Evidence for temporal relationship between the late Mesozoic multistage Qianlishan granite complex and the Shizhuyuan W–Sn–Mo–Bi deposit, SE China

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The world-class Shizhuyuan W–Sn–Mo–Bi deposit is spatially related to the Qianlishan granite complex (QGC) in Hunan Province, China. However, the age and classification of the QGC are still debated, and a better understanding of the temporal genetic relationship between the QGC and the Shizhuyuan deposit is essential. Here, we present chemical compositions the intrusive phases of the QGC and the results of detailed zircon U–Pb dating and muscovite Ar–Ar dating of a mineralized greisen vein. Our new zircon laser ablation inductively coupled plasma mass spectrometry U–Pb age data constrain the emplacement of the QGC to 155–151.7 Ma. According to petrological, geochemical and geochronological data and the inferred redox conditions, the QGC can be classified into four phases: P1, porphyritic biotite granites; P2, porphyritic biotite granite; P3, porphyritic biotite granite; and P4, granitic porphyry dikes. All phases, and especially P1–P3, have elevated concentrations of ore-forming metals and heat-producing elements (U, Th, K; volume heat-producing rate of 5.89–14.03 μW m⁻³), supplying the metal and heat for the metallogenic process of the Shizhuyuan deposit. The Ar–Ar muscovite age (154.0 ± 1.6 Ma) of the mineralized greisen vein in the Shizhuyuan deposit is consistent with the emplacement time of the QGC, suggesting their temporal genetic relationship.

Magmatic fractionation and exsolution of a fluid phase from a cooling pluton plays an important role in metal enrichment for intrusion-related deposits1–3. Reheating of preexisting semi-solidified plutons triggered by the input of a new magma may lead to the exsolution of fluid and element transport, thus contributing to incremental extraction of metals from the magma and their precipitation in the cupola of plutons4,5. Successive magma inputs led to the repeated extraction and precipitation of metals to form ore at the vantage position2,6. The lifespan of the magmatic-hydrothermal system triggered by the emplacement of a set of successive plutons controls the timescale of the ore-forming process and thus the metal grades and tonnages of deposits. Therefore, establishing tight temporal ties between magmatism and its associated mineralization is key to understanding the contribution of magma to mineralization. It is generally considered that lifespans of magmatic-hydrothermal systems is less than 10 million years, and even shorter (< 2 Ma) for porphyry deposits7–12. Accordingly, a time interval between plutons and the associated mineralization of > 10 Ma is interpreted to indicate that they have no genetic ties.

The development of W, Sn, Pb, Zn, and rare earth element (REE) deposits is genetically associated with voluminous Mesozoic granites13–20. The Qianlishan granite complex (QGC) in China is located ~16 km southeast of Chenzhou city, Hunan Province. The QGC is centered in the well-known Shizhuyuan polymetallic ore zone (W–Sn–Mo–Bi–Pb–Zn) which includes the Shizhuyuan W–Sn–Mo–Bi deposit (W: 80 Mt, Sn: 40 Mt, Bi: 20 Mt, Mo: 10 Mt)21–23. The zoned QGC was formed by successive Mesozoic magmatic intrusions24–26, which are

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assumed to have provided heat and metals for mineralization. However, the classification and geochronology of the QGC and the mineralization time of the Shizhuyuan deposit remain debated. Previous research on the QGC obtained intrusion ages ranging from 183 to 131 Ma\textsuperscript{13,14,25–29} and the mineralization ages from 145 to 160 Ma\textsuperscript{28,30,31}. Thus, some phases of the QGC may indeed have a genetic relationship with the deposit, whereas other phases may not.

This study revisited the classification and dating of the QGC and mineralization to clarify their genetic relationship. We present zircon LA-ICP-MS dating results for the QGC and combine these with petrology and field observations to constrain the structure and intrusive history of the QGC. Precise Ar–Ar dating of muscovite from the mineralized greisen vein allows for place constraints on the timing of the Shizhuyuan W–Sn–Mo–Bi deposit. Our results suggest close temporal relationship between the QGC and associated mineralization.

**Geological setting.** The Nanling Range is located in the collision zone between the Yangtze Block and the Cathaysia Block (Fig. 1) where six main (buried) faults strike north and north-northeast. These blocks amalgamated during the early Neoproterozoic along the Qin-Hang deep fault zone\textsuperscript{17,32,33}. This collision zone was reactivated in the early to late Mesozoic at 180–90 Ma, leading to the formation of numerous nonferrous and rare metal mineralized deposits, including W, Sn, Mo, Pb, Zn, U, Cu, Au, and REEs\textsuperscript{34}. The Shizhuyuan ore field is located at the northern end of the Shizhuyuan-Taipingli synclinorium striking northeast. The ore field is surrounded by Sinian metasedimentary rocks, Devonian carbonate and clastic sedimentary rocks, the QGC and Quaternary sediments\textsuperscript{35} (Fig. 2). Sinian metasedimentary rocks occur only on the eastern edge of the ore field. These rocks are mostly weakly metamorphosed clastic sedimentary rocks. Specifically, the rocks comprise gray-green to gray-black, moderately thick, fine-grained quartz-rich sandstones, feldspathic sandstones, siltstones, phyllites and slate\textsuperscript{36}. Devonian carbonate rocks and clastic sedimentary rocks are present as host rocks intensely altered by fracturing and magmatic activity (Fig. 2). From bottom to top, these rocks have been subdivided into four formations: (1) Tiaomajian Formation; (2) Qiziqiao Formation; (3) Shetianqiao Formation; and (4) Xikuangshan Formation. The first two formations belong to the Middle Devonian, and the last two to the Upper Devonian\textsuperscript{37}. The Tiaomajian Formation (D\textsubscript{2t}) is >358 m thick and occurs at the eastern and western sections of the ore field. It is mainly composed of gravel-bearing sandstones and conglomerates. The Qiziqiao Formation (D\textsubscript{2q}, >520 m in thickness) occurs in the middle and southern parts of the ore field. It comprises

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**Figure 1.** Geological map of the Nanling Range, South China (modified after Chen et al. (2016)\textsuperscript{14}, copyright@ Elsevier, 2016). Faults: (1) Jiangshan–Shaoxing–Pingxiang Fault; (2) Zhenghe–Dapu Fault; (3) Changle–Nan’ao Fault; (4) Chenzhou–Linwu Fault; (5) Changlin–Guangchang buried Fault; (6) Wuzhou–Sihui buried Fault.
micritic dolomites, limestones and dolomitic limestones. The Shetianqiao Formation (D₃s, > 296 m in thickness), is present in the Shizhuyuan, Dongpo and Chaishan areas. It contains mainly banded micritic limestones. The Xikuangshan Formation (D₃x, > 363 m in thickness) comprises thick-bedded limestones and dolomitic limestones containing flint concretions. The Quaternary sediments are ~10 m thick, comprising slope wash. They are present only along the rivers in the northern part of the Shizhuyuan ore field.

Petrography. Previous studies have indicated that the QGC (~10 km²) was intruded by lamprophyre and coeval mafic dikes. Since the mafic dikes are ~10 Ma younger than the QGC and the associated mineralization, they are not genetically related. The QGC, which is spatially and temporally associated with W–Sn–Mo–Bi mineralization, can be subdivided into five Sections. The first section (S₁) is a fine-grained porphyritic biotite granite (Fig. 3a,d) that outcrops within an area of ~4.0 km² on the northern edge of the pluton. It is gray-white in color and comprises ~30 vol.% phenocrysts (2–7 mm in diameter), which are mostly potassium feldspar (~10 vol.%), plagioclase (~10 vol.%) and quartz (~10 vol.%), as well as minor biotite (~1 vol.%). The groundmass (0.3–1.0 mm in diameter) contains the same minerals. Dark inclusions within biotite, plagioclase, quartz and apatite occasionally occur in the S₁ stocks and dikes. The accessory minerals in S₁ are zircon, monazite, xenotime and ilmenite.

The second section (S₂) is a gray-white micro-fine-grained porphyritic biotite granite (Fig. 3b,e), occurring in the southern part of the pluton, with an outcrop area of ~1.1 km². It contains phenocrysts of quartz (~17 vol.%) and feldspar (~13 vol.%) that range in size from 1 to 6 mm. The accessory minerals in S₂ are zircon, monazite, xenotime and ilmenite. The second section (S₂) is a gray-white, micro-fine-grained porphyritic biotite granite (Fig. 3b,c), occurring in the southern part of the pluton, with an outcrop area of ~1.1 km². It contains phenocrysts of quartz (~17 vol.%) and feldspar (~13 vol.%) that range in size from 1 to 6 mm. The matrix is dominated by quartz, potassium feldspar, plagioclase and minor biotite (0.1–0.6 mm in diameter). Biotite is locally altered to chlorite (Fig. 3e). Accessory minerals in S₂ are mainly zircon, monazite, xenotime, thorium, and apatite. The third section (S₃) is a gray-white fine- to coarse-grained (mainly 0.3–0.8 mm in diameter) equigranular biotite granite (Fig. 3c,f) with an outcrop area of 4.4 km². It contains quartz (~37 vol.%), plagioclase (~30 vol.%), alkali feldspar (~23 vol.%), biotite (~2 vol.%), and accessory minerals (<3 vol.%) including zircon, monazite,
and fluorite. Plagioclase (An = 0.01–0.03) occasionally exhibits overgrowth and argillization. The fourth section (S4) is a gray-white fine-grained (mostly 0.1–0.3 mm in diameter) equigranular two-mica granite (~0.1 km²;...
Fig. 3g), which comprises quartz (~40 vol.%), plagioclase (~31 vol.%), alkali feldspar (~22 vol.%), and muscovite (~1 vol.%). Plagioclase shows polysynthetic twinning, and alkali feldspar has Carlsbad twinning and perthitic texture. Primary and secondary muscovite were both found in this section. The primary muscovite grains present as euhedral intergranular sheets surrounded by plagioclase and quartz grains, whereas the secondary grains are distributed along the secondary fractures. The S4 has intruded into the first three sections, and pegmatite belts are often found on its top. The accessory minerals in this section are mainly zircon, thorite, topaz and fluorite.

The fifth section (S5) represents a series of NE-striking (25–65°) granite porphyry dikes (Fig. 3h, 3k), comprising quartz (~15 vol.%), orthoclase (~8 vol.%), plagioclase (~15 vol.%), and minor biotite (~2 vol.%). Plagioclase phenocrysts (0.2–2 mm in diameter) within a matrix consisting mainly of quartz, orthoclase, plagioclase, and biotite. This section suffered strong alteration: (1) argillization was widely developed on the surface of plagioclase phenocrysts; (2) almost all biotite has been altered into chlorite and muscovite (Fig. 3k). Plagioclase comprises albite (An = 0.01–0.08) and andesine (An = 0.26–0.37). The Fe/(Fe + Mg) ratio of biotite is 0.74–0.75. The accessory minerals mainly consist of euhedral to subhedral, prismatic allanite and apatite (60–150 μm × 10–60 μm wide), with a small number of zircon, monazite, fluorite, rutile and magnetite. All the studied zircon grains were generally wrapped in plagioclase, suggesting that they occurred as an early crystallization phase during crystal fractionation.

**Alteration and mineralization.**  
*Alteration.*  The alteration of the Shizhuyuan W–Sn–Mo–Bi deposit includes four types: a. skarnization; b. greisenization; c. marmarization; and d. feldspathization.

Skarnization. The skarn located in the contact zone in the southeastern region of the QGC has experienced the most pervasive alteration in the Shizhuyuan deposit (Fig. 2). This skarn is approximately 1.2 km long, 1.0 km wide and 50–500 m thick (with an average thickness of 150–200 m). There are three types of skarns: a. original
skarn; b. retrograde skarn; and c. veinlet skarn. The mineral assemblage of the skarn, whose parent rock is marble, comprises mainly garnet, pyroxene, idocrase and wollastonite. The original skarn has been overprinted by a retrograde skarn. In comparison to the original skarn, the retrograde skarn contains much higher contents of fluorite, epidote, wolframite, scheelite, cassiterite, molybdenite, bismuthinite, magnetite, and pyrite. Generally, mineralization occurs within the retrograde skarn rather than in the original skarn. Skarn veins crosscutting the margin of the retrograde skarn are tens to hundreds meters long and 10–50 cm wide. These skarn veins contain ores with grades of 1% to 6%.

Greisenization. There are two types of greisen: massive greisen and vein-type greisen. Massive greisen occurs mainly as discrete lenses in the upper section of the equigranular granites (S$_1$ and S$_2$); it contains quartz (~ 65%), mica (~ 16%), topaz (~ 8%), feldspar (~ 3%), chlorite (~ 2%) and fluorite (~ 1%). Compared with the massive greisen, the vein-type greisen has a similar mineral assemblage but with wider variations in mineral proportions: quartz (45–85%), mica (3–35%), topaz (5–40%), fluorite (2–10%), and feldspar (1–3%) as well as minor accessory minerals wolframite, scheelite, cassiterite, molybdenite, bismuthinite, magnetite, pyrite, and chalcopyrite (Fig. 3l). The vein-type greisen overlies the massive greisen, and it is distributed much more broadly (Fig. 4). Additionally, in Tunnel 490, a greisen vein is observed cutting through both the massive greisen and the skarn.

Marmarization. The stockwork marble vein, which is located at the contact between the overlying marble and the underlying skarn, is 750 m long, 300–600 m wide and 20–200 m thick. This vein comprises mainly fluorite, mica, tournaline, and feldspar. The mineral grains are smaller than 0.05 mm in diameter.

Feldspathization. Stockwork feldspar is a light-colored altered rock located in the fractures of the skarn. It contains mainly potassium feldspar and plagioclase and occasional quartz, fluorite, garnet, and pyroxene.
Mineralization. Based on their compositions, textures and ore characteristics, the ores are clearly zoned. Pervasive greisenization plays the dominant role in defining these ore type classification. Mao et al. (1998) classified the ores into four types. From top to bottom, these are Type 1—Sn–Cu ore within vein-type greisen superimposed on the porphyritic biotite granites (S1 and S2); Type 2—Sn–Be–Cu ore within the fine stockwork greisen overprinting the marble; Type 3—W–Sn–Mo–Bi ore within thick stockwork greisen and rare stockwork greisen superimposed on the skarn; and Type 4—W–Sn–Mo–Bi ore within massive greisen at the top of the equigranular biotite granite stock (Fig. 4). Of these ores, the Type 3 ore has the greatest tonnage and represents the main mineralization stage.

Results
Zircon LA-ICP-MS age and trace elements. The zircons from Sample GL-13 (S1) are typically transparent, colorless to slightly brown, rectangular to prismatic crystals 100–150 μm long, with aspect ratios ranging from 2:1 to 3:1. Oscillatory zoning, with the occasional appearance of inherited cores, is common in these crystals (Fig. 5). The zircons from Sample 315–36 (S2) are mostly transparent, colorless to pale yellow, euhedral to subhedral crystals 100–200 μm long, with aspect ratios ranging from 2:1 to 3:1. The euhedral grains have concentric zoning with relatively bright cores in CL images (Fig. 5). Compared with those from the S1 and S2 granites, the zircons from the S3 granite (Sample 490–21) are similar in shape and color but are smaller (typically 50–100 μm long), with aspect ratios ranging from 2:1 to 1.5:1, and exhibit weak oscillatory zoning. The zircons of Sample 490–10 (S3) resemble those of Sample 490–21 in terms of their shape, color, and size (Fig. 5). The zircons of Sample 490–2 (S5) are characteristically long (100–250 μm), with aspect ratios ranging from 2:1 to 3:1. They are also transparent, colorless, and euhedral to subhedral. Oscillatory zoning is commonly visible in CL images (Fig. 5).
| Spot  | 206Pb | Th  | U   | Th/U Ratio | 206Pb/238U Ratio | 206Pb/204Pb Ratio | 206Pb/204U Ratio | 206Pb/238U Age | Sample  |
|-------|-------|-----|-----|-----------|-----------------|-------------------|-----------------|-----------------|---------|
| GL-13 | <0.17 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-12 | <0.11 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-13 | <0.27 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-14 | <0.22 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-15 | <0.14 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-16 | <0.02 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-17 | <0.15 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-18 | <0.16 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-19 | <0.25 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-20 | <0.19 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-21 | <0.01 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-22 | <0.13 |...|...|...       |...              |...           |...              |...              |<0.19  |
| GL-23 | <0.11 |...|...|...       |...              |...           |...              |...              |<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–1 | <0.13 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–2 | <0.11 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–3 | <0.15 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–4 | <0.13 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–5 | 0.0160 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–6 | <0.12 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–7 | <0.12 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–8 | <0.13 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–9 | <0.11 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–10 | <0.19 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–11 | <0.15 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–12 | <0.11 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–13 | <0.17 |...|...|...|...|<0.19  |
| Sample 315–36 | 154.4 ± 0.88 Ma | 315–36–14 | <0.18 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–1 | 0.022 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–2 | <0.15 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–3 | 0.012 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–4 | <0.14 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–5 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–10 | 151.7 ± 3.1 Ma | 490–10–6 | <0.06 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–1 | <0.12 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–2 | <0.14 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–3 | <0.10 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–4 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–5 | <0.14 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–6 | <0.14 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–7 | <0.13 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–8 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–9 | <0.12 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–10 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–11 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–12 | <0.26 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–13 | <0.18 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–14 | <0.18 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–15 | <0.17 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–16 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–17 | <0.11 |...|...|...|...|<0.19  |
| Sample 490–2 | 153.7 ± 1.2 Ma | 490–2–18 | <0.10 |...|...|...|...|<0.19  |

Table 1. LA-ICP-MS analyses of zircons in the QGC.
| Spot | Ti  | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| GL-13.1 | 4.7 | <0.0005 | 35 | 0.2 | 2.6 | 6.5 | 0.6 | 29.2 | 10.5 | 135 |
| GL-13.2 | 7.2 | 0.02 | 37.5 | 0.3 | 4.9 | 10 | 1.5 | 51.3 | 16.1 | 186.2 |
| GL-13.3 | 9.3 | 0.01 | 27 | 0.1 | 2 | 3.4 | 0.4 | 18 | 6.9 | 80.3 |
| GL-13.4 | 10.9 | 0.05 | 32.9 | 0.3 | 5.8 | 8.2 | 1.2 | 40.8 | 13.3 | 146.7 |
| GL-13.5 | 12.3 | 0.05 | 18.8 | 0.1 | 1.3 | 3 | 0.5 | 16.6 | 5.4 | 67.8 |
| GL-13.6 | 15.5 | 0.02 | 30.1 | 0.3 | 1.7 | 7.9 | 1.5 | 39.8 | 12.4 | 141.6 |
| GL-13.7 | 5.4 | 2.45 | 36.8 | 1 | 5 | 2.8 | 0.3 | 20.5 | 7.1 | 90.5 |

Sample GL-13 (continued)

| Spot | Ti  | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| GL-13.8 | 13.1 | 0.03 | 28.2 | 0.2 | 4.8 | 9.5 | 1.6 | 41.8 | 13.7 | 165.1 |
| GL-13.9 | 11.6 | <0.001 | 24.7 | 0.1 | 1.5 | 3.7 | 0.9 | 22 | 7.1 | 85.9 |
| GL-13.10 | 6.1 | 0.03 | 31.9 | 0.2 | 2.8 | 7.3 | 0.7 | 41.9 | 13.1 | 165.3 |
| GL-13.11 | 8.7 | 0.01 | 24 | 0.1 | 1.1 | 2.8 | 0.3 | 16.1 | 5.9 | 77.7 |

| Spot GL-13 (continued)

| Spot | Ti  | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| GL-13.1 | 50.4 | 248.9 | 54.1 | 506.2 | 95.6 | 49.4 | 679 | –17.0 | 0.3 | 951.8 |
| GL-13.2 | 5.4 | 2.45 | 36.8 | 1 | 5 | 2.8 | 0.3 | 20.5 | 7.1 | 90.5 |

Sample GL-13 (continued)
Table 2. Zircon Trace element compositions, Ce anomalies, and Ti-in-zircon temperatures. Notes: Ce anomalies (δCe) are calculated based on Nd, Sm, and Gd to Lu using the lattice strain model (Blundy and Wood, 1994).55

| Spot     | Ho  | Er  | Tm  | Yb  | Lu | δCe | T(°C) | lg(fO2) | δFMQ | T(K) | 10⁴/T (1/K) |
|----------|-----|-----|-----|-----|----|-----|-------|---------|------|------|-------------|
| GL-13.2  | 64  | 292.7 | 58.2 | 509.9 | 95 | 20.2 | 716 | −18.3 | −1.9 | 989.1 | 10.1 |
| GL-13.3  | 30.5 | 134.3 | 28.4 | 266.4 | 47.1 | 47.2 | 739 | −14.0 | 1.9 | 1011.9 | 9.9 |
| GL-13.4  | 55.8 | 276 | 60.5 | 562.2 | 19.7 | 754 | −16.5 | −1.0 | 1026.9 | 9.7 |
| GL-13.5  | 24.6 | 114.6 | 23.6 | 218 | 47 | 766 | −12.6 | 2.6 | 1039.0 | 9.6 |
| GL-13.6  | 49.8 | 231.8 | 45.6 | 410.1 | 21.9 | 789 | −14.4 | 0.3 | 1062.0 | 9.4 |
| GL-13.7  | 34.5 | 165.9 | 36.5 | 332.2 | 37.5 | 490 | −17.4 | −0.3 | 963.5 | 10.4 |
| GL-13.8  | 58.2 | 270.6 | 55.8 | 475.8 | 16.4 | 772 | −16.3 | −1.2 | 1044.7 | 9.6 |
| GL-13.9  | 31.4 | 145.6 | 30.9 | 273.4 | 54.1 | 760 | −12.4 | 3.0 | 1032.9 | 9.7 |
| GL-13.10 | 60  | 281.9 | 57.5 | 509.9 | 95.4 | 761 | −17.0 | −0.2 | 974.1 | 10.3 |
| GL-13.11 | 28.7 | 142.2 | 30.2 | 270.2 | 50.8 | 733 | −11.9 | 4.1 | 1005.9 | 9.9 |

Sample 315–36

| Spot     | Ho  | Er  | Tm  | Yb  | Lu | δCe | T(°C) | lg(fO2) | δFMQ | T(K) | 10⁴/T (1/K) |
|----------|-----|-----|-----|-----|----|-----|-------|---------|------|------|-------------|
| 315–36.1 | 24.4 | 115.9 | 24.9 | 230.6 | 44.5 | 130.9 | 736 | −10.3 | 5.7 | 1009.3 | 9.9 |
| 315–36.2 | 33.2 | 156.4 | 33.1 | 300.8 | 59.5 | 67.8 | 753 | −11.9 | 3.6 | 1025.6 | 9.8 |
| 315–36.3 | 22  | 103.4 | 22.1 | 202.2 | 37.5 | 96  | 760 | −10.2 | 5.1 | 1033.4 | 9.7 |
| 315–36.4 | 31.4 | 143.4 | 30.2 | 276.7 | 52.3 | 92.5 | 754 | −12.5 | 4.1 | 999.6 | 10.0 |
| 315–36.5 | 24.6 | 114.6 | 23.6 | 218 | 47 | 766 | −12.6 | 2.6 | 1039.0 | 9.6 |
| 315–36.6 | 49.8 | 231.8 | 45.6 | 410.1 | 21.9 | 789 | −14.4 | 0.3 | 1062.0 | 9.4 |
| 315–36.7 | 34.5 | 165.9 | 36.5 | 332.2 | 37.5 | 490 | −17.4 | −0.3 | 963.5 | 10.4 |
| 315–36.8 | 58.2 | 270.6 | 55.8 | 475.8 | 16.4 | 772 | −16.3 | −1.2 | 1044.7 | 9.6 |

Sample 490–10

| Spot     | Ho  | Er  | Tm  | Yb  | Lu | δCe | T(°C) | lg(fO2) | δFMQ | T(K) | 10⁴/T (1/K) |
|----------|-----|-----|-----|-----|----|-----|-------|---------|------|------|-------------|
| 490–10.1 | 37.6 | 177.7 | 39 | 343.8 | 64.6 | 71.5 | 752 | −11.7 | 3.8 | 1025.4 | 9.8 |
| 490–10.2 | 59.7 | 272.6 | 57.1 | 491.4 | 95.2 | 32.4 | 756 | −14.5 | 0.9 | 1029.2 | 9.7 |
| 490–10.3 | 45.4 | 209.8 | 43.4 | 377.4 | 72.3 | 715 | 751 | −10.0 | 5.6 | 1024.3 | 9.8 |
| 490–10.4 | 26.8 | 136.1 | 29.9 | 285.8 | 54.7 | 367.1 | 723 | −12.1 | 4.1 | 999.6 | 10.0 |
| 490–10.5 | 36.5 | 186.9 | 40.4 | 383.2 | 73.5 | 82.6 | 721 | −12.8 | 3.5 | 993.9 | 10.1 |

Sample 490–2

| Spot     | Ho  | Er  | Tm  | Yb  | Lu | δCe | T(°C) | lg(fO2) | δFMQ | T(K) | 10⁴/T (1/K) |
|----------|-----|-----|-----|-----|----|-----|-------|---------|------|------|-------------|
| 490–2.1  | 41.9 | 191.1 | 38.6 | 343.2 | 62.3 | 13.9 | 766 | −17.2 | −2.0 | 1039.4 | 9.6 |
| 490–2.2  | 46.2 | 76.6 | 16.7 | 155.8 | 28.6 | 167.3 | 727 | −9.8 | 6.3 | 1000.0 | 10.0 |
| 490–2.3  | 22.7 | 108.2 | 21.7 | 200.2 | 36.8 | 118.5 | 746 | −10.2 | 5.5 | 1019.0 | 9.8 |
| 490–2.4  | 15  | 73.4 | 15.7 | 141.2 | 27.1 | 90.4 | 765 | −10.2 | 5.0 | 10382.9 | 9.6 |
| 490–2.5  | 35.5 | 157.9 | 30.8 | 275.9 | 49.1 | 31.4 | 779 | −13.5 | 1.4 | 10523.9 | 9.5 |
| 490–2.6  | 19.1 | 92.5 | 20.1 | 182.6 | 34.7 | 121 | 749 | −9.9 | 5.7 | 1021.6 | 9.8 |
| 490–2.7  | 25.1 | 119.2 | 24.5 | 221.7 | 40.4 | 49.8 | 753 | −13.1 | 2.5 | 1025.9 | 9.7 |

References:
55 Blundy, J. D., & Wood, P. J. (1994).
Zircon dates are summarized in Fig. 6 and Table 1. In total, 40 spots on zircon grains from Sample GL-13 were analyzed. Excluding the spots with abnormally high U content and associated with inherited zircons, 11 analyses yield a 206Pb/238U age of 155 ± 1.9 Ma (MSWD = 2.8, probability 0.002). Similarly, the weighted average 206Pb/238U age of Sample GL-315-36 (154 ± 0.88, MSWD = 1.05, probability 0.001) was obtained by pooling the 11 analyses. The data for Sample 490–21 are too variable to constrain either an intercept age or a concordant age. Sample 490–10 has a slightly younger weighted average 206Pb/238U age (151.7 ± 3.1, MSWD = 2.3, probability 0.04) obtained by 6 analyses. Within error, this date is identical to those of Samples GL-13 and 315–36. Of forty analyses from Sample 490–2, 18 data points give a 206Pb/238U age of 153.7 ± 1.2 (MSWD = 2.2, probability 0.002). Trace element contents in zircon and calculated Ce anomalies and ’Ti-in-zircon’ temperatures are presented in Table 2.

Whole-rock major and trace element chemistry. Twenty representative samples were analyzed for their major and trace element compositions (Table 3). These samples are characterized by high SiO2 (70.32–78.28 wt%) and K2O (3.54–5.92 wt%) contents. Most of the samples plot in the fields of high-K calc-alkaline field, whereas seven samples plot in the shoshone field. The aluminum saturation index (ASI) values of the five phases of Qianlishan granites are 0.95–1.78, 1.04–1.05, 0.88–1.34, 1.04–1.2, and 1–1.2. The S1, S2, and S3 porphyritic granites have higher contents of K2O, CaO, MgO, TiO2, Zr, Sr, Ba, and P2O5 but lower contents of Na2O and Al2O3 than the other granites (Figs. 7, 8). Notably, fluorine concentrations of the S1 and S4 equigranular biotite granites (2500–10,400 ppm) are much higher than those of the S2 granite porphyry (< 2000 ppm), whereas the S5 and S4 porphyritic biotite granites have intermediate F contents (2000–6800 ppm). Moreover, S2, S3, and S4 have relatively high W contents (20–100 ppm), whereas S1 and S5 have lower W contents (< 20 ppm). In the primitive mantle-normalized diagrams (Fig. 9), S3 and S4 exhibit the strongest negative Ba, Sr, P, and Ti anomalies, whereas S1 and S2 show much smaller anomalies. S1 has trace element patterns similar to those of S2 and S5. As presented in Fig. 10 and Table 3, S2 and S5 have the lowest La/Yb (0.88–1.34) and δEu (0.002–0.011), followed by S1 and S4 with La/Yb (3.01–3.71) and δEu (0.15–0.25). S3 has the highest La/Yb (13.16–13.96) and δEu (0.23–0.32).

Muscovite Ar–Ar age. The Ar–Ar analytical data of Sample YJW-8-B are summarized in Table 4. Age spectra and inverse isochrons are plotted in Fig. 11.

Muscovite from Sample YJW-8-B yields a plateau age of 154.2 ± 1.0 Ma (MSWD = 0.65) (Fig. 11a). All errors are quoted at the 2σ level. The plateau age comprises nine steps accounting for 85.9% of the total 39Ar released and agrees with the inverse isochron age of 154.0 ± 1.6 Ma (MSWD = 0.81) (Fig. 11b). The estimated initial 40Ar/36Ar is 296.9 ± 4.1%, which is identical to the present-day initial 40Ar/36Ar (295.5%). The characteristics of the spectra suggest the absence of argon loss and excess argon. In other words, the Ar–Ar system of the muscovite remained closed during the geological history of Sample YJW-8-B.

Discussion

Reclassification of granitic phases. Zoned plutons often require numerous magmatic intrusion pulses continuously emplaced over millions of years, because individual magmatic pulses commonly last for less than 100,000 years.7,8,10,23,43 The QGC exhibits normal zoning with the most differentiated phases (S1 and S2) in the central part. Each phase can be distinguished by their emplacement age, mineral assemblage and geochemistry. Different classification schemes for the QGC have been suggested. According to some studies, the equigranular biotite granite (S1) and the porphyritic biotite granite (S3) have been classified as the QGC.25,28,37,39 In contrast, other studies combined the porphyritic biotite granite (S3) with the porphyritic biotite granite (S4) that is located on the southern margin of the QGC.13,14,22,31,38 Additionally, the porphyritic biotite granite (S4) has been considered a separate phase by Guo et al. (2015)27. To clarify the relationship between different rock types with the QGC, we have undertaken a systematic study of petrology, geochronology and geochemistry of all five sections of the pluton.

Previous geochronological investigations have used diverse methods and obtained a variety of results (Table 5, Fig. 12). For the porphyritic biotite granite (P1), Liu et al. (1997) obtained a potassium feldspar 40Ar/39Ar plateau age of 183.17 ± 3.75 Ma. In contrast, Chen et al. (2016) obtained two zircon U–Pb ages of 157 ± 2 Ma and 158 ± 2 Ma using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)14. Similarly, Chen et al. (2014) obtained two zircon U–Pb ages of 160 ± 1 Ma and 156 ± 1 Ma using LA-ICP-MS35. Furthermore, Guo et al. (2015) obtained four younger ages based on zircon analyses using secondary ion mass spectrometry (SIMS): 153.4 ± 1.6 Ma, 152.5 ± 1.2 Ma, 154.5 ± 1.3 Ma and 152.3 ± 1.2 Ma, which were identical (within error) to the zircon ages of 153 ± 3 Ma27,28 determined using sensitive high-resolution ion microprobe (SHRIMP). Overall, the previous ages of the P1 granite range from 183.2 to 152.3 Ma.

The equigranular biotite granite (P2) can be classified into two groups. (1) One group consists of medium- and coarse-grained equigranular biotite granite, for which Liu et al. (1997) obtained a potassium feldspar 40Ar/39Ar plateau date of 162.55 ± 3.25 Ma. In addition, Chen et al. (2016) obtained two slightly younger zircon U–Pb ages of 157 ± 2 Ma and 158 ± 2 Ma using LA-ICP-MS, which agreed with the younger zircon LA-ICP-MS U–Pb age of 155 ± 2 Ma obtained by Chen et al. (2014)34. However, Li et al. (2004) obtained a SHRIMP zircon U–Pb age of 151 ± 3 Ma, which was consistent with the muscovite 40Ar/39Ar age of 149.3 ± 3.5 Ma obtained by Yin et al. (2002)29,30. (2) The other group is fine-grained equigranular biotite granite, for which Yin et al. (2002) obtained a muscovite 40Ar/39Ar age of 137.4 ± 3.3 Ma. In addition, Chen et al. (2016) did not classify the equigranular granite into two groups with distinct grain sizes, and they obtained two zircon U–Pb ages of 158 ± 2 Ma and 155 ± 1 Ma using LA-ICP-MS35. In summary, the P2 granite was emplaced at 137.4–162.6 Ma.

For the granite porphyry (P3), Chen et al. (2016) obtained a zircon U–Pb age of 154 ± 1 Ma. Liu et al. (1997) obtained a potassium feldspar 40Ar/39Ar plateau date of 144.41 ± 2.83 Ma. Together, these ages indicate that the emplacement of the P3 granite occurred at 154.0–144.4 Ma.
| Phase | LLD (%) |
|-------|---------|
| Sample | GL-12 | GL-13 | 315–35 | 315–36 | 490–21 | 490–24 |
| SiO2 (%) | 19 | 72.97 | 73.18 | 73.13 | 72.88 | 73.61 | 73.49 |
| Al2O3 | 0.3 | 13.41 | 13.97 | 13.76 | 13.89 | 15.07 | 14.30 |
| Fe2O3 | 0.31 | 3.83 | 1.17 | 1.38 | 1.42 | 0.825 | 1.07 |
| MgO | 0.2 | 1.89 | 0.255 | 0.279 | 0.319 | 0.090 | 0.268 |
| CaO | 0.1 | 0.743 | 1.92 | 1.37 | 1.26 | 0.694 | 1.54 |
| Na2O | 0.3 | 6.27 | 3.51 | 3.07 | 3.51 | 4.15 | 1.58 |
| K2O | 0.1 | 5.41 | 4.95 | 5.08 | 4.92 | 4.61 | 5.36 |
| MnO | 0.02 | 0.074 | 0.025 | 0.047 | 0.027 | 0.044 | 0.088 |
| TiO2 | 0.02 | 0.166 | 0.158 | 0.161 | 0.179 | 0.008 | 0.009 |
| P2O5 | 0.01 | 0.079 | 0.066 | 0.062 | 0.070 | 0.041 | 0.039 |
| LOI | 0.0001 | 0.610 | 0.833 | 1.71 | 1.61 | 0.917 | 2.33 |
| FeO | 0.18 | 1.03 | 0.65 | 0.792 | 1.05 | 0.67 | 0.862 |
| Li (ppm) | 7.8 | 67.1 | 50.1 | 67.7 | 63.5 | 192 | 29.7 |
| Be | 0.27 | 12.0 | 11.5 | 15.6 | 7.32 | 7.75 | 19.5 |
| Sc | 1.8 | 8.05 | 7.52 | 8.39 | 8.62 | 5.76 | 6.56 |
| V | 11.5 | 11.2 | 11.0 | 10.5 | 10.9 | 1.77 | 2.04 |
| Cr | 2 | 2.56 | 2.58 | 1.97 | 4.24 | 1.44 | 1.20 |
| Co | 2.4 | 3.33 | 0.76 | 1.06 | 0.99 | 0.901 | 0.13 |
| Ni | 4.9 | 2.85 | 1.61 | 1.25 | 2.13 | 1.26 | 0.97 |
| Cu | 6.4 | 7.12 | 3.14 | 3.67 | 4.46 | 1.31 | 1.65 |
| Zn | 16 | 19.1 | 14.5 | 15.1 | 18.0 | 17.5 | 24.0 |
| Ga | 2.1 | 19.7 | 19.5 | 20.2 | 20.6 | 33.8 | 31.1 |
| Ge | 0.1 |
| Rb | 9.6 | 541 | 532 | 7.44 | 683 | 1072 | 976 |
| Sr | 48 | 52.8 | 66.6 | 71.6 | 55.5 | 9.85 | 16.2 |
| Zr | 21 | 121 | 101 | 112 | 122 | 38.2 | 36.6 |
| Nb | 1.9 | 47.5 | 51.0 | 59.5 | 59.7 | 24.1 | 23.8 |
| Mo | 0.22 | 12.0 | 1.26 | 2.22 | 1.77 | 1.52 | 0.52 |
| Cd | 0.027 |
| In | 0.024 | 0.039 | 0.034 | 0.097 | 0.11 | 0.086 | 0.097 |
| Sn | 0.88 | 0.16 | 0.094 | 0.094 | 0.077 | 0.077 | 0.11 |
| Te | 0.02 |
| Cs | 0.72 | 26.8 | 24.4 | 27.9 | 24.8 | 33.9 | 23.8 |
| Ba | 31 | 149 | 207 | 209 | 150 | 50.2 | 45.0 |
| Hf | 0.54 | 5.89 | 5.49 | 5.57 | 6.06 | 5.14 | 4.47 |
| Ta | 0.124 | 8.02 | 7.84 | 10.7 | 10.8 | 22.8 | 16.5 |
| W | 0.24 | 15.8 | 17.6 | 99.7 | 47.9 | 51.1 | 52.0 |
| Tl | 0.09 | 2.28 | 2.16 | 3.87 | 3.77 | 4.65 | 4.96 |
| Pb | 7.6 | 27.9 | 24.7 | 38.5 | 41.0 | 38.5 | 26.6 |
| Bi | 0.055 | 10.2 | 1.93 | 0.84 | 0.59 | 7.22 | 5.82 |
| Th | 1.5 | 67.8 | 44.1 | 66.3 | 68.2 | 13.3 | 16.1 |
| U | 0.67 | 31.9 | 24.0 | 34.2 | 33.4 | 14.6 | 18.1 |
| Y | 3.3 | 64.3 | 64.1 | 83.1 | 83.8 | 123 | 184 |
| La | 4.8 | 43.3 | 42.9 | 45.4 | 46.3 | 22.6 | 24.7 |
| Ce | 8.7 | 87.1 | 79.6 | 92.8 | 94.1 | 43.9 | 61.3 |
| Pr | 1.2 | 9.97 | 8.66 | 11.1 | 11.6 | 8.46 | 8.84 |
| Nd | 3.9 | 34.2 | 28.9 | 39.6 | 42.0 | 33.7 | 35.7 |
| Sm | 0.8 | 7.43 | 6.48 | 9.54 | 10.1 | 14.5 | 14.7 |
| Eu | 0.17 | 0.53 | 0.54 | 0.50 | 0.48 | 0.022 | 0.023 |
| Gd | 0.67 | 7.33 | 6.66 | 9.27 | 9.75 | 13.6 | 15.4 |
| Tb | 0.11 | 1.49 | 1.40 | 1.96 | 2.07 | 3.61 | 4.12 |
| Dy | 0.54 | 9.57 | 9.08 | 12.6 | 13.2 | 23.2 | 27.2 |
| Ho | 0.1 | 2.04 | 1.98 | 2.66 | 2.77 | 4.43 | 5.34 |
| Er | 0.34 | 6.60 | 6.50 | 8.25 | 8.87 | 13.5 | 19.7 |

Continued
| Phase | Phase 1 | Phase 2 | Phase 3 |
|-------|---------|---------|---------|
| Section | LLD (%) | Section 1 | Section 2 | Section 3 | Section 4 | Section 5 |
| Sample | | GL-12 | GL-13 | 315–35 | 315–36 | 490–21 | 490–24 | 490–9 | 490–10 | SZY-490-5a | SZY-490-5b | SZY-490-4a | SZY-490-4b | 490–2 | 490–3 | SZY-490-1a | SZY-490-1b |
| Tm | 0.053 | 1.16 | 1.13 | 1.41 | 1.54 | 2.48 | 2.93 | | | | | | | | | | | |
| Yb | 0.3 | 8.48 | 8.31 | 10.1 | 11.0 | 18.4 | 21.2 | | | | | | | | | | | |
| La | 0.046 | 1.34 | 1.33 | 1.59 | 1.70 | 2.68 | 3.14 | | | | | | | | | | | |
| Lu/Y | 3.66 | 3.71 | 3.24 | 3.01 | 0.88 | 0.84 | | | | | | | | | | | | |
| Si | 0.22 | 0.25 | 0.16 | 0.15 | 0.005 | 0.005 | | | | | | | | | | | |
| Phase 2 | Phase 3 | |
| Section | LLD (%) | Section 4 | Section 5 |
| Sample | | GL-12 | GL-13 | 315–35 | 315–36 | 490–21 | 490–24 | 490–9 | 490–10 | SZY-490-5a | SZY-490-5b | SZY-490-4a | SZY-490-4b | 490–2 | 490–3 | SZY-490-1a | SZY-490-1b |
| SiO₂ (%) | 73.76 | 73.69 | 76.63 | 76.72 | 74.52 | 74.52 | 70.32 | 71.17 | 73.64 | 73.62 | | | | | | | | |
| Al₂O₃ | 14.96 | 14.80 | 13.17 | 13.20 | 14.38 | 14.37 | 14.53 | 14.43 | 12.47 | 12.45 | | | | | | | | |
| TiO₂ | 0.836 | 0.953 | 0.046 | 0.030 | 0.40 | 0.39 | 2.33 | 2.37 | 0.88 | 0.86 | | | | | | | | |
| MgO | 0.104 | 0.107 | 0.11 | 0.11 | 0.055 | 0.067 | 0.466 | 0.456 | 0.43 | 0.43 | | | | | | | | |
| CaO | 0.746 | 0.797 | 1.06 | 1.05 | 0.61 | 0.61 | 1.38 | 1.41 | 1.45 | 1.45 | | | | | | | | |
| Na₂O | 3.66 | 3.71 | 3.24 | 3.01 | 0.88 | 0.84 | | | | | | | | | | | | |
| δEu | 0.22 | 0.25 | 0.16 | 0.15 | 0.005 | 0.005 | | | | | | | | | | | | |
| Phase 3 | |
| Section | LLD (%) | Section 4 | Section 5 |
| Sample | | GL-12 | GL-13 | 315–35 | 315–36 | 490–21 | 490–24 | 490–9 | 490–10 | SZY-490-5a | SZY-490-5b | SZY-490-4a | SZY-490-4b | 490–2 | 490–3 | SZY-490-1a | SZY-490-1b |
| SiO₂ (%) | 73.76 | 73.69 | 76.63 | 76.72 | 74.52 | 74.52 | 70.32 | 71.17 | 73.64 | 73.62 | | | | | | | | |
| Al₂O₃ | 14.96 | 14.80 | 13.17 | 13.20 | 14.38 | 14.37 | 14.53 | 14.43 | 12.47 | 12.45 | | | | | | | | |
| TiO₂ | 0.836 | 0.953 | 0.046 | 0.030 | 0.40 | 0.39 | 2.33 | 2.37 | 0.88 | 0.86 | | | | | | | | |
| MgO | 0.104 | 0.107 | 0.11 | 0.11 | 0.055 | 0.067 | 0.466 | 0.456 | 0.43 | 0.43 | | | | | | | | |
| CaO | 0.746 | 0.797 | 1.06 | 1.05 | 0.61 | 0.61 | 1.38 | 1.41 | 1.45 | 1.45 | | | | | | | | |
| Na₂O | 3.66 | 3.71 | 3.24 | 3.01 | 0.88 | 0.84 | | | | | | | | | | | | |
| δEu | 0.22 | 0.25 | 0.16 | 0.15 | 0.005 | 0.005 | | | | | | | | | | | | |

Continued
Table 3. Major and trace element composition of samples from the main intrusive stages of the QGC. LOI, Loss on ignition; LLD, Lower limit of detection.

| Phase | Phase 2 | Phase 3 |
|-------|---------|---------|
| Section 4 | Section 5 | Section 5 |
| Sample | 490–9 | 490–10 | SZY-490-5a | SZY-490-5b | SZY-490-4a | SZY-490-4b | 490–2 | 490–3 | SZY-490-1a | SZY-490-1b |
| Nd | 46.7 | 44.7 | 37.6 | 40.3 | 48.3 | 45.4 | 59.5 | 58.8 | 61.4 | 64.0 |
| Sm | 17.1 | 17.2 | 14.9 | 16.0 | 18.8 | 17.1 | 10.3 | 10.3 | 10.9 | 11.2 |
| Eu | 0.06 | 0.051 | 0.007 | 0.009 | 0.019 | 0.016 | 1.02 | 0.93 | 0.78 | 0.77 |
| Gd | 16.3 | 17.7 | 13.0 | 7.02 | 7.90 | 7.91 | 9.53 | 9.49 | 9.35 | 9.61 |
| Tb | 3.99 | 4.33 | 3.60 | 3.85 | 4.16 | 3.78 | 1.48 | 1.48 | 1.58 | 1.60 |
| Dy | 23.3 | 27.9 | 22.2 | 24.4 | 25.2 | 23.4 | 7.97 | 8.10 | 8.39 | 8.42 |
| Ho | 4.90 | 5.48 | 4.31 | 4.67 | 4.85 | 4.27 | 1.55 | 1.59 | 1.57 | 1.62 |
| Er | 14.3 | 15.8 | 12.5 | 14.1 | 14.0 | 12.5 | 4.57 | 4.80 | 4.60 | 4.76 |
| Yb | 16.6 | 17.5 | 16.6 | 19.4 | 17.1 | 15.2 | 4.56 | 4.65 | 4.68 | 4.73 |
| Lu | 2.41 | 2.53 | 2.44 | 2.94 | 2.43 | 2.19 | 0.67 | 0.70 | 0.69 | 0.69 |
| La/Y | 2.41 | 2.56 | 2.62 | 3.07 | 2.74 | 2.48 | 0.69 | 0.71 | 0.82 | 0.82 |
| Y | 0.011 | 0.009 | 0.001 | 0.002 | 0.002 | 0.005 | 0.005 | 0.32 | 0.29 | 0.23 | 0.23 |

...
Genetic relationship between plutonism and mineralization. Liu et al. (1997) obtained a garnet/pyroxene Sm–Nd age for the QGC of 160.8 ± 2.4 Ma, which was consistent (within error) with the Sm–Nd age for the massive-type skarn of 157 ± 6.2 Ma obtained by Lu et al. (2003)\textsuperscript{25,39}. In contrast, according to the analyses of samples from massive-type skarn and vein-type greisen, Li et al. (2004) obtained a much younger Sm–Nd age of 149 ± 2 Ma, which matched the molybdenite Re-Os age of 151 ± 3.5 Ma obtained by Li et al. (1996) and a quartz fluid inclusion Ar–Ar age of 153.7 ± 0.9 Ma obtained by Wang et al. (2016)\textsuperscript{28,30,31}. Furthermore, Yin et al. (2002) used muscovite 40Ar/39Ar dating to suggest that the timing of greisenization and its associated W–Sn–Mo–Bi mineralization ranged from 145 to 148 Ma\textsuperscript{29}. Collectively, the age discrepancy is up to ~ 20 Myr.

Based on our field observations, the W–Sn–Mo–Bi mineralization of the Shizhuyuan deposit is intimately associated with greisenization; therefore, muscovite Ar–Ar dating is ideal candidate for assessing the timing of hydrothermal mineralization. According to our analytical results, greisen-type mineralization occurred ca. 154.2 ± 1.0 Ma. Within error, this age is consistent with molybdenite Re-Os dating (151 ± 3.5 Ma) conducted by Li et al. (1996)\textsuperscript{31}. Wang et al. (2016) obtained a muscovite Ar–Ar age of 153.7 ± 0.9 Ma by carrying out

Figure 7. Harker diagram for the QGC.
geochronological Ar–Ar dating on a fluid inclusion in quartz and coexisting muscovite. This age also agrees with our dates.

In conclusion, the QGC has two impacts on the Shizhuyuan deposit. (1) Heat supply: According to the thermal model of McLaren et al. (1999), the heat derived from the high-heat-producing granites reaches a maximum ~ 10 Myr after its emplacement. Furthermore, the thermal disturbances caused by the high-heat-producing granites can drive hydrothermal fluid convection, resulting in mineralization. For instance, the mineralization in the Mount Elliott Cu-Au deposits, Australia, was produced by hydrothermal convection driven by the heat released from its associated high-heat-producing granite. The volume heat of the QGC estimated by the U, Th, and K contents is 5.89–14.30 μWm⁻³ (volume heat of high-heat-producing granite > 5 μWm⁻³), indicating their high heat production. Therefore, when mineralization occurred, the heat anomaly resulting from the QGC was quite strong (nearly its maximum strength), which promoted the development of hydrothermal convection around the QGC, leading to the generation of the Shizhuyuan deposit. (2) Metal supply: Field observations reveal that the Shizhuyuan W–Sn–Mo–Bi deposit is located at the endo-contact of the skarn and the porphyritic biotite granite (S₁, S₂) and equigranular granite (S₃, S₄), demonstrating their close spatial relationship. In addition, as shown in Fig. 8a, the W contents in the S₁, S₂, S₃, and S₄ granites are mostly 40–60 ppm; therefore, the QGC can supply sufficient metal for mineralization.

Figure 8. SiO₂ vs Sr, Ba, Zr, P₂O₅, W and F for the QGC.
Figure 9. REE patterns for the QGC.

Figure 10. La/Y vs δEu for the QGC.

Table 4. Ar–Ar stepwise heating data for muscovite samples from the QGC and the Shizhuyuan deposit.

| Sample  | T (°C) | (40Ar/39Ar)m | (36Ar/39Ar)m | (37Ar0/39Ar)m | (38Ar/39Ar)m | 40Ar(%) | 40Ar*/39Ar | 39Ar Age ± 1σ (Ma) | Age (Ma) ± 1σ | Ar* (Cum.) (%) |
|---------|--------|--------------|--------------|---------------|--------------|---------|------------|------------------|----------------|----------------|
| YJW-8-B | 700    | 6.8485       | 0.0000       | 1.3186        | 2.4          | 49.7199 | 0.1        | 350 23           |                |                |
|         | 760    | 58.7071      | 0.1103       | 0.0376        | 44.48        | 26.1126 | 0.87       | 192.3 2.2       |                |                |
|         | 800    | 35.7398      | 0.0364       | 0.0215        | 69.87        | 24.9724 | 2.63       | 184.3 2.1       |                |                |
|         | 840    | 27.9391      | 0.0189       | 0.0175        | 79.96        | 22.3392 | 14.1       | 165.7 1.6       |                |                |
|         | 870    | 23.4786      | 0.009        | 0.0156        | 88.7         | 20.8253 | 36.67      | 155 1.5         |                |                |
|         | 900    | 21.9468      | 0.0043       | 0.0148        | 94.16        | 20.6644 | 62.73      | 153.8 1.5       |                |                |
|         | 930    | 22.1158      | 0.0051       | 0.015         | 93.11        | 20.5911 | 81.93      | 153.3 1.5       |                |                |
|         | 960    | 22.4984      | 0.0063       | 0.0157        | 91.67        | 20.6253 | 86.51      | 153.5 1.5       |                |                |
|         | 1000   | 22.6302      | 0.0066       | 0.0154        | 91.3         | 20.662   | 90.32      | 153.8 1.5       |                |                |
|         | 1040   | 25.2333      | 0.0137       | 0.0149        | 83.91        | 21.1641 | 91.16      | 157.4 1.7       |                |                |
|         | 1080   | 22.7969      | 0.0075       | 0.0158        | 90.22        | 20.5658 | 96.05      | 153.1 1.5       |                |                |
|         | 1200   | 25.0391      | 0.0146       | 0.017         | 82.71        | 20.7107 | 98.83      | 154.1 1.5       |                |                |
|         | 1400   | 50.3407      | 0.0999       | 0.0332        | 41.32        | 20.8003 | 100        | 154.8 1.9       |                |                |
In summary, the QGC is temporally and spatially associated with the formation of the Shizhuyuan W–Sn–Mo–Bi deposit. Furthermore, the QGC provided heat and metals for these deposits.

Conclusions

1. According to zircon LA-ICP-MS dating, the emplacement time of the Qianlishan granite complex is constrained to 155–151.7 Ma.

2. Based on petrological and geochemical characteristics, the Qianlishan granite complex can be classified into four phases: porphyritic biotite granites (Phase 1, Section 1); porphyritic biotite granites (Phase 2, Section 2); equigranular biotite granite (Phase 3, Sections 3 and 4); and granite porphyry dikes (Phase 4, Section 5).

3. The Qianlishan granite complex is temporally and spatially associated with the formation of the Shizhuyuan W–Sn–Mo–Bi deposit (mineralization time: 154 Ma).

Appendix: Sampling and analytical methods—General remarks on sampling

Granite samples. Five samples (Samples GL-13, 315–36, 490–21, 490–10, and 490–2) were collected from the QGC for dating analysis of accessory minerals (Figs. 2, 4; Table 6). Sixteen samples (Samples GL-12, GL-13, 315–35, 315–36, 490–21, 490–24, 490–9, 490–10, SZY-490-4a, SZY-490-4b, SZY-490-5a, SZY-490-5b, 490–2, 490–3, SZY-490-1a, and SZY-490-1b) were obtained for whole-rock geochemical analysis (Figs. 2, 4; Table 6).

Samples GL-12 and GL-13, which represent fine-grained porphyritic biotite granite ($S_2$), were collected on the sides of Taipingli Road (25°46′04″ N, 113°09′42″ E). Samples 315–36 and 315–35 were collected from a microfine-grained porphyritic biotite granite ($S_2$) in the main transport tunnel on Level 500. Samples 490–21 and 490–24 are medium- to coarse-grained equigranular biotite granites ($S_3$) that were collected in Tunnel 490. Samples 490–9, 490–10, SZY-490-4a, SZY-490-4b, SZY-490-5a, and SZY-490-5b are fine-grained equigranular...
biotite granites (S4) that were collected in Tunnel 490. Samples 490–2, 490–3, SZY-490-1a and SZY-490-1b were collected from granite porphyry dikes (S5) in Tunnel 490.

In total, sixteen granite samples and one stockwork greisen were collected with a sledgehammer. Each sample weighed 5 to 10 kg. Samples GL-12 and GL-13 were fresh massive rocks sampled from the outcrops of granites

| Phase | Section | Lithology | Mineral for dating | Method | Age (Ma) | Age |
|-------|---------|-----------|--------------------|--------|----------|-----|
| 1     | 1       | Fine-grained porphyritic biotite granite | Zircon | (LA-ICP-MS) | 155 ± 1.9 | 155 |
|       |         |          | K-feldspar | (40Ar-39Ar) | 183.17 ± 3.75 | 183.17 |
|       |         |          | Zircon     | (LA-ICP-MS) | 160.3 ± 1.1 | 160.3 |
|       |         |          | Zircon     | (SIMS U-Pb) | 153.4 ± 1.6; 152.5 ± 1.2 | 153.4 |
|       |         |          | Biotite    | (K-Ar)     | 144.5 ± 3.4 | 144.5 |
|       |         |          | Muscovite  | (K-Ar)     | 142.6 ± 2.8 | 142.6 |
|       |         |          | Zircon     | (SIMS U-Pb) | 154.5 ± 1.3; 152.3 ± 1.2 | 154.5 |
|       |         |          | Zircon     | (LA-ICP-MS) | 157 ± 2; 158 ± 2 | 157 |
|       |         |          | Zircon     | SHRIMP     | 153 ± 3 | 153 |
|       |         |          | whole-rock | (Rb-Sr)    | 152 ± 9 | 152 |
|       | 2       | Microfine-grained porphyritic biotite granite | Zircon | (LA-ICP-MS) | 154 ± 0.88 | 154.4 |
|       |         |          | Zircon     | (SIMS U-Pb) | 154.5 ± 1.3; 152.3 ± 1.2 | 154.5 |
|       |         |          | Zircon     | (LA-ICP-MS) | 157 ± 2; 158 ± 2 | 157 |
|       |         |          | Zircon     | SHRIMP     | 153 ± 3 | 153 |
|       |         |          | whole-rock | (Rb-Sr)    | 152 ± 9 | 152 |
|       | 3       | Medium- and coarse-grained equigranular biotite granite | K-feldspar | (40Ar-39Ar) | 162.5 ± 3.25 | 162.55 |
|       |         |          | Muscovite  | (K-Ar)     | 149.3 ± 3.5 | 149.3 |
|       |         |          | Zircon     | (SIMS U-Pb) | 152.4 ± 1.2; 151.6 ± 1.2 | 152.4 |
|       |         |          | Zircon     | (LA-ICP-MS) | 158 ± 2; 158 ± 8 | 158 |
|       |         |          | Zircon     | SHRIMP     | 151 ± 3 | 151 |
|       |         |          | whole-rock | (Rb-Sr)    | 137 ± 7 | 137 |
|       | 4       | Fine-grained equigranular biotite granite | Zircon | (LA-ICP-MS) | 151.7 ± 3.3 | 151.7 |
|       |         |          | K-feldspar | (40Ar-39Ar) | 158.07 ± 3.16 (Pegmatite) | 158.07 |
|       |         |          | Muscovite  | (K-Ar)     | 137.4 ± 3.3 | 137.4 |
|       | 5       | Granite porphyry dykes | Zircon | (LA-ICP-MS) | 153.7 ± 1.2 | 153.7 |
|       |         |          | K-feldspar | (40Ar-39Ar) | 144.41 ± 2.83 | 144.41 |
|       |         |          | Zircon     | (LA-ICP-MS) | 154 ± 1 | 154 |
|       |         |          | whole-rock | (Rb-Sr)    | 131 ± 1 | 131 |

Table 5. Ages of the QGC from this study and the literature. Reference: 1. This study; 2. Chen et al. (2016)13; 3. Guo et al. (2015)27; 4. Li et al. (2004)28; 5. Yin et al. (2002)29; 6. Mao et al. (1998)26; 7. Liu et al. (1997)25; 8. Chen et al. (2014)13.

Figure 12. Summary of the dating of the QGC from previous publications and this study. Zrn, Zircon; Kfs, K-feldspar; Bt, Biotite; Ms, Muscovite (Whitney DL and Evans BW et al. 2010)53. WR, whole-rock. Reference: 1. This study; 2. Chen et al. 201613; 3. Guo et al. 201527; 4. Li et al. 200428; 5. Yin et al. 200229; 6. Mao et al. 199826; 7. Liu et al. 199725; 8. Chen et al. 201413.

In total, sixteen granite samples and one stockwork greisen were collected with a sledgehammer. Each sample weighed 5 to 10 kg. Samples GL-12 and GL-13 were fresh massive rocks sampled from the outcrops of granites.

Figure 12. Summary of the dating of the QGC from previous publications and this study. Zrn, Zircon; Kfs, K-feldspar; Bt, Biotite; Ms, Muscovite (Whitney DL and Evans BW et al. 2010). WR, whole-rock. Reference: 1. This study; 2. Chen et al. 2016; 3. Guo et al. 2015; 4. Li et al. 2004; 5. Yin et al. 2002; 6. Mao et al. 1998; 7. Liu et al. 1997; 8. Chen et al. 2014.
beside Taipingli Road, and the weathered parts were chipped off using a hammer. All the other samples were fresh rocks collected with sledgehammers from granite outcrops in the tunnels.

**Stockwork greisen.** Sample YJW-8-B, consisting of massive rock, was collected using a sledgehammer from stockwork greisen in the main transport tunnel, Level 350. It represents the greisen associated with W–Sn–Mo–Bi mineralization.

In summary, we conducted zircon LA-ICP-MS U–Pb dating and whole-rock major and trace element analyses on all five sections of the QGC. Muscovite Ar–Ar dating was carried out on the stockwork W–Sn–Mo–Bi to constrain the ore-forming age of the Shizhuyuan deposit.

**Thin-section preparation and optical petrography.** Billets with a size of ~ 45 × 25 × 15 mm were cut from fresh field samples using a diamond blade. Then, they were planed and mounted on a 28 × 48 mm standard petrographic carrier glass using epoxy. After polishing with abrasive powders, the thin sections reached a thickness of 30 μm. To identify the mineralogies and textures of the rocks, polished thin sections were studied under a binocular microscope and an Olympus BX 51 polarizing microscope at China University of Geosciences (Beijing) (CUGB).

**Zircon LA-ICP-MS U–Pb dating.** Five fresh samples weighing approximately 5 kg (Samples GL-13, 315–36, 490–21, 490–10, and 490–2) of the Qianlishan plutonic rocks were processed at the Central Laboratory of China Railway Resources Group. Zircon grains subjected to U–Pb dating were separated from these samples using conventional heavy liquid and magnetic techniques. Then, approximately 100 of the best-quality zircon grains from each sample were handpicked under a binocular microscope. These grains were mounted in epoxy and then polished. After the mounts were prepared, the grains were photographed using optical microscopy and cathodoluminescence (CL) imaging to reveal their internal morphologies, which were used to select grains and choose analytical spots. The CL images were obtained using a HITACHI S3000-N scanning electron microscope equipped with a Robinson backscattered-electron detector and a Gatan Chroma CL imaging system. These samples were analyzed using an Agilent 7900 quadrupole ICP-MS with a 193 nm coherent Ar-F laser and Resonetics S155 ablation cell in CODES (Centre for Ore Deposit and Earth Sciences) of Tasmania University. The NIST610 standard used for Pb correction was analyzed after every 15 unknowns. Th/U and Pb/Th mass bias downhole fractionation and instrument drift were corrected with the 91,500 zircon standard according to Wiedenbeck et al. (1995)38. Each zircon analysis comprised 30 s of blank gas measurements and 30 s of analysis time. The analyzed spots were 29 μm in size, and the laser was emitted at a frequency of 5 Hz with an energy density of approximately 2 J/cm². Particles ablated by the laser were carried out by the flow of He carrier gas at a rate of 0.35 l/min into the chamber to be mixed with argon gas. Then, they were carried to the plasma torch. The Temora standard of Black et al. (2003) and the Plesovice standard of Sláma et al. (2008) were applied36,57. Data processing was carried out using concordia intercept ages on the Tera-Wasserburg plot utilizing ISOPLOT (Ludwig, v. 3.75, 2012, copyright@ BGC Berkeley Geochronology Center, 2006, available from: http://www.bgc.org/isoplot_etc/isoplot.html). The method of data reduction was described in Halpin et al. (2014)36. The estimation of random and systematic uncertainties followed the method in Paton et al. (2010)39.

**Whole-rock major and trace element analyses.** Billets ~ 70 × 50 × 30 mm in size were cut from the selected fresh samples. They were cleaned with tap water and powdered to a grain size of < 200 mesh using an agate mill. Major and trace element analyses were carried out at the Central Laboratory of China Railway Resources Group. Zircon grains subjected to U–Pb dating were separated from these samples using a diamond blade. Then, they were planed and mounted on a 28 × 48 mm standard petrographic carrier glass using epoxy. After polishing with abrasive powders, the thin sections reached a thickness of 30 μm. To identify the mineralogies and textures of the rocks, polished thin sections were studied under a binocular microscope and an Olympus BX 51 polarizing microscope at China University of Geosciences (Beijing) (CUGB).

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### Table 6. Lithology and location of samples.

| Section | Sample       | Lithology                                      | Location                                      |
|---------|--------------|------------------------------------------------|-----------------------------------------------|
| 1       | GL-13        | Fine-grained porphyritic biotite granite       | Taipingli Road, N 25°46′04″, E113°09′42″, H 272 m |
| 2       | GL-12        | Fine-grained porphyritic biotite granite       | Taipingli Road, N 25°46′04″, E113°09′42″, H 272 m |
| 3       | 315–36       | Fine-grained porphyritic biotite granite       | Main transport tunnel, Lever 500              |
| 3       | 315–35       | Fine-grained porphyritic biotite granite       | Main transport tunnel, Lever 500              |
| 3       | 490–21       | Coarse-grained equigranular granite           | Crossing between Tunnel C1 and P1, Level 490  |
| 3       | 490–24       | Coarse-grained equigranular granite           | Crossing between Tunnel C1 and P1, Level 490  |
| 4       | 490–10       | Fine-grained equigranular granite             | Crossing between Tunnel P4 and C6–C7, Level 490 |
| 4       | SZY-490-5a   | Fine-grained equigranular granite             | Crossing between Tunnel C6 and P4, Level 490  |
| 4       | SZY-490-5b   | Fine-grained equigranular granite             | Crossing between Tunnel C6 and P4, Level 490  |
| 4       | SZY-490-4a   | Fine-grained equigranular granite             | Main transport tunnel, Lever 350              |
| 4       | SZY-490-4b   | Fine-grained equigranular granite             | Main transport tunnel, Lever 350              |
| 5       | 490–2        | Granitic porphyry                             | Main transport tunnel, Level 490              |
| 5       | 490–3        | Granitic porphyry                             | Main transport tunnel, Level 490              |
| 5       | SZY-490-1a   | Granitic porphyry                             | Main transport tunnel, Level 490              |
| 5       | SZY-490-1b   | Granitic porphyry                             | Main transport tunnel, Level 490              |
| YJW-8-B |              | Greisen                                        | Main transport tunnel, Lever 350              |
Muscovite Ar–Ar dating. The stockwork W–Sn–Mo–Bi (Type 3) ore has the highest average ore grade and the largest amount of ore; it thus represents the main stage of mineralization and is an ideal candidate for studying the mineralization time of this deposit.

In this study, one fresh sample (~120 × 80 × 30 mm) was collected for muscovite dating from a greisen vein with mineralization (Type 3) at the contact with the skarn in Tunnel 450. As shown in Fig. 3, this sample contained mainly muscovite (~92%) and minor quartz (~5%) and K-feldspar (~2%). This muscovite sample was crushed to a size of 40–60 mesh, and muscovite separates were carefully handpicked to a purity of over 99% under a binocular microscope. After being washed in an ultrasonic bath using methanol and deionized water, the muscovite crystals were wrapped in aluminum foil and stacked in quartz vials. Then, they were irradiated for 1442 min in the B4 position of the swimming pool reactor at the Chinese Institute of Atomic Energy, Beijing. The Fangshan biotite standard (ZBH-25), which has an age of 132.7 ± 1.2 Ma and a potassium content of 7.6%, was used to monitor the neutron flux (2.65 × 10^{13} n cm^{-2} s^{-1}). After the samples underwent cooling for approximately 100 days, step-heating Ar/Ar analyses were conducted using an MM1200B mass spectrometer at the Ar–Ar laboratory, Institute of Geology, Chinese Academy of Geological Sciences, Beijing. The instrumental conditions and analytical methodology were described by. Step-heating analyses were performed in a double-vacuum resistance furnace; at each temperature step, the muscovite crystals were heated for 10 min and then purified for 30 min. The Ca and K correction factors calculated based on the analyses of K_2SO_4 and CaF_2 double-vacuum resistance furnace; at each temperature step, the muscovite crystals were heated for 10 min and then purified for 30 min. The Ca and K correction factors calculated based on the analyses of K_2SO_4 and CaF_2 were (36Ar/37Ar)_Ca = 0.0002389, (40Ar/39Ar)_K = 0.004782 and (39Ar/37Ar)_Ca = 0.000806. A 40K decay constant of 5.543 × 10^{-10} year^{-1} was used in the age calculations. ISOPLOT software (Ludwig, v. 3.75, 2012, copyright@ BGC Berkeley Geochronology Center, 2006, available from: http://www.bgc.org/isoplot_etc/isoplot.html) was used for data processing. The errors in the plateau ages are quoted at the 2σ level.

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**Author contributions**
B.Z. provided the scientific idea of this paper. Y.L., T.L. and F.L. complete the field investigation. Y.L., B.Z., L.V.D. conducted the U-Pb dating analysis. Y.L., L.V.D. completed all the data analysis. Y.L. wrote the main manuscript text and prepared all the figures and tables. Y.L., D.Z. and F.L. provided funding. All authors reviewed the manuscript. L.V.D., B.Z., D.Z., M.W. offered constructive comments on this manuscript and improved the manuscript significantly.

**Competing interests**
The authors declare no competing interests.

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