The origin of the world class tin-polymetallic deposits in the Gejiu district, SW China: Constraints from metal zoning characteristics and $^{40}$Ar–$^{39}$Ar geochronology

Yanbo Cheng a,b,c,*, Jingwen Mao c, Zhaoshan Chang b, Franco Pirajno d

a Faculty of Earth Science and Mineral Resources, China University of Geosciences, Beijing, 100083, China
b School of Earth and Environmental Sciences, James Cook University, Townsville, 4811, Australia
c School of Earth and Environment, University of Western Australia, 35 Stirling Highway, Crawley WA 6008, Australia
d MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, 100037, China

A B S T R A C T

The Gejiu tin-polymetallic deposits in the Western Cathaysia Block of South China comprise the world’s largest primary tin district, with a total resource of approximately 300 million metric ton ores, at an average grade of 1 wt% Sn. Tin polymetallic mineralization occurs in five deposits and has four ore types, i.e., greisen, skarn, stratabound cassiterite-sulfide (mostly oxidized) and vein type ore. In each deposit the orebodies typically occur in an extensive hydrothermal system centered on a shallow Late Cretaceous granitoid cupula. Metal zoning is well developed both vertically and horizontally over the entire district, from W+Be+Bi±Mo±Sn ores inside granite intrusions, to Sn+Cu-dominated ores at intrusion margins and farther out to Pb+Zn deposits in the surrounding host carbonate. This zoning pattern is similar to that of other hydrothermal deposits in other parts of the world, indicating a close genetic relationship between magmatism and mineralization. In this paper, we dated thirteen mica samples from all types of mineralization and from the five deposits in the Gejiu district. The ages range from $77.4 \pm 0.6$ Ma to $95.3 \pm 0.7$ Ma and are similar to the existing zircon U–Pb ages of the granitic intrusions ($77.4 \pm 2.5$–$85.8 \pm 0.6$), indicating a genetic relationship between the mineralization and the intrusions. Geological characteristics, metal zoning patterns and new geochronological data all indicate that the tin-polymetallic ores in the Gejiu district are hydrothermal in origin and are genetically related to the nearby granitic intrusions. It is unlikely that the deposits are syngenic, as has been proposed in recent years.

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1. Introduction

The Gejiu tin-polymetallic ore district is located approximately several tens of kilometers southeast of Gejiu city, Yunnan Province, SW China. It is one of the largest and oldest mining districts in the world. It has been mined since the Han dynasty (202 B.C. to 220 A.D.), intermittently for more than 2000 years. The Gejiu district comprises five Sn–Cu–Pb–Zn polymetallic deposits, namely Malage, Songshujiao, Gaosong, Laochang and Kafang, each containing approximately 300 Mt of Sn ores at an average grade of 1% Sn, another 300 Mt of Cu ores averaging 2% Cu, and 400 Mt of Pb–Zn ores with an average grade of 7% Pb + Zn. It is the largest tin deposit in the world. Exploration in this district is still finding more orebodies to date.

Tin polymetallic ores in the Gejiu district, characterized by extensive skarn alteration, multiple mineralization styles and well defined metal zoning around granitic cupolas, have long been considered genetically related to Cretaceous granites (e.g., 308 Geological Party, 1984; Luo, 1995; Mao et al., 2008; Peng, 1985; Zhao and Li, 1987; Zhuang et al., 1996). Theories based on this understanding have contributed a great deal to exploration efforts (e.g., 308 Geological Party, 1984; Jiang et al., 1997; Peng, 1985; Zhuang et al., 1996). However, as many orebodies are approximately stratabound, some authors have challenged this view, arguing that the ores may be syngenic (Jin, 1991; Peng, 1992; Zhou, 1988). Metacolloidal textures and resembling oolites aggregates have been found in some of the orebodies, leading to the speculation of a submarine exhalation hypothesis (Zhang et al., 2004; Zhou et al., 1997, 1999). Based on K–Ar, Ar–Ar and Pb–Pb dating on different minerals (see below for details), it has been argued that Sn polymetallic mineralization may be of VHMS style and/or SEDEX deposits (Li et al., 2006, 2009; Qian et al., 2011a, 2011b; Qin and Li, 2008; Qin et al., 2006). Dating is one of the most powerful tools that place constraints on the genesis of ore. However, the above-mentioned mineralisation ages have a wide range and are somewhat inconsistent. Qin et al. (2006) obtained several mica $^{40}$Ar–$^{39}$Ar ages ranging from $83.23 \pm 2.07$ to $205.11 \pm 4.38$ Ma, while another group of $200$ to $240$ Ma ages were obtained through the use of Pb–Pb methods on sulfides. Qin et al. (2006) and Li et al. (2009) reported K–Ar ages of $43.49 \pm 0.87$ Ma to $186.01 \pm 3.72$ Ma for cassiterite. These data were viewed as important evidence for the syngenetic model (Li et al., 2009; Qin and Li, 2008; Qin et al., 2006), as the ores were considered to be of Triassic ages.
In this study, we document the geological characteristics of the Gejiu district, demonstrating the clear metal zoning, both vertically and horizontally, around granitic intrusions in all deposits in the Gejiu district. Moreover, due to lack of precise and systematic mineralization dating, we have also completed Ar–Ar dating of 13 representative muscovite and phlogopite samples from all ore types to constrain the age of mineralization. Comparing these dating results with U–Pb zircon ages of the granitic intrusions in the Gejiu district provides further constraints on the ore genesis.

2. Regional geologic setting

The world class Gejiu tin polymetallic ore district is located on the western margin of the South China Block, adjacent to the Yangtze Craton in the north and the Sanjiang Fold Belt in the west (Fig. 1). It is bounded by the Mile–Shizong Fault to the north, the regional strike–slip Ailaoshan–Honghe Fault to the west, and the North Vietnam Block to the south. The Gejiu District is ~1600 km² in area and was a tectonic sag or depression for much of its geological history. Cambrian to Quaternary rock successions are well-preserved (mostly not exposed and not shown in Fig. 1), and the late Triassic to Cretaceous strata are preferentially exposed near and at the surface due to uplift associated with Yanshanian (Mesozoic) tectonic movements (308 Geological Party, 1984). Most of the outcrops in the Gejiu area consist of Middle Triassic Gejiu Formation carbonate (>3000 m thick), and Middle Triassic Falang Formation fine-grained clastic sediment and carbonate with interlayering mafic lavas (1800 to 2800 m thick; Qin and Li, 2008). Numerous faults are present in the Gejiu region, including the NNE-trending Longchahe, Jiaodingshan and Yangjiatian faults, the NE-trending Baishachong fault and the NS-trending Gejiu fault. The Gejiu fault, which is the dominant structure in the Gejiu District, divides the Gejiu area into its eastern and western sectors (Fig. 1), with the major deposits in the eastern sector. The Gejiu batholith is a prominent igneous body in this area, composed of Mesozoic gabbro, mafic microgranular enclaves (MMEs; Cheng et al., 2012), porphyritic biotite granite, equigranular biotite granite, syenites and mafic dykes. Mafic-intermediate rocks and alkaline rocks occur mostly in the western sector, while granitoids are distributed throughout the region. Granites in the vicinity of orebodies have intense greisen alteration, albite alteration and K-feldspar alteration, with or without skarns in carbonate wallrocks.

3. Characteristics of the Gejiu granitic batholith

The Gejiu granitic batholith has an outcrop area of ~300 km² and is one of the largest intrusions in the western Cathaysia Block (Fig. 1).
intruding the Mid-Triassic sedimentary rocks. Based on texture and mineralogy, the Gejiu granitic batholith comprises six phases (308 Geological Party, 1984; Cheng and Mao, 2010; Dai, 1996; Li, 1985; Lu, 1987; Zhuang et al., 1996), which are summarized below.

Phase 1 is represented by porphyritic biotite granite with large euhedral K-feldspar phenocrysts that mostly measure 3–5 cm in length, but that may reach up to 10 cm. Phase 1 is represented by the Longchahe stock in the western sector. The rock-forming minerals include plagioclase (–40%), quartz (15–20 vol.%), K-feldspar (10–25 vol.%) and biotite (10–20 vol.%). Accessory minerals are magnetite, titanite, apatite, zircon and allanite. Phase 2 is fine-grained porphyritic biotite granite, typically distributed around the Baishaya area, which is close to the Longchahe stock. The size and shape of phenocrysts vary in this phase. The major minerals are K-feldspar (–40 vol.%), plagioclase (–25 vol.%), quartz (–25 vol.%), and biotite (5–10 vol.%). The accessory minerals are the same as those from Phase 1. Phase 3 is porphyritic biotite granite with medium-grained euhedral to subhedral K-feldspar phenocrysts, which is best represented in the Malage, Songshujiao and Laochang ore deposits. Phenocryst size is generally between 1 and 3 cm, with larger phenocrysts reaching 6 cm. Minerals include plagioclase (–25 vol.%), K-feldspar (10–20 vol.%), quartz (–30 vol.%), and biotite (–10 vol.%), with magnetite, zircon, apatite, titanite, fluorite, allanite and tourmaline as accessory minerals. Phase 4 is a coarse to medium-grained equigranular biotite granite, mostly distributed in the Laongchong ore deposit and in the Shenxianshui, Baishachong and Kele areas. The major minerals include quartz (–30 vol.%), K-feldspar (–40 vol.%), plagioclase (–20 vol.%), and biotite (–5 vol.%). Accessory minerals include zircon, magnetite, monazite, apatite and minor titanite. Phase 5 is medium to fine-grained leucogranite in the Xinshan area of the Kafang deposit. Rocks of this phase are fine-grained equigranular and light in color, containing little or no biotite, and with a high content of quartz (–40 vol.%), K-feldspar (–35 vol.%), and plagioclase (–30 vol.%). Accessory minerals include zircon, apatite and monazite. Phase 6 refers to the fine-grained equigranular granite dyke swarm and small stocks around granite margins, especially around the Baishachong and Shenxianshui stocks. The major minerals are quartz (–60 to –70 vol.%) and K-feldspar (–25 vol.%), with minor occurrences of plagioclase, muscovite, zircon.

Recent studies have revealed that the Gejiu granite batholith formed between ~85 Ma and 77 Ma, is transitional from metaluminous to weakly peraluminous and is high-K and alkali-rich (Cheng and Mao, 2010). Geochemical and Sr–Nd–Hf isotopic data suggest that the Gejiu granitic magma experienced high degrees of fractional crystallization following its formation due to the partial melting of the Mesoproterozoic crust with minor input from mantle-derived magmas (Cheng and Mao, 2010). The geochemical data indicate that degrees of fractional crystallization are distinctive from each other and that the later phases tend to be more evolved. Mineralization is spatially related to highly evolved granitic phases.

4. Ore deposit geology

4.1. Malage Sn–Cu deposit

The Malage deposit is located in the northernmost part of the Gejiu district and occurs over approximately 40 km². The deposit is mostly underlain by the Mid-Triassic Gejiu Formation, which reaches a thickness of more than 1000 m and consists of limestone, dolomitic limestone, and dolomite. The NW-trending Masong anticline and its associated faults are the major ore-controlling structures of the Malage ore (Sun et al., 1987). The faults in Malage deposit are considered crucial for the ore-forming fluid migration and ore genesis as they affected the interaction between fault deformation and fluid flow (Jiang et al., 1997). The Late Cretaceous granites, the Baishachong equigranular granite in the north and the Beipaotai porphyritic granite in the south, are the main igneous rocks in this area. Although they have different petrological and geochemical compositions, they are believed to be derived from the same magma chamber, with different degrees of fractionation (Cheng and Mao, 2010; Lu, 1987).

The Malage deposit is Sn–Cu-dominant, with varying amounts of Pb, Zn, W, Mo and Be mineralization. Two types of ore styles have been recognized in this deposit (Fig. 2). The first is skarn, located in the contact areas between porphyritic granite and carbonate wallrocks. Tin and Cu grades range from 0.02% to 0.05% and 0.3% to 1.56%, respectively (308 Geological Party, 1984). Ore minerals include pyrrhotite, chalcopyrite, pyrite, beryl, bismuth, molybdenite, scheelite, sphalerite, galena, cassiterite and arsenopyrite. These ore minerals commonly occur as disseminations and/or as veins in skarn. The orebodies are generally lenticular, centered on Beipaotai porphyritic granite and are characterized by a clear metal zoning (308 Geological Party, 1984). The second type of ore style found in the Malage deposit is stratabound ore (weathered), examples of this ore style are present in some layers of various sedimentary rocks and are commonly distal to granite, with an average tin grade of 2.39% (308 Geological Party, 1984). Tin is the major metallic element in this stratabound ore and is generally associated with varying amounts of Cu, Pb, Zn, In and Bi, with a few gangue minerals of quartz. The shape of these orebodies is quite complicated, including stratabound, vein and tabular. Alteration in the Malage deposit is extensive, with skarn being the major alteration type, comprising garnet, pyroxene, tremolite, actinolite, wollastonite, epidote and phlogopite. However, other alteration types also occur, including alkali metasomatism (potassic and sodic), greisen (quartz-muscovite), sericite and chlorite alteration of the intrusive rocks.

4.2. Songshujiao Sn–Pb deposit

The Songshujiao Sn–Pb deposit is located to the southeast of the Malage deposit and to the northeast of the Gaosong deposit (Fig. 1). The Mid-Triassic Gejiu Formation in this deposit consists of dolomite, interbedded dolomitic limestone and limestone. The NNE-trending Wuzishan anticline and the NW-trending Baishachong fault, together with various folds and fractures, are the main structural components in the area of the Songshujiao deposit. Centered on granitic “humps” of the batholith are well developed fault slip zones between layers of different rock types (Fig. 2) that provide critical conduits for granitic magma-derived hydrothermal fluids and space for the precipitation of ore minerals. Three groups of faults occur in the Songshujiao deposit that trend NW, NE and E-W. The fault zones are usually approximately 3 m wide and are infilled with small amounts of oxidized ores. Igneous rock in the Songshujiao deposit is porphyritic biotite granite. Skarn has commonly developed around the contact areas between granite and carbonate wallrocks.

Two types of mineralization are recognizable in the Songshujiao deposit. Skarn Sn–Cu ores have developed mainly along the contact areas between porphyritic granite and Gejiu Formation carbonates. This type of ore occurs as lenses, strata-bound bodies or as veins, and it is generally distributed around granitic cupolas. Thus, the size of the orebodies generally varies from ~5 to ~50 m thick (locally up to ~100 m thick), and from 100 m to 500 m long. The skarn minerals include pyroxene, scapolite and garnet. The ore minerals are pyrrhotite, chalcopyrite, arsenopyrite, marmatite, pyrite, magnetite, cassiterite, scheelite, and molybdenite. The deposit contains Sn, Cu, Zn and W with minor amounts of In, Bi and Ag. Skarn type ore constitutes approximately 66% of the Sn and ~80% of the Cu resources in the Songshujiao deposit.

Stratabound Sn–Pb ore, the second type of ore, is mainly hosted in interbedded limestone and dolomite and is distal from the granite (Fig. 2). Lead ore of this type accounts for approximately 60%–70% of the total Pb resources in the Songshujiao deposit. The occurrence of such ores is relatively complex and commonly controlled by fault, fold and/or fault slip structures. The strike length of the stratabound orebodies is 20–50 m, with a few reaching more than 100 m; their thickness is commonly >20 m. Most of these ores are weathered, containing limonite.
(~ 70%), calcite (~ 15%), and quartz (~ 5%), with minor concentrations of fluorite, cassiterite, pyrite, arsenopyrite, cerussite and malachite.

4.3 Gaosong Sn–Pb–Zn deposit

The Gejiu Formation in Gaosong consists of the following three units: 1) the Bainidong Unit, consisting primarily of light gray to gray limestone, with minor banded and lenticular calcareous dolomite; 2) the Malage Unit, consisting primarily of dark gray to gray limey dolomite, with minor dolomitic limestone; 3) the Kafang Unit, which is mainly composed of gray to light gray limestone and limey dolomite interlayers. The Kafang Unit is the main host of the Gaosong mineralisation. The 8-km long NE-trending Lutangba fault and its associated subsidiary faults are the major structures controlling ore. They cut the Kafang Unit, acting as major conduits for ore-forming fluids. Greisen (quartz–muscovite) alteration, muscovite, sericite and skarn minerals have developed intensively on the margins of the granitic cupola and in the contact zone between granite and carbonate.

Two types of ore occur in Gaosong. Type 1 skarn-sulfide ore occurs along the contact zones between granite and limestone and/or dolomite, with disseminated, veinlet and massive ores hosted by skarn. The primary skarn minerals are pyroxene, garnet and scapolite. The sulfides are associated with retrograde skarn minerals (actinolite, tremolite and chlorite). The major ore minerals include arsenopyrite, pyrrhotite, chalcopyrite and marmatite, with lesser amounts of cassiterite, pyrite, scheelite, native bismuth, molybdenite and magnetite. The average Sn grade is ~0.5–1%, with the highest grade up to 3%.

Type 2 ores are weathered and have complex orebody shapes, including stratabound, irregular banded, lenticular and veinlet. The orebodies occur in different layers that are controlled by fault slip zones and fractures (Fig. 2) and typically consist of several ore layers at different levels, generally 3–5 layers, locally up to 8–9 layers. Type 2 orebodies can be tens to hundreds of meters long and 100–200 m wide. The weathered ores consist of limonite, hematite, goethite and clay minerals, with minor amounts of cassiterite, marmatite, anglesite, pyrolusite and malachite. Gangue minerals include primarily scorodite, siderite, calcite, quartz, phlogopite, fluorite, tourmaline, chlorite, garnet, tremolite, pyroxene, with minor amounts of plagioclase, jarosite and kaolinite. The average Sn grade is ~2%.

4.4 Laochang Sn–W–Cu polymetallic deposit

The Laochang Sn–W–Cu polymetallic deposit is situated between the Gaosong deposit in the north and the Kafang deposit in the south. It is the most important deposit in the Gejiu district, containing ~50% of the tin resources of the whole district. The Laochang deposit is bounded by the Beiyinshan fault in the north and the Laoxiongdong fault in the south. In Laochang, six EW-trending faults provided conduits for the ore forming fluids and the space for the precipitation of ore minerals. Six NE- and/or NW-trending faults cut the Laochang deposit. The stratigraphy is similar to the deposits described above (Fig. 1), and the interlayer zones are the same ore-hosting locations.

**Fig. 2. Cross sections of the five deposits in the Gejiu district that show the spatial relationship of granite, orebodies and host rocks (modified from Mao et al., 2008).**
Equigranular and porphyritic granites are the major igneous rocks in this area, which intruded into the Mid-Triassic Gejiu Formation. The major mineralization styles in the Laochang deposit are skarn ores, strataboroud ores and carbonate hosted veins (Fig. 2).

Skarn ores include skarn W ores, skarn-sulfide Sn ores and Cu ores, associated with minor amounts of Bi, In and Ga mineralization. Tin in skarns accounts for ~60% of all the Sn resources in Laochang. The distribution of orebodies is influenced by the geometry of the granite contact areas, with most ores occurring around granitic “humps”. Major metallic minerals are pyrrhotite, arsenopyrite, chalcopyrite, pyrite, marmatite, cassiterite and scheelite. Major gangue minerals are pyroxene, garnet, plagioclase, fluorite, phlogopite, quartz, and chlorite. Small amounts of ores are weathered to an assemblage of limonite, goethite, malachite and plumbojarosite, and these are associated with sericite, phlogopite, muscovite, quartz and calcite.

Stratabound ores occur in the interlayer zones of limestone and dolomite, and these types of ores contain approximately 25% of the total Sn resources in Laochang. The ores have been strongly weathered, currently primarily composed of cassiterite, hematite, limonite, goethite, malachite, scordaitic, conichalcite, anglesite, cerusite, plumbojarosite and wadite, with minor amounts of arsenopyrite, pyrite, chalcopyrite, sphalerite, galena and marmatite.

Vein-type mineralization comprising tourmaline–quartz veins, tourmaline–K feldspar–skarn veins, tourmaline–skarn–cassiterite veins, and tourmaline–phlogopite veins in Gejiu Formation carbonate. The scale of mineralization and vein distribution is influenced by host rock type, stratigraphy, structure, and association with nearby granite (Cheng et al., 2012). The host rocks are folded and faulted limestone and dolomite of the Mid-Triassic Gejiu Formation. The ore zone has an approximately thomson shape, bordered by the Huangnidong fault in the east, the Aotoushan fault in the west, the Meiychong fault in the north and the Longshupo fault in the south. Granite bodies occur 200–1000 m beneath the surface and are aligned along a NE trend beneath the ore veins. The dimensions of the veins vary in length from several centimeters to more than 200 meters and in width from several millimeters to approximately 1 meter. Tin is the major metal produced from these ore veins and the average grades of Sn, Be and WO3 of the vein-type orebodies are 0.42%, 0.13%, and 0.11%, respectively.

4.5. Kafang Cu–Sn deposit

The Kafang Cu–Sn deposit is located in the southernmost part of the Gejiu district (Fig. 1), to the east of the Gejiu fault and between the parallel EW-striking Laoxiongdong and Xianrendong Faults. Basaltic lava flows with a thickness of 60–100 m are intercalated with the Gejiu Formation carbonate beds (Fig. 2). The Xinshan granitic pluton is fine-grained equigranular biotite granite intruded into the Gejiu Formation carbonates and the interbedded lava. Three types of ores are recognizable in Kafang (Fig. 2).

Type 1 skarn Cu–Sn–Mo–W–Au–Bi polymetallic ores occur in the contact areas between Xinshan granite and carbonate wallrocks (Fig. 2). Ore minerals include magnetite, chalcopyrite, pyrrhotite and cassiterite, and minor minerals include pyrite, scheelite, native bismuth, native gold, sphalerite, galena, molybdenite, wolframite and arsenopyrite. Skarn minerals include garnet, pyroxene, epidote, actinolite, tremolite, sericite, chloride, calcite and quartz.

Type 2 strataboroud Cu-dominant ores are hosted in the basaltic lavas. The orebodies are ~200–400 m long and up to 10 m wide. The gangue minerals include actinolite, phlogopite and tremolite, with minor amounts of pyroxene, calcite and fluorite. The ore minerals are primarily chalcopyrite, pyrite, arsenopyrite, molybdenite and pyrrhotite. The orebodies are roughly sheet-like or tabular.

Type 3 strataboroud Cu–Sn–Pb–Zn polymetallic ores are hosted in limestone and/or dolomitic limestone layers up to 2000 m from the granitic pluton. The metallic minerals include pyrrhotite, cassiterite and pyrite, and the gangue minerals are variable amounts of quartz, tourmaline, tremolite and fluorite. The contact areas between orebodies and host rocks are sharp. Localized ore veins, emanating from the main orebodies, cut the host rock. Alteration around these orebodies is minor, but some banded skarns (garnet, pyroxene, wollastonite and calcite) occur parallel to the bedding of the host rocks and parallel to the orebodies; these are better developed closer to the orebodies.

5. Metal zoning

The metal deposits in the Gejiu district are distinctly zoned outward from W + Be + Bi ± Mo ± Sn deposits in the granite cuppolas, to Sn + Cu-dominated deposits at the granite contact zones, and Pb + Zn deposits in the surrounding host rocks (Fig. 3). This metal zoning is developed both vertically and horizontally (Fig. 3).

(1) Inner W–Be–Bi ± Mo ± Sn zone

This zone mostly occurs in the interior of granite (endogranitic) or its margins. The size of the W, Be, Bi, Mo orebodies are usually limited. Examples of this style of mineralization include the Malage and Laochang Be deposits, the Xinshan W deposit and the Xinshan Bi deposit. Tungsten is generally more abundant and more widespread than Be and Bi (308 Geological Party, 1984). Be–Bi mineralization is most common around equigranular (non-porphyritic) granite, whereas W (scheelite) is developed in both equigranular and porphyritic granites (Fig. 4). Gangue minerals include large quartz/feldspar crystals, garnet and pyroxene.

(2) Middle Cu–Sn zone

Copper and Sn are the most abundant metals in this zone, which hosts almost 90% of the Cu–Sn resources in the Gejiu area. The tin and Cu orebodies generally occur together, although the Cu ores are generally located closer to the granites than the Sn ores (Fig. 3). The ore minerals are mainly cassiterite and chalcopyrite, occurring locally primarily with pyrrhotite, pyrite, arsenopyrite, molybdenite and with minor amounts of sphalerite and galena. Prograde and retrograde skarn minerals are represented by garnet, pyroxene, wollastonite, tremolite, epidote, chlorite and phlogopite in this zone (Fig. 4).

(3) Distal Pb–Zn zone

Outwards from the Cu–Sn zone is a zone with dominant Pb and Zn sulfides (Fig. 3) that is closer to the surface and distal to granite. Examples include the Malage Pb–Zn deposit, the Songshujiao Pb deposit and the Laochang Pb deposit. Field evidence indicates that there were at least two episodes of Pb mineralization (308 Geological Party, 1984), with the above-mentioned deposits belonging to the early stages. A later Pb ± Zn mineralization stage exists as veins in both wall rocks and granites with no Sn mineralization (Fig. 4) (308 Geological Party, 1984).

6. Ar–Ar dating techniques and results

6.1. Analytical techniques

For our study, thirteen samples containing 0.18 to 0.28 mm mica grains were wrapped in aluminum foil, loaded into an aluminum tube, then sealed into a quartz bottle and irradiated for 24 h in the Swimming Pool Nuclear Reactor at the Chinese Institute of Atomic Energy in Beijing by fast neutrons with a flux of 2.2464×10 18 n cm −2 s −1 . The monitor used in this analysis was an internal standard of Fangshan biotite (Z8H25) with an age of 132.7 ± 1.2 Ma and a potassium content of 7.579 ± 0.030 wt% (Wang, 1983). The measured isotopic ratios were corrected for mass discrimination, atmospheric argon components, blanks and irradiation-induced mass interference. The correction factors of interfering isotopes produced during irradiation were determined by an analysis of irradiated pure K2SO4 and CaF2. Their values
corresponded to the following: \( \frac{^{39}\text{Ar}}{^{37}\text{Ar}} \) Ca = 0.000271; \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) k = 0.00703; \( \frac{^{39}\text{Ar}}{^{37}\text{Ar}} \) Ca = 0.000652. The \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) step-heating analysis was performed at the ME Key Laboratory of Orogenic Belt of Crustal Evolution in Peking University and the detailed experimental process has been previously reported (Gong et al., 2008). The \( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \) vs \( \frac{^{39}\text{Ar}}{^{36}\text{Ar}} \) isochron diagram was defined by using the ISOPLOT version 3.0 program of Ludwig (2003).

### 6.2. Results

The \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) analytical results are summarized in Table 1 and the details are listed in Appendix 1 and Appendix 2, which are available as a digital supplement to this paper. In this study, apparent ages obtained from \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) analyses at low temperatures are not considered to have geological significance because of the low percentage of \( ^{39}\text{Ar} \) released (Guo et al., 2011), which was likely caused by the initial loss of small quantities of Ar from the edges of mineral grains (Hanson et al., 1975). Plateau ages of this study were determined from six or more contiguous steps that comprise >75% of the total \( ^{39}\text{Ar} \) released. The uncertainties of the ages are reported at a 95% confidence level (2\( \sigma \)).

Two muscovite samples were collected from the Malage deposit for \( \text{Ar–Ar} \) analysis to constrain the age of the weathered ore (sample 8255) and the retrograde-skarn ore (sample 8253). \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) stepwise heating analyses of muscovite over the higher temperature intervals yielded uniform and remarkably flat \( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \) age spectra with plateau ages for 90.3% of the total \( ^{39}\text{Ar} \) released (Fig. 6), indicating the absence of excess argon or any diffusive argon loss. Six plateau ages were obtained from sample 8255 at temperatures between 1000 and 1400 °C. These 6 pieces of data are consistent with the release of 90.2% of the total \( ^{39}\text{Ar} \). The 95.4 ± 0.7 Ma and 89.7 ± 0.7 Ma ages for samples 8253 and 8255, respectively, are believed to be reliable estimates of the crystallization age of muscovite from the oxidized ore and skarn ore in the Malage deposit.

One muscovite sample (sample SSJ-01) from greisen ore and one phlogopite sample (sample 7060) from skarn ore in Songsuishuiao deposit were collected. Ten plateau ages were obtained from sample SSJ-01 at temperatures between 900 and 1400 °C, and these constitute a flat age plateau comprising 98.8% \( ^{39}\text{Ar} \) released. Eight plateau ages were obtained from sample 7060 at temperatures between 1000 and 1400 °C with 91.7% \( ^{39}\text{Ar} \) released. The plateau ages of 85.5 ± 0.7 Ma and 92.3 ± 0.6 Ma are believed to be the best estimates of the age of the greisen ore and the skarn ore in the Songsuishuiao deposit, respectively.

Two muscovite samples from Gaosong deposit were collected to represent the retrograde skarn ore (sample GS-01) and weathered ore (sample 7091). Eight plateau ages were obtained from sample 7091 at temperatures between 1000 and 1350 °C, with 96.2% \( ^{39}\text{Ar} \) released, yielding a well-defined plateau age of 85.6 ± 0.7 Ma. Twelve step-heating experiments at temperatures ranging from 850 °C to 1400 °C were performed for sample GS-01; of these, seven steps during 950 °C to 1250 °C constituted a flat age plateau encompassing 94% \( ^{39}\text{Ar} \) released and yielded a well-defined plateau age of 84.3 ± 0.6 Ma.

Four muscovite samples, including samples 8145 and 8187 from greisen ores in different locations, sample 8180 from oxidized ore, and sample 8120 from vein ore, were collected from the Laochang deposit to represent four different mineralization types. Greisen samples yielded well-defined plateau ages of 85.6 ± 0.6 Ma and 87.4 ± 0.6 Ma. Sample 8145 was analyzed at a temperature between 950 °C to 1250 °C with 79.3% \( ^{39}\text{Ar} \) released, and sample 8187 was analyzed at a temperature between 950 °C to 1400 °C with 89.2% \( ^{39}\text{Ar} \) released. Seven plateau ages were obtained from the oxidized ore sample (sample 8180) at temperatures between 1000 and 1300 °C with 84.4% \( ^{39}\text{Ar} \) released to yield a
plateau age of $77.4 \pm 0.6$ Ma. The plateau age of the vein ore (sample 8120) yielded $87.5 \pm 0.6$ Ma, based on $76.4\%$ $^{39}$Ar released between 950 °C to 1400 °C. As shown in Appendix 2, the isochron ages and inverse isochron ages of these samples are indistinguishable from their plateau ages, and we therefore believe that these $^{36}$Ar/$^{39}$Ar dates are reliable.

Fig. 4. Photographs showing field characteristics, mineral associations, mica analyzed in this study and their relationships with other intergrowth minerals from the Gejiu ore district.
One muscovite sample and two phlogopite samples were collected from the Kafang deposit to constrain the age of greisen ore (sample ZKF08-49), basalt host stratabound ore (sample ZKF08-29) and altered basalt (sample ZKF08-62). The plateau ages of these samples are 79.5 ± 0.6 Ma, 79.6 ± 0.5 Ma and 85.5 ± 0.6 Ma, respectively. Temperatures were relatively high (>850 °C) and the 40Ar released at more than 80%. These three plateau ages agree with their isochron and inverse isochron ages, indicating that they are reliable and of high quality.

7. Discussions and conclusions

7.1. Timing of mineralization

The 13 representative muscovite/phlogopite samples from different mineralization environments in this study show excellent agreement between the plateau age, the isochron age and the inverse isochron age, within the applicable analytical uncertainty, indicating the absence of excess argon or any diffusive argon loss (Appendix 1 and 2). Therefore, the 13 well-defined plateau ages, from 77.4 ± 0.6 Ma and 95.3 ± 0.7 Ma, that we report are accurate and believed to be a reliable estimate for the crystallization time of these mica (Fig. 5).

As shown in published works (308 Geological party, 1984; Cheng and Mao, 2010; Cheng and Mao, 2012; Dai, 1996; Li, 1985; Li et al., 2011; Lu, 1987; Mo, 2006; Zhuang et al., 1996), diverse textures, mineral associations, major and trace elements and isotopic compositions of granites in the Gejiu district indicate multi-stage crystal fractionation. However, as opposed to the intrusive rocks in the western sector of granites in the Gejiu district indicate multi-stage crystal fractionation, major and trace elements and isotopic compositions (2011; Lu, 1987; Mo, 2006; Zhuang et al., 1996), diverse textures, mineral associations, major and trace elements and isotopic compositions of granites in the Gejiu district indicate multi-stage crystal fractionation. Existing zircon U-Pb dating results, from approximately 100 Ma to 80 Ma (Cheng and Mao, 2010; Mao et al., 2008), which supports the contention that the mineralization ages of the Sn–Cu ores in the Gejiu district lie in the range of ~77 Ma to ~95 Ma, as measured by this work.

7.2. Implications of metal zonings

Metal/mineral/alteration zoning of granite-related ore systems has been recognized since the 1920s (Emmons, 1924; Park, 1955; Wong, 1920) and has been identified by many scientists all over the world. This is exemplified by Sn–W deposits from around the world, including in the Bolivian tin deposits (Ahfeld, 1941; Lehmann, 1990), the Cornwall Sn polymetallic district (Bromley and Holl, 1986), the Erzgebirge Sn deposits (Stemprok, 2003), and in the Dachang Sn district (Chen and Li, 1993). Metal zoning also found with other ores, such as Au-polymetallic deposits (James and Baker, 2001; Markowski et al., 2006; Meinert et al., 1997; So et al., 1998) and Pb–Zn–Ag deposits (Baumgartner et al., 2008; Newberry et al., 1991; Plumlee and Whitehouse-Veres, 1994). For the origin of these metal zonings and their implications, Ashley and Plimer (1989) re-examined the controversial Zn/Sn skarn deposits in eastern Australia and proved that the mineralization of these deposits is closely associated with granites, emphasizing that there was no possibility that the ores were of syngenetic origin. Newberry et al. (1991) further strengthened the theory that the genesis of the Pb–Zn–Ag zoning of the Darwin deposit in California should be attributed to the variations of temperature, pH and oxidation state of the granitic magma-derived ore-forming fluids. Temperature changes of hydrothermal fluids are very important for the precipitation of ore minerals and therefore metal zoning, as revealed by several studies (Pirajno, 1992; Wu and Jin, 1993). Audétat et al. (2000) suggested that the metal zonation of Sn–W deposits around the Mole Granite reflected both compositional variations of the source fluid and sequential metal precipitation. For the Erzgebirge Sn-bearing granite batholith, Stemprok (2003) proposed that the tectonics along the granite contact areas and several deep-seated fault zones were also important for the mobilization of the hydrothermal fluids and distribution of the ore zoning around the granite pluton. Thus, we can conclude that the above-mentioned metal/alteration zonings are genetically related to intrusions (mostly granitic) and are influenced by the nature of the hydrothermal fluids and surrounding geological characteristics.

Fig. 3 shows that metal zoning occurs both vertically and laterally away from the various granitic bodies in the Gejiu Sn-polymetallic district. The general sequence of zoning is upward and outward from W–Be–Bi±Mo±Sn to Cu–Sn to Pb–Zn at the periphery. Mineralization types change consistently upward, from disseminated in granite outward to skarn along the contact area with carbonate beds, to oxidized ores and eventually to veins in limestone units distal to granites. This pattern is similar to those established for the Cornwall W–Bi–Sn–Cu–Pb–Zn–Ag ore district in SW England (Bromley and Holl, 1986). The zonings suggest a close genetic relationship between magmatism and mineralization. The metal zonings are believed to have been caused by the progressive cooling of magma-derived hydrothermal fluids, perhaps combined with fluid-
rock interaction or fluid–fluid mixing, as they move upward and outward away from the magmatic source.

### 7.3. Genetic implications and exploration significance

Controversies are long-standing about the genesis of the Gejiu Sn–Cu polymetallic district, with arguments focusing on whether the deposits are of the SEDEX type or granitic intrusion-related (Geological Party, 1984; Mao et al., 2008; Qian et al., 2011a, 2011b; Qin et al., 2006; Yu et al., 1988; Zhang et al., 2003, 2005; Zhou et al., 1997, 1999; Zhuang et al., 1996; and the references therein). The genetic link between magmatism and mineralization is demonstrated by the distinctive spatial association and zoning around granitic cupolas and their greisen-style alteration with Sn–W mineralization.

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**Fig. 5.** $^{40}$Ar/$^{39}$Ar age spectra of muscovite and phlogopite separate from the Gejiu tin polymetallic district, SW China. Data uncertainty is given as 2σ.

![Age spectra of muscovite and phlogopite](image)

**Key:**
- 8253: skarn ore; 8255: oxidized ore; SSJ-01: greisen ore;
- 7060: skarn ore; 8180: oxidized ore; GS-01: skarn ore;
- 7091: oxidized ore; 8187: greisen ore;
- 7120: vein ore; 8145: greisen ore; ZKF08-49: greisen ore;
- ZKF08-29: basalt hosted stratiform Cu ore; ZKF08-62: mineralized basalt.
that leads outward to a sequence of exoskarns with metal associations from proximal to distal. Importantly, the granite-mineral system genetic coupling is supported by systematic geochronologic constraints from the Ar–Ar ages in this study. The age data show a mineralization age of 77 Ma to 95 Ma, much younger than the age of the host Mid-Triassic Gejiu Formation sedimentary carbonate rocks and correlating closely with the timing of the granite intrusions (Cheng and Mao, 2010; Fig. 6). We conclude that the Sn–Cu polymetallic ores of the Gejiu ore district are of hydrothermal origin and granite-related.

**Acknowledgments**

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**Appendix 1**

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7091, Oxidized ore sample from Gaosong deposit, J=0.005243

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7120, Vein ore sample from Laochang deposit, J=0.005154

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8180, Oxidized ore from Laochang deposit, J=0.005123

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8187, Greisen ore from Laochang deposit, J=0.005501
Science Foundation of China (40930419), the Special Research Funding for the Public Benefits Sponsored by MLR (200911007–12), the Research Program of Yunnan Tin Group (2010–04A), and the Fundamental Research Funds for the Central Universities (2–9–2010–21).

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