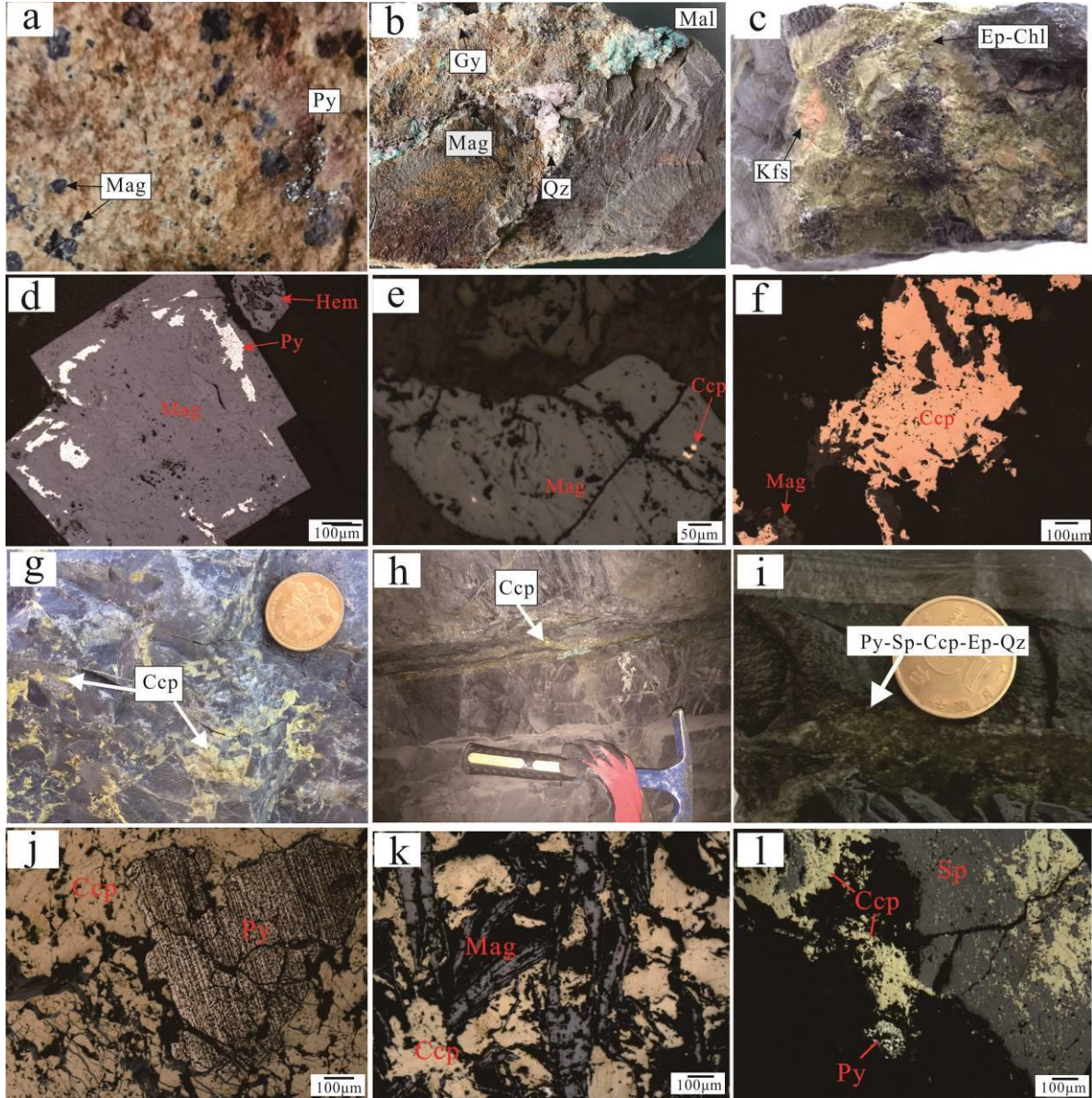


Figure 2. Photographs showing the ore from the Tonggou porphyry and vein mineralization. (a) disseminated pyrite and magnetite occurring in granodiorite; (b) stockwork magnetite-malachite-quartz vein from porphyry mineralization; (c) potassic and propylitic alteration from porphyry mineralization; (d) early pyrite replaced by magnetite showing a metasomatic relict texture from porphyry mineralization; (e) disseminated chalcopyrite occurring in magnetite from porphyry mineralization; (f) allotriomorphic magnetite and chalcopyrite from porphyry mineralization; (g) disseminated chalcopyrite from vein mineralization; (h) sulfide ore vein from vein mineralization; (i) pyrite-chalcopyrite-sphalerite-epidote-quartz assemblages from vein mineralization; (j) euhedral pyrite replaced by allotriomorphic chalcopyrite from vein mineralization; (k) allotriomorphic chalcopyrite and leaf-shaped magnetite; (l) allotriomorphic pyrite, chalcopyrite and sphalerite from vein mineralization; Abbreviations: Mag = Magnetite, Py = Pyrite, Ccp = chalcopyrite, Sp = Sphalerite, Gy = Gypsum, Qz = Quartz; Chl = chlorite; Ep = epidote; Kfs = K-feldspar.

4. Methods

4.1. Sample preparation

We collected ore-bearing granodiorite from the Tonggou deposit and barren granodiorite from the Daheyan area. The Daheyan granodiorite was collected from an intrusion to the west of Daheyan [43]. The Tonggou granodiorite displays a medium- to fine-grained texture, a massive structure (Figure 3a), and contains quartz (15%), plagioclase (67%), alkali-feldspar (10%, including orthoclase and perthite), hornblende (5%) and biotite (3%) (Figure 3b). Due to hydrothermal alteration, plagioclase has undergone epidotization, and hornblende and biotite are chloritized. On the other hand, the Daheyan granodiorite commonly shows a subhedral and allotriomorphic texture, as well as a massive structure (Figure 3c). It consists of quartz (10%), plagioclase (77%), alkali-feldspar (6%, including orthoclase and perthites), chlorite (4%) and biotite (2%) (Figure 3d).

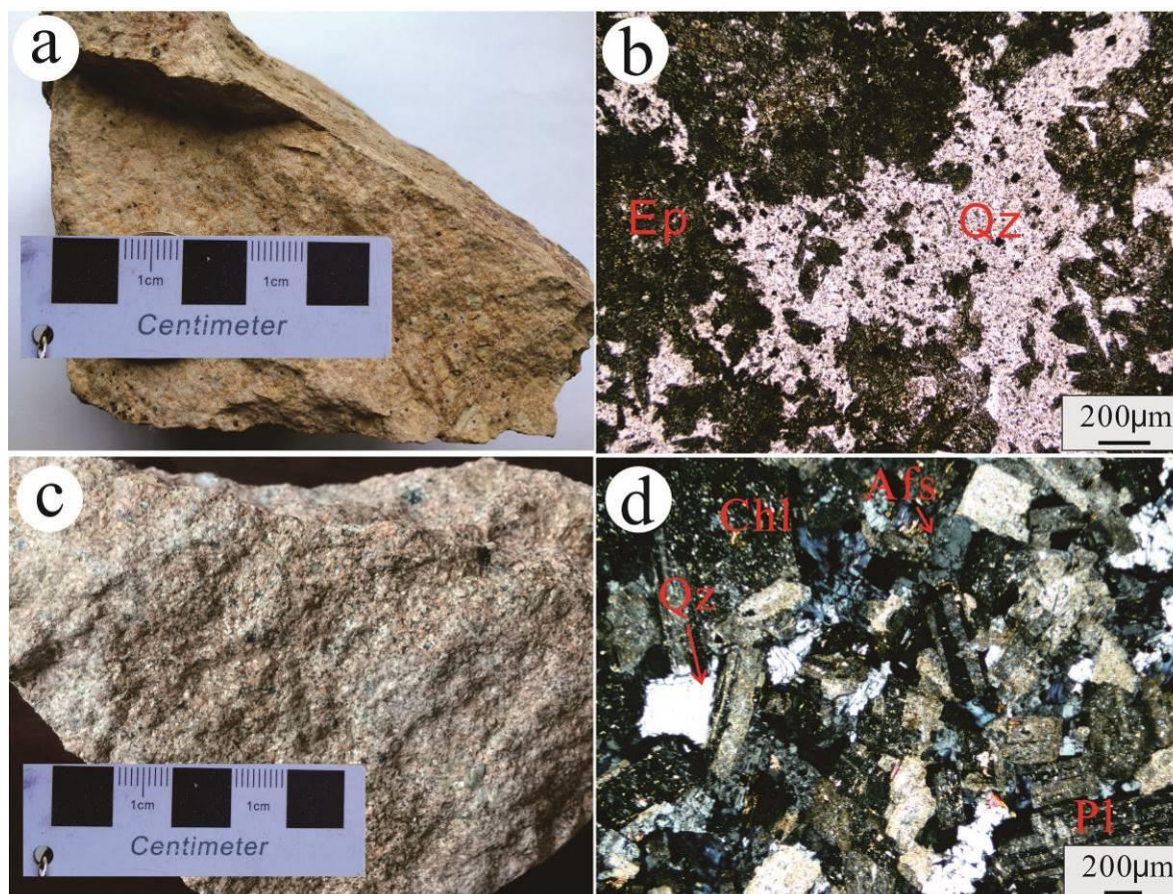


Figure 3. Representative photographs of the intrusions in hand specimen and thin-section. **a, b** granodiorite from the Tonggou deposit; **c, d** granodiorite from the Daheyan area.

4.2. Analytical methods

Zircon U–Pb ages were determined for granodiorite samples from the Tonggou deposit (Figure 4). The samples were crushed, zircon grains were extracted, and cathodoluminescence (CL) images were generated at the Faith Geological Service Company, Langfang, Hebei province, China. U–Pb–Hf isotopic and trace element analyses of the zircons were performed at Wuhan Samplesolution Analytical Technology Co., Ltd., Wuhan, China. Zircon grains were mounted on epoxy blocks and polished to expose grain centers. CL images are shown in Figure 4. U–Pb dating, Hf isotopic and trace element analyzes of zircons were obtained using an Agilent 7700e inductively coupled plasma (ICP) mass spectrometer (MS) and a GeolasPro laser ablation system. $^{206}\text{Pb}/^{238}\text{U}$ ratios were calculated by ICPMSDataCal [50–51], while concordia diagrams and weighted mean calculations were made using Isoplot 3.0 [52].

Four Tonggou granodiorite samples of major, trace and rare earth elements were measured and analyzed at ALS Minerals-ALS Chemex, Guangzhou. The samples were crushed in a steel jaw

crusher and then powdered to 200 mesh in an agate mill. Major-element compositions were analyzed using ME-XRF06 X. Trace element compositions were analysed using ICP–AES and ICP–MS (ME-MS61 and ME-MS81), respectively. The analytical results for the Chinese standard GDW07104 indicated that the analytical precision was better than 5% for major elements and 10% for trace elements and REEs [53].

5. Results

5.1. Zircon LA-ICP-MS U–Pb ages

Zircons from the Tonggou granodiorite exhibit oscillatory or planar zoning under CL and have Th/U ratios ranging from 0.39 to 2.00, consistent with a magmatic origin [54]. U–Pb dating results for 23 zircons, collected from granodiorite (sample TG1) of the Tonggou deposit, are listed in Table 1. The $^{206}\text{Pb}/^{238}\text{U}$ ages can be divided into two sets. One group plots near the concordia curve (Figure 4a) and has $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 298 to 305 Ma, with a mean of 302.2 ± 2.5 Ma (MSWD = 0.38; Figure 4), which represents the crystallization age of the Tonggou granodiorite. In addition, three samples near the concordia curve have $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 321 to 372 Ma, which represent the crystallization age of zircons captured or entrained from the wall rock during magma ascent. The other points measured deviate from the concordia curve. Moreover, the U–Pb age of the Tonggou granodiorite is consistent with that of the Daheyan granodiorite [43], and both are associated with Late Carboniferous magmatism.

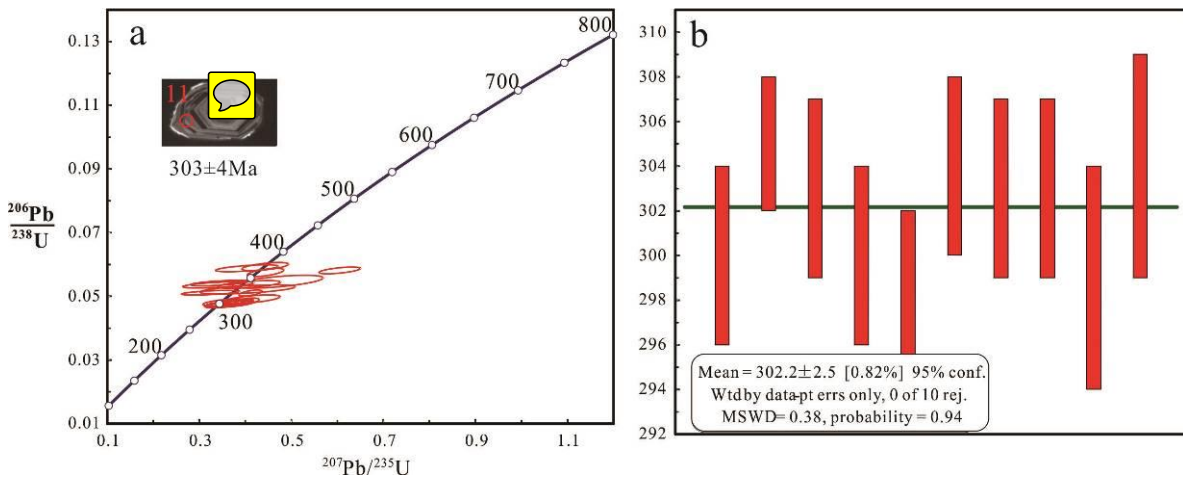


Figure 4. Zircon concordia diagram and weighting diagram for granodiorite samples from Tonggou deposit.

5.2. Whole-rock geochemistry

Samples of Tonggou granodiorite show high SiO_2 (68.58–70.85; Table 2), low K_2O and Na_2O contents due to epidotization and chloritization (molar $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 < 0.01$) [55], it is consistent with geological evidences of Tonggou porphyry Cu mineralization (Fig. 3c). The Zr/TiO_2 vs. Nb/Y of most samples plot in the fields of granodiorite on a discrimination diagram for the Tonggou intrusion (Figure 5).

Tonggou granodiorite samples display a narrow range of ΣREE values (89.41 ppm–102.06 ppm), LREE values vary from 75.96 to 89.22, and HREE values range from 12.84 to 13.47. The samples are enriched in LREE and depleted in HREE ($\text{LREE}/\text{HREE} = 5.64\text{--}6.95$; $(\text{La}/\text{Yb})_{\text{N}} = 5.24\text{--}9.82$). Granodiorite shows weak negative Eu anomalies ($\delta\text{Eu} = 0.76\text{--}1.02$) on the chondrite-normalized REE diagram (Figure 6a; Table 2). The primitive-mantle-normalized trace-element diagram indicates that the Tonggou granodiorite is enriched in incompatible elements (e.g. Th, U, and Zr) and some LILEs (e.g. Sr), as well as depleted in HFSEs (e.g. Ta, Nb and Ti) (Figure 6b).

Table 1. LA-ICP-MS U–Pb data on zircons from the Granodiorite.

Sample No.	Th (10 ⁻⁶)	U (10 ⁻⁶)	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb		²⁰⁷ Pb/ ²³⁵ U		²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²⁰⁶ Pb		²⁰⁷ Pb/ ²³⁵ U		²⁰⁶ Pb/ ²³⁸ U	
				1σ	1σ	1σ	1σ	1σ	1σ	Age (Ma)	1σ	Age (Ma)	1σ	Age (Ma)	1σ
TG1-01	1018	1802	0.57	0.0711	0.0055	0.5880	0.0470	0.0604	0.0008	184	251	344	32	368	4
TG1-02	640	878	0.73	0.0753	0.0035	0.6053	0.0298	0.0581	0.0007	1078	80	481	19	364	4
TG1-03	449	630	0.71	0.0739	0.0056	0.5396	0.0402	0.0535	0.0008	1039	129	438	27	336	5
TG1-04	441	625	0.71	0.0905	0.0085	0.6825	0.0663	0.0543	0.0007	-	241	286	32	322	3
TG1-05	370	730	0.51	0.0681	0.0035	0.4500	0.0221	0.0483	0.0007	471	200	320	24	300	4
TG1-06	557	1072	0.52	0.0551	0.0020	0.3682	0.0130	0.0484	0.0005	415	61	318	10	305	3
TG1-07	935	468	2.00	0.0577	0.0030	0.3855	0.0215	0.0481	0.0007	517	98	331	16	303	4
TG1-08	762	937	0.81	0.0700	0.0037	0.4612	0.0217	0.0485	0.0006	386	189	310	22	300	4
TG1-09	753	788	0.96	0.0720	0.0035	0.4833	0.0240	0.0483	0.0006	530	196	326	24	298	4
TG1-10	666	959	0.70	0.0551	0.0024	0.3650	0.0142	0.0483	0.0006	415	64	316	11	304	4
TG1-11	697	1088	0.64	0.0630	0.0032	0.4191	0.0184	0.0487	0.0007	347	202	308	23	303	4
TG1-12	427	1087	0.39	0.0644	0.0025	0.5188	0.0182	0.0581	0.0009	453	140	373	19	360	5
TG1-13	252	480	0.53	0.0640	0.0031	0.4314	0.0205	0.0487	0.0006	480	166	325	20	303	4
TG1-14	377	587	0.64	0.0676	0.0036	0.4515	0.0238	0.0483	0.0007	411	208	312	24	299	5
TG1-15	673	829	0.81	0.0627	0.0030	0.5182	0.0239	0.0600	0.0008	378	177	373	24	372	5
TG1-16	228	349	0.65	0.0899	0.0141	0.6507	0.1081	0.0524	0.0009	955	435	411	66	321	6
TG1-17	1014	1181	0.86	0.0584	0.0024	0.4113	0.0167	0.0510	0.0006	543	67	350	12	321	4
TG1-18	574	709	0.81	0.0742	0.0064	0.5592	0.0433	0.0550	0.0008	417	256	348	33	337	5
TG1-19	386	481	0.80	0.0853	0.0049	0.5972	0.0330	0.0507	0.0009	642	226	351	29	309	5
TG1-20	406	409	0.99	0.0597	0.0035	0.3958	0.0228	0.0483	0.0007	594	98	339	17	304	5
TG1-21	673	598	1.13	0.0827	0.0055	0.6372	0.0470	0.0542	0.0009	465	366	345	49	328	6
TG1-22	511	533	0.96	0.0899	0.0061	0.7090	0.0480	0.0568	0.0007	6	273	298	39	337	4
TG1-23	122	213	0.57	0.0894	0.0074	0.6840	0.0574	0.0564	0.0013	693	314	392	45	343	8

Table 2. Major (%) and trace element (ppm) data for the Tonggou granodiorite.

Sample	TG-1	TG-2	TG-3	TG-4	Sample	TG-1	TG-2	TG-3	TG-4
SiO ₂ (%)	69.12	69.73	70.85	68.58	Ga (ppm)	23.7	22.1	20.1	22.5
TiO ₂ (%)	0.46	0.47	0.38	0.37	Hf (ppm)	3.5	3.7	3.6	3.5
Al ₂ O ₃ (%)	12.10	11.48	12.60	13.65	Ho (ppm)	0.74	0.77	0.69	0.74
TF ₂ O ₃ (%)	5.77	5.66	4.50	4.91	La (ppm)	16.9	15.7	27.1	24.8
MnO (%)	0.10	0.10	0.10	0.11	Lu (ppm)	0.33	0.33	0.30	0.32
MgO (%)	0.16	0.15	0.17	0.30	Nb (ppm)	6.2	6.1	4.9	4.6
CaO (%)	10.85	10.40	9.54	10.20	Nd (ppm)	17.3	17.3	23.3	22.4
Na ₂ O (%)	0.08	0.05	0.19	0.22	Pr (ppm)	4.53	4.54	6.47	6.08
K ₂ O (%)	0.08	0.08	0.05	0.05	Rb (ppm)	1.8	1.6	1.4	1.6
P ₂ O ₅ (%)	0.07	0.07	0.06	0.07	Sm (ppm)	3.78	3.81	4.80	4.83
LOI (%)	1.50	1.31	1.45	1.65	Sn (ppm)	2.6	2.5	7.0	8.5
(La/Yb) _N	5.83	5.24	9.82	8.68	Sr (ppm)	774	735	688	709
LREE/HREE	5.77	5.64	6.95	6.40	Ta (ppm)	0.44	0.49	0.36	0.33
δEu	1.02	1.01	0.76	0.77	Tb (ppm)	0.55	0.58	0.55	0.58
ΣREE	89.41	89.43	102.06	98.62	Th (ppm)	6.30	6.50	4.98	4.87
Ba (ppm)	48.9	49.8	21.8	22.1	Tl (ppm)	0.03	0.04	<0.02	<0.02
Ce (ppm)	32.5	33.4	26.5	26.1	Tm (ppm)	0.32	0.33	0.31	0.32
Cr (ppm)	78	54	36	34	U (ppm)	1.84	1.89	1.51	1.56
Cs (ppm)	0.07	0.07	0.12	0.12	Y (ppm)	20.3	21.0	19.8	20.7
Dy (ppm)	3.53	3.58	3.24	3.38	Yb (ppm)	2.08	2.15	1.98	2.05
Er (ppm)	2.21	2.19	2.03	2.11	Zr (ppm)	128	132	137	129
Eu (ppm)	1.20	1.21	1.05	1.08	Cu (ppm)	1.7	5.1	1.8	1.3
Gd (ppm)	3.44	3.54	3.74	3.83	V (ppm)	105	102	68	75

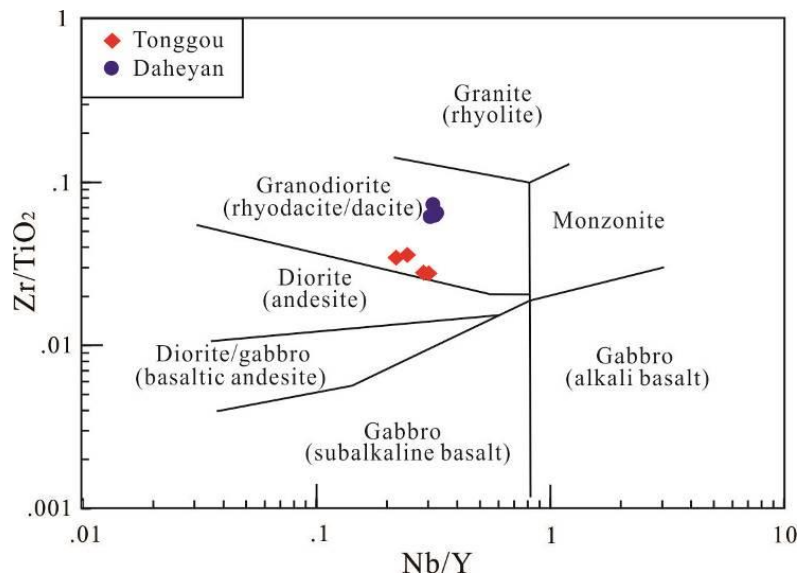


Figure 5. Zr/TiO₂ vs. Nb/Y of Tonggou and Daheyan samples following the classification [56-57]. Partial data for Daheyan granodiorite cited from [43].

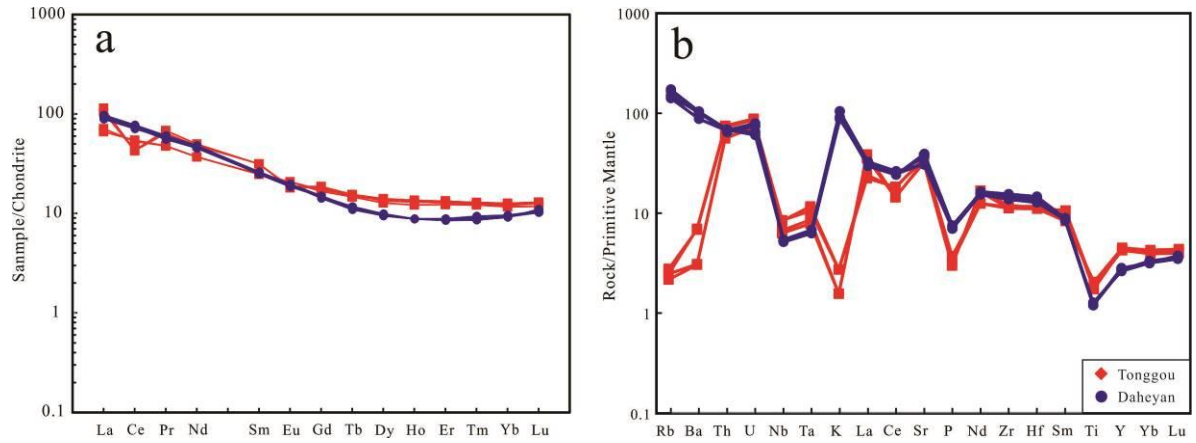


Figure 6. Chondrite-normalized REE pattern and primitive-mantle-normalized spider diagrams from whole rocks analyses. Chondrite and primitive mantle values used for normalization are from [58] and [59], respectively. Partial data for Daheyan granodiorite cited from [43].

5.3. Hf isotopes

In situ Hf isotopic compositions of zircon from the Tonggou granodiorite are listed in Table 3. The 9 analyses obtained from samples of the Tonggou granodiorite show $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.2826–0.2830, and have $\epsilon_{\text{Hf}}(t)$ values varying from +1.9 to +14.1 (with an average of 8.6). The corresponding T_{DM1} is ca. 375–870 Ma, whereas the T_{DM2} is ca. 414–1189 Ma.

Table 3. Zircon Lu–Hf isotopic data from the Tonggou granodiorite.

Sample spot	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Yb}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf} (t)$	$\epsilon_{\text{Hf}} (0)$	$\epsilon_{\text{Hf}} (t)$	σ	T_{DM1}	T_{DM2}	f_s
TG1-05	0.0018	0.0496	0.2826	0.2826	-4.3	1.9	0.44	870	1189	-0.95
TG1-06	0.0007	0.0227	0.2826	0.2826	-4.3	2.2	0.34	848	1175	-0.98
TG1-08	0.0016	0.0470	0.2828	0.2828	2.3	8.6	0.36	597	765	-0.95
TG1-09	0.0013	0.0451	0.2829	0.2829	3.7	10.0	0.33	535	672	-0.96
TG1-12	0.0022	0.0698	0.2829	0.2829	4.2	11.6	0.47	529	620	-0.93
TG1-13	0.0022	0.0758	0.2830	0.2830	7.9	14.1	0.39	375	414	-0.94
TG1-18	0.0011	0.0383	0.2828	0.2828	1.9	8.7	0.29	607	775	-0.97
TG1-20	0.0013	0.0423	0.2828	0.2828	2.3	8.7	0.28	594	762	-0.96
TG1-22	0.0017	0.0558	0.2829	0.2829	4.0	11.0	0.34	530	639	-0.95

5.4. Trace elements in Zircon

Minor and trace-element concentrations in zircon are listed in Table 4, and chondrite-normalized REE patterns are shown in Figure 8. Zircon grains commonly contain minute inclusions of REE-bearing minerals (e.g., apatite, titanite, monazite, and allanite), which may yield higher LREE and lower $\text{Ce}^{4+}/\text{Ce}^{3+}$ values than their true concentrations in zircon. For this reason, zircon grains for LA-ICP-MS analysis were carefully examined with CL to make sure that they contained no inclusions. In addition, the possible presence of such inclusions was monitored by measuring Sr, Th, Al, and P content during LA-ICP-MS analysis; when spikes of these elements were encountered, the analysis was discarded. In this study, most zircon analyses have very low P, Ca, Sr, and Al (Table 4).

Tonggou granodiorite zircons show a narrow range of ΣREE values (1162 ppm–1196 ppm), and are enriched in HREE and depleted in LREE. These samples show obviously negative Eu anomalies ($\delta\text{Eu} = 0.21$ – 0.22) on the chondrite-normalized REE diagram (Figure 7a; Table 4). Daheyan granodiorite zircons show low ΣREE values (322 ppm–695 ppm), and are also enriched in HREE and depleted in LREE. The samples show weakly negative Eu anomalies ($\delta\text{Eu} = 0.33$ – 0.57) on the chondrite-normalized REE diagram (Figure 7b; Table 4).

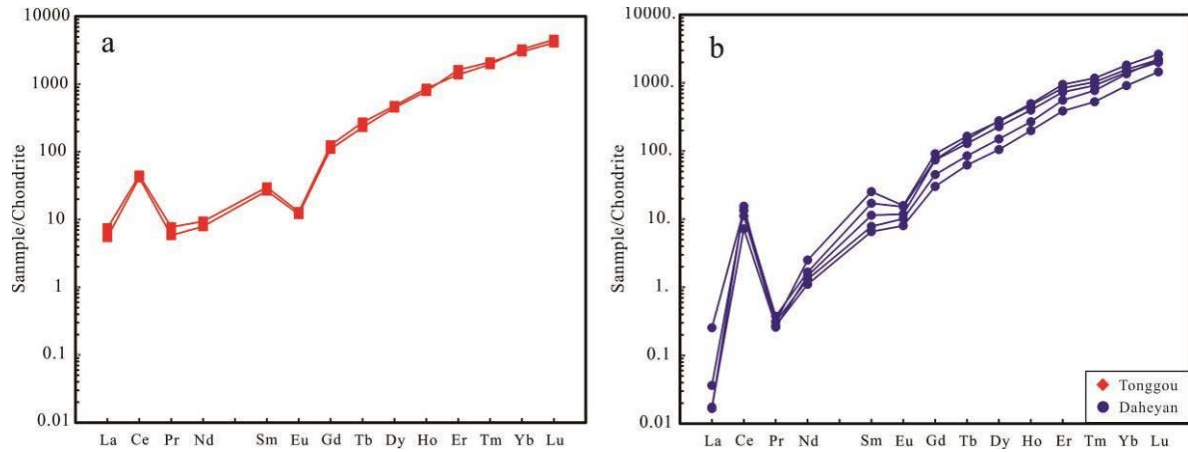


Figure 7. Chondrite-normalized REE pattern diagrams from zircon [58].

The calculation of Ce anomalies requires an estimation of the concentration of Ce^{3+} and Ce^{4+} . The concentration of Ce^{3+} is commonly based on La and Pr values with the assumption that the normalized values of La, Ce^{3+} , and Pr plot along a smooth curve. The concentration of Ce^{4+} is commonly based on the Hf and U values with the assumption that the normalized values of Hf, Ce^{4+} , and U plot along a smooth curve as well [60]. Due to the fact that P contents of the Tonggou and Daheyan intrusions are low, <0.2 wt % (Table 2, [43]), the effects of apatite and monazite on whole-rock compositions should be small. Thus, the compositions of whole-rock samples are assumed to represent those of the parental melt for calculation of Ce anomalies. The calculated $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratios for Tonggou and Daheyan intrusions vary from 159 to 286, and from 72 to 138 (Table 4), respectively.

6. Discussion

6.1. Timing of Tonggou porphyry Cu mineralization

The LA-ICP-MS zircon U-Pb age for granodiorite of the Tonggou deposit is 302.2 ± 2.5 Ma, which represents Tonggou porphyry mineralization. Similar ages of porphyry and vein mineralization in the Tonggou deposit indicate that vein Cu polymetallic mineralization is closely associated with porphyry Cu mineralization in temporal and spatial terms. Furthermore, the time of Tonggou porphyry Cu mineralization differs from porphyry Cu mineralization in the Jueluotage Belt (e.g., Tuwu, Yandong, and Fuxing deposits [27, 61-62]). The Late Carboniferous was a time of significant porphyry Cu mineralization in Eastern Tianshan.

6.2. Source of magmas and petrogenesis

Zircon $\epsilon_{\text{Hf}}(t)$ values from Tonggou granodiorite range from 1.8 to 14.1 with a wide range of values (Table 4), indicating that the primary magma of the Tonggou granodiorite was derived from multiple sources. On the $\epsilon_{\text{Hf}}(t)$ vs. age diagram, all samples from Tonggou and Daheyan plot between the depleted mantle and CHUR reference line (Figure 8), suggesting that the Tonggou and Daheyan granodiorites were mainly derived from crustal melting with some contribution from mantle-derived materials. Early Carboniferous-Devonian zircon xenocrysts in the Tonggou and Daheyan granodiorites both show positive $\epsilon_{\text{Hf}}(t)$ values, suggesting that Devonian juvenile crustal rocks possibly existed in the basement of the Bogda Orogenic Belt. Moreover, two-stage Hf model ages ($T_{\text{DM}2}$) of the Tonggou and Daheyan granodiorites correspond to 427-872 Ma and 414-1189 Ma [43], respectively. These values are younger than those of basement rocks in the Cathaysia Block (1.8-2.2 Ga) [63], also indicating that these granodiorites were both mainly derived from a juvenile crustal source and some mixed mantle materials.

Table 4. Trace Element Abundance (in ppm), Ce⁴⁺/Ce³⁺ and Eu Anomalies in Zircon, and Ti-in-Zircon Temperature.

Analysis	TG1-8	TG1-11	D03-6	D03-7	D03-8	D03-16	D03-21	Analysis	TG1-8	TG1-11	D03-6	D03-7	D03-8	D03-16	D03-21		
	Tonggou, granodiorite				Daheyan, granodiorite					Tonggou, granodiorite				Daheyan, granodiorite			
Al	57.0	18.2	1.9	1.4	13.9	4.7	7.6	Tm	53.8	49.8	23.3	19.7	29.9	13.4	26.3		
P	547	576	341	267	555	229	323	Yb	513	557	243	230	309	155	267		
Ti	6.60	6.63	10.16	8.07	13.16	9.56	12.44	Lu	103	115	51	55	67	37	56		
Sr	5.10	1.63	0.08	0.20	0.31	0.11	0.14	Th	252	229	42	48	48	53	51		
Y	1528	1605	746	557	941	389	866	U	371	366	70	103	89	103	70		
La	1.296	1.770	0.004	0.000	0.061	0.004	0.009	Zr	489886	487745	494258	494658	494103	487071	485058		
Ce	25.5	27.4	9.5	6.8	8.3	4.4	8.2	Hf	10182	10703	9670	9634	9786	9106	10023		
Pr	0.56	0.74	0.02	0.03	0.04	0.03	0.03	Ta	1.36	1.54	0.26	0.28	0.20	0.18	0.24		
Nd	3.69	4.37	0.69	0.61	0.78	0.52	1.17	Nb	3.50	3.81	0.67	0.53	0.68	0.20	0.44		
Sm	4.06	4.59	1.75	1.20	2.62	1.01	3.89	ΣREE	1162	1196	552	472	695	322	624		
Eu	0.69	0.75	0.69	0.59	0.88	0.46	0.92	LREE/HREE	0.034	0.032	0.020	0.023	0.023	0.020	0.019		
Gd	22.5	25.9	15.2	9.3	15.4	6.2	18.7	δEu	0.22	0.21	0.41	0.54	0.43	0.57	0.33		
Tb	8.64	10.15	4.81	3.17	5.55	2.32	6.18	Ce ⁴⁺ /Ce ³⁺	159	286	138	134	121	106	72		
Dy	113.3	121.3	57.9	38.1	70.5	26.6	69.5	T(°C)	762	761	805	781	833	798	826		
Ho	44.3	48.8	22.5	15.2	28.1	11.3	26.5	Eu/ Eu*	0.25	0.24	0.41	0.54	0.43	0.57	0.33		
Er	268.0	228.0	121.0	92.1	157.0	64.0	139.0	△NNO	-0.02	-0.22	2.21	3.84	2.43	4.21	1.16		

256 Note: Ti-in-zircon temperatures are calculated using the equation proposed by [64]; the activities of SiO₂ and Ti are set to 1 and 0.75, respectively.

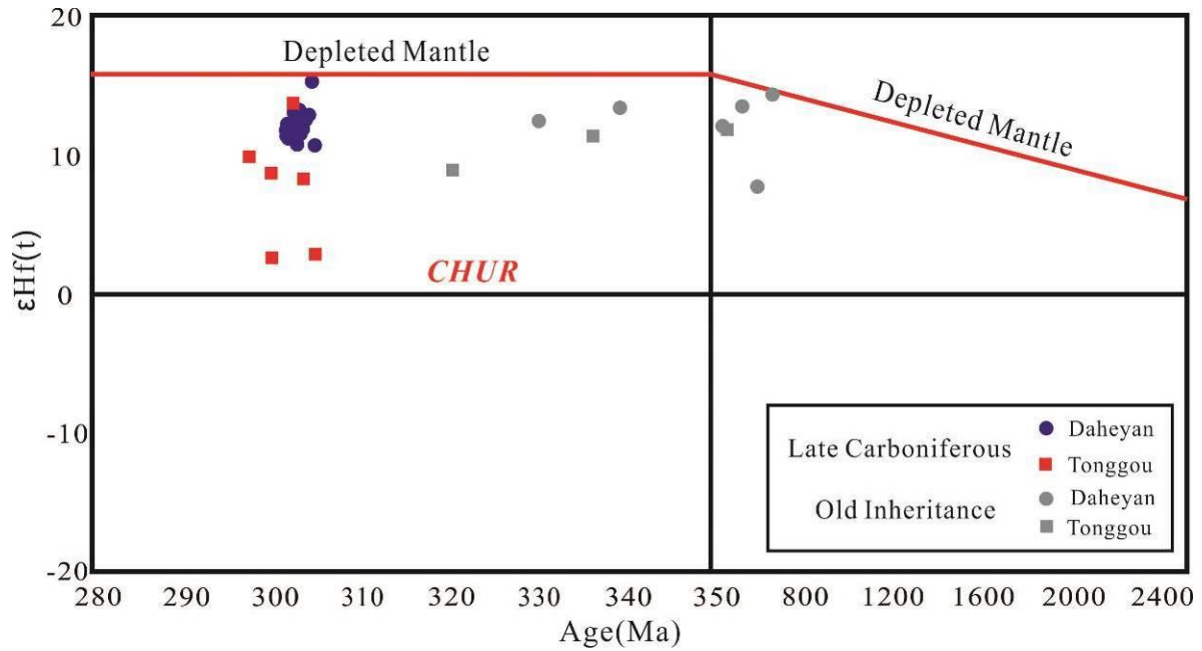


Figure 8. Zircon U–Pb ages vs. $\epsilon\text{Hf}(t)$ plots for Tonggou and Daheyan samples. Partial data for Daheyan granodiorite cited from [43].

The Tonggou granodiorite is characteristically enriched in SiO_2 and Sr, but the values of Y (19.8–21.0) and Yb (1.98–2.15) are obviously higher than the related values of adakitic rocks [65]. The Sr/Y vs. Y of samples plot in the fields of non-adakite on a discrimination diagram for the Tonggou granodiorite (Figure 9a). However, the Daheyan granodiorite is enriched in SiO_2 (≥ 68.14) and Al_2O_3 (≥ 15.54) and depleted in Y (≤ 12.9) and Yb (≤ 1.64). The Sr/Y vs. Y of samples plot in the fields of adakite on a discrimination diagram for the Daheyan granodiorite (Figure 9a), which suggests that Daheyan granodiorite is adakite. Generally, adakitic rocks have higher initial contents of Cu, which are essential for porphyry Cu mineralization [66–67]. Porphyry Cu mineralization does not occur in the Daheyan granodiorite for the following two reasons. Firstly, the porphyry Cu mineralization did indeed formed at the top of the Daheyan granodiorite, however, this mineralization was mostly eroded away. Secondly, although the Daheyan granodiorite had a high initial Cu value, porphyry Cu mineralization did not form due to other factors (such as water content and the magma oxidation state).

6.3. Fractional crystallization of magmas

Due to alteration of epidote, chlorite, and kaolinite, some major elements in samples from the Tonggou granodiorite have suffered large compositional variations. However, fractional crystallization of granitic magma can be identified by its REE and trace elements compositions in whole rocks and zircon. Compared to the Daheyan barren granodiorite, the Tonggou mineralized granodiorite has lower ΣREE values, LREE/HREE ratios (Figure 9b), and clearly negative Eu anomalies (Fig. 6) in whole rocks, indicating that fractional crystallization was more evident in the Tonggou granodiorite [68–69]. Furthermore, Tonggou granodiorite is more depleted in compatible elements (e.g., Ba ≤ 49.8 ppm, Sr ≤ 774 ppm, Zr ≤ 137 ppm, and Hf ≤ 3.7 ppm) compared to granodiorite from Daheyan in whole rocks (Figure 6; [43]), which indicates that Tonggou granodiorite is of a more fractionated nature [69–70]. In addition, Zr/Hf and Nb/Ta ratios in whole rocks decrease significantly in the Tonggou granodiorite (Table 4, Figure 9c), which is also regarded as a sign of fractional crystallization [21, 71–72].

According to Zr/Hf ratios in zircon, granites can be classified into three types: common granites (Zr/Hf > 55), moderately evolved granites ($25 < \text{Zr/Hf} < 55$), and highly evolved granites (Zr/Hf < 25) [73]. Zircon Zr/Hf ratios from the Tonggou and Daheyan granodiorite vary from 45.8 to 47.9 and 43.7 to

54.3 (Table 4), respectively. The Tonggou and Daheyan granodiorite both belong to moderately evolved granites. Furthermore, highly fractionated granites are characteristically enriched in P and Hf in zircon [74–75], and the Tonggou granodiorite has higher P and Hf values in zircon than the Daheyan granodiorite. On the Zr/Hf vs. P diagram for zircon, the Tonggou granodiorite has a more obviously fractionated trend compared with Daheyan granodiorite (Figure 9d).

A more important issue is that the crystallization temperature of granites decreases with fractional crystallization [76]. We evaluated the crystallization temperatures of the Tonggou and Daheyan granodiorites based on the Ti-in-zircon thermometer [64]. This is supported by calculated temperatures that decrease from Daheyan (781–826 °C) to Tonggou (761–762 °C), the Tonggou granodiorite is more highly evolved unit (Figure 9e). Moreover, the zircon Th/U ratio may increase along with temperature due to fractionation (Figure 9f; [25]).

Based on REE and trace elements in whole rock, trace elements in zircon and crystallization temperatures of granites, it is evident that the Tonggou mineralized granodiorite experienced a higher degree of fractional crystallization than the Daheyan barren granodiorite.

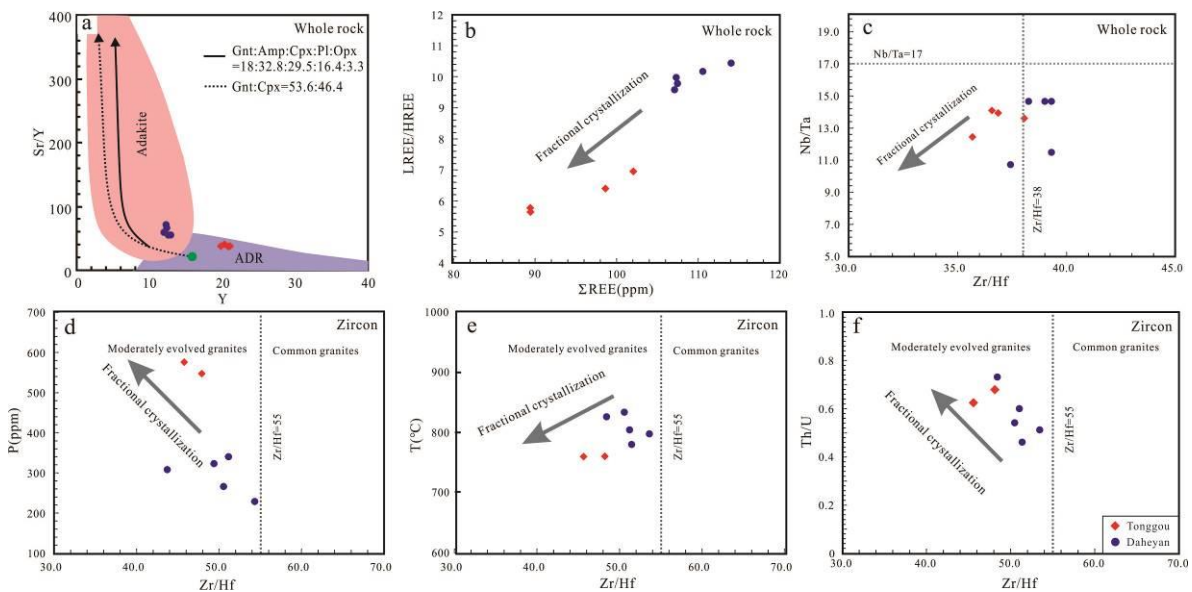


Figure 9. Geochemical characteristics of the Tonggou and Daheyan samples, which record a high degree of fractionation. (a) Sr/Y vs. Y in whole rocks [76]; (b) Σ REE vs. LREE/HREE in whole rocks; (c) Zr/Hf vs. Nb/Ta in whole rocks; (d) Zr/Hf vs. P in zircon; (e) Zr/Hf vs. T in zircon; (f) Zr/Hf vs. Th/U in zircon. Partial data for Daheyan granodiorite cited from [43]. Partial melting curves are calculated for accumulated fractional melting of lower crust, with starting values from [77]. ADR = island andesite-dacite-rhyolite.

6.4. Factors affecting Ce anomalies

The oxidation conditions of magmas show a positive correlation with Ce^{4+}/Ce^{3+} ratios, a high Ce^{4+}/Ce^{3+} ratio usually indicating oxidizing magmatic conditions [13, 17, 20, 79]. The calculated Ce^{4+}/Ce^{3+} ratios for the Tonggou mineralized granodiorite range from 159 to 286 (Table 4). In addition, we plotted the Ce^{4+}/Ce^{3+} values of our samples on the Ce^{4+}/Ce^{3+} vs. $10^4/T$ diagram for granitoids (Figure 10). The Ce^{4+}/Ce^{3+} ratios of the Tonggou porphyry deposits plot close to the magnetite-hematite (MH) buffer and are similar to the Ce^{4+}/Ce^{3+} ratios of large porphyry deposits of the CAOBS (Fig. 10). Moreover, the oxygen fugacity of the magmas lower than the hematite–magnetite buffer, which is favorable for porphyry copper deposits since it can provide ferrous iron in the porphyry Cu system [67]. The high oxygen fugacity of Tonggou granodiorite is also verified by the widespread presence of magnetite and hematite. Thus, since ore-forming fluids from oxidized magmas are likely to have higher Cu contents, this suggests that the Tonggou deposit is likely to host a large porphyry Cu deposit.

To further evaluate the relationship between the oxidation state of magmas and porphyry Cu mineralization, we also examined the Ce^{4+}/Ce^{3+} ratios in zircon from the Daheyan barren granodiorite. The calculated Ce^{4+}/Ce^{3+} ratios of Daheyan granodiorite vary from 72 to 138 (Table 4). Thus, the Daheyan barren granodiorite plots between the NNO and the MH buffer on the Ce^{4+}/Ce^{3+} vs. $10^4/T$ diagram (Fig. 10). However, Ce^{4+}/Ce^{3+} ratios and crystallization temperatures of the Daheyan barren granodiorite are indeed distinctly different from the related values of intermediate- to large porphyry deposits at the CAOB.

There is therefore a correlation between the Ce^{4+}/Ce^{3+} ratio in zircon and the potential of an intrusion to produce a large porphyry deposit, and thus Ce^{4+}/Ce^{3+} ratios in zircon can be used as a parameter to evaluate porphyry Cu deposit potential.

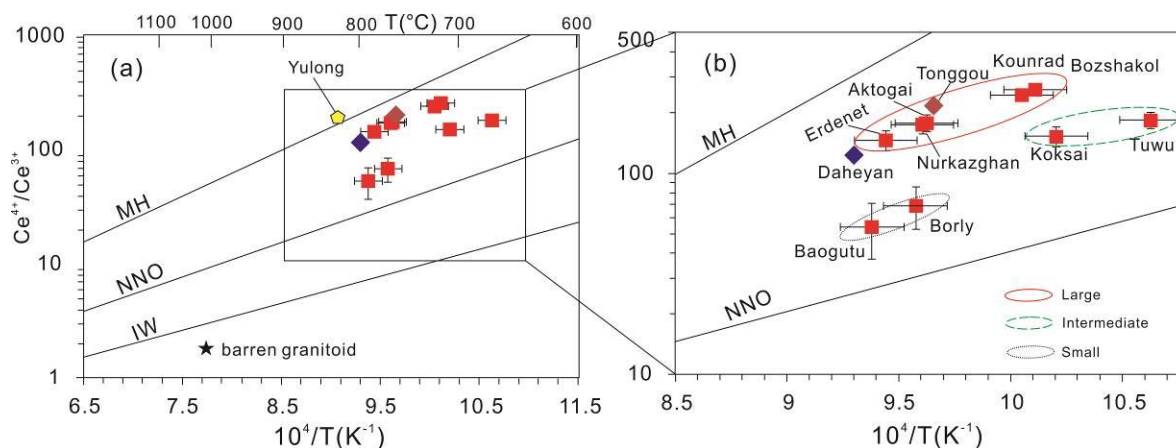


Figure 10. Average Ce^{4+}/Ce^{3+} vs. $10^4/T$ for porphyry Cu deposits of the CAOB. Temperatures were calculated using the Ti-in-zircon thermometer [64]. Partial data for porphyry Cu deposits of the CAOB cited from [13]. Curves for oxygen fugacity buffers include magnetite-hematite (MH), Ni-Ni oxide (NNO), and Fe-wustite (IW) buffers.

7. Conclusion

(1) The zircon U-Pb age of the Tonggou granodiorite is of 302.2 ± 2.5 Ma, which indicates that porphyry Cu mineralization of the Tonggou deposit was associated with Late Carboniferous magmatism.

(2) The geochemical characteristics of whole rocks and zircon suggest that the Tonggou mineralized granodiorite experienced more fractional crystallization than the Daheyan barren granodiorite.

(3) Zircon grains from the Tonggou mineralized granodiorite show higher Ce^{4+}/Ce^{3+} ratios than those of the Daheyan barren granodiorite, which indicates that the Tonggou granodiorite formed at a higher magmatic oxidation state.

(4) Significant porphyry Cu mineralization is expected to be associated with fractional crystallization and oxygen fugacity.

Author Contributions: Conceptualization, X.-B. Z.; Methodology, F.-M. C.; Software, S.-D. L. and S.-S. W.; Validation, X.-B. Z.; Formal Analysis, X.-B. Z.; Investigation, C. C. and X.-B. Z.; Resources, X.-B. Z.; Data Curation, X.-B. Z.; Writing–Original Draft Preparation, X.-B. Z.; Writing–Review & Editing, H.-Y. Q. and K.-Y. W.; Visualization, X.-B. Z. and S.-D. L.; Supervision, F.-M. C.; Project Administration, X.-B. Z.; Funding Acquisition, X.-B. Z.

Funding: This research was supported by the Natural Science Foundation of Xinjiang Province, China (Grant No. 2018D01C042).

Acknowledgments: We would like to thank the staff of the Wuhan Samplesolution Analytical Technology Co., Ltd. for LA-ICP-MS zircon U-Pb dating and Hf isotope and trace element analysis. We also thank the staff of the ALS Laboratory Group for whole-rock geochemical analyses.

Conflicts of Interest: The authors declare no conflict of interest.

361 References

- 362 1. Sillitoe, R.H. Porphyry copper systems. *Econ. Geol.* **2010**, 105, 3-41.
- 363 2. Sun, W.D.; Huang, R.F.; Li, H.; Hu, Y.B.; Zhang, C.C.; Sun, S.J.; Ling, M.X. Porphyry deposits and oxidized
364 magmas. *Ore Geol. Rev.* **2015**, 65, 97-131.
- 365 3. Zarasvandi, A.; Rezaei, M.; Raith, J.G.; Pourkaseb, H.; Asadi, S.; Saed, M.; Lentz, D.R. Metal endowment
366 reflected in chemical composition of silicates and sulfides of mineralized porphyry copper systems,
367 Urumieh-Dokhtar magmatic arc, Iran. *Geochim. Cosmochim. Acta*, **2018**, 223, 36-59.
- 368 4. Richards, J.P. Tectono-magmatic precursors for porphyry Cu-(Mo-Au) deposit formation. *Econ. Geol.* **2003**,
369 98, 1515-1533.
- 370 5. Sillitoe, R.H. Why No Porphyry Copper Deposits in Japan and South Korea. *Resour. Geol.* **2018**, 68, 107-125.
- 371 6. Cooke, D.R.; Hollings, P.; Walshe, J.L. Giant Porphyry Deposits: Characteristics, Distribution, and Tectonic
372 Controls. *Econ. Geol.* **2005**, 100, 801-818.
- 373 7. Richards, J.P. Tectonic, magmatic, and metallogenic evolution of the Tethyan orogen: From subduction to
374 collision. *Ore Geol. Rev.* **2015**, 70, 323-345.
- 375 8. Hou, Z.Q.; Yang, Z.M.; Lu, Y.; Kemp, A.; Zheng, Y.; Li, Q.; Duan, L. A genetic linkage between
376 subduction- and collision-related porphyry Cu deposits in continental collision zones. *Geology* **2015**, 43,
377 247-250.
- 378 9. Richards, J.P. High Sr/Y arc magmas and porphyry Cu $\pm$ Mo $\pm$ Au deposits: Just add water. *Econ. Geol.*
379 **2011**, 106, 1075-1081.
- 380 10. Hattori, K.H.; Keith, J.D. Contribution of mafic melt to porphyry copper mineralization: Evidence from
381 Mount Pinatubo, Philippines, and Bingham Canyon, Utah, USA. *Miner. Depos.* **2001**, 36, 799-806.
- 382 11. Hou, Z.Q.; Yang, Z.M.; Wang, R.; Zheng, Y.C. Further discussion on porphyry Cu-Mo-Au deposit
383 formation in main-land China. *Earth Sci. Front.* **2020**, doi.org/10.13745/j.esf.sf.2020.3.8.
- 384 12. Cherniak, D.J.; Watson, E.B.; Hanchar, J.M. Rare-earth diffusion in zircon. *Chem. Geol.* **1997**, 134, 289-301.
- 385 13. Shen, P.; Hattori, K.; Pan, H.D.; Jackson, S.; Seitmuratova, E. Oxidation Condition and Metal Fertility of
386 Granitic Magmas: Zircon Trace-Element Data from Porphyry Cu Deposits in the Central Asian Orogenic
387 Belt. *Econ. Geol.* **2015**, 110, 1861-1878.
- 388 14. Zhang, C.C.; Sun, W.D.; Wang, J.T.; Zhang, L.P.; Sun, S.J.; Wu, K. Oxygen fugacity and porphyry
389 mineralization: A zircon perspective of Dexing porphyry Cu deposit, China. *Geochim. Cosmochim. Acta*,
390 **2017**, 206, 343-363.
- 391 15. Rezeau, H.; Moritz, R.; Wotzlaw, J.F. Zircon Petrochronology of the Meghri-Ordubad Pluton, Lesser
392 Caucasus: Fingerprinting Igneous Processes and Implications for the Exploration of Porphyry Cu-Mo
393 Deposits. *Econ. Geol.* **2019**, 114, 1365-1388.
- 394 16. Smythe, D.J.; Brenan, J.M. Magmatic oxygen fugacity estimated using zircon-melt partitioning of cerium.
395 *Earth Planet. Sci. Lett.* **2016**, 453, 260-266.
- 396 17. Dilles, J.H.; Kent, A.J.R.; Wooden, J.L.; Tosdal, R.M.; Koleszar, A.; Lee, R.G.; Farmer, L.P. Zircon
397 compositional evidence for sulfur-degassing from ore-forming arc magmas. *Econ. Geol.* **2015**, 110, 241-251.
- 398 18. Cao, M.J.; Qin, K.Z.; Li, G.; Evans, N.J.; McInnes, B.I.; Li, J.; Zhao, J. Oxidation state inherited from the
399 magma source and implications for mineralization: Late Jurassic to Early Cretaceous granitoids, Central
400 Lhasa subterrane, Tibet. *Miner. Depos.* **2018**, 53, 299-309.
- 401 19. Sobolev, A.; Chaussidon, M. H₂O concentrations in primary melts from supra-subduction zones and
402 mid-ocean ridges: Implications for H₂O storage and recycling in the mantle. *Earth Planet. Sci. Lett.* **1996**,
403 137, 45-55.
- 404 20. Richards, J.P.; Kerrich, R. Adakite-like rocks: Their diverse origins and questionable role in metallogenesis.
405 *Econ. Geol.* **2007**, 102, 537-576.
- 406 21. Ballouard, C.; Poujol, M.; Boulvais, P.; Branquet, Y.; Tartèse, R.; Vigneresse, J.L. Nb-Ta fractionation in
407 peraluminous granites: A marker of the magmatic-hydrothermal transition. *Geology* **2016**, 44, 231-234.
- 408 22. Gelman, S.E.; Deering, C.D.; Bachmann, O.; Huber, C.; Gutiérrez, F.J. Identifying the crystal graveyards
409 remaining after large silicic eruptions. *Earth Planet. Sci. Lett.* **2014**, 403, 299-306.
- 410 23. Chudík, P.; Uher, P.; Kohút, M.; Bačík, P. Accessory columbite to tantalite, tapiolite and zircon: Products of
411 extreme fractionation in highly peraluminous pegmatitic granite from the Považský Inovec Mountains,
412 Western Carpathians, Slovakia. *J. Geosci.* **2008**, 53, 323-334.
- 413 24. Belousova, E.; Griffin, W.; O'Reilly, S.Y.; Fisher, N.I. Igneous zircon: trace element composition as an
414 indicator of source rock type. *Contrib. Mineral. Petrol.* **2002**, 143, 602-622.

- 415 25. Kirkland, C.L.; Smithies, R.H.; Taylor, R.J.M.; Evans, N.; McDonald, B. Zircon Th/U ratios in magmatic
416 environs. *Lithos* **2015**, 212-215, 397-414.
- 417 26. Coldwell, B.; Adam, J.; Rushmer, T.; Macpherson, C.G. Evolution of the East Philippine arc: Experimental
418 constraints on magmatic phase relations and adakitic melt formation. *Contrib. Mineral. Petrol.* **2011**, 162,
419 835-848.
- 420 27. Wang, Y.F.; Chen, H.Y.; Baker, M.J.; Han, J.S.; Xiao, B.; Yang, J.T.; Jourdan, F. Multiple mineralization
421 events of the Paleozoic Tuwu porphyry copper deposit, Eastern Tianshan: Evidence from geology, fluid
422 inclusions, sulfur isotopes, and geochronology. *Miner. Depos.* **2019**, 54, 1053-1076.
- 423 28. Wang, Y.H.; Zhang, F.F.; Liu, J.J.; Que, C.Y. Genesis of the Fuxing porphyry Cu deposit in Eastern
424 Tianshan, China: Evidence from fluid inclusions and C-H-O-S-Pb isotope systematics. *Ore Geol. Rev.*
425 **2016**, 79: 46-61.
- 426 29. Han, C.M.; Xiao, W.J.; Wan, B.; Ao, S.J.; Zhang, J.E.; Song, D.F.; Zhang, Z.Y.; Wang, Z.M. Late
427 Palaeozoic-Mesozoic endogenetic metallogenic series and geodynamic evolution in the East Tianshan
428 Mountains. *Acta Petrol. Sin.* **2018**, 34:1914-1932.
- 429 30. Wang, J.B.; Wang, Y.W.; He, Z.H. Ore deposits as a guide to the tectonic evolution in the east Tianshan
430 mountains NW China. *Geol. China* **2006**, 33, 461-469. (in Chinese).
- 431 31. Allen, M.B.; Windley, B.F.; Zhang, C. Paleozoic collisional tectonics and magmatism of the Chinese Tien
432 Shan, central Asia. *Tectonophysics* **1993**, 220, 89-115.
- 433 32. Carroll, A.R.; Graham, S.A.; Hendrix, M.S.; Ying, D.; Zhou, D.; Late Paleozoic tectonic amalgamation of
434 northwestern China: sedimentary record of the northern Tarim, northwestern Turpan, and southern
435 Junggar basins. *Geol. Soc. Am. Bull.* **1995**, 107, 571-594.
- 436 33. Wu, F.Y.; Sun, D.Y.; Ge, W.C.; Zhang, Y.B.; Grant, M.L.; Wilde, S.A.; Jahn, B.M. Geochronology of the
437 Phanerozoic granitoids in northeastern China. *J. Asian Earth Sci.* **2011**, 41, 1-30.
- 438 34. Xu, B.; Charvet, J.; Chen, Y.; Zhao, P.; Shi, G. Middle Paleozoic convergent orogenic belts in western Inner
439 Mongolia (China): framework, kinematics, geochronology and implications for tectonic evolution of the
440 Central Asian Orogenic Belt. *Gondwana Res.* **2012**, 23, 1342-1364.
- 441 35. Xiao, W.J.; Zhang, L.C.; Qin, K.Z.; Sun, S.; Li, J.L. Paleozoic accretionary and collisional tectonics of the
442 eastern Tianshan (China): implications for the continental growth of Central Asia. *America. J. Sci.* **2004**, 304,
443 370-95.
- 444 36. Wu, Y.S.; Chen, Y.J.; Zhou, K.F. Mo deposits in Northwest China: Geology, geochemistry, geochronology
445 and tectonic setting. *Ore Geol. Rev.* **2016**, 81, 641-671.
- 446 37. BGMRXUAR (Bureau of Geology and Mineral Resources of Xinjiang Uygur Autonomous Region) (1993)
447 Regional geology of Xinjiang Uygur Autonomous Region. Geological Publishing House, Beijing, pp 1-841.
448 (in Chinese).
- 449 38. Xiao, Q.H.; Qin, K.Z.; Xu, Y.X.; San, J.Z.; Ma, Z.L.; Sun, H.; Tang, D.M. A discussion on geological
450 characteristics of Hongxingshan Pb-Zn (Ag) deposit in Central Tianshan massif, eastern Xinjiang, with
451 reference to regional metallogenesis. *Miner. Depos.* **2009**, 28, 120-132.
- 452 39. Ma, X.H.; Chen, B.; Wang, C.; Yan, X.L. Early Paleozoic subduction of the Paleo-Asian Ocean: Zircon U-Pb
453 geochronological, geochemical and Sr-Nd isotopic evidence from the Harlik pluton, Xinjiang. *Acta Petrol.*
454 *Sin.* **2015**, 31:89-104. (in Chinese).
- 455 40. Han, B.F.; Guo, Z.J.; Zhang, Z.C.; Zhang, L.; Chen, J.F.; Song, B. Age, geochemistry, and tectonic
456 implications of a Late Paleozoic stitching pluton in the North Tian Shan suture zone, Western China. *Geol.*
457 *Soc. Am. Bull.* **2010**, 122, 627-640.
- 458 41. Wang, C.; Chen, B.; Ma, X.H.; Yan, X.L. Petrogenesis of early and late Paleozoic plutons in Sanchakou area
459 of east Tianshan and their implications for evolution of Kangur Suture Zone. *J. Earth Sci. Environ.* **2015**, 37,
460 52-70. (in Chinese).
- 461 42. Lei, W.; Guo, J.F.; Ma, J.; Xiao, L.; Li, X.C.; Liu, J.; Li, Y. Lithogeochemistry and LA-ICP-MS zircon U-Pb age
462 and its tectonic significance of Sujishan A-type granite pluton, eastern Bogda Mountains. *Geol. J. China*
463 *Univ.* **2016**, 22, 231-241. (in Chinese).
- 464 43. Zhang X.B.; Chai, F.M.; Chen C.; Quan H.Y.; Gong X.P. Geochronology, geochemistry and tectonic
465 implications of late Carboniferous Daheyuan intrusions from the Bogda Mountains, eastern Tianshan, *Geol.*
466 *Mag.* **2020**, 157, 289-306.
- 467 44. Gu, L.X.; Hu, S.X.; Yu, C.S.; Li, H.Y.; Xiao, X.J.; Yan, Z.F. Carboniferous volcanites in the Bogda Mountains
468 of eastern Tianshan: their tectonic implications. *Acta Petrol. Sin.* **2000**, 16, 305-16. (in Chinese).

- 469 45. Yuan, C.; Sun, M.; Wilde, S.; Xiao, W.; Xu, Y.; Long, X.; Zhao, G. Post-collisional plutons in the Balikun
470 area, East Chinese Tianshan: Evolving magmatism in response to extension and slab break-off. *Lithos* **2010**,
471 119, 269–88.
- 472 46. Li, P.; Li, Q.; Zhu, Z.; Chen C.; Liu, X. The Study on Fluid Inclusions and Stable Isotopes of Suoerbasitao
473 Gold Deposit in the Eastern Tianshan Mountain, NW China. *Acta Geol. Sin.* **2014**, 88, 757–758.
- 474 47. Zhang, X.B.; Chen C.; Xia F.; Gao, L.L.; Quan, H.Y. Metallogenesis and hydrothermal evolution of the
475 Tonggou Cu deposit in the eastern Tianshan: Evidence from fluid inclusions, H-O-S isotopes, and Re-Os
476 geochronology. *Geosci. Front.* **2019**, 10, 2301–2312.
- 477 48. Zhang, X.B. The research progress of Tonggou porphyry-vein Cu deposit in Eastern Tianshan. *The abstract*
478 *books of 9th national colloquium metallogenic theory and prospecting methods*, **2019**, 310. (in Chinese).
- 479 49. NGPXGEICMGB (No.704 Geological Party, Xinjiang Geological Exploration Institute of China
480 Metallurgical Geology Bureau) (1975) 1: 10000 detailed investigation report of Cu multi-metal belt.
481 Chaiwopu, Xinjiang, pp 1–175. (in Chinese).
- 482 50. Liu, Y.S.; Hu, Z.C.; Gao, S.; Günther, D.; Xu, J.; Gao, C.G.; Chen, H. In situ analysis of major and trace
483 elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chem. Geol.* **2008**,
484 257, 34–43.
- 485 51. Liu, Y.S.; Hu, Z.C.; Zong, K.Q.; Gao, C.G.; Shan, G. Reappraisal and refinement of zircon U-Pb isotope
486 and trace element analyses by LA-ICPMS. *Sci. Bull.* **2010**, 55, 1535–46.
- 487 52. Ludwig, K.R. ISOPLLOT 3.0: A Geochronological Toolkit for Microsoft Excel. Berkeley, California: Berkeley
488 Geochronology Center. *Special Publication*, **2003**, pp. 1–70
- 489 53. Yang, H.; Ge, W.C.; Zhao, G.C.; Dong, Y.; Xu, W. L.; Ji, Z.; Yu, J.J. Late Triassic intrusive complex in the
490 Jidong region, Jiamusi-Khanka Block, NE China: Geochemistry, zircon U-Pb ages, Lu-Hf isotopes, and
491 implications for magma mingling and mixing. *Lithos* **2015**, 224–225, 143–159.
- 492 54. Hoskin, P.W.O. Black, L.P. Metamorphic zircon formation by solidstate recrystallization of protolith
493 igneous zircon. *J. Metamorph. Geol.* **2000**, 18, 423–439.
- 494 55. Davies, J.F.; Whitehead, R.E. Alkali/Alumina Molar Ratio Trends in Altered Granitoid Rocks Hosting
495 Porphyry and Related Deposits. *Explor. Min. Geol.* **2010**, 19, 13–22.
- 496 56. Winchester, J.; Floyd, P.; Geochemical discrimination of different magma series and their differentiation
497 products using immobile elements: *Chem. Geol.* **1977**, 20, 325–343.
- 498 57. Vry, V.H.; Wilkinson, J.J.; Seguel, J.; Millán, J. Multistage intrusion, brecciation, and veining at El Teniente,
499 Chile: Evolution of a nested porphyry system. *Econ. Geol.* **2010**, 105, 119–153.
- 500 58. Boynton, W.V. Geochemistry of the Rare Earth Elements: Meteorite Studies. In: Rare Earth Element
501 Geochemistry (ed. P Henderson), **1984**, pp. 63–114.
- 502 59. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: implications for mantle
503 composition and processes. In *Magmatism In Ocean Basins* (eds AD Saunders and MJ Norry), Geological
504 Society of London, Special Publication. London, UK, **1989**; Volume 32, pp. 313–345.
- 505 60. Blundy, J.; Wood, B. Prediction of crystal-melt partition coefficients from elastic moduli. *Nature* **1994**, 372,
506 452–454.
- 507 61. Wang, Y.F.; Chen, H.Y.,; Xiao, B.; Han, J.S.; Fang, J.; Yang, J.T. Overprinting mineralization in the Paleozoic
508 Yandong porphyry copper deposit, eastern Tianshan, NW China—evidence from geology, fluid inclusion
509 and geochronology. *Ore Geol. Rev.* **2018**, 100, 148–167.
- 510 62. Wang, Y.H.; Zhang, F.F.; Liu, J.J.; Que, C.Y. Carboniferous magmatism and mineralization in the area of
511 the Fuxing Cu deposit, Eastern Tianshan, China: evidence from zircon U–Pb ages, petrogeochemistry, and
512 Sr–Nd–Hf–O isotopic compositions. *Gondwana Res.* **2016**, 34, 109–128.
- 513 63. Chen, J. F.; Guo, X.S.; Tang, J.F.; Zou, T.X. Nd isotopic model ages: implications of the growth of the
514 continental crust of southeastern China. *J. Nanjing Univ.* **1999**, 35, 649–658. (in Chinese).
- 515 64. Ferry, J.M.; Watson, E.B. New thermodynamic models and revised calibrations for the Ti-in-zircon and
516 Zr-in-rutile thermometers: *Contrib. Mineral. Petrol.* **2007**, 154, 429–437.
- 517 65. Defant M.J.; Drummond M.S. Derivation of some modern arc magmas by melting of young subducted
518 lithosphere. *Nature* **1990**, 347, 662–665.
- 519 66. Sun, W.; Zhang, H.; Ling, M.X.; Ding, X.; Chung, S.L.; Zhou J.B.; Yang X.Y.; Fan W.M. The genetic
520 association of adakites and Cu–Au ore deposits. *Inter. Geol. Rev.* **2011**, 53, 691–703.
- 521 67. Sun W D , Liang H Y , Ling M X , Zhan, M.Z.; Ding, X.; Zhang, H.; Yang X.Y.; Li, Y.L.; Ireland, T.R.; Wei,
522 Q.R.; Fan, W.M. The link between reduced porphyry copper deposits and oxidized magmas. *Geochim.*
523 *Cosmochim. Acta*, **2013**, 103, 263–275.

68. Miller, C.F.; Mittlefehldt, D.W. Extreme fractionation in felsic magma chambers: A product of liquid-state diffusion or fractional crystallization? *Earth Planet. Sci. Lett.* **1984**, *68*, 151–158.
69. Gelman, S.E.; Deering, C.D.; Bachmann, O.; Huber, C.; Gutiérrez, F.J. Identifying the crystal graveyards remaining after large silicic eruptions. *Earth Planet. Sci. Lett.* **2014**, *403*, 299–306.
70. Lee, C.T.A.; Morton, D.M. High silica granites: Terminal porosity and crystal settling in shallow magma chambers. *Earth Planet. Sci. Lett.* **2015**, *409*, 23–31.
71. Pérez-Soba, C.; Villaseca, C. Petrogenesis of highly fractionated I-type peraluminous granites: La Pedriza pluton (Spanish Central System). *Geol. Acta* **2010**, *8*, 131–149.
72. Wu, F.Y.; Liu, X.C.; Liu, Z.C.; Wang, R.C.; Xie, L.; Wang, J.M.; Ji, W.Q.; Yang, L.; Liu, C.; Khanal, G.P.; He S.X. Highly fractionated Himalayan leucogranites and associated rare-metal mineralization. *Lithos* **2020**, *352–353*, 1–24.
73. Breiter, K.; Lamarão, C.N.; Borges, R.M.K.; Dall'Agnol, R. Chemical characteristics of zircon from A-type granites and comparison to zircon of S-type granites. *Lithos* **2014**, *192–195*, 208–225.
74. Chudík, P.; Uher, P.; Kohút, M.; Bačík, P. Accessory columbite to tantalite, tapiolite and zircon: Products of extreme fractionation in highly peraluminous pegmatitic granite from the Považský Inovec Mountains, Western Carpathians, Slovakia. *J. Geol. Sci.* **2008**, *53*, 323–334.
75. Cerný, P.; Teertstra, D.K.; Chapman, R.; Selway, J.B.; Hawthorne, F.C.; Ferreira, K.; Chackowsky, L.E.; Wang, X.J.; Meintzer, R.E. Extreme fractionation and deformation of the leucogranite-pegmatite suite at Red Cross Lake, Manitoba, Canada. IV. Mineralogy. *Can. Mineral.* **2012**, *50*, 1839–1875.
76. Sun, W.D.; Ling, M.X.; Chung, S.L.; Ding, X.; Yang, X.Y.; Liang, H.Y.; Fan, W.M.; Goldfarb, R.; Yin, Q.Z. Geochemical constraints on adakites of different origins and copper mineralization. *J. Geol.* **2012**, *120*, 105–120.
77. Rudnick, R.L.; Fountain, D.M. Nature and composition of the continental crust: a lower crustal perspective. *Rev. Geophys.* **1995**, *33*, 267–309.
78. Nadia, Mohammadi.; Lentz, D.R.; Chris, R.M.; McFarlane, B.C. Geochemistry of the highly evolved Sn-W-Mo-bearing Mount Douglas Granite, New Brunswick, Canada: Implications for origin and mineralization, *Ore Geol. Rev.* **2020**, *117*, 103266.
79. Chelle-Michou, C.; Chiaradia, M.; Ovtcharova, M.; Ulianov, A.; Wotzlaw, J.F. Zircon petrochronology reveals the temporal link between porphyry systems and the magmatic evolution of their hidden plutonic roots (the Eocene Corocohuayco deposit, Peru). *Lithos* **2014**, *198–199*, 129–140.



© 2020 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).