The origin of the Zhangjialong tungsten deposit, South China: Implications for W-Sn mineralization in large granite batholiths.

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Abstract. The Nanling region is the largest W-Sn metallogenic district in the World and hosts a number of giant W-Sn deposits, all of which are spatially and genetically associated with highly evolved Mesozoic granitic stocks. Volumetrically, however, Caledonian granites (Paleozoic), mainly batholiths, approach their Mesozoic equivalents in importance and have been the target of recent exploration. This has resulted in the discovery of a number of economic tungsten deposits in or near these granite batholiths, including the giant Zhangjialong deposit, which is located on the southern margin of the Caledonian Penggongmiao granite batholith. The unresolved question is whether or not this is evidence for an important Caledonian epoch of W-Sn mineralization. In this contribution, we report the results of high precision SIMS zircon U-Pb, muscovite Ar-Ar, and molybdenite Re-Os age determinations that constrain the timing relationships among granitic magmatism, greisenization and tungsten mineralization related to the Zhangjialong deposit. The molybdenite Re-Os age of the tungsten mineralization is 160.2±2.2 Ma, which is similar to, albeit slightly older than, the muscovite Ar-Ar age of the greisen (153.5±1.0 Ma). These ages, however, are considerably younger than the zircon SIMS U-Pb age of 441.3 ± 2.4 Ma for the spatially associated granite. These data...
demonstrate that the tungsten mineralization and greisenization of the Zhangjialong W deposit is of Late Jurassic rather than Silurian age, which precludes a temporal and genetic link between the hydrothermal tungsten mineralization and the regional Caledonian magmatism. Instead, the tungsten mineralization is interpreted to be related to a hidden Late Jurassic granitic pluton. A compilation of published whole-rock geochemical data indicate that the large granite batholiths are less differentiated than the W-Sn bearing granite stocks, irrespective of whether they are Paleozoic or Mesozoic in age. This suggests that the metallogenic potential of the large granitic batholiths is limited, and that W-Sn deposits hosted within granite batholiths are likely to be genetically related to highly evolved granitic stocks that in some cases have not been exposed.

Keywords Re-Os Molybdenite; Ar-Ar muscovite; SIMS zircon U-Pb; Caledonian batholiths; Late Mesozoic tungsten mineralization; Nanling region

1. Introduction

Most giant W-Sn deposits are temporally, spatially and genetically related to highly evolved granitic stocks (Sillitoe et al., 1975; Romer and Kroner, 2016; Korges et al., 2017). However, there are also many W-Sn deposits within or at the margins of large granitic batholiths (Willis-Richards and Jackson, 1989; Sun and Higgins, 1996; Yokart et al., 2003; Hulsbosch et al., 2016), for which a genetic relationship with the spatially associated granite is unclear (Kelly and Turneaure, 1970; Kelly and Rye, 1979; Hulsbosch et al., 2016). This is an important issue to resolve, because granitic batholiths provide very large exploration targets for W-Sn mineralization. A better understanding of the temporal and genetic association of the mineralization with the spatially associated granitic batholith is an essential first step towards developing an effective strategy for discovering potentially economic W-Sn deposits in this environment.

The Nanling region in the northwestern part of the Cathaysia block of the South China hosts more than 54% of the tungsten resources of the World as well as important resources of tin and rare metals (Lu, 1986;
USGS, 2017). Most of the deposits making up this resource are spatially associated with highly evolved Mesozoic granitic stocks (Fig. 1). Numerous precise age determinations have shown that the tungsten, tin and rare metal mineralization and the spatially-associated granitic intrusions are of Mesozoic age, and were emplaced in three distinct episodes (Mao et al., 2013), namely a Late Triassic W-Sn-Nb-Ta episode (Indosinian, 230-210 Ma; Cai et al. 2006; Yang et al. 2009), a Late Jurassic W-Sn episode (Early Yanshanian, 160-150 Ma, Peng et al. 2006, 2007; Jiang et al. 2008; Yuan et al. 2008a, 2011; Zhao et al. 2012; Hu et al. 2012a,b), and a Late Cretaceous Sn-Be-F episode (Late Yanshanian, ~90 Ma, Yuan et al. 2015).

In addition to the Mesozoic granites, there are also large granite batholiths of Caledonian age in the Nanling region (Chen et al. 2013; Hua et al. 2013) (Fig. 2), which are second in importance volumetrically only to the Yanshinian granites but have been thought to be unimportant from the perspective of W-Sn mineralization. Recent successful exploration of the giant Zhangjialong tungsten deposit, however, is changing this view (Hua et al. 2013). This deposit has proven WO₃ reserves of 57,300 t at a grade of 0.317% WO₃ (Guo et al. 2017) and is located within the Penggongmiao granite batholith, which has been dated at 426.5 ± 2.5 Ma based on a LA-ICP-MS zircon U-Pb age for a scheelite-bearing aplitic dyke (Zhang et al., 2011). As a result, a consensus is developing that there was also an important episode of tungsten mineralization during the Caledonian (Qiao et al. 2011; Chen et al. 2013; Hua et al. 2013; Li et al. 2013), and that the Caledonian granites and the adjacent pre-Silurian strata are favorable targets for regional W-polymetallic mineralization (Qiao et al. 2011; Li et al. 2013; Guo et al., 2017). However, although the Zhangjialong tungsten deposit is spatially associated with the Penggongmiao granite batholith, the age of the mineralization has not been determined and thus a genetic association with the batholith has not been established.

In this paper, we report results of systematic in-situ SIMS U-Pb, Ar-Ar and Re-Os dating of zircon,
muscovite and molybdenite, respectively, from greisen ore of the Zhangjialong tungsten deposit. Our new geochronological data provide compelling evidence that the tungsten mineralization and greisenization of the Zhangjialong deposit is of Late Jurassic, rather than Silurian age as previously thought. Our data therefore preclude a temporal and genetic link between the tungsten mineralization and regional Caledonian magmatism. Based on a regional geochronological data set, and a compilation of published whole-rock geochemical data, we evaluate the potential of the granite batholiths for W-Sn mineralization from other perspectives and in so doing advance our understanding of the W-Sn metallogenic potential of large granite batholiths.

2. Regional geological setting

The Nanling region is located in the northwestern part of the Cathaysia block of South China (longitude 110°E-116°E, latitude 24°N-27°N), and covers a surface area of about 170,000 km². This region is characterized by five separate granitic mountain ranges (the Yuechengling, Dupanling, Mengzhuling, Qitianling and Dayuling), and is located at the junction of four provinces in southern China, namely Hunan; Jiangxi; Guangdong; and Guangxi (Figs.1, 2) (Chen et al. 2002; Yuan et al. 2015). Previous age determinations have shown that assembly of the Yangtze Craton and Cathaysia Block along the Qinhang tectonic belt took place at ~1.1 to 0.83 Ga and coincided with the development of an Early Neoproterozoic unconformity and the formation of the Jiangnan fold belt (e.g., Shui 1987; Chen and Jahn, 1998; Zhao et al. 2011).

After assembly, the Nanling region in the central part of the South China Block was extensively reworked during Caledonian, Indosinian, and Yanshanian tectonic-thermal events. These tectonic-thermal events created a regional basement consisting of Sinian-Silurian clastic and metamorphic clastic rocks that
was overlain by a cover sequence of Devonian to Jurassic marine and marine-continental strata, including carbonate rocks, marlstone and clastic beds (Mao et al., 2007). Between the Jurassic and Cretaceous, many small fault-controlled depressions were filled by terrestrial clastic and volcanic rocks (Mao et al., 2007). In addition, multiple episodes of granitic magmatism generated large volumes of granitic rocks in the Nanling and neighboring regions (Mao et al., 2007; Hu and Zhou 2012), which are considered to have played an important role in the W-Sn polymetallic pre-enrichment that culminated in large-scale Mesozoic W-Sn mineralization (Hua et al. 2013).

The earliest granites are of Caledonian age and occur mainly as large batholiths along the boundaries of Hunan, Jiangxi, Guangxi and Guangdong provinces (Fig. 2, Chen et al. 2013). These granites mainly belong to the S-type class and formed in a regional Caledonian syn- or post-orogenic setting (Chen et al., 2013; Hua et al., 2013; Ji et al., 2016). Until recently, they were not considered to be significant from the perspective of W-Sn mineralization. Indosinian granitic magmatism in the Nanling region was triggered mainly by the Indosinian orogeny and culminated in a series of post-collisional S-type granite batholiths (e.g., the Xitian and Dengfuxian granite batholiths) or highly evolved granitic stocks (e.g., Limu; Zhou et al., 2003; Hua et al., 2005). The Indosinian W-Sn mineralization in the Nanling region is mainly associated with highly evolved Late Triassic post-collisional granitic stocks such as those hosting the Limu Sn deposit, the Liguifu W-Sn deposit and the Shuiyuanshan and Yejiwo W deposits (Fig. 2, Yang et al., 2009; Zou et al., 2009; Mao et al., 2013; Zhang et al., 2015). This was followed by large-scale Middle to Late Jurassic granitic magmatism that was triggered by the westward subduction of the Paleo-Pacific Plate (Mao et al., 2013). The result was the emplacement of large volumes of post-arc S-type or A-type granitic rocks and the formation of the largest W-Sn metallogenic district in the World (Jiang et al., 2009; Mao et al., 2013; Chen et al., 2016) (Fig.2).

Most of the Middle to Late Jurassic W-Sn deposits are temporally, spatially, and genetically related to...
highly evolved granitic stocks (Mao et al., 2007, 2013; Hu et al., 2012; Yuan et al., 2017). Recent exploration, however, has revealed that a number of tungsten deposits or occurrences are located within Caledonian granite batholiths or at their contact zones. Examples of these deposits are the giant Zhangjialong tungsten deposit and the smaller Zhenkou and Yangmeikeng tungsten deposits at the southern margin of the Penggongmiao granite batholith (Lei et al., 2009; Li et al. 2013), the Yuntoujie, Jiepai, and Niutangjie tungsten deposits at the southern margin of the Mia'ershan-Yuechengling granite batholith (Yang et al. 2014), and the Liuyuan tin and the Zhuyuanli tungsten deposits within the Guidong granite batholith (Yuan et al., 2018) (Fig. 2).

3. Deposit geology

The Zhangjialong ore deposit occurs at the southern margin of the Penggongmiao granite batholith (975 km²), which is located in eastern Hunan Province (Fig. 2). It comprises 46 orebodies, the largest nine of which are mainly hosted in the granite batholith. The latter comprise disseminated and vein-style tungsten mineralization in greisenized granite and provide much of the economic value of the deposit. They are referred to hereafter as greisen-type orebodies. The five next most important orebodies comprise individual quartz veins but are hosted within Sinian-Ordovician meta-sandstone intercalated with slate near the contact with the batholith. The remaining ore bodies are of much less importance, occur as veins or disseminations and are equally distributed between the granite and the host meta-sandstone. There are three sets of faults developed in the area, with EW-, NW- and NE trends. Among these, the EW-trending faults are the dominant regional structures and controlled the emplacement of the Penggongmiao granite batholith. The NW-trending faults are well developed in the Zhangjialong area and cut the Penggongmiao granite batholiths. They formed the main conduits for the fluids that altered the rocks and formed the tungsten orebodies (Figs. 4 and 5).
NE-trending faults are the youngest and cut the Penggongmiao granite batholiths and the NW-trending faults.

Granitic magmatism in the Penggongmiao area occurred mainly between 447 and 426 Ma (Zhang et al. 2014). Based on detailed petrographic observations and zircon U-Pb dating, Zhang et al. (2014) divided the Penggongmiao granite into two units, namely a fine-grained biotite granite with minor hornblende (G1 with LA-ICP-MS zircon U-Pb ages of 447-442 Ma), and a medium- to coarse-grained porphyritic biotite monzogranite (G2 with LA-ICP-MS zircon U-Pb ages of 436-431 Ma). The giant Zhangjialong W deposit is hosted mainly in the G2 granite, and contains phenocrysts of K-feldspar and plagioclase in a groundmass of K-feldspar, plagioclase, quartz and biotite (Fig. 6). Accessory minerals include apatite, rutile, titanite and zircon (Zhang et al. 2011). In addition to the two main granitic units (G1 and G2), fine-grained scheelite-bearing aplite dikes with a LA-ICP-MS zircon U-Pb age of 426.5 Ma occur locally (Zhang et al. 2011).

Hydrothermal alteration and mineralization were controlled mainly by NW-trending faults that cut the medium- to coarse-grained porphyritic biotite monzogranite (G2) and Sinian clastic rocks (Figs. 4, 5). Greisen is the dominant alteration associated with the tungsten mineralization (Fig.6) and developed mainly in the medium- to coarse-grained porphyritic biotite monzogranite around the NW-trending faults (Figs. 4, 5). Silicification accompanied quartz vein-type tungsten mineralization developed along NW-trending faults in the granite and Sinian clastic rocks (Figs.4, 5). As noted above, 46 separate orebodies have been discovered in the Zhangjialong area. They represent a cumulative strike length of 100-3010 m, and width of 0.4-3.27 m (1.38 m on average) and include the nine, main greisen-type orebodies and five main quartz-vein-type orebodies mentioned above (Fig.4, Li et al. 2013; Guo et al., 2017). Among these, the No. 2 greisen-type orebody is by far the largest one, with a strike length of 2320 m, and a width of 0.85-2.45 m. The most common ore mineral of the greisen-type ore is scheelite (accounting for 90.5% of the tungsten resource in this deposit) and is accompanied by minor amounts of molybdenite and pyrite. The main gangue and
alteration minerals are quartz and muscovite, which are intergrown with scheelite and molybdenite in the greisen ore (Fig. 6). The most common ore mineral of the quartz-vein-type ore is scheelite, which is accompanied by minor proportions of wolframite, molybdenite, bismuthinite, chalcopyrite, galena, sphalerite, arsenopyrite and pyrite. The main gangue mineral is quartz, which occurs with small proportions of muscovite; both are intergrown with scheelite, wolframite and molybdenite. Rocks hosting the vein-type mineralization have been silicified for distances of 1-3 cm from the orebodies (individual veins).

4. Sampling and analytical procedures

The zircon used for U-Pb dating (Sample ZJL-2), molybdenite for Re-Os dating (Samples ZJL-5,6,7,8,9) and the muscovite for Ar-Ar dating (Sample ZJL-2) were extracted from drill core containing greisenized medium- to coarse-grained porphyritic biotite monzogranite and associated tungsten mineralization (Fig. 5). The molybdenite is intergrown with muscovite and scheelite (Fig. 6). Zircon, muscovite and molybdenite grains were separated using standard magnetic and heavy liquid techniques and were subsequently handpicked under a binocular microscope at Chenxin Services Ltd., Langfang, China.

4.1 Zircon SIMS U-Pb dating

Representative zircon grains together with chips of the zircon standards, Plešovice and Qinghu, were mounted in epoxy discs and polished to expose the longitudinal section of crystals for analysis. All zircon crystals were examined in transmitted and reflected light, and with scanning electron microscopy (SEM), and cathodoluminescence (CL) images were prepared to reveal their internal structures. The SEM was operated with an accelerating voltage of 15 kV.

Measurements of U, Th and Pb isotope ratios were conducted using a Cameca IMS-1280HR SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. The analytical procedures
used during this study are similar to those described by Li et al. (2009), and only a brief summary is given here. The primary O²⁻ ion beam spot is about 20×30 μm in area. Positive secondary ions were extracted with a 10 kV potential. A 60 eV energy window was used in conjunction with a mass resolution of ca. 5400 (at 10% peak height) to separate Pb⁺ peaks from isobaric interferences. A single electron multiplier was used in ion-counting mode to measure secondary ion beam intensities in peak jumping mode. Analyses of the zircon standard, Plesovice, were alternated with analyses of unknown grains. Each measurement consisted of seven cycles. The Pb/U calibration was performed relative to the zircon standard, Plesovice (2⁰⁶Pb/²³⁸U age = 337 Ma, Sláma et al. 2008); U and Th concentrations were calibrated against zircon standard 91500 (Th = 29 ppm, and U = 81 ppm, Wiedenbeck et al. 1995). A long-term uncertainty of 1.5% (1s RSD) for 2⁰⁶Pb/²³⁸U measurements of the standard zircon crystals was propagated to the unknowns (Li et al. 2010), although the measured 2⁰⁶Pb/²³⁸U error in a specific session was generally ≤1% (1s RSD). Measured compositions were corrected for common Pb using non-radiogenic ²⁰⁴Pb. The corrections were sufficiently small to be insensitive to the choice of a common Pb composition. An average present-day crustal composition (Stacey and Kramers 1975) was used for the common Pb assuming that the latter was largely present due to surface contamination during sample preparation. The data reduction was carried out using the Isoplot/Ex v. 2.49 program (Ludwig 2001). Uncertainties for individual analyses are reported at the 1σ level; Concordia U-Pb ages are quoted with a 95% confidence interval, except where otherwise noted.

In order to monitor the external uncertainties associated with SIMS U-Pb zircon age determinations calibrated against the Plesovice standard, an in-house zircon standard, Qinghu, was alternately analyzed as an unknown with the other unknown zircon crystals. Twenty-two measurements of the Qinghu zircon yielded a Concordia age of 160 ± 1 Ma, which is identical within error to the recommended value of 159.5 ± 0.2 Ma (Li et al. 2013).
4.2 Muscovite $^{40}$Ar-$^{39}$Ar dating

The muscovite grains were sealed into a quartz bottle for irradiation in a nuclear reactor at the Chinese Institute of Atomic Energy, Beijing; the total time for irradiation was 1444 min, the neutron flux was about $2.60 \times 10^{13} \text{ n cm}^{-2} \text{S}^{-1}$, and the integrated neutron flux was $2.25 \times 10^{18} \text{ n cm}^{-2}$. The Fangshan biotite (ZBH-25), with an age of $132.7 \pm 1.2 \text{ Ma}$ and a potassium content of 7.6%, was used as the internal standard. The sample and monitors were heated in a graphite furnace after irradiation; the heating-extraction step for each temperature increment was 30 minutes, with 20 minutes for purification. Mass analysis was carried out using a Helix C Plus multiple collector noble gas mass spectrometer, and 20 sets of data were obtained for each peak value. The analyses were performed in the Isotope Laboratory of the Institute of Geology, Chinese Academy of Geosciences. The measured isotopic ratios were corrected for mass discrimination, atmospheric Ar, blanks and irradiation-induced mass interference. The correction factors of interfering isotopes produced during irradiation were determined by analysis of irradiated pure $\text{K}_2\text{SO}_4$ and CaF$_2$, and yielded the following ratios: $\left( ^{36}\text{Ar} / ^{37}\text{Ar}_0 \right)_{\text{Ca}} = 0.0002389$; $\left( ^{40}\text{K} / ^{39}\text{Ar} \right)_K = 0.004782$; $\left( ^{39}\text{Ar} / ^{37}\text{Ar}_0 \right)_{\text{Ca}} = 0.000806$. Lambda, the decay constant, was taken to be $5.543 \times 10^{-10} \text{ year}^{-1}$ (Steiger and Jager, 1977) and all $^{37}\text{Ar}$ abundances were corrected for radiogenic decay (half-life 35.1 days). The plateau age, and the isochron and inverse isochron were calculated using the ISOPLOT program (Ludwig, 2003); the uncertainties in the ages are reported at the 95% confidence level (2$\sigma$). Details of the operating and data processing procedures were described by Chen et al. (2006).

4.3 Molybdenite Re-Os dating

Molybdenite Re-Os isotopic analyses were performed using a Thermo Electron TJA X-series ICP-MS instrument in the Re-Os laboratory at the National Research Center of Geoanalysis, Chinese Academy of Geosciences, Beijing, China. The analytical procedures used during this study were similar to those described...
by Du et al. (2009), Mao et al. (1999) and Stein et al. (2001). The Re-Os model ages were calculated using

\[ t = \frac{\ln(1+^{187}{\text{Os}}/^{187}{\text{Re}})}{\lambda}, \]

where \( \lambda \) is the decay constant of \(^{187}\text{Re}\) of \(1.666 \times 10^{-11}\) year\(^{-1}\) (Smoliar et al. 1996). The Re-Os isochron age was calculated using the ISOPLOT 2.49 program (Ludwig 2001). The uncertainty in the Re-Os model ages includes a 1.02% uncertainty in the \(^{187}\text{Re}\) decay constant, an uncertainty in the spike calibration, and the mass spectrometry analytical error (Du et al., 2009).

5. Results

5.1. SIMS Zircon U-Pb age

Spot analyses were conducted on 28 zircon grains in sample ZJL-2 from greisenized granite associated with tungsten mineralization using in situ SIMS U-Pb. The zircon grains and grain fragments are generally colorless, transparent, euhedral, and range between 50 and 250 \(\mu m\) in length with length/width ratios of 1-4. In CL images, most of the zircon crystals show evidence of oscillatory zoning with fine bands (Supplementary Fig. 1). Together, these features indicate that the zircon is of magmatic origin (Hoskin and Schaltegger 2003). Results of in-situ zircon U-Th-Pb analyses on domains showing oscillatory zoning are presented in Supplementary Table 1. Zircon crystals from sample ZJL-2 have U contents and Th/U ratios varying from 202 ppm to 1751 ppm and from 0.23 to 0.53 (Supplementary Table 1), respectively. All the data from the 28 analyses are concordant and yield a Concordia age of \(441.3 \pm 2.4\) Ma (MSWD=0.043) (Fig. 7a), which is the best estimate of the crystallization age of sample ZJL-2. Our new SIMS U-Pb age for the greisenized granite is indistinguishable within error from previously published LA-ICP-MS U-Pb zircon ages of \(436.2\pm3.1\) Ma to \(435.3\pm2.7\) Ma for the medium coarse-grained biotite granite and is significantly older than the LA-ICP-MS U-Pb zircon age of \(426.5\pm2.5\) Ma for the aplitic dykes crosscutting the porphyritic biotite granite (Zhang et al. 2011).

5.2 Muscovite Ar-Ar dating


\[ ^{40}\text{Ar}^{39}\text{Ar} \]

\[ ^{40}\text{Ar}^{39}\text{Ar} \] age determinations were carried out on muscovite grains intergrown with scheelite and molybdenite from the greisen-type ore (separate ZJL-2); the analytical results are listed in Supplementary Table 2, and illustrated in Figure 8. The apparent ages obtained from the low-temperature steps are not considered to have geological significance because of the low percentage of \(^{39}\text{Ar} \) released (Yuan et al. 2007, 2010, 2015), which was likely caused by the initial loss of small quantities of Ar from the edges of mineral grains (Hanson et al. 1975). In contrast, the eleven continuous steps at temperatures of 770-1400 °C are almost coincident and constitute a uniform and remarkably flat \(^{40}\text{Ar}^{39}\text{Ar} \) age spectrum with 99.35% \(^{39}\text{Ar} \) released. These steps yield a well-defined plateau age of 153.5 ± 1.0 Ma (MSWD=1.2), an isochron age of 153.0 ± 1.5 Ma (MSWD = 3.1) for an initial \(^{40}\text{Ar}^{36}\text{Ar} \) ratio of 300.6 ± 5.8, and an inverse isochron age of 152.9 ± 1.5 Ma (MSWD = 6.4) for an initial \(^{40}\text{Ar}^{36}\text{Ar} \) ratio of 301.9 ± 5.3 (MSWD = 6.4) (Fig. 8). The agreement among the plateau age, the isochron age and the inverse isochron age is excellent, and within the applicable analytical uncertainty. The plateau age (153.5 ± 1.0 Ma) is considered to represent the best estimate of the crystallization age of the muscovite.

### 5.3 Molybdenite Re-Os dating

The Re and Os abundances and isotopic data for the molybdenite samples are listed in Supplementary Table 3. Total Re and \(^{187}\text{Os} \) concentrations vary from 1665 ng/g to 2135ng/g, and from 2.821 ng/g to 3.535 ng/g (Supplementary Table 3), respectively. The Re-Os model ages of the five molybdenite samples range from 157.9 ± 2.3 Ma to 161.7 ± 2.4 Ma with a weighted mean of 160.4 ± 2.2 Ma (MSWD=2.2). The isochron age for all five samples is 150 ± 25 Ma with a MSWD of 3.9 (Fig. 7b). Considering that the Re-Os model ages vary in a relatively narrow range and the error of the weighted mean age (MSWD=2.2) is smaller than that of the isochron age (MSWD=3.9), the weighted mean of 160.4 ± 2.2 Ma is interpreted as the age of...
6. Discussion

6.1 Timing of granite emplacement and tungsten mineralization

Zhang et al. (2011) reported zircon LA-ICP-MS U-Pb ages for the biotite granite and a scheelite-bearing aplitic dyke cross-cutting the granite of 436-435 Ma and 426.5±2.5 Ma, respectively. Because of this and the fact that that the Zhangjialong tungsten deposit is mainly hosted by the Penggongmiao granite batholith, most researchers have taken this deposit to be an example of tungsten mineralization genetically related to Caledonian granite magmatism (Qiao et al. 2011; Chen et al. 2013; Li et al. 2013). Our direct Re-Os dating of molybdenite, however, has provided a precise age of 160.4 ± 2.2 Ma for the quartz-vein-hosted mineralization, which is broadly consistent with the $^{40}$Ar-$^{39}$Ar plateau age (153.5 ±1.0 Ma) of muscovite intergrown with scheelite in the greisen and considerably younger than the zircon SIMS U-Pb age of 441.3 ± 2.4 Ma for greisenized granite that hosts the ore. This shows clearly that the hydrothermal tungsten mineralization is temporally and genetically unrelated to Caledonian granite magmatism.

Our new molybdenite Re-Os age (160.4 ± 2.2 Ma) and muscovite Ar-Ar age (153.5 ±1.0 Ma) are well within the range of those for Late Jurassic W-Sn deposits (160-150 Ma) in the Nanling region (Yuan et al. 2007, 2008a, 2012a, b; Peng et al. 2006, 2007; Hu et al. 2012a, b; Hu and Zhou, 2012; Mao et al. 2004, 2007, 2013). Accordingly, we propose that the tungsten mineralization of the Zhangjialong deposit was introduced by hydrothermal fluids associated with a concealed Late Jurassic granite pluton. Late Jurassic granite magmatism therefore satisfactorily explains the tungsten mineralization of the Zhangjialong area, and thus any exploration of the Penggaozhan batholith for tungsten based on a model involving a genetic relationship between this mineralization and Caledonian magmatism is fundamentally flawed.
6.2 Genesis of the W-Sn deposits hosted within large granite batholiths

As mentioned in the introduction to this paper, most W-Sn deposits typically occur in close proximity to differentiated granites. This also applies to the Nanling region, where most of the giant W-Sn deposits are spatially associated with small, highly evolved granitic Mesozoic granite stocks (ca.160-150 Ma; Fig. 2) with which they are considered to be genetically related (Mao et al. 2004; Yuan et al., 2008b, 2011, 2015; Liu et al. 2012).

However, mineral exploration during the past few years has shown that, in addition to the Zhangjialong W deposit, several other large W and W-Sn deposits occur within or near Caledonian granite batholiths. For example, in the western part of the Nanling region, the Niutangjie, Jiepai and Gaoling W deposits and the Yuntoujie W-Mo deposit are distributed along the southern and eastern margin of the Miaoershan (MES)-Yuechengling (YCL) granite batholith (with an exposure area of about 3000 km²) (Fig. 2). Significantly, however, the Niutangjie W deposit has been shown recently to be genetically related to a highly evolved Caledonian granite stock rather than the batholith (Yang et al., 2014). The spatial association with Caledonian granitic batholiths also applies to the Liguifu W-Sn and the Limu Sn deposits, which are located within the eastern and southeastern margin of the Haiyangshan (HYS)-Dupangling (DPL) granite batholith (with an exposure area of about 650 km²) (Fig. 2).

The above association extends to the Mesozoic batholiths. Thus, for example, the giant Xitian tin deposit in southern Hunan Province is located within the Indosinian (230-210 Ma) Xitian granite batholith (with an exposure area of about 240 km²) near its contact with Devonian dolomitic limestone (Fig. 2). This is also true for the nearby large Dengfuxian tungsten deposit, which occurs within the Indosinian Dengfuxian granite batholith (with an exposure area of about 170 km²) (Fig. 2). High precision zircon U-Pb, molybdenite Re-Os...
and muscovite Ar-Ar data now show, however, that both the Xitian Sn and Dengfuxian W deposits formed at 160-150 Ma, and are genetically related to highly evolved Late Jurassic (Early Yanshanian) granite stocks (Liu et al. 2008; Ma et al. 2008; Fu et al. 2009; Guo et al. 2014; Cai et al. 2012; Huang et al. 2013; Liang et al. 2016) rather than the Indosinian granite batholiths (Cai et al., 2013; Liu et al. 2015).

In other parts of the World, notably the Southeast Asian Sn belt, the Central Portuguese W-Sn district, the Erzgebirge tin province in Germany and the Blue Tier tin district in Australia, W-Sn deposits also occur commonly within or adjacent to granite batholiths. Most of these deposits, however, are genetically related to highly evolved younger granite stocks or cupolas (Durisova et al., 1979; Föster et al., 1999; Yokart et al., 2003; Webster et al., 2004).

6.3 The W-Sn metallogenic potential of large granite batholiths

Tin and tungsten are present in higher concentrations in reduced ilmenite-series S-type granitic magmas than other granitic magmas and, owing to their incompatibility, accumulate in the residual liquid during magmatic differentiation (Ishihara et al., 1979). Consequently, advanced magmatic fractionation has been considered a key criterion for identifying S-type granites that might host genetically related Sn-W deposits (Lehmann 1982, 1987, 1990; Lehmann and Mahawat 1989). For the same reason, the granites are thought to be more likely to occur as small stocks rather than larger intrusions.

In order to further evaluate the hypothesis that economic W-Sn mineralization in granite batholiths is genetically related to small, highly evolved stocks that intrude these batholiths, we have compiled the available whole-rock geochemical data for the granitic rocks that form the batholiths and the W-Sn-bearing granite stocks in the Nanling region (Figs. 1, 2, Supplementary Table 4). These data show that the large granite batholiths in the region (such as the Miao’eshan, Yuechengling, Haiyangshan, Dupangling, ...
Dengfuxian, Xitian, Penggaomiao and Wanyangshan granite batholiths) are less differentiated than W-Sn-bearing granite stocks such as the Qianlishan (QLS), the Laiziling (LZL), the Jiangfengling (JFL), and Xihuashan (XHS) stocks (Figs. 9, 10; Yao et al. 2005; Cheng et al. 2012, 2013; Xuan et al. 2014; Chen et al. 2014). The granites of the stocks can be distinguished from those of the batholiths by their chondrite-normalized REE profiles and their Rb/Sr, K/Rb, Nb/Ta, Zr/Hf ratios (Fig. 9 and 10). Thus, the granite stocks are characterized by flat to moderate heavy REE enrichment, whereas the granites of the batholiths display heavy REE depletion (Fig. 9). Similarly, the granitic stocks have high Rb/Sr ratios (>9), and low Nb/Ta ratio (<5), Zr/Hf ratio (<20) and K/Rb ratio (<60), whereas the opposite is the case for the granitic batholiths (Fig. 10; Soloviev 2011, 2014; Ballouard et al. 2016). Most significantly, and consistent with the incompatibility of W and Sn, the concentrations of these elements in the granitic stocks range from 23 to 51 ppm, which contrasts strongly with those of the granitic batholiths that are in the range 1.2 to 21ppm (Cheng et al., 2013).

In view of the much higher W and Sn contents of the evolved stocks relative to their batholithic parents, it is reasonable to predict that the granites of the stocks are more likely to be the source of economic W-Sn mineralization than those of the batholiths. An additional and potentially more important reason for the stocks being the source of the metals is that the granite batholiths are emplaced at mid-crustal levels and thus relatively high pressure. Consequently, there is limited development of hydraulic fracturing and the release of magmatic hydrothermal fluids is unfocussed, both of which are unfavorable for the formation of economic deposits. In contrast, small, highly evolved stocks represent cupolas that develop kilometers above the general level of emplacement of the batholiths. As such, they are emplaced at shallow crustal levels where hydraulic fracturing is intense and the release of hydrothermal fluids from the magma is highly focused. This, and the convective magma overturn that ensures the introduction of multiple batches of H2O-rich magma into the cupolas, facilitating the large-scale hydrothermal alteration and, in principle, the multi-stage W-Sn rare metal...
mineralization that are the signatures of economic W-Sn deposits.

6.4 Differential competence as a control of W-Sn mineralization in granite batholiths

Although, as discussed above, granite batholiths are not predicted to produce W-Sn deposits directly, the occurrence of economic deposits within, albeit close to their margins, suggests that this spatial association is more than coincidence. We propose that the reason for this association in the Nanling region is that, because there is a large difference in the competence of the granite and the adjacent metasedimentary rocks, fractures developed preferentially along the contacts between the two rock-types in response to tectonic events, and these fractures provided the conduits for the subsequent emplacement of later granitic stocks. As the Caledonian granites occur mainly in the form of large batholiths, we further propose that most of the higher level Caledonian stocks have been eroded and that the Caledonian W-Sn mineralization is now of minor importance. However, because late Mesozoic magmatism, corresponding to the Yanshanian event, produced large volumes of evolved granitic magma that could be emplaced along fractures immediately adjacent to older batholiths of Caledonian and Indosinian age (after considerable erosion of these batholiths), there is now a strong spatial association between the batholiths and economic W-Sn mineralization. Thus, although Caledonian batholiths were not the source of the economic W-Sn mineralization exemplified in the Zhangjialong W deposit, their contacts represent very favourable locations for the discovery of new economic W-Sn deposits.

7. Conclusions

A combination of Re-Os dating of molybdenite and Ar-Ar dating of muscovite intergrown with scheelite and molybenite shows that the Zhangjialong W deposit formed during the Yanshanian event, i.e., between 160 and 150 Ma, whereas SIMS U-Pb dating of zircon (441.3 ± 2.4 Ma) in the greisenized granite confirms
that the latter is of Caledonian age. This precludes a temporal and genetic link between hydrothermal tungsten
mineralization and the regional Caledonian granite magmatism. Instead, the geochronological data and
evidence that granitic stocks are more evolved and more enriched in W and Sn suggests strongly that the
latter are the source of the W-Sn mineralization in these and the younger Indosinian batholiths. We propose
1) that the W-Sn mineralization, which is spatially associated with the batholiths originated from younger
stocks emplaced at high crustal levels, thereby enabling focused release of W-Sn enriched hydrothermal
fluids, and 2) that the location of the deposits near the margins of the batholiths was a result of differential
competence between the granites and the host metasedimentary rocks, which facilitated tectonic-induced
fracturing and emplacement of the magmas that produced W-Sn fertile stocks.

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Captions for Figures and Tables
Fig. 1 Geological map of the South China Block (modified after Wang et al., 2013 and Zhou et al., 2006)
Fig. 2 Geological map of the Nanling Range showing the distribution of granites and associated tungsten/tin deposits (modified after Mao et al., 2007).
Fig. 3 Geological sketch map of the Penggongmiao area, showing the distribution of tungsten deposits (modified after Li et al., 2013).
Figure 4 Geological sketch map of the Zhangjialong tungsten deposit (modified after Li et al., 2013)
Fig. 5 Geological cross-section of No. 50 exploration line from the Zhangjialong tungsten deposit

Fig. 6 Photographs of hand specimens and micrographs of ore-hosted granite and molybdenite-bearing ores collected from the Zhangjialong W deposit. (a) and (b) medium coarse-grained biotite monzonite granite; (c) and (d) Greisen-type tungsten ore; (e) and (f) Molybdenite-bearing greisen-type tungsten ore.

Ccp=chalcopyrite; Kfs= K-feldspar; Ms=muscovite; Pl=plagioclase; Py=pyrite; Qtz=quartz; Sch=scheelite.
Fig. 7 SIMS zircon U-Pb Concordia diagram (a) for the medium coarse-grained biotite monzonite granite and Re-Os age (b) for molybdenite from the Zhangjialong W deposit.

Fig. 8 Plateau, isochron and inverse isochron $^{40}$Ar-$^{39}$Ar ages of muscovite from the greisen-type W ore in the Zhangjialong W deposit.
Fig. 9 Plot of (a) Nb/Ta versus Zr/Hf, (b) Rb/Sr versus K/Rb, (c) W versus TiO₂, (d) Sn versus TiO₂, (e) and (f) Chondrite-normalized REE patterns for W-Sn related granite and ore-barren granite for differentiating the barren granite batholiths and ore-bearing granitic stocks in the Nanling Range region (Data are from the references of Supplementary Table 4).
Supplementary Figure 1 Cathodoluminescence (CL) images of representative zircons separated from medium coarse-grained biotite monzonite granite of the Penggongmiao granite batholith. Also shown is the SIMS spot for U-Pb dating. The white bars are 100 μm in length for scale.

Supplementary Table 1 SIMS zircon U-Pb data of the biotite granite sample ZJL-2 in the Zhangjialong W deposit, Nanling Range.

Supplementary Table 2 ⁴⁰Ar-³⁹Ar data for muscovite from sample ZJL-2 of the Zhangjialong W deposit,
Supplementary Table 3 Re-Os isotopic data for molybdenites from the Zhangjialong W deposit, Nanling Range.

Supplementary Table 4 Summary of the features of representative ore-barren batholiths and ore-bearing stocks in the Nanling Range and surrounding area.