Geology and genesis of Kafang Cu–Sn deposit, Gejiu district, SW China

Yanbo Cheng a,b, Jingwen Mao a,c,d, Brian Rusk b, Zongxi Yang d

Abstract

Kafang is one of the main ore deposits in the world-class Gejiu polymetallic tin district, SW China. There are three main mineralization types in the Kafang deposit, i.e., skarn Cu–Sn ores, stratiform Cu ores hosted by basalt and stratiform Cu–Sn ores hosted by carbonate. The skarn mainly consists of garnet and pyroxene, and retrograde altered rocks. These retrograde altered rocks are superimposed on the skarn and are composed of actinolite, chlorite, epidote and phlogopite. Major ore minerals are chalcopyrite, pyrrhotite, cassiterite, pyrite and scheelite. Sulfur and Pb isotopic components hint that the sources of different types of mineralization are distinctive, and indicate that the skarn ore mainly originated from granitic magma, whereas the basalt-hosted Cu ores mainly derived from basalt. Microthermometry results of fluid inclusions display a gradual change during the ore-forming process. The homogenization temperature of different types of inclusions continuously decreases from early to late mineralization stages. The salinities and freezing temperatures exhibit similar evolutionary tendencies with the homogenization temperature, while the densities of the different types keep constant, the majority being less than 1. Oxygen and hydrogen isotopic values (δ18O and δD) of the hydrothermal fluids fall within ranges of 3.1 to 7.7‰ with an average of 6.15‰, calculated at the corresponding homogenization temperature, and —73 and —98‰ with an average of —86.5‰, respectively. Microthermometry data and H–O isotopes indicate that the ore-forming fluid of the Kafang deposit is mainly derived from magma in the early stage and a mixture of meteoric and magmatic water in late stage. Molybdenite Re–Os age of the skarn type mineralization is 83.4±2.1 Ma, and the stratiform ores hosted by basalt is 84.2±7.3 Ma, which are consistent with the LA-ICP-MS zircon age of the Xinxian granite intrusion (83.1±0.4 Ma). The evidence listed above reflects the fact that different ore styles in the Kafang deposit belong to the same mineralization system.

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1. Introduction

The genesis of co-existing skarn and stratiform orebodies in the Gejiu ore district, the largest polymetallic tin area in the world, has been the subject of debate for decades. Theories to account for the origin of the orebodies include syngenetic (Li et al., 2009; Qian et al., 2009; Qin et al., 2006; Zhang et al., 2005; Zhou et al., 1998) and granite-related hydrothermal origin (308 Geological Party, 1984; Cheng and Mao, 2012; Cheng et al., 2008, 2009; Mao et al., 2008a; Peng, 1985; Xu et al., 2009; Yang et al., 2008, 2009, 2010; Yu et al., 1988; Zhuang et al., 1996). Most researchers accept that the skarn-type ores in the district are related to Cretaceous granites; however, in recent years, the origin of the stratiform ores has been interpreted as syngenetic based on their morphology and some K–Ar/Ar–Ar dating results (Li et al., 2009; Qin et al., 2006; Zhang et al., 2007). The Kafang Cu–Sn orefield, a complex area containing two different types of stratiform ores, is located in the south Gejiu tin ore district. Mining began there during the Han Dynasty (2000 years ago) but large-scale exploration was not carried out until the 1970s. The Kafang deposit has defined reserves of about 40 Mt Cu at 1% and >10 Mt Sn at 0.7%. The Kafang deposit, which has significant mineralization hosted by Triassic volcanics and sediments, has a higher Cu/Sn ratio than most other deposits in the Gejiu district, which are predominantly hosted in granites and skarns. (Figs. 1 and 2). This is reflected at Kafang by higher Cu/Sn ratios in the stratiform ore bodies than in the skarn ore bodies. In this study we present new field observations, LA-ICP-MS zircon U–Pb dating, molybdenite Re–Os dating, S–Pb–H–O isotopes, and fluid inclusion microthermometry data, to constrain the origin of the Kafang Cu–Sn deposit and its relation to mineralization throughout the Gejiu ore deposits.

2. Geological setting

The Gejiu mining district is located in southeastern Yunnan province, approximately 300 km SE of Kunming, the capital of Yunnan
(Fig. 1). Tectonically, the Gejiu ore district is located at the western-most end of the Cathysian block (South China fold belt, adjacent to the Yangtze craton in the north and to the Sanjiang fold belt in the west (Fig. 1a, b). Strata in the Gejiu area are made up of a 3-km-thick sequence of Permian and Triassic clastic rocks with interlayered basic lavas in the Middle Triassic sequence. The strata consist of 170 to 390 m of sandstone and shale of the Lower Triassic Feixian-guan Formation; ~400 to 460 m of sandstone and mudstones of the Lower Triassic Yongningzhen Formation; ~400 to 1400 m of the Mid-Triassic Gejiu Formation of carbonate with intercalations of mafic lavas; ~1800 to 2800 m of fine-grained sandstones and limestones, with interlayers of mafic lavas of the Middle-Triassic Falang Formation; and ~500 to 1200 m of the Upper Triassic Niagao Formation (fine-grained clastic rock). No Jurassic or Cretaceous units exist in the region. The carbonate rocks of the Gejiu and Falang Formations, including the interlayered Triassic basic lavas in the Gejiu Formation, are the most important ore-hosting strata.

Numerous faults exist in the Gejiu area, including the NNE-trending Longchahe fault, fadongsfhan fault, Yangjiaqian fault, NE-trending Baishachong fault, and the N–S-trending Gejiu fault. The latter divides the Gejiu district into two parts (Fig. 1c). The ore deposits are mainly located in the eastern part. Structures in the eastern part include NS-, NNE- and EW-trending anticlines and faults. The NNE-trending Wuzhishan anticline is one of main structures controlling the location of the orebodies in the eastern Gejiu district (308 Geological Party, 1984). The EW-trending Longshujiao, Beiyingshan, Longxiongdong, Xianrendong and Bailong faults separate the Gejiu district into five distinct ore deposit areas, i.e., Malage, Songshujiao, Gaosong, Laochang and Kafang from north to south (Fig. 1c).

In addition to the Triassic lavas, the Mesozoic igneous rocks in the Gejiu district include gabbro, mafic microgranular enclaves (MME)-bearing granites, porphyritic biotite granite, equigranular biotite granite, alkaline rocks and mafic dikes (Fig. 1c). Cheng and Mao (2010) reported SHRIMP and LA-ICP-MS zircon age data of 80~85 Ma for the following granitic rocks: Longchahe porphyritic granite (83.2 Ma), Songshujiao porphyritic granite (82.8 Ma), Laochang porphyritic granite (83.3 Ma), Shenxianshui equigranular granite (83.0 Ma), Baishachong equigranular granite (79.0 Ma), Laochang equigranular granite (85.5 Ma). These are consistent with the \( {^{40}}\text{Ar} - {^{39}}\text{Ar} \) age of 82.74 \pm 0.68 Ma on plagiogopite from the Laochang vein-type orebody (Yang et al., 2009). These results demonstrate the magmatism and at least some mineralization were coeval in the Late Cretaceous.

### 3. Geology of Kafang Cu–Sn deposit

The Kafang Cu–Sn deposit is located in the southernmost part of the Gejiu ore district (Fig. 1), to the east of Gejiu fault and between the parallel EW-striking Laoxiongdong and Xianrendong Faults (Fig. 2A). Several EW trending faults occur in this area. The host rocks and wall rocks in the Kafang deposit are the Triassic Gejiu Formation of limestone, argillaceous limestone, dolomite limestone and dolomite. The limestones and dolomite range from ~50 to >800 m in thickness. A Triassic basalt layer (60 to 100 m-thick) is intercalated in the Gejiu Formation (Fig. 2A).

The basalt includes olivine basalt and amygdaloidal basalt. Geologic and geochemical data indicate that both basalts are silica-unsaturated, alkaline-rich, high-titanium, high-magnesium and low-aluminum, exhibiting the typical characteristics of continental alkali olivine basalt (Li et al., 2008). The Xinshan granitic pluton intruded into the Gejiu Formation carbonate and the intercalated basalt about 2 km NE of Kafang town. The Xinshan granite is a phase of the fine-grained equigranular biotite granite. It contains plagioclase feldspar, quartz and biotite, with accessory magnetite, apatite, and zircon. Similar to other granitic plutons in the Gejiu district, the Xinshan granite is an alkali feldspar granite characterized by high silica and alkali content. Trace elements and REE patterns show that this is highly fractionated granite that was likely generated in an intraplate setting (Cheng and Mao, 2010).

The Kafang orefield strikes >2 km N–S and 4–6 km E–W (Fig. 2A, B). Different from other four orefields, which are characterized by dominant Sn mineralization and lesser Cu ore, the Kafang orefield contains more Cu than Sn. Spatially, all the orebodies in Kafang occur around the Xinshan granite, but are hosted by different rocks (Fig. 2). In general, orebodies at Kafang occur at the contact of granite and carbonate, and are hosted by basalt, dolomitic limestone, and limestone, and the distance between ores and granite are generally ~<2 km (Fig. 2B). The ores at the contact are associated with extensive skarn-type alteration, and alteration is commonly weaker in the sediments and volcanic rocks more distal from the granite.

### 4. Hydrothermal alteration and mineralization styles

In the Kafang deposit, there are three mineralization styles: (1) skarn type Cu–Sn ores located at the contact of granite and carbonate; (2) stratiform Cu ores hosted by basalt; and (3) stratiform Cu–Sn ores hosted by carbonate (Fig. 2B). Copper orebodies are widely distributed in all the three mineralization types, whereas Sn mineralization only developed in the skarn type and stratiform orebodies hosted by carbonate.

#### 4.1. Skarn type Cu–Sn mineralization

Skarn mineralization mainly developed at the contact zone between the Xinshan granite and carbonate sediments (Figs. 2–4). Ore minerals include chalcopyrite, pyrrhotite and cassiterite, and minor pyrite, native bismuth, native gold, sphalerite, galena, molybdenite and wolframite. Skarn minerals include grossularite, andradite, diopside, hedenbergite, actinolite, tremolite, sericite, magnetite, calcite and quartz. A characteristic feature of this type of alteration is the skarn mineral assemblage commonly occurs as bands intercalated in the host carbonate rocks (Figs. 2–4). Large calcareous skarn zones, ranging from several to tens of meters in thickness, occur at the contact of the Xinshan granite pluton (Fig. 3). In light of the mineral assemblages, the skarn can be sub-divided into garnet skarn, diopside–hedenbergite skarn, and diopside–garnet–magnetite skarn. The ore minerals corresponding to these skarn include scheelite, bismuthinite, chalcopyrite, pyrite and arsenopyrite. Retrograde skarn minerals including epidote, amphibole, chlorite, calcite and magnetite, typically overprint primary skarn minerals. Ore minerals associated with retrograde alteration are mainly sulfides, including arsenopyrite, pyrrhotite, and pyrite, with minor cassiterite and native bismuth. Two uncommon phenomena observed are a wiggly texture, mainly composed of garnet and diopside, and breccias containing fragments of white carbonate encapsulated by diopside ± chlorite ± epidote (Fig. 4).

#### 4.2. Stratiform Cu mineralization hosted by basalt

The stratiform copper orebodies hosted by basalt contain actinolite, phlogopite and tremolite, with minor diopside and fluorite (Fig. 5), accompanying pyrrhotite and chalcopyrite mineralization. Generally, the basalt-hosted orebodies are about 200 to 400 m in length and the thickness ranges between 0.1 and 10 m. The ore minerals are commonly chalcopyrite, pyrite, arsenopyrite, molybdenite and pyrrhotite, and gangue minerals include calcite, actinolite, phlogopite, tremolite, and chloride (Fig. 5). These massive ores generally are sheet- or tabular-like in morphology. The Cu content is generally higher in the central part of the host basalt and is always below economic grade towards the margins (Fig. 5). Calcite and/or fluorite veins are occasionally observed in these ores (Fig. 5).

#### 4.3. Stratiform Cu–Sn mineralization hosted by carbonate

Stratiform orebodies also exist within limestones and dolomitic limestones distal to the granite pluton from 0 to 500 m (Fig. 2B),
and ore metals include both Cu and Sn. The contacts of Cu–Sn stratiform orebodies and the wall rocks are clear. In some locations, veins from the ore bodies cut the host rocks, indicating mineralization is not coeval with carbonate formation (Fig. 6). Ore minerals include pyrrhotite, cassiterite, pyrite, and other sulfides, and variable amounts of quartz, tourmaline, tremolite, fluorite, and other gangue minerals. Unlike the basalt-hosted ore, the carbonate-hosted ore commonly contains coarse grained cassiterite. Little alteration exists around these orebodies, but some banded skarns, interbedded with the host strata extend along the same trend as the orebodies, and are developed close to these orebodies (Fig. 6). Minerals mainly include garnet, diopside, and wollastonite. Carbonate minerals, such as calcite, dolomite and siderite, accompanied with weak cassiterite mineralization, and calcite±fluorite veins cross-cut the orebodies.

5. Analytical methods and sample description

5.1. Fluid inclusions

We chose 12 quartz and calcite samples from the granite interior (CYB1008224, CYB0912032, CYB0912033), granite margin (CYB0912050, ZKF08-23), the contact between granite and carbonate

Fig. 2. a. Geology of Kafang ore field. b. Geological section of 24–24′. The location of investigation areas are marked on the cross-section. Panel a is modified after 308 Geological party (1984).

Fig. 1. (a) Simplified geological map of eastern Asia, showing major tectonic units (Wang et al., 2005). (b) Distribution of tin deposits in the Cathaysia block (Mao et al., 2004). (c) Sketch map showing the geology and the distribution of tin-polymetallic deposits in the Gejiu ore district. SCB = South China Block; NCB = North China Block; YC = Yangtze Craton; IC = Indochina Block; SI = Sibumasu Block; G = Songpan-Ganze Accretionary Complex; WB = West Burma; Hi = Himalayas; LS = Lhasa; QT = Qiangtang. Sketch map in Panel (c) is after 308 Geological Party (1984).
Fig. 3. Schematic profile of the contact of granite, skarn and carbonate, including photographs of main alteration and mineralization styles in the profile. The location of this investigation area is marked on the cross-section. Parallel-like skarn bands in carbonate rocks, minerals are garnet, diopside and wollastonite. 1—Banded skarn in carbonate. 2—Quartz and garnet skarn in the margin the granite. 3—Banded skarn in carbonate in the contact of granite and carbonate. 4—Banded skarn in carbonate. 5—Banded skarn in carbonate.

Fig. 4. Schematic profile of the contact of granite, carbonate and skarn, including photographs of the main alteration and mineralization styles in the profile. The location of this investigation area is marked on the cross-section. 1—Tourmaline and quartz vein in the granite. 2—Quartz vein and associate mineralization in granite. 3—Banded garnet ± diopside exoskarn. 4—Contact of garnet and diopside skarn and massive quartz in the margin of granite. 5—Mineralization in the skarn zone. 6—Massive carbonate enveloped by chlorite ± diopside skarn.
(CYB0912006, CYB0912005, ZKF08-85), basalt interlayers (ZKF08-90, ZKF08-92, ZKF08-109), and the carbonate interlayer (CYB1007029) to study the characteristics and evolution of the ore-forming fluid in different mineralization units (Tables 1 and 2).

Microthermometric measurements were carried out at Resources Exploration laboratory, China University of Geosciences, Beijing. Fluid inclusion microthermometry data were obtained on a Linkam MDS 600 heating-freezing stage, coupled to a Zeiss microscope. The stage enables measurements within the range of −196 and 600 °C. For freezing runs, the precision is about ±0.3 °C for melting CO2 and ±0.2 °C for ice melting; for heating runs, the precision is about ±1 °C for critical point of H2O.

5.2. Isotopes

5.2.1. Lead isotopes

Although published data have been presented, we collected several new samples from Kafang to complement these. The new samples were from Qianjin adit (QJK-16CP, QJK-19PR and QJK-29CP) and Donggualin adit (DGL-16PR, DGL-15CP, DGL-7PR and DGL-2CP) to represent mineralization in basalt interlayers and contact (Table 3). The mineral Qianjin adit samples mainly include chalcopyrite, pyrrhotite, actinolite and chlorite, while the Donggualin adit samples contain chalcopyrite, pyrrhotite, garnet, diopside and epidote.

Fresh chalcopyrite and pyrrhotite with >99% purity were hand-picked and cleaned ultrasonically in purified Milli-Q H2O (18.2 MΩ). The purified samples were measured for Pb isotopes on a Nu Instruments multiple collector plasma source mass spectrometer at the Laboratory of Isotope Geology, MLR, Institute of Geology, Chinese Academy of Geological Sciences. The mass discrimination of instrument has been corrected by using the “Tl-doping” method (He et al., 2005). The amount of Tl is about 1/2 of Pb content. Pb isotope ratios of samples are reported relative to the measured ratio for NBS981 standard material.

5.2.2. Sulfur isotopes

We collected 27 samples from granite (CYB1008143, CYB1008193, CYB1008196, CYB1008210, CYB1008248), basalt (ZKF08-11, ZKF08-12, ZKF08-14, ZKF08-26, CYB1008194), carbonate (TSY-1, TSY-2, TSY-3), skarn ores (JZL-2CP, JZL-3PR, JZL-4PR, DGL-6PR, DGL-7PR, DGL-15CP, DGL-15PR, DGL-16CP) and basalt hosted ores (QJK-16CP, Fig. 5. Photographs of the main alteration and mineralization styles in the stratiform Cu ore hosted by basalt. 1—Contact of granite and basalt. 2—Skarn vein associate with mineralization in basalt. 3 and 4—Pyrrhotite mineralization in basalt. 5—Quartz vein and associate mineralization in basalt. 6—Fluorite vein in basalt.
QJK-16PR, QJK-10CP, QJK-43CP, QJK-29CP, QJK-3CP) to study the S isotopic evolution in different parts of the Kafang orefield. Sulfur isotope measurements were performed on pyrite and pyrrhotite. SO$_2$ was prepared from pyrite using the method of Robinson and Kusakabe (1975), and was analyzed with a MAT 251 EM mass spectrometer at the Stable Isotope Laboratory of Institute of Mineral Resources, Chinese Academy of Geological Sciences. Sulfur isotope ratios are reported as $\delta^{34}$S relative to the Cañon Diablo Troilite (CDT); the analytical reproducibility is $\pm 0.2‰$ (Mao et al., 2008b).

5.2.3. Oxygen and hydrogen isotopes

Samples for H–O isotopes study were collected from the granite margin (ZYK-4), skarn Cu–Sn ores (JZL-5), and basalt interlayer-hosted Cu ores (ZYK-1), and carbonate-hosted ores (DGL-1) to represent the different mineralization environments of the Kafang deposit. Oxygen was liberated from quartz by reaction with BrF$_5$ (Clayton and Mayeda, 1963) and converted to CO$_2$ on a platinum-coated carbon rod. The $\delta^{18}$O analyses were made on a Finnigan Mat 253 mass spectrometer at the Stable Isotope Laboratory of Institute of Mineral Resources, Chinese Academy of Geological Sciences. Reproducibility for isotopically homogeneous pure quartz is about $\pm 0.2‰$ ($1\sigma$) (Mao et al., 2008b).

Hydrogen isotope ratios on bulk fluid inclusions in quartz were measured by mechanical crushing of about 5 g of quartz grains, 1 to 5 mm in size, according to the method described by Simon (2001). Samples were first degassed of labile volatiles and low temperature fluid inclusions by heating under vacuum to 120 °C for 3 h. The released water was trapped, reduced to H$_2$, and then analyzed with a Finnigan Mat Delta 251 S mass spectrometer at the Stable Isotope Laboratory of Institute of Mineral Resources, Chinese Academy of Geological Sciences. Analyses of standard water samples suggest a precision for $\delta D$ of $\pm 2‰$ ($1\sigma$) (Mao et al., 2008b).

5.3. Geochronology

5.3.1. Re–Os dating

Five molybdenite samples (C009-8, C009-12, C010-1, C010-2, C010-3) were collected from a Mo-bearing skarn, and another five molybdenite samples (CYB1008231, CYB1008225, CYB1008228, CYB1008230, CYB1008232) were collected from basalt interlayers associated with the Cu mineralization for Re–Os dating, to constraint the ages of these two styles of mineralization. Gravitational and magnetic separation were applied and molybdenite grains were handpicked under a binocular microscope (purity >99%). The analyzed molybdenite is fine-grained (<0.1 mm), and thus likely avoided the decoupling of Re and Os within large molybdenite grains (Selby and Creaser, 2004; Stein et al., 2003). Re–Os isotope analyses were performed in the Re–Os Laboratory, National Research Center of Geoanalysis of Chinese Academy of Geological Sciences in Beijing using a Thermo Electron TJA X-series ICP-MS. The analytical procedures followed those of Shirey and Walker (1995), Mao et al. (1999) and Du et al. (2004). The model ages were calculated on following the equation: $t = \frac{\ln (1 + \frac{187\text{Os}}{187\text{Re}})}{\lambda}$, where $\lambda$ is the decay constant of $^{187}$Re, 1.666 $\times 10^{-11}$/yr$^{-1}$ (Smoliar et al., 1996).

5.3.2. LA-ICP-MS

Zircons for analysis were separated from 10 kg bulk samples of Xinshan granite, using conventional heavy liquid and magnetic techniques. Representative zircon grains were handpicked under a binocular microscope, mounted in epoxy resin, polished, and coated with gold, which was used for CL imaging and removed before laser ablation.
6.1. Magmatism and mineralization dating

6.1.1. LA-ICP-MS zircon U–Pb dating

The zircon U–Pb analytical results are presented in Table 4. Most zircon grains have uniform U concentrations ranging from 142 to 1210 ppm and variable Th concentrations from 98 to 3287 ppm, with Th/U ratios ranging between 0.14 and 1.14. In the analyses, 18 spots in 18 different zircons from 10 kg samples yielded $^{206}\text{Pb}/^{238}\text{U}$ ages of 81.9–83.8 Ma with a weighted mean age of 83.1±0.4 Ma, and MSWD = 0.21 (Fig. 7), which is interpreted as the crystallization age of the Xishan granite.

6.2. Re–Os molybdenite Re–Os dating

Results of molybdenite Re–Os dating are listed in Table 5. For the samples associated with skarn Cu–Sn mineralization, the concentrations of $^{187}\text{Re}$ and $^{187}\text{Os}$ range from 23.60 to 39.10 ppm and 20.69 to 34.14 ppb, respectively. Five samples give a Re–Os model age of 82.95–83.54 Ma and a weighted mean age of 83.30±0.4 Ma. The data, processed using ISOPLOT/Ex (Ludwig, 2004), yielded an isochron age of 83.4±2.1 Ma, with MSWD = 0.37 (Fig. 8a).

For samples associated with stratiform Cu mineralization in basalt interlayers, the concentrations of $^{187}\text{Re}$ and $^{187}\text{Os}$ range from 7.72 to 13.16 ppm and 6.81 to 11.56 ppb, respectively. Five samples give a Re–Os model age of 83.82–85.74 Ma and a weighted mean age of 85.30±0.4 Ma.

### Table 1: Classification of characteristics of samples.

<table>
<thead>
<tr>
<th>Location</th>
<th>Granite interior</th>
<th>Granite margin</th>
<th>Skarn ores</th>
<th>Stratiform Cu ores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dongguain +1800 m</td>
<td>Qianjin +1800 m</td>
<td>Dakeng +1800 m</td>
<td>Qianjin +1800 m</td>
</tr>
<tr>
<td>CYB0910050</td>
<td>5</td>
<td>5</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>CYB0108224</td>
<td>25</td>
<td>40</td>
<td>40</td>
<td>150</td>
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<td>–</td>
</tr>
<tr>
<td>CYB0912033</td>
<td>40</td>
<td>–</td>
<td>40</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 2: Characteristics and parameters of primary fluid inclusion in Kafang Cu–Sn deposit.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Mineral</th>
<th>Location</th>
<th>Representation</th>
<th>Type</th>
<th>Inclusion number</th>
<th>Homogenization T (°C)</th>
<th>Freezing point T(°C)</th>
<th>w(NaCl)/ Density (g/cm³)</th>
</tr>
</thead>
<tbody>
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<td>CYB1008224</td>
<td>Quartz</td>
<td>1870 m in Pianjin</td>
<td>Granite interior</td>
<td>A 5</td>
<td>279.3–355.5</td>
<td>331.0</td>
<td>17.1–20.3</td>
<td>20.30–22.58</td>
</tr>
<tr>
<td>CYB0912032</td>
<td>Quartz</td>
<td>1800 m in Dakeng</td>
<td>Granite margin</td>
<td>A 2</td>
<td>287.4–376.7</td>
<td>323.5</td>
<td>3.6–4.7</td>
<td>5.86–7.45</td>
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<tr>
<td>CYB0912033</td>
<td>Quartz</td>
<td>1800 m in Dongguain</td>
<td></td>
<td>A 9</td>
<td>293.2–341.7</td>
<td>319.3</td>
<td>18.5</td>
<td>21.33</td>
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<tr>
<td>CYB0912050</td>
<td>Quartz</td>
<td>1800 m in Dongguain</td>
<td></td>
<td>A 9</td>
<td>302.5–338.8</td>
<td>318.9</td>
<td>20.7</td>
<td>22.85</td>
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<tr>
<td>CYB0912006</td>
<td>Quartz</td>
<td>1800 m in pianjin</td>
<td>Contact</td>
<td>B 5</td>
<td>257.2–294.0</td>
<td>278.7</td>
<td>15.0–14.6</td>
<td>18.30–18.73</td>
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<td>ZKX08-23</td>
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<td>1800 m in pianjin</td>
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<td>C 1</td>
<td>109.7–201.8</td>
<td>169.6</td>
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<td>215.3</td>
<td>10.7</td>
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<td>ZKX08-90</td>
<td>Calcite</td>
<td>1820 m in Basalt</td>
<td>Contact</td>
<td>C 6</td>
<td>131.5–183.5</td>
<td>155.4</td>
<td>5.0–4.3</td>
<td>6.88–7.86</td>
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<td>1820 m in Basalt</td>
<td>Contact</td>
<td>C 6</td>
<td>131.5–183.5</td>
<td>155.4</td>
<td>5.0–4.3</td>
<td>6.88–7.86</td>
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<tr>
<td>ZKX08-109</td>
<td>Quartz</td>
<td>1690 m in Carbonate</td>
<td></td>
<td>A 15</td>
<td>323.8–443.8</td>
<td>394.3</td>
<td>20.3</td>
<td>22.58</td>
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<tr>
<td>ZKX08-109</td>
<td>Quartz</td>
<td>1690 m in Carbonate</td>
<td></td>
<td>B 3</td>
<td>2055.2–2454</td>
<td>237.8</td>
<td>15.5–6.1</td>
<td>9.34–19.05</td>
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<tr>
<td>ZKX08-109</td>
<td>Quartz</td>
<td>1690 m in Carbonate</td>
<td></td>
<td>C 15</td>
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<td>147.1</td>
<td>12.9–3.8</td>
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<td>248.4</td>
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A: vapor volume is 15% to 40%; B: vapor volume is 5% to 15%; C: vapor volume is less than 5%.
The study of sulfur isotopes is crucial for understanding the mineralization processes. Sulfur isotopes can distinguish between different ore types and provide insights into the geological setting of deposition. The δ34S values for different ore types range from -3.2‰ to +3.7‰, indicating a range of isotopic compositions that can be attributed to various ore types.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minerals</th>
<th>208Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>206Pb/204Pb</th>
<th>Location</th>
<th>Style</th>
<th>Reference</th>
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<td>Basalt hosted</td>
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<td>This paper</td>
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<td>15.6130</td>
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<td>Gejiu Formation</td>
<td>Wall rock</td>
<td>Wang, 1983</td>
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</table>

84.41 ± 0.92 Ma. The data, processed using the ISOPLOT/Ex program (Ludwig, 2004), yielded an isochron age of 84.2 ± 7.3 Ma, with MSWD = 2.40 (Fig. 8b). The identical model ages and isochron ages for the two samples suggest that the analytical results are reliable.

### Table 4

<table>
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<tr>
<th>Spots</th>
<th>Th/U</th>
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<th>±1σ (‰)</th>
<th>208Pb/204Pb</th>
<th>±1σ (‰)</th>
<th>207Pb/235U</th>
<th>±1σ (‰)</th>
<th>208Pb/235U</th>
<th>±1σ (‰)</th>
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<td>O22-17</td>
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<td>0.000</td>
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<td></td>
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The slightly depleted in δ18O suggests that some meteoric water could have mixed with a magmatic fluid during the mineralization process.

### 6.2. Isotopes

#### 6.2.1. Sulfur isotopes

Sulfur isotope data are presented in Table 6. 24 samples of this study and 3 samples from the literature covered all the mineralization units of the Kafang deposit. Large variations are exhibited by our samples, yielding δ34S values in the range —3.2 to 11.1 per mil. All samples from skarn orebodies have negative δ34S values (−3.2 to −0.9), and are in the range of the samples from granite (−3.7 to 0.1); whereas the samples from basalt-hosted stratiform Cu orebodies yield positive values (1.5 to 2.9), close to the range of the basalt (2.6 to 3.8). However, all the data of the four mentioned locations is distinguished from the Gejiu Formation sediments (Qin and Li, 2008).

#### 6.2.2. Hydrogen and oxygen isotope data

The oxygen isotope ratios of ore-forming fluid in equilibrium with the quartz are calculated using the fractionation formulas from Clayton and Mayeda (1963). The results show that the δ18O values fall within a range between 3.1 and 7.7‰ (the calculated temperature as listed in Table 2). The granite sample has a value of 7.7‰, the basalt-hosted ores are 7.2‰, skarn ores are 6.6‰, and the carbonate-hosted ores are 3.1‰. δD values vary between −73 and −98‰ with an average of −86.5‰. The values of δ18O are similar to those of magmatic fluids (+5.5 to +9.5 per mil) (Ohmoto and Goldhaber, 1997; Ohmoto and Rye, 1979) (Table 7).
an average of 18.500 and $^{207}\text{Pb}/^{204}\text{Pb}$ from 15.629 to 15.666, with an average of 15.646.

6.4. Fluid inclusion studies

6.4.1. Petrography and types

Most fluid inclusions are primary and pseudosecondary and are distributed in groups or isolated (Fig. 9), with size generally $8 \times 6 \mu m$, up to $14 \times 8 \mu m$. Secondary inclusions are presenting fractures cross-cutting host minerals. The majority of the inclusions are liquid-rich two-phase inclusion. Based on their compositions and physical properties, inclusions of this study can be classified into three types: (1) vapor-rich type (A type), where the volume of vapor is about 20% and generally 15% to 40%, with a few having larger bubbles and the vapor phase occupies ~50 vol.% (Fig. 9); (2) vapor phase-moderate type (B type), where the volume of vapor is about 10% and generally 5% to 15%; and (3) vapor phase-poor type (C type), with the volume of vapor is generally less than 5%. Coexistence of the three types of fluid inclusions in the Kafang ores indicates that the fluid inclusions captured heterogeneous fluids, i.e., boiling may have occurred during mineralization.

6.4.2. Microthermometry

Table 2 summarizes the microthermometric data. Salinities are calculated using the data of Bodnar (1985), and density is calculated from the empirical formula of Liu and Shen (1999).

For the A-type inclusions, 99 inclusions were analyzed from all the samples collected from the five mineralization environments (i.e., interior granite, granite margin, skarn, basalt-hosted and carbonate-hosted ores) (Table 2). The homogenization temperatures range from 279.3 to 452.0 °C, with an average of 336 °C, and the ice-melting temperatures were between $-15.8$ and $-20.7$ °C. The corresponding salinities of the inclusions were from 15.37 to 22.85 wt.% NaCl equiv., averaging 20.70 wt.% NaCl equiv., and all the densities range between 0.773 and 0.934.

The B-type inclusions, 88 inclusions were analyzed and the homogenization temperatures ranged from 161.6 to 342.4 °C, with an average of 243 °C, and the freezing temperature were $-6.0$ to $-15.5$ °C. The corresponding salinities of the inclusions were from 9.21 to 19.05 wt.% NaCl equiv., averaging 13.42 wt.% NaCl equiv., and most the densities are between 0.823 and 1.036.

52 inclusions were analyzed for the C-type inclusions, and the homogenization temperature ranged from 105.2 to 227.8 °C, with an average of 168 °C, and the freezing temperature were $-1.1$ to $-12.9$ °C.

### Table 5

mo®ybdenite Re–Os dating results of Kafang ore field.

<table>
<thead>
<tr>
<th>Sample from skarn mineralization</th>
<th>Weight/g</th>
<th>Re/10^{-6}</th>
<th>Os ng/g</th>
<th>Re187/10^{-6}</th>
<th>Os187/10^{-9}</th>
<th>Model age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C009-8</td>
<td>0.05046</td>
<td>23.6 ± 0.2</td>
<td>0.0145 ± 0.0150</td>
<td>14.9 ± 0.2</td>
<td>20.69 ± 0.18</td>
<td>83.54 ± 1.31</td>
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<tr>
<td>C009-12</td>
<td>0.05055</td>
<td>29.8 ± 0.2</td>
<td>0.0274 ± 0.0149</td>
<td>18.7 ± 0.2</td>
<td>25.87 ± 0.15</td>
<td>82.95 ± 1.16</td>
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<td>C010-1</td>
<td>0.05046</td>
<td>39.1 ± 0.4</td>
<td>0.0204 ± 0.0049</td>
<td>24.6 ± 0.2</td>
<td>34.14 ± 0.20</td>
<td>83.35 ± 1.24</td>
</tr>
<tr>
<td>C010-2</td>
<td>0.04999</td>
<td>25.09 ± 0.2</td>
<td>0.0203 ± 0.0086</td>
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<td>21.80 ± 0.12</td>
<td>83.25 ± 1.14</td>
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<td>C010-3</td>
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<td>31.98 ± 0.21</td>
<td>83.49 ± 1.19</td>
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</table>

<table>
<thead>
<tr>
<th>Sample from stratiform ore hosted by basalt</th>
<th>Weight/g</th>
<th>Re/10^{-6}</th>
<th>Os ng/g</th>
<th>Re187/10^{-6}</th>
<th>Os187/10^{-9}</th>
<th>Model age (Ma)</th>
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<td>9.271 ± 0.1</td>
<td>1.5680 ± 0.0320</td>
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<td>8.16 ± 0.1</td>
<td>83.96 ± 1.21</td>
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<tr>
<td>CYB1008225</td>
<td>0.05066</td>
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<td>0.3523 ± 0.0126</td>
<td>8.274 ± 0.1</td>
<td>11.56 ± 0.1</td>
<td>83.82 ± 1.20</td>
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<tr>
<td>CYB1008228</td>
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<td>4.850 ± 0.1</td>
<td>6.81 ± 0.1</td>
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<td>0.05194</td>
<td>10.70 ± 0.1</td>
<td>0.9783 ± 0.0194</td>
<td>6.723 ± 0.1</td>
<td>9.49 ± 0.1</td>
<td>84.68 ± 1.32</td>
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<tr>
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<td>6.744 ± 0.1</td>
<td>9.64 ± 0.1</td>
<td>85.74 ± 1.41</td>
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</table>
The corresponding salinities of the inclusions were from 1.91 to 16.80 wt.% NaCl equiv., averaging 5.05 wt.% NaCl equiv., and the densities range from 0.860 to 1.055.

7. Discussion

7.1. Timing of magma emplacement and Cu–Sn mineralization

Numerous geochronological studies have been carried out on Xinshan granite and results vary widely, including 81 Ma by Rb–Sr (Wu et al., 1984), and 64–84 Ma by unknown methods (308 Geological Party, 1984; Dai, 1996). Qin and Li (2008) obtained several mica $^{40}$Ar–$^{39}$Ar ages ranging from of 83.23 ± 2.07 Ma to 205.11 ± 4.38 Ma. An age range of 43.49 ± 0.87 Ma to 186.01 ± 3.72 Ma of cassiterite was also reported by Qin and Li (2008) by K–Ar methods. Previous age determinations for the granite and the ores vary widely and are not consistent. In this study, we obtained a zircon LA-ICP-MS U–Pb weighted mean age of 83.1 ± 0.4 Ma from the Xinshan granite and two Re–Os isochron ages for molybdenite samples of 83.4 ± 2.1 Ma and 84.2 ± 7.3 Ma from the skarn Sn–Cu ores and stratiform Cu ores interpreted to represent the age of the Xinshan granite, skarn Cu–Sn ores, and stratiform Cu ores hosted by basalt, respectively. These ages are consistent, and indicate that granite emplacement and the Cu–Sn mineralization were largely synchronous, in the Late Cretaceous.

Fig. 8. Re–Os isochron of molybdenites from skarn and basalt hosted stratiform Cu ores.
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7.2. Source and fluid evolution

7.2.1. Source of ore-forming materials

As described above, Cu mineralization is found in all the three types of orebodies while the Sn mineralization only developed in skarn orebodies and stratiform ores hosted by carbonate. Here, we attempt to constrain the key factors responsible for the formation of two types of stratiform ores and skarn-type ores using Pb and S isotope systematics.

Lead isotope compositions of basalt-hosted ores mainly plot between the orogenic belt evolution curve and the mantle evolution curve (Fig. 11), indicating a mixed origin between mantle and crust according to the "orogenic" reservoir of Zartman and Doe (1981). Pb isotope compositions of the stratiform orebody are similar to those of basalt; however, they are different from the limestone of the Gejiu Formation and K-feldspar from the Xinshan granite.

Lead isotope compositions of basalt-hosted ores is 2.6 to 3.8. Based on the S and Pb isotopic data of this study, our results and previous results show that the S isotopes of skarn orebodies are mainly derived from the granite. Sulfur isotopic compositions of the skarn orebodies falls within a narrow range between −3.2%o and −0.9%o with an average of −1.7%o and are similar with the data of the granite (Fig. 12). Sulfur isotopes in the Gejiu Formation carbonate range from 7.14 to 11.1 (Qin and Li, 2008). This suggests that there is little contribution of sedimentary S for the skarn-type mineralization. Moreover, δ34S values of skarn orebody in this study are consistently lower than those of the basalt (Fig. 12). Our data is therefore inconsistent with a sedimentary or basaltic S source. Considering both the Pb and S isotopes, we suggest that the source of sulfides in skarn orebody is the Cretaceous granite.

7.2.2. Fluid evolution

It is clear that from the granite outward, there is a progressive decrease trend in homogenization temperature and salinity for all the samples of the 5 mineralization environments i.e., interior granite, granite margin, skarn, basalt-hosted and carbonate-hosted ores. We suggest all the fluids of the 5 environments should belong to a same ore-forming fluid system. Moreover, as the similar microthermometric results of the granite and the 3 different mineralization environments, according to the coeval relationships of the magmatism and mineralization, we suggest that all the ore-forming fluids of the whole Kafang deposit derived from the same granitic magma, i.e., the Xinshan granite.

Hydrogen and oxygen isotopes are important monitors for the evolutionary history of ore-forming fluids. Zhao et al. (1990) and Zhao et al. (2003) pointed out that the δD (−90.3‰ to −48.3‰)}

<table>
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<th>Sample</th>
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<th>δ18OδHSMOW(‰)</th>
<th>δ18OδHSMOW(‰)</th>
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<td>Quartz</td>
<td>Donggualin tunnel</td>
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<td>15.20</td>
<td>−92</td>
<td>3.1</td>
</tr>
<tr>
<td>JZL-5</td>
<td>Quartz</td>
<td>Zhulin tunnel</td>
<td>317</td>
<td>12.92</td>
<td>−73</td>
<td>6.6</td>
</tr>
<tr>
<td>ZYK-1</td>
<td>Quartz</td>
<td>Zhulin tunnel</td>
<td>317</td>
<td>13.54</td>
<td>−83</td>
<td>7.2</td>
</tr>
<tr>
<td>ZYK-4</td>
<td>Quartz</td>
<td>Zhulin tunnel</td>
<td>320</td>
<td>13.88</td>
<td>−98</td>
<td>7.7</td>
</tr>
</tbody>
</table>
−67‰ in average) and δ18O H2O (3.35‰–9.59‰, 5.9‰ in average) of granite-related skarn deposits are consistent with a predominantly magmatic source with a minor meteoric water contribution. In this study, the δ18O H2O values of the quartz vary from 3.1 to 7.7‰ with an average of 6.15‰, δ18O H2O values of sample JZL5 (from Jinzhulin adit) plot within the magmatic water box (δD H2O: −80‰−−40‰, δ18O H2O: 5.5‰–9.0‰; Taylor, 1974), which indicates that these ore-forming fluids are dominantly magmatic water (Fig. 13). Two other samples (ZYK-1 and ZYK-2) have similar δ18O H2O values as JZL5, but δD values are below the magmatic water box. Sample DGL-1 (from Donggualin adit) indicates significant mixing of meteoric water. The compositions of hydrogen–oxygen isotopes indicate that the ore forming fluid dominated by magmatic water in the early stage and it mixed with meteoric water in a later stage. This is supported by the large variations of fluid inclusion homogenization temperatures and salinities as discussed above (Fig. 10).

### 7.3. Mineralization process and ore genesis

Between ~83 and ~84 Ma, the Xinshan granitic magma intruded into the Triassic Gejiu Formation and associated mafic lavas, causing skarn and retrograde alteration in the wall rocks of the Kafang area. Temperature decrease decreases metal solubility in the ore-forming fluids (Barnes et al., 1967; Bourcier and Barnes, 1987; Crerar and Barnes, 1976; Giordano and Barnes, 1979; Romberger and Barnes, 1970). In the Kafang deposit, the homogenization temperatures of fluid inclusions range widely, which can be ultimately beneficial for the economic viability of the deposit. The wide temperature range, with corresponding salinities and densities, suggests multiple stages of evolution of the ore-forming fluid in Kafang deposit, which is also supported by the different H–O isotopes compositions of different mineralization styles. Therefore, we suggest the mixing of granitic magma-derived fluid and meteoric water, along with decreasing temperature had a key role in the precipitation of the ore minerals.

Both S and Pb isotopes indicate that the Cu and Sn have distinct parental magmas: Cu was likely sourced from the basaltic magma, whereas Sn was likely sourced from the granite. Ore metals were transported by magma-derived hydrothermal fluids. This model is supported by the following observations: (1) both copper and tin are spatially centered around the Xinshan granite; (2) the alteration minerals are present throughout the whole orefield, including in the two stratiform types and the skarn ores; (3) in Kafang area, Cu is more widely distributed than Sn, as the former can be found in all the mineralization types, while the Sn ores only developed as skarn-type or carbonate–carbonate; (4) the Cu and Sn abundance in different units of this area (Table 8). The average Cu abundance of Xinshan granite is 15.6×10−6, and Gejiu Formation is 20×10−6, but the Cu abundance of basalt in Kafang orefield is 500×10−6 (Peng, 1992). The Cu abundance of basalt is 32 and 25 times higher than the granite and sedimentary rocks.

Much research has shown that high oxygen fugacity is beneficial for the enrichment of Cu in magmatic melts and the continuous release from ore-forming fluid (Sun et al., 2004; Wyborn and Sun, 1994). Conversely, the deposition environment of Sn in the granitic magma favors low oxygen fugacity, which is common for most tin granite world-wide, under a NNO system (Heinrich, 1990). Available published data show that the Xinshan granite has a low oxygen fugacity (Li, 1985), which means that granitic magma in Kafang Sn–Cu mine with low oxygen fugacity decreases the Cu solubility and thus decreases the potential for Cu mineralization, but is favorable for tin mineralization. Though controversies about the genesis of Kafang Cu–Sn mineralization have existed for many years (308 Geological Party, 1984; Jin, 1991; Mao et al., 2008a; Peng, 1985; Qin et al., 2006; Yang et al., 2008; Zhuang et
al., 1996), geological evidence and the new data of this study, led us to conclude that both granite and basalt played important role for the formation of the Kafang Cu–Sn deposit, where the granite acted as a source of fluids, S and some metals, but the Triassic basalt also contributed metals and S upon interaction with magmatic hydrothermal fluids.

We propose the following genetic model for the Kafang deposit. A high temperature granitic magma-derived hydrothermal fluid interacted with cooler incoming meteoric water and formed the Sn ores and developed the related skarns and retrograde alteration along contact zones. The same hydrothermal fluid leached Cu from the basalt when it interacted with the basalt during its outward migration. As this fluid cooled and interacted with meteoric water, the stratiform Cu orebodies formed. Some of the magma-derived ore-forming fluid, transported Cu and Sn along the detachment structure of the Gejiu Formation (Mao et al., 2008a), and sulfide and cassiterite precipitated upon interaction with the carbonate layers, forming the carbonate-hosted stratiform Cu–Sn ores.

8. Conclusions

New LA-ICP-MS zircon U–Pb ages of the Xinshan granite (83.1 ± 0.4 Ma) and molybdenite Re–Os ages of the skarn ore (83.4 ± 2.1 Ma) and basalt-hosted ore (84.2 ± 7.3) in the Kafang orefield indicate a coeval relationship between magmatism and mineralization in Kafang deposit. Microthermometric results of fluid inclusions and H-O isotope data indicate that ore-stage minerals precipitated by the mixing of magma-derived fluid and meteoric water. According to the homogenization temperature, salinity and density data, it is inferred that fluid mixing along with fluid cooling played a key role in the formation of the Cu–Sn deposits in the Kafang area. A similar evolutionary trend of fluids suggests that the skarn, basalt-hosted and carbonate-hosted ores belong to a same ore-forming fluid system, which derived from the crystallizing Xinshan granite. S and Pb isotope indicate that the ore metals came from different sources, i.e., Cu was likely sourced from the basalt, whereas Sn was likely sourced from the granite. Thus we conclude that the metallogeny of the Cu–Sn ores in Kafang area should be attributed to be the same intrusion-related hydrothermal system.
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