Revision 2

The ore-forming magmatic-hydrothermal system of the Piaotang W-Sn deposit (Jiangxi, China) as seen from Li-mica geochemistry

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Abstract

Many studies have proved the usefulness of Li-mica and chlorite geochemistry as indicators of the chemical and thermal evolution of magmatic systems. This study highlights the suitability of Li-micas as tracers of hydrothermal mineralizing events in world-class W-Sn deposits associated with Jurassic (190–150 Ma) granites in China through the complex magmatic–hydrothermal evolution of the Piaotang deposit (South Jiangxi). A paragenetic sequence has been established for the Piaotang deposit comprising (i) a first “silicate-oxide” stage that hosts abundant W-Sn mineralization ( wolframite and cassiterite), (ii) a “calcic” stage with scheelite and wolframite, (iii) a “base metal sulphides” stage with cassiterite and wolframite, and (iv) a late “sulphide” stage, involving for the first time a polyphase emplacement of the mineralization. Li-micas from the underlying granite, greisen, and the different stages represented in the veins, were studied. The chemistry of the micas (characterized by intermediate compositions between phlogopite-zinnwaldite-muscovite poles) demonstrates the presence of end-members representing three different fluids that were involved in the emplacement of the Piaotang deposit. These end-members can be linked to previous fluid inclusion studies conducted on this deposit. The three fluids are identified to be magmatic, meteoric (as previously reported in the literature), and also metamorphic, and are shown to have mixed throughout the different stages. Moreover, it appears that the magmatic fluids could not have been derived from the Piaotang biotite granite but rather must have originated from a more evolved rare metal granite that is presently unidentified. These fluids were responsible for the greisenization.

Finally, chlorite geochemistry reveals the occurrence of a heating process (from 200°C in stage II to 300°C in stage III) during the post-mineralizing stages, which was responsible for the precipitation of new generations of ore-bearing minerals (cassiterite and wolframite).
concomitant with a continuous gain of metals during the emplacement of the Piaotang deposit.

Keywords

Piaotang, W-Sn deposit, Yanshanian, Lithium-mica, Chlorite, Magmatic-hydrothermal

Introduction

Constraining the origin and evolution of mineralizing fluids in W-Sn-quartz vein-type deposits remains challenging. Current models refer to (i) metal-rich magmatic fluids exsolved from granitic magmas (e.g., Kamenetsky et al., 2004; Audétat et al., 1998; Thomas et al., 2005), (ii) “external” fluids (metamorphic or meteoric) that circulate around cooling peraluminous granitoids and leach metals from the peraluminous granitoid or the country rocks (e.g., Wilkinson 1990; Blamart 1991; Smith et al. 1996; Zhao and Jiang, 2004), or (iii) combinations of the two (e.g., Beuchat et al., 2004; Carruzo et al., 2004; Marignac and Cathelineau 2009; Wei et al., 2012; Chicharro et al., 2016). In association with stable isotope (O, H) studies of minerals (Beuchat et al., 2004; Carruzo et al., 2004; Wei et al., 2012; Chicharro et al., 2016), fluid inclusion studies have contributed greatly to these models in recent years, by providing valuable information about the origins and physical–chemical evolution of the mineralizing fluids (e.g., Audétat et al. 1998; Beuchat et al., 2004; Carruzo et al., 2004; Wei et al., 2012; Chicharro et al., 2016). However, fluid inclusion studies are restricted to just a few favourable mineral species (e.g., topaz, quartz, wolframite, and cassiterite) and even then, primary fluid inclusions are often hard to identify. Consequently, several stages of the deposit formation cannot be studied by this approach, and can only be
investigated indirectly using detailed paragenetic successions and in-depth geochemical analysis. In this perspective, Li-mica and chlorites, which are frequently found in W–Sn vein-type deposits (Giuliani, 1985; Tischendorff et al., 1997; Costi et al., 2002; Johan et al., 2012; Nieva, 2013) show interesting potential. The majority of chlorite species are sensitive to temperature in hydrothermal and geothermal systems (Walshe, 1986), and thus provide a useful geothermometer in many geological settings and, in particular, in hydrothermal metallogenic systems. Moreover, Legros et al. (2016) showed that, in the case of the Maoping deposit (Jiangxi, China), the detailed chemistry of magmatic and hydrothermal Li-mica can be used to interpret the relative contributions of magmatic, meteoric and metamorphic fluids in the formation and evolution of W-Sn deposits. Based on this work, the present study focuses on the Piaotang W-Sn deposit, located in the southern Jiangxi Metallogenic Province (SE China), the most important W-Sn province in the world (USGS, 2016). The Piaotang W–Sn deposit exhibits several generations of magmatic and hydrothermal Li-mica, as well as two generations of chlorite, that crystallized during multiple stages of the ore-forming system. This study uses combined optical microscopy, SEM, EPMA and LA-ICPMS to establish for the first time a detailed paragenetic succession for the Piaotang deposit and to determine the major and trace element compositions of Li-mica and chlorite geothermometers, with the aim of providing new constraints on the physical–chemical evolution of fluids involved in the formation of such deposits.

Geological Setting and sampling

The southern Jiangxi Metallogenic Province
The southern Jiangxi W-Sn province, also referred as Nanling metallogenic belt, is located in the Cathaysia Block of the South China Craton (SCC) and is currently the main W repository in China (90% of the reserves: Wang et al. 2016). The SCC resulted from late Grenvillian suturing between two terranes: the Yangtze Block to the north and the Cathaysia Block to the south, during the Jiangnan orogeny (Charvet 2013 and references therein). The final age of the collision is still under debate, with estimates ranging between 900 and 800 Ma (e.g., Li et al. 2009, Hu and Zhou 2012, Yao et al. 2013). Mostly coinciding with the southern boundary of the orogen, the major Jiangshan-Shaoxi fault zone is considered the northern boundary of the Cathaysia block (Figure 1).

After the Neoproterozoic collage of the Yangtze and Cathaysia terranes, the newly formed SCC was strongly reworked, becoming progressively metacratonized through a sequence of intra-continental events starting in the late Neoproterozoic (the failed Nanhua Rift: Wang et al. 2006), and followed by the Middle Palaeozoic (“Caledonian”) Kwangsian orogenesis, the Early Mesozoic Indosinian events and the Jurassic-Cretaceous Yanshanian events. Although the entire SCC was affected, the metacratonisation and the most pervasive magmatic activity during the Yanshanian were observed in the Cathaysia Block. Consequently, the Phanerozoic magmatism was responsible for producing one of the largest igneous provinces in the world (Zhang et al. 2012, Wang et al. 2013). A variety of granites were produced, including S-, I- and peralkaline-types. Metaluminous A-type granites remain the most frequently found. Nb-Ta-rich peraluminous rare metal granites (RMG) also form part of this magmatic diversity. Sporadic occurrences of RMG were first recorded in the Kwangsian (Wang et al., 2011), whereas both the Indosinian (270–200 Ma) (with the world-class Yichun deposit) and the early Cretaceous (ca. 130 Ma) appear to have been the most productive episodes of RMG magmatism.
The Middle Palaeozoic Kwangsian (Caledonian) orogeny, which produced a double-verging NE-trending belt, is commonly interpreted to have resulted from the inversion of the Nanhua Rift (e.g., Charvet et al., 2010, Charvet 2013). This first intra-cratonic event, which was restricted to the Cathaysia Block, culminated with crustal thickening and a HT metamorphic event at ca. 450 Ma, yielding a high-grade belt composed of migmatites and granulites (e.g., Liu et al. 2010), followed by basaltic underplating, dehydration melting in the lower crust, and the emplacement of large syn-kinematic S-type granite bodies (covering more than 20,000 km²: Li et al. 2011) at ca. 430–420 Ma (e.g., Wang et al. 2013, Xia et al. 2014).

At the end of the Triassic, a second major intracratonic event, which reworked the earlier Kwangsian structures (with the same NE-trending direction but a NW vergence), recorded the suturing of the SCC with the North China craton (e.g., Wang et al. 2001). This Indosinian event, which affected both the Cathaysia Block and the Jiangnan orogen, was associated with HT metamorphism (metamorphic core complexes: Faure et al. 1996), and produced large volumes of magma (presently covering 14,300 km²), with the subsequent emplacement of I-type granites (245-230 Ma) and S-type granites (220-210 Ma) (Shu et al. 2008 and references therein). The first cycle of Nb–Ta granites occurred in the Nanling Range (Mao et al. 2013).

The Yanshanian event (Late Jurassic-Cretaceous) was essentially marked by magmatism that led to the generation of the large igneous province (Li et al., 2014). However, the event was also associated with alternating transpressive and transtensional deformation along the same NE-SW lineaments that controlled the Kwangsian and Indosinian events (Li et al., 2014, Liu et al., 2012, Shu et al., 2009). The Yanshanian events are currently interpreted as reflecting a major change in the overall plate tectonic regime, with a shift from a Palaeo-Tethyan to a Pacific control, marked by the inception of subduction of the Paleo-Pacific (Izanagi) plate under the SCC (e.g. Zhou et al., 2002). The Yanshanian is subdivided into the Early (Jurassic)
and Late (Cretaceous) Yanshanian. The Jurassic (190–150 Ma) is characterized by extensive
magmatic activity, today represented by the outcropping of granitic rocks over an area of
about 100,000 km². The peak of magmatic activity is dated at 160–150 Ma, with several
pulses, and the granitic province exhibits all the characteristics of a felsic large igneous
province. The majority of the Cathaysia W-Sn deposits were formed during the same 160–150
Ma interval, although this was recently challenged (ca. 130 Ma ages proposed by Wang et al.
2016). Coeval with this, the E-W trending Nanling Range, which is composed of three
roughly parallel granitic belts and associated wolframite deposits (Zhao et al. 2017), was
formed. The Cretaceous event (135–80 Ma) was characterized by granites (mainly intruded in
the Cathaysian interior) and rhyolites (mainly erupted along the coastal area). Renewed rare-
metal deposition occurred in the Nanling Range, characterized notably by large magmatic-
related Sn and U mineralizations, while Au-Cu-Pb-Zn-Ag mineralizations were deposited
along the southeastern coast (Hua et al., 2005).

The Piaotang W-Sn deposit

The polymetallic W-Sn-(Nb) Piaotang deposit is one of several giant tungsten deposits in the
Nanling Range and produces 1,500 t WO₃ per year, ranking it eighth in the top ten reserves in
China with 47,775 t WO₃ (MB Company database: www.metalbulletin.com). The deposit is
composed of mineralised veins emplaced in Cambrian metasediments that lie above the
concealed Piaotang biotite granite (Figure 2). Two sets of faults can be observed in the field:
E-W-oriented faults intersecting NE-SW-oriented faults (Figure 2A). The granite was
emplaced during the Jurassic (159.8 ± 0.3 Ma, U-Pb zircon dating; Zhang et al., 2017), coeval
with the W mineralization (159.5±1.5 Ma, U-Pb cassiterite dating; Zhang et al., 2017). A
Kwangsian quartz diorite body (439 ± 2 Ma, U-Pb zircon dating; He et al. 2010) also occurs at depth.

**The vein system:** The vein system extends vertically over 300 m, down to the Piaotang biotite granite (Figure 2B). The vein system includes flat-lying and steep veins, associated with evidence for brittle tectonics. Field observations at different levels show (i) a first generation of, more or less lenticular, flat-lying (N80-90°E 30-40°N) quartz veins, displaying some evidence of faint extensional tectonics, (ii) a second generation of similar flat-lying veins (N0-30°E 30-40°W) corresponding to inverse faulting (as demonstrated by their intersections with the first generation veins), and (iii) a third generation of steep veins, with clear evidence for both faint inverse and sinistral strike-slip tectonics. Whereas the first generation of veins is scarce and the second generation is moderately frequent, the third generation of veins is ubiquitous. Only the third generation of veins shows mineralizations of economic interest. The thickness of the veins increases from the bottom to the top, from a few centimetres at the 556 level, to more than one meter at the 268 level.

**Relationship with the granite:** At the bottom of the system, a fine-grained biotite granite is observed. The interaction between this granite and the vein system appears to be complex.

- The granite exhibits a locally steep and sharp contact with the country rocks, striking 30°N. Outside the main body, several gently dipping dike-like expansions are observed, which themselves present complex digitations in the form of crackle breccias. No ductile deformation is observed along the contact between the granite and country rocks.

- Inside the granite body, a gently dipping vein system is observed. The veins show borders composed of feather-like K-feldspars megacrysts, and a filling of greisenized fine-grained rock that forms a cement around large quartz crystals (stockscheider).
The granite overprints a generation of flat-lying quartz veins which likely represent
the first generation of veins. Some dike-like expansions appear to be associated with inverse
brittle faulting as they intersect earlier flat-lying quartz veins. These dikes are likely coeval
with the second generation of veins.

Granite and greisen: The primary granite mineralogy consists of quartz, orthoclase, albite and
biotite (see below, Figure 5a). The texture is microgranular with porphyric perthitic K-
feldspar and quartz. No ductile or brittle deformation is observed: the granite is always
macroscopically isotropic. The micas enclose a variety of accessory minerals—apatite, quartz,
xenotime, rutile, monazite, fluorite and zircon—that are not observed in quartz or feldspars.
W, Sn or Nb-Ta minerals have not been observed in the granite. The feldspars are altered to
muscovite but also exhibit clay mineral alteration. This may be considered as incipient
greisenization, even if a clear granite to greisen transition is not observed in the mine.
The greisen at the top of the granite body is composed exclusively of quartz, muscovite and
fluorite (see below, Figure 5b). All minerals are corroded and very weakly deformed. Fluorite
is observed exclusively as inclusions in muscovite.

Analytical methods

Thirty samples of the mineralized veins, granite and greisen (Figure 3) were collected in the
Piaotang mine site at the 268, 388 and 556 levels (respective depths). The relationships
between host-rocks and veins are easily observed in the mine. As discussed previously, the
third generation of veins is the mineralization-bearing vein and thus only this vein is
considered in the remainder of the manuscript.
All preparations and analyses described below were carried out at the GeoRessources laboratory (Nancy, France). Petrographic observations were performed on polished thin-sections using conventional transmitted and reflected light microscopy and a HITACHI FEG S4800 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), using a Si(Li) semi-conductor detector.

Electron microprobe analyses (EMPA) of Si, Al, Ti, Na, Mg, Mn, Fe, K, Ca, Rb and F were performed on chlorites and Li-bearing micas using a CAMECA SX100 instrument equipped with a wavelength dispersive spectrometer (WDS) and calibrated using natural and synthetic oxides and silicates (albite, olivine, Al₂O₃, orthose, andradite, MnTiO₃, hematite, cassiterite, RbTiPO₅, topaz, scheelite, LiTaO₃ and LiNbO₃). A current of 12nA and an accelerating voltage of 15kV was used with a counting time of 10s per element. Special attention was paid to fluorine determination by using a spectrometer dedicated to this element (average detection limit of 1300 ppm). The analyses have a spatial resolution of 1 to 2 µm. The reproducibility of standard analyses was 1% for each element analyzed. Total Fe is presented as FeO.

Major, minor and trace elements (Mg, Si, Al, Ti, Mn, Fe, Co, Nb, Mo, Sn, Ba, Ta, W) were measured in Li-bearing micas using a LA-ICPMS instrumental setup described in Leisen et al. (2012) and Lach et al. (2013), composed of a GeoLas excimer laser (ArF, 193 nm, Microlas, Göttingen, Germany) (Günther et al., 1997) and an Agilent 7500c quadrupole ICPMS. The laser beam was focused onto the sample within a 24.5 cm³ cylindrical ablation cell with a Schwarzschild reflective objective (magnification ×25; numerical aperture 0.4) mounted on an optical microscope (Olympus BX41), equipped with a X–Y motorized stage and a CCD camera. Si (determined by EPMA) was chosen as an internal standard and precisely quantified by EPMA for all analysed micas. NIST SRM 610 (values from Jochum et al., 2011) was chosen as the external standard (accuracy was verified by analysing NIST SRM 612). The parameters used were a fluence of 8J/cm² and a laser shot.
frequency of 5 Hz, \( \text{He} = 0.5 \text{ L.min}^{-1} \) as a carrier gas mixed with \( \text{Ar} = 0.7 \text{ L.min}^{-1} \) via a cyclone mixer prior to entering the ICP torch, spot sizes of 120 µm, and an ablation duration of 40 s. Quantifications were performed using Iolite software (Paton et al., 2011) and concentrations were calculated following Longerich et al. (1996).

The temperature of chlorite formation was calculated using the graphical geothermometer of Cathelineau and Bourdelle (2015) for each composition that plotted between the sudoite, corundophilite and Al-free chlorite end-members on the Si-R\(^{2+}\) diagram of Wiewiora and Weiss (1990). This method assumes that quartz and water activities are equal to 1 and is valid for a temperature range of 50–350°C, which seems reasonable in the case of quartz-bearing rocks formed under low-grade metamorphic conditions, such as those in the Piaotang deposit.

All Fe was assumed to be ferrous in the calculations of the structural formulas.

Paragenetic sequence

A paragenetic succession was previously established by Tanelli (1982), providing a common chart for the Piaotang and Xihuashan deposits. According to Tanelli (1982), the succession can be divided into three stages: (i) a first “oxide stage” with quartz, K-feldspar, beryl, topaz, wolframite and cassiterite; (ii) a second “sulphide stage” with quartz, bismuthinite, sphalerite, galena, cassiterite and wolframite; and (iii) a third “carbonate stage” with quartz, chlorite, sericite, fluorite, calcite, pyrite and scheelite.

In the present study, a new paragenetic sequence was established from field observations in the mine galleries, as well as from petrographic observations by optical microscope, SEM and EPMA analyses in the laboratory (Figure 4). Hereafter, minerals refer to (i) their recommended IMA mineral abbreviations, (ii) their generation number (1 to 4, from the oldest to the youngest), and (iii) the paragenetic stage to which they belong (I to III, from the oldest to the youngest).
to the youngest). For example, Wf$_{2-III}$ stands for the second generation of wolframite in the
whole paragenetic sequence, occurring during stage III (sulphide stage).

As seen in Figure 4, our detailed study has led to some modification of the Piaotang
paragenetic succession. The main difference is seen in the “calcic stage”, now intercalated
between the “oxide” and “sulphide” stage on the basis of crosscutting relationships between
major minerals of the different stages. The succession obtained in this study is valid for the
entire vertical extent of the mineralized system (all levels).

*The silicate-oxide stage* (Stage I) represents the main stage of crystallization of the ore-
bearing minerals, wolframite and cassiterite. The Stage I minerals are Fe-Li-mica (Fe-Li-
mca$_{1,2,3-I}$), cassiterite (Cst$_{1,2-I}$), wolframite (Wf$_{1-I}$), topaz (Toz$_{1,2-I}$), quartz (Qtz$_{1,2-I}$), molybdenite
(Mlb$_{1-I}$), and possibly beryl (Brl$_{1-I}$). Stage I can be subdivided into two sub-stages: the first
(Ia) is the main ore stage and the second (Ib) is the main Fe-Li mica stage. There is however,
considerable overlap: (i) the earliest Fe-Li-mca$_{1-I}$ are coeval with Cst$_{1-I}$, and (ii) Cst$_{2-I}$ is
observed to have crystallized coevally with later Fe-Li-mca$_{2-I}$.

The wolframite Wf$_{1-I}$ shows maximum growth perpendicular to the walls, with crystals up to
15 cm in size found in the largest veins (Figure 3). Wf$_{1-I}$ is coeval with quartz growth (Qtz$_{1-I}$),
which shares similar comb textures and size. However, the initial morphologies of both the
quartz and wolframite were considerably altered by a succession of crack-seals (up to
brecciation) and recrystallization phenomena, with the growth of small newly formed
wolframite prisms on previous crystals (Figure 5c). Nevertheless, the wolframite composition
is homogeneous, with an average structural formula of Fe$_{0.5}$Mn$_{0.5}$WO$_4$ (SEM). The main
cassiterite (Cst$_{1-I}$) crystallization occurred after the main wolframite deposition, and cassiterite
growth is often observed on wolframite crystals (Figure 5c). Cst$_{1-I}$ deposition was coeval with
crack-sealing and Cst$_{1-I}$ is therefore frequently found at the vein selvages. The cassiterite
composition is pure SnO$_2$ (SEM). The earliest Fe-Li-mca$_{1-1}$ are associated with Cst$_{1-1}$, and have often grown in dissolution cavities affecting Qtz$_{1-1}$ (Figure 5d). A second generation of Fe-Li mica (Fe-Li-mca$_{2-1}$) occurs as infilling of vein openings, most often at the vein selvage, where it separates early cassiterite from the wall-rocks. Small overgrowths of Cst$_{2-1}$ are observed at the mica-Cst$_{1-1}$ boundary. Crack-seals filled with Fe-Li-mca$_{2-1}$ are also observed within Fe-Li-mca$_{1-1}$ aggregates and Cst$_{1-1}$, with overgrowths of Cst$_{2-1}$ associated with Qtz$_{2-1}$.

Cst$_{2-1}$ is compositionally identical to Cst$_{1-1}$. A last episode of crack-seal is observed in Fe-Li-mca$_{2-1}$ at the vein boundary and is associated with the deposition of the third generation of Fe-Li micas (Fe-Li-mca$_{3-1}$).

Topaz (Toz$_{1-1}$) has been deposited in fractures affecting Qtz$_{1-1}$, with symplectic topaz-quartz local associations indicating partial dissolution of the quartz. The exact timing of the topaz deposition is ambiguous. Local observations indicate that the topaz post-dates the Cst$_{1-1}$ deposition and has been altered by stage III micas, but no relationship between the topaz and the main micas was observed. Topaz was most probably emplaced during stage I as it experienced the same plastic deformation as the surrounding Qtz$_{1-1}$ as well as molybdenite (see below).

Tanelli (1982) listed K-feldspar, beryl, tourmaline, helvite and biotite in the oxide stage. These minerals were not observed in the present study, with the possible exception of beryl. Some euhedral prismatic crystals with hexagonal sections are observed in association with Qtz$_{1-1}$, which, being totally pseudomorphosed by stage III Li-msc$_{4-III}$, could originally have been beryl (Brl$_{1-1}$).

An episode of ductile deformation separates stage I from stage II. This episode affected both Qtz$_{1,2-1}$, all the Fe-Li micas, the topaz and the molybdenite. This deformation consists of very low intensity kinking of the micas and molybdenite, but is pervasive in quartz (subgrain
boundaries, undulose extinction). Such ductile-brittle transition separation (only observed microscopically) between early minerals and later stage minerals was also observed in the nearby Maoping deposit (Legros et al. 2016), where it may have been related to extensional tectonics.

**Calcic stage II**: Stage II is characterized by the partial transformation of wolframite into scheelite (Sch$_{1-II}$), followed by a first generation of chlorite (Chl$_{1-II}$) and fluorite (Fl$_{1-II}$) (Figure 6a and b). Small euhedral prismatic crystals of W-rich (up to 8.5 wt% WO$_3$) mangano-columbite (Clb$_{1-II}$), up to 5 µm in size, are systematically dispersed in the Chl$_{1-II}$. It is likely that the Clb$_{1-II}$ is the result of mobilization of Nb and W during wolframite transformation into scheelite. However, no particular textures were observed in Wf$_{1-I}$ using the SEM.

**Sulphide stage III**: Although mainly marked at the macroscopic scale by sulphide deposition, this stage is characterized by a complex succession of phyllosilicates, sulphides and late wolframite and cassiterite. The Fe-Li-mica (Fe-Li-mca$_{4-III}$) developed first, mainly at the expense of a pervasively corroded Qtz$_{1,2-I}$ or in the form of small veinlets overprinting earlier minerals as Chl$_{1-II}$. Fe-Li-mca$_{4-III}$ is also observed in thin crack-seal re-openings at the vein boundaries (exhibiting shearing features) and in alteration of Toz$_{1-I}$ (Figure 6c). Fe-Li-mca$_{4-III}$ also appears as spherolites (up to 150 µm in diameter) in vuggy microcavities. Some overgrowths on earlier micas (mainly Fe-Li-mca$_{1-I}$) are associated with these spherolites. As seen in Figure 7, these overgrowths (Z1 to Z4) are zoned and associated with reworking of the early zinnwaldite/Li-Ms association, which is overprinted by micas similar to the first zone of the overgrowth. The zones consist of an alternation of Li-Fe-Ms and Li-Ms. In the Monier and Robert diagram (1986) (Figure 8c), these zones plot along the Fe-Li-mca$_{4-III}$ trend. The end of the overgrowth is marked by distinctly Mg-rich (and Mn-poor) compositions, very
similar to those of the Fe-Li-mca$_{4-III}$ micas (Figure 7). Consequently, these overgrowths are considered to be coeval with the latter (Fe-Li-mca$_{4b-III}$). Sulphide deposition, coeval with a second generation of chlorite (Chl$_{2-III}$) (Figure 6d), follows chalcopyrite deposition (Ccp$_{1-III}$). Small euhedral prisms of a phenakite (Phk$_{1-III}$) are found as inclusions in the chalcopyrite. This phenakite could have trapped the beryllium leached from Brl$_{1-I}$ when replaced by Fe-Li-mca$_{4-III}$. Chl$_{2-III}$ deposition started with a Fe-chamosite composition and then evolved towards an Al-Fe clinochlore composition. Sphalerite (Sp$_{1-III}$) and stannite (Stn$_{1-III}$) followed the chalcopyrite deposition and appear as trails of more-or-less rounded inclusions (a few tens of µm in size). In detail, the sphalerite inclusions are zoned, with a core that is spotted with multiple chalcopyrite micro-inclusions and a rim that exhibits symplectic stannite-sphalerite associations (Figure 6e). Chalcopyrite micro-inclusions in sphalerite are known as “chalcopyrite disease”, which is classically interpreted to result from a reaction between sphalerite and a permeating Cu-rich fluid (Barton et al., 1978, Bortnikov et al., 1991). In the present case, the texture could therefore be referred to as “sphalerite disease”, interpreted as the healing of cracks affecting chalcopyrite. In systematic spatial association with sphalerite and stannite in the chalcopyrite, small euhedral cassiterite crystals (Cst$_{3-III}$) are observed, which locally contain inclusions of Mn-wolframite (Fe$_{0.43}$Mn$_{0.57}$WO$_4$, Wf$_{2-III}$) (Figure 6f). Cst$_{3-III}$ is also present in the form of microcracks lining the chalcopyrite boundary. Wf$_{2-III}$ microcracks of hübneritic composition (from Fe$_{0.20}$Mn$_{0.80}$W$_4$ to Fe$_{0.12}$Mn$_{0.88}$WO$_4$) are also observed. A late fluorite (Fl$_{2-III}$) is coeval with Cst$_{3-III}$ and Wf$_{2-III}$ (Figure 5f and g).

**Sulfosalt stage IV:** Overprinting all preceding mineral assemblages, a late generation of sulphured minerals has precipitated in the following sequence: galena (Bi-rich, up to 1 wt%), members of the lillianite series (Ag$_{0.8-1.3}$Pb$_{1.6-1.3}$Bi$_{2.6-2.7}$S$_6$), lead-rich bismuthinite (up to 5 wt%), and finally, native bismuth (Figure 6h).
Composition of micas

Major elements

All mica generations from the granite, greisen and the veins were studied by SEM and analysed by EPMA for major elements and LA-ICPMS for minor and trace elements. Representative EPMA analyses are presented in Table 1. A total of 170 EPMA and 98 LA-ICPMS analyses were performed.

The problem of Li content: The LA-ICPMS analyses (Table 2) showed that all Piaotang micas are Li-bearing micas. However, the micas appear to display complex internal patterns (see below) and the diameter of the LA-ICPMS spots (44 to 120 µm) was not small enough to measure most of the microstructures related to EPMA measurements (internal standardization for LA-ICPMS). Moreover, being a highly volatile element, lithium remains difficult to quantify with precision by LA-ICPMS (up to 0.5 wt. % Li₂O). To avoid this “lithium issue”, the empirical regressions of Tischendorff et al. (1997) are used. The suitable regressions in our system would be SiO₂ for tri-octahedral micas and F for di-octahedral micas, and both were used in the present study. However, the results were inconsistent: in the Li-Al-R²⁺ diagram of Foster (1960), the Piaotang micas plot within the immiscibility gap determined by Monier and Robert (1986), meaning that our calculated LiO₂ contents (Li₂O*) are underestimated. This problem was also encountered by Legros et al. (2016) in a study of the Maoping deposit and was resolved by adjusting the Li₂O* contents (by adding a constant to the Li₂O* values estimates from the Tischendorff et al. (1997) regressions). However, this method would be very complicated to apply in the case of the Piaotang deposit, where more
trends are exhibited (Figure 8). Consequently, the lithium content of the micas has been
removed from the diagrams.

Micas from granite: With an average Fe# \((\text{Fe}/(\text{Fe}+\text{Mg}+\text{Mn}) \text{ ratio})\) of 0.55 and an average
\(\text{R}^{2+}/(\text{R}^{2+}+\text{Al})\) of 0.53, the granite micas plot between annite-phlogopite and eastonite-
siderophyllite compositions (Figure 8a) and may be classified as lithian biotite.

\(\text{Fe-Li-mca}_{1,2}:\) The two first generations of micas appear as intergrowths of tri-octahedral and
di-octahedral components. Two converging trends are displayed in the Monier and Robert
(1986) diagram (Figure 8b): (i) a zinnwaldite-phlogopite trend (referred to as zinnwaldite in
the following) and (ii) a trend towards Li-muscovite (about 0.5 trilithionite), referred to as Fe-
Li muscovite in the following (Figure 8b). In detail, the micas consist of a succession of
alternating compositions between Fe-Li muscovite (Li-Fe-ms) and zinnwaldite (Znw). Both
Li-Fe-ms and Znw show a significant manganese content even though the zinnwaldite
components always exhibit higher Mn contents (up to 1.9 wt. % MnO). In addition, the
earliest Fe-Li-mca_{1,4} are characterized by the development of a large overgrowth, on a core
formed by the complex intergrowths described above (Figure 7). This overgrowth is zoned,
showing a succession of Fe-Li-ms toward Li-ms trends with distinct Fe#, similar to the
composition of the core (Figure 7). In addition, the outer zones are characterized by very low
Fe# and Mn contents.

End of stage I micas: The Fe-Li-mca_{3,4} are either Znw or Li-Fe-ms, and exhibit very similar
compositions to the earliest Fe-Li micas (Figure 8b).

Stage III micas: The Fe-Li-mca_{4,III} micas are all Fe-Li-ms, which, in the Al-Si-R^{2+} diagram,
are displaced from their equivalent from stage I (Figure 8c). However, they exhibit distinctive
low Fe# (0.2–0.4) and MnO (less than 1.0 wt. %) contents.
Greisen: The greisen micas are Fe-Li-ms, which, in the Monier and Robert (1986) diagram, are very similar to the Fe-Li-mca\(_{1-I}\) and Fe-Li-mca\(_{3-III}\) Fe-Li muscovites. It is noteworthy that these data exhibit similar trends to the Maoping Li-micas analysed by Legros et al. (2016) in the same district (Figure 8d).

Trace elements

Micas from granite: These micas are characterized by elevated Nb and Ta contents (Nb+Ta>100 ppm; Figure 9a), with variable Nb\# (Nb/(Nb+Ta)) ranging from 0.91 to 0.67. They have the lowest W (<10 ppm) and Sn (<200 ppm) contents of all micas analysed in this study. A vertical positive correlation between Nb\# and Mn content is observed in these micas (Figure 9b).

Vein micas: As seen in Figures 9a and 9c, the first (Fe-Li-mca\(_{1-I}\)) and fourth (Fe-Li-mca\(_{4-III}\)) generations of micas display positive correlations between Mn and W or Nb+Ta, the Fe-Li-mca\(_{4-III}\) being the most depleted. A group of Fe-Li-mca\(_{1-I}\) analyses are displaced from the overall trend and most likely represent the Fe-Li-mca\(_{4-III}\) overgrowth (Z1 to Z4, Figure 7) and, indeed, these micas plot with the Fe-Li-mca\(_{4-III}\) micas in all diagrams. In contrast, the Fe-Li-mca\(_{2-I}\) micas plot as a cluster in all diagrams (Figures 9a, c and d). Compared to other generations of micas, the Fe-Li-mca\(_{2-I}\) micas are the most W-enriched (20 to 30 ppm), whereas the Fe-Li-mca\(_{1-I}\) micas are distinguished by higher Nb+Ta (up to 1.4 ppm). The Fe-Li-mca\(_{4-III}\) micas are characterized by elevated Sn contents (up to 820 ppm) and very low W and Nb+Ta values. Due to the LA-ICPMS spot size, Fe-Li-mca\(_{3-III}\) micas could not be analysed for trace element contents.
Greisen micas: Compared to the micas analysed in veins, the greisen micas are enriched in Nb and Ta (Figure 9a) and exhibit constant (close to the granite average) Nb# (Figure 9b). In Figure 8a and b, the greisen micas also share some similarities with the stage I micas.

Composition of chlorites

A total of 33 EMPA analyses were performed on chlorites (Chl\textsubscript{1-II} and Chl\textsubscript{2-III}) that crystallized in the veins in stages II and III. Analyses were carried out on homogeneous Chl\textsubscript{1-II} and 100-µm size spherolites of Chl\textsubscript{2-III}, perpendicular to their Fe-Mg zonation (Table 3, Figure 10). All of these chlorites were found to be tri/dioctahedral Fe–chlorites with compositions that lie between ripidolite-brunsvigite and pycnochlorite fields. In the Al\textsuperscript{IV} versus Al\textsuperscript{VI} plot, both generations of chlorite are displaced from the Tschermak line, which is always the case for low-temperature chlorites (Figure 10c; Cathelineau and Nieva, 1985). The Chl\textsubscript{2-III} chlorites present FeO contents of 17 to 35%, with Fe/(Fe+Mg) ratios of 0.3 to 0.8 (Table 3). From the core to the margin of the spherolites, major elements, especially FeO and MgO concentrations, show oscillatory variations (Figure 10a and b), but no general trend can be distinguished.

Temperatures were calculated using the graphical geothermometer of Cathelineau and Bourdelle (2015) and plotted in the Si-R\textsuperscript{2+} diagram of Wiewiora and Weiss (1990) (Figure 10d). This thermometer is based on the chlorite-quartz equilibrium. It does not require prior knowledge of the valence state of iron and is calibrated for low-T chlorites (T<350°C and pressures below 4kbar). The temperatures obtained range from 180 to 260°C for Chl\textsubscript{1-II} (average temperature of 200°C) and 200 to 380°C for Chl\textsubscript{2-III} (average temperature of 300°C) and correspond to temperatures reached during the second and third stages of crystallization.
of the veins. No correlation between the calculated temperatures and the petrographic zoning in the Chl$_{2-III}$ or chemical composition was observed.

**Discussion**

**Major elements in hydrothermal micas: evidence for fluid mixing**

*Fe-Li-mca$_{1,2,I}$ micas:* In the Al-Si-R$^{2+}$ diagram (Figure 8), the early Fe-Li-mca$_{1,2,I}$ display two trends: a “phlogopite-zinnwaldite” trend between two poles a and b, and a “zinnwaldite-muscovite” trend between the same b pole and a muscovite c pole (Figure 8b).

The systematic alternation between zinnwaldite and muscovite compositions during the growth of Fe-Li-mca$_{1,2,I}$ indicates the coexistence, at this time in the Piaotang hydrothermal system, of three distinct hydrothermal fluids responsible for the a-b and b-c trends. The b-c trend may be interpreted as a mixing trend between two fluids, one richer in Fe and Mg and the other, richer in Al, that co-precipitate in either Fe-Li-mca$_{1,2,I}$ or Fe-Li-mca$_{2,4}$. By contrast, the zinnwalditic a-b trend can be interpreted in terms of closed system crystallization (correlated Fe and Mg contents). The a-pole is in fact associated with a primitive fluid end-member (F$_A$), whereas the b-pole is associated with the evolution of F$_A$ towards a F$_B$ composition by fractional crystallization (closed system). Moreover, the b-c trend might be interpreted to be the result of an opening of the system, with the arrival of a new F$_C$ fluid end-member (associated with the c-pole), and a mixing of F$_C$ with the residual F$_B$ fluid. This trend is also observed in the greisen micas (g-h trend). According to this interpretation, the complex structure of the Fe-Li-mca$_{1,2,I}$ would result in a combination of alternating influxes of F$_A$ and F$_C$, with repeated periods of closure of the system, allowing the evolution of F$_A$ into F$_B$. This is consistent with the continuous presence of tectonic activity recorded during the
hydrothermal process and the repetitive occurrence of crack-seal phenomena. These early micas share similar compositions and processes with early micas observed in the mineralizing stage of the Maoping deposit (also from the Dayu district) by Legros et al. (2016).

*Fe-Li-mca*$_{3,4}$: The late stage I micas, either zinnwaldite, or Li-Fe-ms, display similar trends to the other Piaotang micas (Figure 8b). The same pattern of a double trend converging towards the same mica composition is observed. Fe-Li-mca$_{3,4}$ are therefore likely to result from the same combination of closed system crystallization and mixing as the Fe-Li-mca$_{1,2,4}$ micas.

*Fe-Li-mca*$_{4,III}$: The Fe-Li-mca$_{4,III}$ display a single trend between a zinnwalditic d pole and a muscovite e pole (Figure 8c), consistent with a scheme of fluid mixing between the two end-members. Direct evidence for mixing is found in zoned overgrowths at the microscopic scale, where compositional changes could not be caused by a fractional crystallization (closed system) process (i.e., either Fe and Mg co-vary or Fe decreases when Mg increases) (Figure 7). The consistency between these d and e poles and the previous b and c poles will be addressed in the following sections. These post-mineralization micas are similar in composition to micas observed in the post-mineralizing stages of the Maoping deposit (also from the Dayu district) (Legros et al. 2016).

**Conditions of interpretation of trace element compositions**

The chemical composition of a given hydrothermal mineral is a record of the fluid composition, generally controlled by the partition coefficients of the incorporated elements between the mineral and the fluid. These are in turn controlled by crystal chemistry constraints and intensive parameters (P, T, pH, fO$_2$, etc.). Crystal chemistry constraints are clear for major elements, and may also be significant for trace elements. For instance,
incorporation of Li (likewise Nb and Ta) in trioctahedral micas depends on Al, due to the
Li\textsubscript{+1}(Fe, Mg\textsubscript{+1})\textsubscript{Al\textsubscript{-1}} mechanism of incorporation. In the same way, Sn and W are incorporated
by exchanges involving Ti (and also Fe, Mg in the case of W) (Bos, 1990). Generally
speaking, crystal chemistry constraints are not well established for most trace elements in
micas. Nevertheless, it may be suggested that, at the 1000 ppm level (and below), the ability
of sites and the major elements needed for the substitution mechanisms are always sufficient
to allow element incorporation. In this respect, the presence, or not, of a given trace element
in a mica, is only governed by the presence of the element in the hydrothermal fluid. The
abundance of the element in the mica is however controlled by the fluid-to-mica partition
coefficient of the element, and under a given set of intensive parameters, significant
differences between the partition coefficients of distinct trace elements might exist.

Experimental data related to mica-fluid partition coefficients are scarce and very limited for
hydrothermal conditions, experiments usually being conducted at high temperature (over
500°C). For instance, concerning F entry into micas, Zhu and Sverjensky (1991) conclude that
the higher the temperature, the lower the amount of fluorine that partitions into minerals. In
contrast, following the experimental results of Munoz and Ludington (1977), the F/(F+OH)
ratio of muscovite and phlogopite correlates positively with temperature (but only
significantly at T > 500°C). According to Munoz and Ludington (1977), when muscovite
equilibrates with biotite, it is systematically poorer in fluorine with no dependence upon
octahedral occupancy (i.e., the Al content). Nevertheless, both Li and Mg should increase F
partitioning in muscovite. Experiments on Rb and Cs partitioning between phlogopite and
fluid performed at 800°C and 0.2 to 4 GPa by Melzer and Wunder (2001) show that while Rb
partitions in the mineral, Cs partitions into the fluid. Thus, the Rb/Cs ratio in phlogopite is not
representative of the fluid composition. However, from experiments on phlogopite at 650°C
and 0.2 GPa, Bos (1990) concluded that the Rb, Zn, Pb and Cu contents of the mica are only
controlled by their concentrations in the fluid. From these limited data, it may be estimated
that the main control on the incorporation of elements into a mica structure, is their abundance
in the hydrothermal fluids, and that their ratios in the mineral should therefore be close to
their ratios in the fluids. The large compositional differences between the different Piaotang
mica generations may thus be safely interpreted in terms of differences in the hydrothermal
fluid compositions.

**Trace elements: characterization of fluid end-members**

The data obtained from the Fe-Li-mca\(_{1,4}\) and Fe-Li-mca\(_{2,1}\) micas represent combinations of
both the a-b and b-c trends, depending on the local proportion of zinnwaldite and Fe-Li-ms
components at the spot site. Considering the mica structures, it seems that the Fe-Li-ms
components are statistically more abundant in the Fe-Li-mca\(_{1,1}\) micas, which should
consequently yield more information on the b-c trend. Conversely, in the Fe-Li-mca\(_{2,1}\)
structure, the zinnwaldite and Fe-Li-ms components are more equally distributed and are
more likely representative of the b pole. The data in Figure 8b are quite consistent with these
suggestions: the Fe-Li-mca\(_{1,1}\) micas lie along trends suggestive of mixing, whereas the Fe-Li-
mca\(_{2,1}\) data plot in a more homogeneous cluster, likely representing an average composition.

Given the trace element data for these micas, it is possible to simplify our interpretation with a
two-fluid model. Indeed, all hydrothermal mica generations (Fe-Li-mca\(_{1,4}\), Fe-Li-mca\(_{2,4}\), Fe-
Li-mca\(_{4,III}\) and greisen) are characterized by trends in the trace element diagrams (Figure 9).
According to major element interpretations, these trends may be considered as reflecting
mixing events and therefore may define four pairs of potential end-members (a and b for Fe-
Li-mca\(_{1,1}\), c and d for Fe-Li-mca\(_{2,1}\), e and f for Fe-Li-mca\(_{4,III}\), and g and h for greisen micas)
(Figure 9e and f). Owing to the fact that Mn is more abundant in zinnwaldite and other Fe-rich micas, and in reference to the W-Mn diagram (Figure 9c), a and e correspond to the F_B end-member while b and d, reflect the F_C end-member. The W-Ba and Sn-Ba diagrams allows us to refine our interpretation of the trace element data. It appears (Figure 9e and f) that two series of end-members (g, a, f and h, d, b, respectively) display well-defined trends, connecting the earliest vein micas to the greisen micas. In contrast, the later Fe-Li-mca_{4-III} micas form their own trend and result from the F_E-F_F mixing process. Following this logic, the greisen micas appear to result from the interaction of two series of fluids associated with the stage I micas (F_B and F_C). These fluids evolve from a metal-poor to a metal-rich composition with a constant fractionation vs mixing model (see section above).

**Relationships with the ore-forming process**

Given that both the F_B and F_C fluids carry significant concentrations of metal, both are potentially able to contribute to the ore-forming process. However, micas precipitating from the mixing ore-depositing fluid record a lower saturation value than micas from the pre-mixing stages. Thus, micas from the ore-stage are expected to be depleted in rare metals. This may explain, for instance, why the Fe-Li-mca_{1-1} micas are depleted in W (coeval with wolframite) and the Fe-Li-mca_{2-4} micas are depleted in Sn (coeval with cassiterite). Correlatively, the relative enrichment in Nb in the Fe-Li-mca_{1-1} micas could result from the incompatible character of Nb, which was also not detected at a significant level in wolframite or in cassiterite, whereas other vein micas would be very Nb-poor. Therefore, the Fe-Li-mca_{2-4} micas and the greisen micas have recorded a period where the conditions for ore-deposition were not encountered. Moreover, greisen micas are considered to be the result of the biotite granite transformation, which includes alteration of the initial Nb-Ta-rich biotite into an
enriched Fe-Li muscovite in the greisen with inherited rare metals. This interpretation is supported by the constant Nb# in greisen micas, fixed at the average value of the biotite precursors. In their study of the Dajishan deposit, Wu et al. (2017) observed that the muscovite in RMG granites was enriched in Nb, Ta, Rb and Cs relative to the vein-hosted muscovite, whereas both displayed similar Sn and W contents (similar to the Piaotang case).

In Wu et al. (2017), muscovites in the granite were interpreted to have formed by the same fluids that formed the veins but modified through reaction with the HFSE-enriched granite in the same way as in the Piaotang deposit. The lower Nb and Ta contents in the greisen micas relative to the granite micas reflect the leaching of these rare metals out from the granite body.

The late Fe-Li-mca₄₋₃ micas, which were deposited at the very beginning of stage III, characterized by renewed Sn deposition (abundant Stn₁₋₃ and minor Cst₃₋₃), are enriched in Sn and depleted in W, and may thus be considered as having recorded a Sn-rich fluid, which would, in this case, be identified as the Fₑ end-member (Figure 9b and f).

Comparison with published fluid inclusion studies

Fluid inclusion (FI) studies were performed at the Piaotang deposit on quartz (Wang et al. 2013b; Ni et al. 2015), cassiterite (Zeng et al. 2002; Wang et al. 2013b) and wolframite (by infrared microscopy; Ni et al. 2015). The corresponding data are summarized in Figure 11. For each mineral presented in Figure 11, the primary FI were plotted. Secondary inclusions were only analysed in quartz by Ni et al. (2015) and are referred to as “post stage I”. The FI display a trend of decreasing temperature from wolframite (400 to 300°C) to cassiterite (350 to 300°C) and finally to post-ore fluids trapped in quartz (300 to 150°C). Fluid mixing is attested to by salinity variations in wolframite (between 4.6 and 8.9 wt. % eq. NaCl) and...
quartz (0 to 11 wt. % eq. NaCl), whereas cassiterite trapped the most saline fluids (8.5 to 9.5 wt. % eq. NaCl).

The preceding interpretations of mica compositions are consistent with these results. Moreover, the decrease in temperature revealed by the FI studies would explain why the Fe-Li-mca$_{2-1}$ micas are not associated with wolframite deposition in that the temperature decrease could have inhibited wolframite precipitation.

**Origin of the fluids**

**Stage I fluids:** As discussed in the preceding sections, the $F_B$ fluid, or, more precisely, its $F_A$ parent, are likely to be representative of the ore-forming fluids at stage I. The interpretative model detailed in the previous section implies that each $F_B^x$ should be associated with an $F_A^x$ fluid (Figure 9) involving a renewal of the source. According to the major and trace element composition data, (except for their W (and Sn) content) the $F_A$ fluids are characterized by high contents of F, Fe+Mg (Fe# of 0.75) and Mn. Such characteristics could be interpreted as reflecting a magmatic-hydrothermal origin, involving a rare metal granite (RMG) with a high F content. However, such fluids are unlikely to be Mg-rich as they are associated with evolved granites. Moreover, the enrichment in F should be associated with Al enrichment. In any case, this RMG could not be the Piaotang granite. Interaction of an evolved granite with an external fluid, which (based on the Fe and Mg contents) could be of metamorphic origin, would be more likely. However, no volatile component was observed in the FI studies (Zeng et al. 2002; Wang et al. 2013b, Ni et al. 2015).

The $F_C$ fluid, poorer in F, represents the diluting fluid recorded in the FI studies. Wang et al. (2009) characterize this fluid as a meteoric air-saturated fluid, interpreted to have recorded
downward infiltration of meteoric water through faults and fractures. This shallow water could have infiltrated through tectonically-activated regional drains. However, the trace element content of this F_c fluid, notably in terms of rare metals, suggests that this end-member equally interacted with the same granite as the F_A fluids.

Stage III fluids: The stage III F_E and F_F fluid end-members are interpreted in the same terms as the stage I end-members, with F_E being the Sn-rich ore-forming fluid (Figure 9f) and F_F, the external, diluting end-member.

Geothermometry implications

Fluid inclusion analyses have only been performed on stage I wolframite, quartz and cassiterite, as presented previously (Zeng et al., 2002, Wang et al., 2008, Ni et al., 2015). Chlorite geothermometry allows us to constrain post-mineralization temperatures at the Piaotang deposit. At the end of stage I, a brittle to ductile (based on microscopic observations only) environment is recorded (Figure 4). According to Stöckhert et al. (1999), the temperature of the brittle–plastic transition in quartz is between 310±30 and 350±50 °C. Cassiterite was the last of the three minerals to crystallize (Figure 4) and recorded homogenization temperatures of between 300 and 350°C (Zeng et al., 2002). Moreover, as fluids were circulating, a hydrostatic gradient should be considered in our system. Given this, even if a wide gradient of 30°C/km to 90°C/km is considered, the cassiterite crystallizing fluids should have been at higher temperatures (at least 400°C). Thus, the fluids must have been cooling at the end of stage I, supporting the idea of involvement of a meteoric fluid (F_c).

Stage II and III temperatures have not been constrained in the literature. However, scheelite (Sch_{1-II}) development at the expense of wolframite is usually interpreted as reflecting a
temperature decrease (Wood and Samson 2000). Moreover, Chl$_{1-II}$ compositions applied to the Cathelineau and Bourdelle (2015) geothermometer indicate that the Piaotang system cooled to a temperature of close to 200°C during stage II. Moreover, the Chl$_{2-III}$ geothermometer indicates that the hydrothermal fluids were reheated to a temperature of at least 300°C during stage III. The increase in temperature at this stage could explain the crystallization of new generations of cassiterite and wolframite.

**Implications**

A new paragenesis of the Piaotang deposit has been established here, composed of four stages of emplacement, three of which involve W-Sn minerals: (i) the “silicate-oxide” stage, which hosts the main mineralization; (ii) a “calcic” stage with scheelite and columbo-tantalite; (iii) a “base metal sulphides” stage with wolframite and cassiterite; and finally (iv) a late “sulphide” stage. This detailed paragenesis highlights for the first time the deposition of W-Sn minerals during three successive stages with a complementary Nb-Ta occurrence during the “calcic” stage.

Fe-Li-mica and chlorite are common in W-Sn deposits, which are usually emplaced during multiple magmatic and hydrothermal events that affect granites and other country rocks. In this work we have presented a detailed study of Fe-Li-mica and chlorites that can be correlated with fluid inclusion studies in order to observe diverse magmatic and hydrothermal influences. The correlation between the W-Sn content of Fe-Li-micas and its concordance with the crystallization of wolframite and cassiterite confirms that Li-micas are good tracers of mineralization in this kind of deposit.

Moreover, by correlating the geochemistry of micas and chlorite with the findings of previous fluid inclusion studies, it appears that two mixing end-members (magmatic and meteoric), clearly identified in both approaches, are associated with the deposition of wolframite and...
 cassiterite during the first stage. However, it should be noted that this study also highlights
involvement of a third fluid (external and possibly metamorphic) during deposition of the
mineralization and that the circulation of fluids during stage I is responsible for the
greisenization. More importantly, the now buried Piaotang biotite granite cannot be the source
of the mineralizing magmatic fluids and that the source should instead be linked to a more
evolved RMG granite that has not yet been identified.

Finally, our study of Fe-Li-mica and chlorite in the post-mineralizing stages has allowed, for
the first time, the different processes involved after the “silicate-oxide” stage to be
constrained. A new source of heat was induced into the system during stage III, enabling the
crystallization of new generations of minerals of economic interest (cassiterite and
 wolframite). A fluid inclusion study of the post-mineralizing stages could help to identify the
fluid at the origin of this heat advection.

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References


European Journal of Mineralogy, 25, 967-985.


evolved tin-granite magmas: a melt-fluid inclusion study. Contributions to Mineralogy
and Petrology, 148, 582-641.


Walsche, J.L. (1986) A six-component chlorite solid solution model and the conditions of
chlorite formation in hydrothermal and geothermal systems. Economic Geology, 81,
681-703.

dome in the Wugongshan Massif, Jiangxi province and their genetical relationship to
the tectonic events in southeast China. Tectonophysics, 339, 259-277.

of the chemical index of alteration and discussion of subdivision and correlation of the

fluid in the Piaotang tungsten deposit in Jiangxi Province: Evidence from helium and

crustal anatexis within the eastern South China Block: geochemical, zircon U–Pb
geochronological and Hf isotopic fingerprints from the gneissoid granites of Wugong

Wang, X-D., Ni, P., Yuan, S-D., and Wu, S-H. (2013b) Fluid inclusion studies on coexisting
cassiterite and quartz from the Piaotang tungsten deposit, Jiangxi Province, China. Acta
Geologica Sinica, 87, 850–859 In Chinese with English abstract.

South China Block: key observations and controversies. Gondwana Research, 23, 1273-
1305.


Yao, J., Shu, L., Santosh, M., and Li, J. (2013) Geochronology and Hf isotope of detrital zircons from Precambrian sequences in the eastern Jiangnan Orogen: Constraining the


**Figure captions**
Figure 1: (a) Ore mining districts and metal deposits of the Cathaysia Block, (b) Detailed map of the southern part of the Jiangxi Province, SE China, showing the distribution of Jurassic and Cretaceous granitoids. The Piaotang deposit is located in the Dayu district in the south-western part of the Jiangxi province (Modified after Legros et al. (2016) and references therein).

Figure 2: Simplified geological map (a) and cross-section with associated strikes (b) of the Piaotang W-Sn deposit, showing the relationships between the deep granite, Cambrian host rocks, and mineralized veins and the sampling levels ((a) modified after Tanelli 1982 and (b) modified after Ni et al., 2015).

Figure 3: Mineralized veins as observed in the mine galleries at different levels of sampling. (a) Wolframite-cassiterite-quartz vein. (b) Fluorite-cassiterite-quartz vein. (c) Accumulated sulphides in the vein. (d) Fluorite accumulation in the vein.

Figure 4: Paragenetic sequence of veins in the Piaotang W–Sn deposit based on petrographic observations of samples from mine galleries at levels 268, 388 and 556. See text for details of the different stages, mineral abbreviations and notations.

Figure 5: Microphotographs of the mineralogical textures and associations of the Piaotang deposit. (a) Micrograined-granite with porphyritic feldspar and biotite (crossed polars). (b) Slightly deformed quartz grains and corroded muscovite from the greisen (crossed polars). Thin-section in (c) natural light and (d) crossed polars of the main minerals that crystallized in stage I (Cst$_{1-1}$, Wf$_{1-1}$, Qtz$_{1-1}$ and Fe-Li-mca), showing the multiple crack-seal episodes observed in quartz and wolframite. Abbreviations
according to the IMA: Ab = albite; Cst = cassiterite; Mca = micas; Or = orthoclase;
Qtz = quartz; Wf = wolframite.

Figure 6: Microphotographs of the mineralogical textures and associations of the Piaotang
deposit. (a) Alteration of Wf$_1$-I into Sch$_1$-I followed by the crystallization of
associated Chl$_{1-II}$, Fl$_{1-II}$ and Clb$_{1-II}$ during stage II (SEM). (b) Textures of stage II
retromorphosis of wolframite into scheelite associated with early stage I minerals
(crossed polars). (c) Alteration of early stage I Toz$_{1-I}$ by Fe-Li-mca$_{4-III}$ in stage III
(crossed polars). (d) Spherulites of chlorite that crystallized during the stage II
(SEM). (e) Microcracks lining the Ccp$_{1-IV}$ boundary with inclusions of Cst$_{3-III}$, Wf$_2$.
III, Stn$_{1-III}$, and symplectic textures observed between Ccp$_{1-III}$, Sp$_{1-III}$ and Stn$_{1-III}$
(SEM). (f) Association of the second generation of Wf$_2$-III with Fl$_2$-III and Fe-Li-mca$_4$-
III in stage III (SEM). (g) Association of a third generation of cassiterite Cst$_{3-III}$ and
Stn$_{1-III}$ to stage IV sulphides (SEM) replacing second stage chlorite Chl$_{1-II}$. (h)
Texture and association of Ccp$_{1-III}$, Sp$_{1-III}$, Gln$_{1-IV}$, Bmt$_{1-IV}$, Bi$_{1-IV}$ in stage IV (SEM).
Abbreviations according to the IMA: Bi = native bismuth; Bmt = bismuthinite; Ccp
= chalcopyrite; Chl = chlorite; Clb = Colombo-tantalite; Cst = cassiterite; Fl =
fluorite; Gln = galena; Mca = micas; Mlb = molybdenite; Py = pyrite; Qtz = quartz;
Sch = scheelite; Sp = sphalerite; Stn = stannite Toz = topaz; Wf = wolframite.

Figure 7: Detailed study of an altered Fe-Li-mca$_{1-1}$ spherolite into Fe-Li-mca$_{4-III}$. The chemical
profiles show the oscillatory changes in composition during alteration. All elements
are presented as apfu values, calculated from EPMA data.
Figure 8: Compositions of micas plotted on a Monier and Robert (1986) phase diagram as a function of $R^{3+}$ (Al), $R^{2+}$ (Fe+Mg+Mn) and Si (apfu). Each generation of micas from the veins, granite and greisen displays an evolution trend that can be described using end-member compositions from (a) to (h) and be compared to similar published data from the Maoping deposit (Legros et al., 2016). See discussion section for explanations.

Figure 9: Trace element binary diagrams for three generations of micas from the veins, the granite and the greisen in the Piaotang deposit (data from LA-ICPMS analysis). The chosen binary diagrams aim to unravel the behavior of different metals observed in trace amounts in micas and separate the evolution of each generation. “Fx” refer to fluids identified in the discussion section (see text for further explanation). The granite mica data have been removed from (e) and (f) binary diagrams for better visibility.

Figure 10: (a) Zoning in stage II chlorites and an example of the spatial distribution of analytical points across the zoning (SEM). (b) Compositional profiles corresponding to chemical variations in FeO and MgO along the transect shown in (a) (EMPA data). (c) Octahedral Al (apfu) vs. tetrahedral Al (apfu) in stage II and stage III chlorites (EMPA data). The line corresponds to the Tschermak line. (d) Distribution of temperature determined by chlorite graphical thermometry (Cathelineau and Bourdelle, 2015) and plotted in a T-$R^{2+}$-Si diagram.

Figure 11: Fluid inclusion data plotted on a binary salinity vs. homogenization temperature diagram after Ni et al., (2015), Wang et al., (2008) and Zeng et al., (2002).
Table 1. Selected major oxide contents from EPMA analyses and calculated structural formulae for micas from each stage, granite and greisen. Li$_2$O contents were calculated using Tischendorff et al. (1997). Values preceded by the symbol ‘<’ indicate element concentrations below the limit of detection.

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Table 2. LA-ICPMS analyses of trace elements in micas from three generations in veins, granite and greisen. Zr, U, Y, and REE were also analyzed but were systematically below 1 ppm.

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*DOI: http://dx.doi.org/10.2138/am-2016-6196*

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Table 3. Electron microprobe analyses of chlorites from the Piaotang mineralized veins sampled at the level -388 m. Values preceded by the symbol ‘<’ indicate element concentrations below the limit of detection.

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Atoms per 14 O

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| AlO^3     | 1.51       | 1.51       | 1.51       | 1.51       | 1.51       | 1.51       |
| Mg        | 1.32       | 1.32       | 1.32       | 1.32       | 1.32       | 1.32       |
| FeO       | 2.39       | 2.39       | 2.39       | 2.39       | 2.39       | 2.39       |
| Mn        | 0.25       | 0.25       | 0.25       | 0.25       | 0.25       | 0.25       |
| Ti        | 0.06       | 0.06       | 0.06       | 0.06       | 0.06       | 0.06       |

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**Figure 1**

![Map of economic resources and Mesozoic intrusions in Southern Jiangxi Province](image1)

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<td>Jurassic granitoids (190-150 Ma)</td>
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**Figure 2**

![Geological map of Piaotang area](image2)

- Quaternary: red soil, alluvium
- Cambrian: quartz sandstone, biotite-quartz sandstone, phyllite and minor limestone, hornfels
- Sinian: quartz micaceous schists and sandstone hornfels
- Jurassic biotite granite
- Deep Jurassic Piaotang granite
- Mineralized veins
- Tungsten mines
- Faults
- Sampling levels

**Legend:**
- Red: Jurassic biotite granite
- Orange: Deep Jurassic Piaotang granite
- Gray: Quartz sandstone, biotite-quartz sandstone, phyllite and minor limestone, hornfels
- Brown: Sinian quartz micaceous schists and sandstone hornfels
- Green: Quaternary red soil, alluvium
- Black: Mineralized veins
- Blue: Tungsten mines
- Purple: Faults
- Yellow: Sampling levels
Figure 3

![Figure 3](image)

Figure 4

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<td>Native Bismuth</td>
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</table>

Corrosion and zoning deformation: 1 - 2 - 3 - 4
Figure 5

(a) Granite
(b) Greisen
(c) Stage I
(d) Stage I

Mineral Abbreviations:
Ab - Albite
Qtz - Quartz
Or - Orthoclase
Fe-Li-mca - Ferro-Lithium-Mica
Cst - Cassiterite
Wf - Wolframite

Scale:
1 mm for (a) and 5 mm for (c) and (d)
Figure 6
Figure 7
Figure 8

Stage I
- Fe-Li-mca$_{14}$
- Fe-Li-mca$_{24}$
- Fe-Li-mca$_{54}$

Stage III
- Fe-Li-mca$_{34}$

Data from granite, greisen, and veins from the similar Meining deposit (Lehre et al., 2016)
Figure 10

Figure 11