Miner Deposita (2006) 41: 661–669
DOI 10.1007/s00126-006-0084-4

ARTICLE

Jiantang Peng · Mei-Fu Zhou · Ruizhong Hu · Nengping Shen · Shunda Yuan · Xianwu Bi · Andao Du · Wenjun Qu

Precise molybdenite Re–Os and mica Ar–Ar dating of the Mesozoic Yaogangxian tungsten deposit, central Nanling district, South China

Received: 12 June 2006 / Accepted: 8 July 2006 / Published online: 25 August 2006

Abstract The Yaogangxian deposit in the central Nanling region, South China consists of vein-type ore bodies hosted in Cambrian to Jurassic strata and Mesozoic granitic intrusions. Wolframite and molybdenite are the dominant ore minerals intergrown with gangue minerals of quartz, feldspar, phlogopite, and muscovite. We have carried out molybdenite Re–Os and phlogopite and muscovite $^{40}Ar/^{39}Ar$ dating to better understand the timing and genesis of mineralization. Re–Os dating of eight molybdenite samples yielded model ages ranging from 152.0±3.5 to 161.1±4.5 Ma, with an average of 156.0 Ma. The Re–Os analyses give a well-defined $^{187}Re/^{187}Os$ isochron with an age of 154.9±2.6 Ma (MSWD=2.4). Hydrothermal phlogopite and muscovite display extremely flat $^{40}Ar/^{39}Ar$ age spectra. Phlogopite yields a $^{40}Ar/^{39}Ar$ plateau age of 153.0±1.1 Ma, whereas muscovite yields a plateau age of 155.1±1.1 Ma. Both $^{40}Ar/^{39}Ar$ ages are in good agreement with the Re–Os ages, placing the timing of tungsten mineralization at about 154 Ma. This age is consistent with the field relationships. Our new data, when combined with published geochronological results from other major deposits in this region, suggest that large scale W–Sn mineralization occurred throughout the central Nanling region in the Late Jurassic.

Editorial handling: B. Lehmann

J. Peng · R. Hu · N. Shen · S. Yuan · X. Bi
Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, People's Republic of China

J. Peng (✉) · R. Hu · N. Shen · S. Yuan · X. Bi
State Key Laboratory of Ore Deposit Geochemistry,
Guiyang 550002, People's Republic of China
e-mail: pengjiantang@vip.gyig.ac.cn

M.-F. Zhou
Department of Earth Sciences, University of Hong Kong,
Hong Kong, People's Republic of China

A. Du · W. Qu
National Research Center of Geoanalysis,
Beijing 100037, People's Republic of China

Keywords Re–Os · Molybdenite · Ar–Ar · Mica · Tungsten · Nanling region · China

Introduction

China is the world's largest producer of tungsten both in terms of reserves and production. According to USGS (2006), the tungsten production of China in 2004 accounted for 90.9% of the total world production for that year, and China hosts 62.1% of the world's total tungsten reserves. More than 90% of the Chinese tungsten resources are distributed in the Nanling region, South China (Hsu 1943; RGNTD 1985; Lu 1986), and the Yaogangxian deposit is the largest of these.

Previous studies have significantly advanced our understanding of the tungsten ore formation in the Nanling region (e.g., RGNTD 1985; Lu 1986), but the exact timing of tungsten mineralization has been poorly constrained. Early isotopic dating, which focused mainly on granites related to the mineralization, yielded very scattered dates ranging from 195 to 65 Ma (RGNTD 1985). These have led to great ambiguity in our understanding of the timing of regional ore formation. Thus, direct dating of the deposits is required.

Molybdenite Re–Os (Suzuki et al. 1993; McCandless and Ruiz 1993; Huang et al. 1994; Stein et al. 1997, 1998; Mao et al. 1999, 2003; Selby et al. 2002; Kohút and Stein 2005; Zhang et al. 2005) and mica Ar–Ar dating (Snee et al. 1988; Cheilletz et al. 1993; Marsh et al. 1997; Reynolds et al. 1998; Garnier et al. 2002; Mello et al. 2006) have been used elsewhere to date in hydrothermal ore deposits. In this paper, we report first Re–Os ages of molybdenite and Ar–Ar ages of hydrothermal phlogopite and muscovite from the Yaogangxian tungsten deposit. The Re–Os ages and $^{40}Ar/^{39}Ar$ ages are indistinguishable and coincide well with the field geological relationships and other published geochronological results for W–Sn mineralization in the central Nanling region. Our work provides the first precise constraints on the absolute timing of hydrothermal tungsten mineralization in this deposit and further documents a regional tungsten–tin mineralization event in the central Nanling region, South China.

Geological background

South China comprises the Yangtze Block to the west and the Cathaysian Block to the east. The two blocks amalgamated along a Neoproterozoic collision belt at about 1000 Ma. The Cathaysian Block consists of a Proterozoic basement overlain by a cover sequence of Sinian to Triassic sedimentary strata (Chen and Jahn 1998). The Yaogangxian tungsten deposit is located in the Nanling district, which lies in the northwestern part of the Cathaysian Block (Fig. 1).

Late Paleozoic sedimentary strata, especially Devonian and Carboniferous limestone, are widespread in the central Nanling region. Mesozoic granitoid intrusions are well developed throughout the region, and Jurassic and Cretaceous granites are abundant in the central part (Institute of Geochemistry 1979; Mo et al. 1980). The Jurassic plutons consist predominantly of biotite granite with lesser amounts of two-mica granite, and they were previously considered to be typical S-type granites (Mo et al. 1980; RGNTD 1985), but some have recently been identified as A-type (Zhao et al. 2000; Zheng and Jia 2001; Fu et al. 2005; Bo et al. 2005). Spatially, these granitoid rocks are controlled by Mesozoic NE-striking faults.

The central Nanling region, covering an area of 6,600 km^2, contains numerous tungsten and tin deposits (Huang et al. 2003). These deposits are typically enriched in Mo, Bi, Pb, Zn, Cu, and Ag, and in some cases, Pb–Zn are the dominant metals. Several giant ore deposits in this region include the Shizhuyuan W–Sn–Mo–Bi–F deposit (Lu et al. 2003), the Furong Sn deposit (Huang et al. 2001, 2003; Li et al. 2006; Peng et al. 2006, submitted for publication), the Yaogangxian W deposit, the Xianghualing Sn–W–Pb–Zn deposit (Xiong et al. 2002; Yuan et al. 2006, submitted for publication), and the Huangshaping Pb–Zn–W–Sn–Ag deposit (Fig. 1). The Furong Sn deposit was discovered in the late 1990s and is expected to become a world-class tin producer (Huang et al. 2001). Despite extensive mining since the 1930s, the central Nanling region is still rich in W and Sn, with metal reserves of 1.7 million tons (metric) tungsten and 1.2 million tons tin (Che et al. 2005).

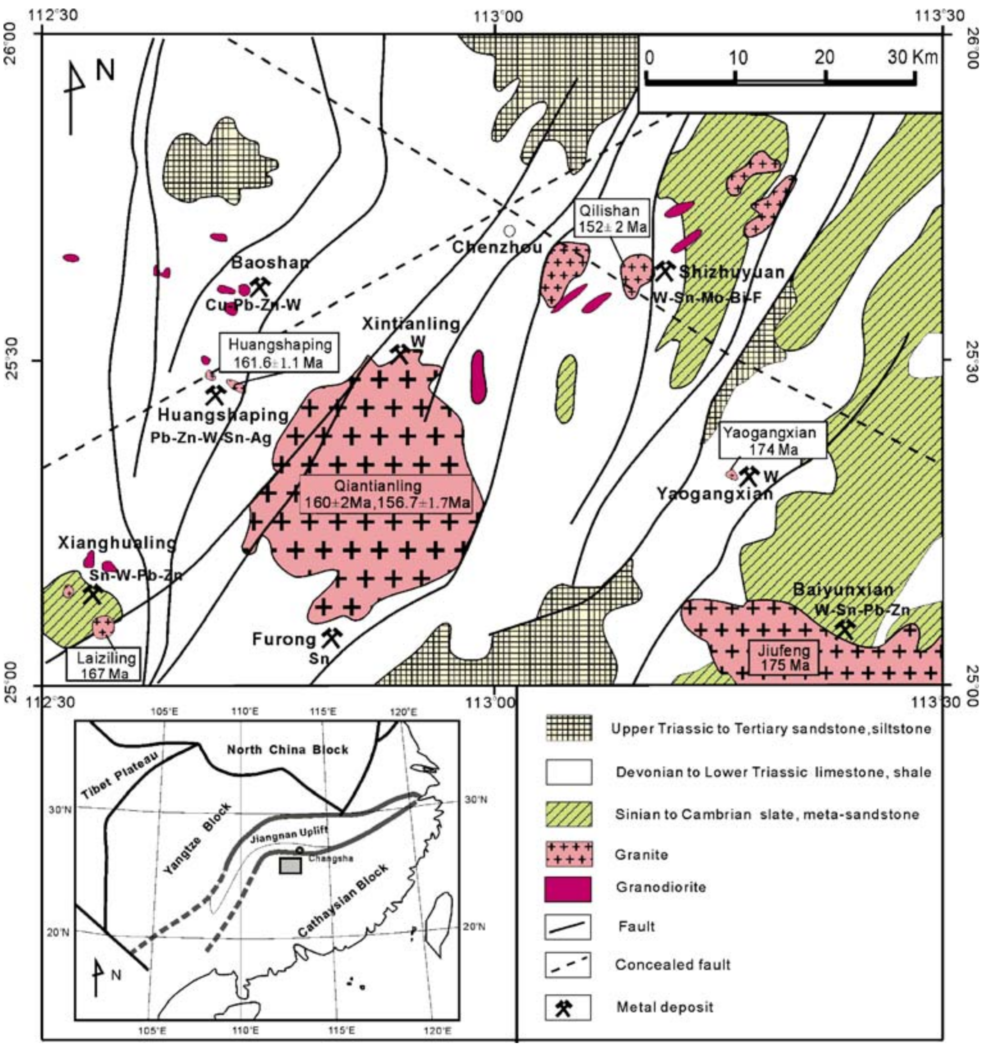

Fig. 1 Sketch map of tungsten and tin deposits in the central Nanling region, South China. Modified after Huang et al. (2003), age data for Qitianling granite from Fu et al. (2004) and Li et al. (2005), Qianlishan granite from Li et al. (2004), Huangshaping granite from Yao et al. (2005), Jiufeng granite from RGNTD (1985), and others from HBGMR (1988)

There are three main types of tungsten mineralization in this region, i.e., greisen-, skarn-, and quartz vein-type. All three types are commonly found together in most deposits but they can also occur individually. In addition to these three types, tin mineralization also occurs as stratiform cassiterite + sulfide type, altered granite type, and stockwork or network type in some deposits. Spatially, all these deposits are associated with the widespread Mesozoic granitic intrusions. Tungsten and tin mineralization usually occurs along the contact zones between the granitic intrusions and the sedimentary strata and is hosted in both Devonian to Permian sedimentary rocks and in granitic rocks. The field relations suggest that W–Sn deposits in this region are essentially coeval with the host Mesozoic granites (RGNTD 1985).

Yaogangxian tungsten deposit

The Yaogangxian tungsten deposit is mined since 1914 and has an average ore grade of about 1.27% WO_3 (Zhu 1999). The total production of the Yaogangxian mine until 2000 was 65,000 tons of refined tungsten concentrates (WO_3> 65%). Being the largest W producer in China, the Yaogangxian mine currently has an annual production of refined tungsten concentrates of about 2,300 metric tons (Yaogangxian Mine, unpublished data). The proven reserve of wolframite ores is estimated to be 2,360,000 tons.

In the Yaogangxian mining district, the stratigraphic sequence consists of Cambrian metasandstone and slate, unconformably overlain by Devonian and Carboniferous sandstone and limestone, and Jurassic sandstone (Fig. 2)

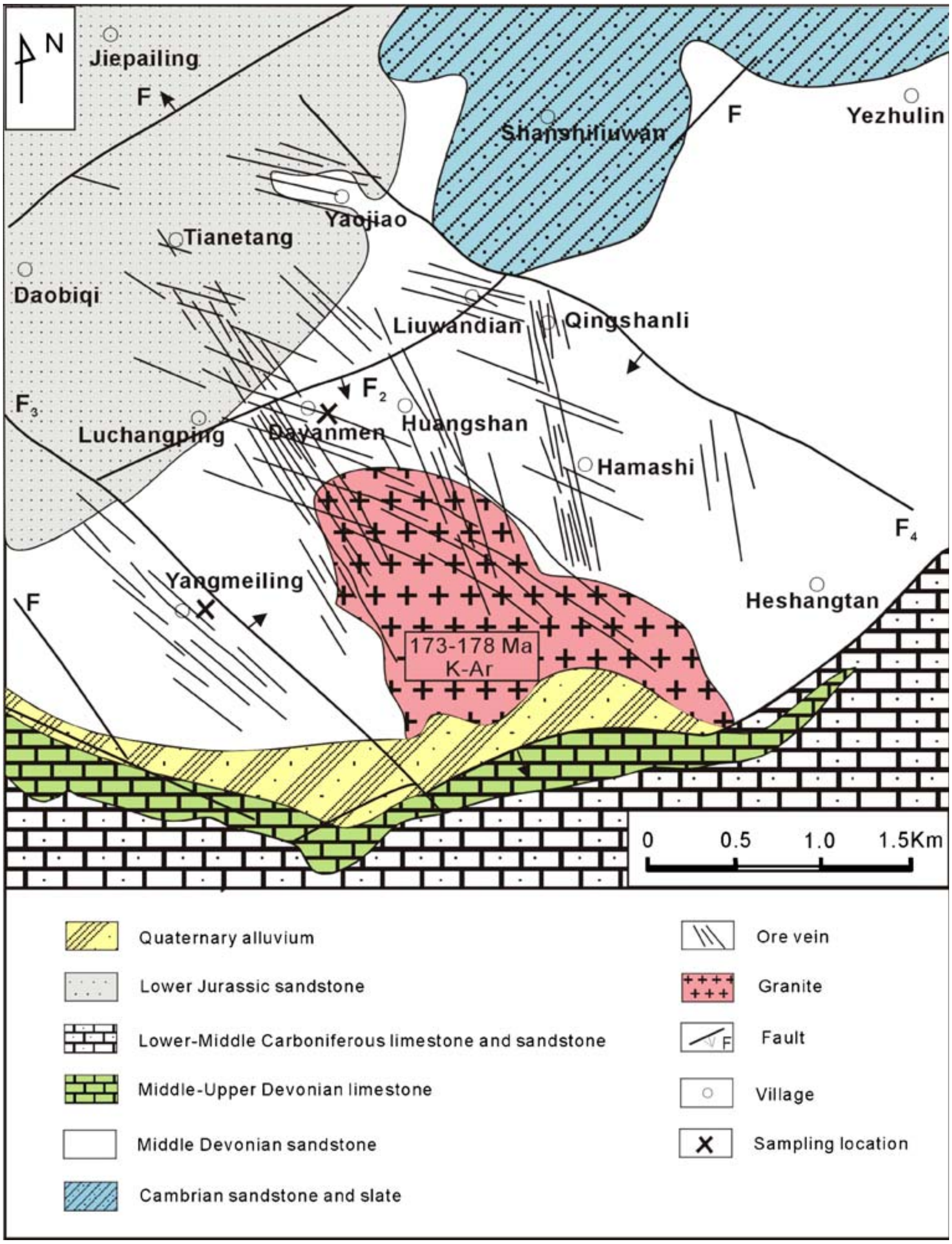

Fig. 2 Geological map of the Yaogangxian tungsten deposit, South China. Modified after Chen (1981)

(Chen 1981). A two-mica granite, with an exposed surface area of 1.2 km^2, intruded Cambrian and Devonian strata at 173–175 Ma (muscovite, biotite, K–Ar method) (Institute of Geochemistry 1972; HBGMR 1988). Some small dikes including diabase, aplite, and granite porphyry also occur in the mining district. They postdate the emplacement of the two-mica granite (Chen 1981).

The Yaogangxian deposit consists of more than 200 ore veins. These veins are usually NNW-, NW-, and NWW-striking (Fig. 2). Most ore veins occur along the northern contact zone between the granite and the sedimentary strata and commonly crosscut both lithologies. Individual veins are up to 1,200 m long, 1.5 m wide, and typically extend for 100 to 1,000 m downdip (Chen 1981). Generally, the veins increase in thickness with depth, but the number of veins decreases.

Ore minerals in this deposit are mainly wolframite and molybdenite, with minor amounts of arsenopyrite, cassiterite, chalcopyrite, pyrite, bournonite, and bismuthinite. The gangue minerals in the ores are predominately quartz, with minor amounts of mica, feldspar, fluorite, and calcite. The veins display mineral zoning, with quartz, sulfides, and occasionally wolframite in the innermost part, whereas the selvages of the veins typically contain wolframite, molybdenite, and mica. These minerals are usually oriented perpendicular to, or oblique to, the vein walls.

Sampling and analytical methods

Molybdenite occurs as fine- to coarse-grained euhedral platelets along the margins of the veins (Fig. 3a,b) where it is typically intergrown with other minerals such as wolframite, mica, fluorite, and pyrite. Molybdenite separates were collected from underground exposures of quartz–molybdenite veins hosted in the Cambrian metasandstones in the Yangmeiling mining adit (Fig. 2).

The phlogopite sample was collected from a quartz–feldspar–mica vein hosted in Devonian sandstone in the Dayanmen mining adit (Fig. 2). The vein has a sharp contact with the wall rocks, and phlogopite forms aggregates of euhedral crystals oriented perpendicular to the vein walls (Fig. 3c). The central part of the vein consists of feldspar, fluorite, and chalcopyrite, with minor quartz and fine-grained wolframite. The muscovite sample was collected in the Yangmeiling mining adit, and it is from a mica–quartz vein in Cambrian slate that contains disseminated fine-grained aggregates of sulfide. The mica forms euhedral aggregates with a diameter of about 1 to 3 mm (Fig. 3d).

Molybdenite for Re–Os dating was magnetically separated and then handpicked under a binocular microscope. The selected separates were crushed in an agate mortar to about 200 mesh. The analytical procedures followed those of Du et al. (2004). Molybdenite separates were digested using the Carius tube method (Shirey and Walker 1995) and equilibrated with ^{185}Re and ^{190}Os spikes in HNO_3-HCl by sealing in a thick-walled glass ampoule. The tube was then placed in a stainless steel jacket and heated for 10 h at 230°C. Osmium was recovered by distilling directly from the Carius tube and purified by microdistillation. The Re was recovered by anion exchange. Re and Os concentrations and isotopic compositions were determined using a TJA PQ-Excell inductively

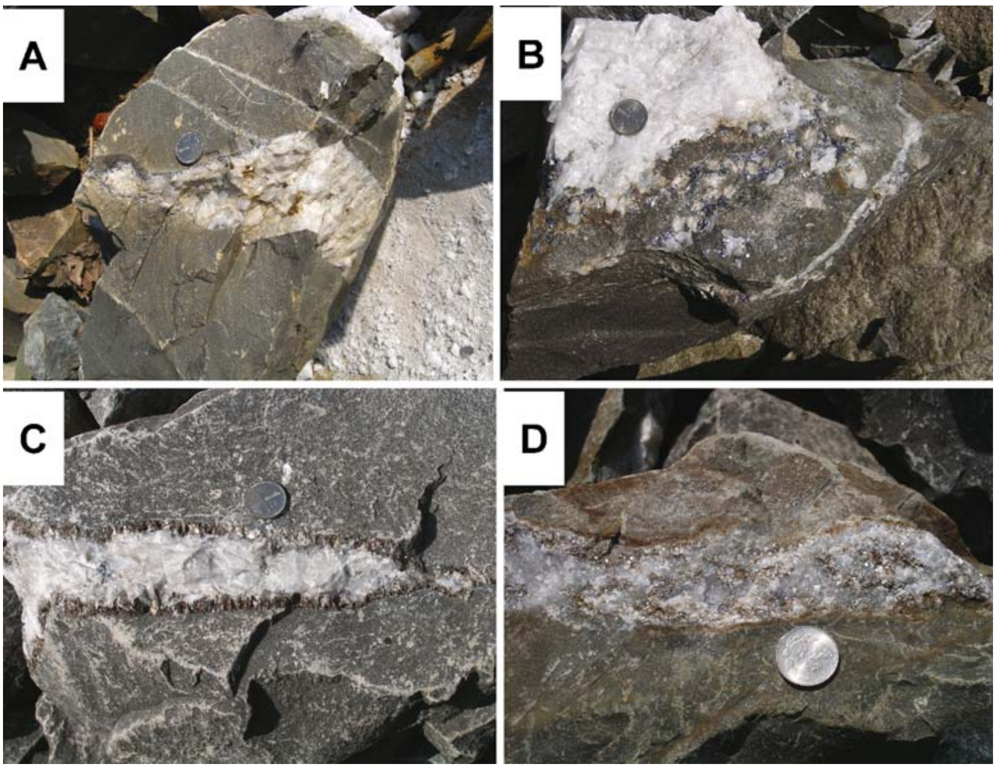

Fig. 3 Photographs of ore veins from the Yaogangxian tungsten deposit, South China. **a** Quartz–molybdenite ore vein. **b** Quartz–molybdenite ore vein. **c** Quartz–feldspar–phlogopite–sulfide vein. **d** Quartz–muscovite vein

coupled plasma mass spectrometer (ICP-MS) in the National Research Center of Geoanalysis, Beijing. The molybdenite standard GBW04436 (JDC) used in this study gave a mean value of 139.0±3.3 Ma compared with the certified value of 139.6±3.8 Ma (Du et al. 2004). Blanks during this study were 26–88 pg for Re and 1.6–1.7 pg for Os. The Re–Os isochron age was calculated using the least-squares method of York (1969), as implemented in the ISOPLOT 3.00 program (Ludwig 2004). The decay constant used in the age calculation is λ^{187}Re=1.666× 10^{-11} year^{-1} (Smoliar et al. 1996).

Phlogopite and muscovite grains (about 60 mesh) for Ar–Ar dating were carefully handpicked under a binocular microscope from the crushed materials and washed in an ultrasonic bath using ultrapure water. The mineral concentrates were analyzed by X-ray diffraction to ensure their purity. Samples were irradiated with fast neutrons for 62 h at the Chinese Academy of Nuclear-Energy Sciences and subsequently cooled for about 100 days. ^{40}Ar/^{39}Ar stepwise heating analyses were performed at the Guilin Institute of Geology and Mineral Resources using an MM-1200 gas-source mass spectrometer. Samples were analyzed in 11 temperature steps from 300°C to total fusion at 1,300°C. The biotite standard JBH (132.5 Ma) was used to monitor the neutron flux in the study. ^{40}Ar/^{39}Ar plateau ages were calculated using ISOPLOT 3.00 (Ludwig 2004).

Analytical results

Re–Os age of molybdenite

The eight molybdenite samples have a relatively narrow range of Re–Os mineral ages varying from 152.0±3.5 to 161.1±4.5 Ma, with an average of 156.0 Ma (Table 1), showing excellent reproducibility. The samples yield a well-constrained ^{187}Re–^{187}Os isochron, which corresponds to an isochron age of 154.9±2.6 Ma (MSWD=2.4) and an intercept of 0.0006±0.0034 (Fig. 4). A zero intercept confirms that all the ^{187}Os in the molybdenite are radiogenic and that the molybdenite contains no measurable common Os. This indicates that the model age for the molybdenite samples is reliable (Hintenberger et al. 1954; Luck and Allègre 1982). Noticeably, no correlation between Re and Os contents and molybdenite type (2H or 3R) was found in this study (Table 1).

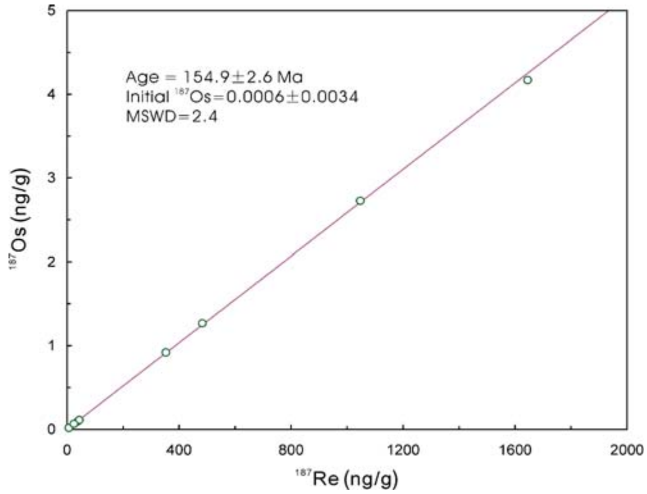

Fig. 4 ^{187}Re–^{187}Os isochron diagram for eight molybdenite samples from the Yaogangxian tungsten deposit, South China

Ar–Ar age determination of phlogopite and muscovite

Ar–Ar analytical results for phlogopite and muscovite are summarized in Tables 2 and 3, respectively, and illustrated in Fig. 5. In this study, an age plateau is defined as a sequence of five or more consecutive steps corresponding to at least 60% of the total ^{39}Ar released that yield apparent ages reproducible at the 95% confidence level (2σ). The two samples yielded well-defined plateau ages at 153.0± 1.1 and 155.1±1.1 Ma (Fig. 5), and both dates overlap the Re–Os date within uncertainties. The plateaus comprise ten continuous steps accounting for 99% of the total ^{39}Ar released. The characteristics of the spectra suggest that argon loss and excess argon did not occur in the samples and that the hydrothermal minerals host their radiogenic and nucleogenic gas fractions in tight crystallographic reservoirs which remained closed during the geological history of the sample.

Table 1 Re and Os isotopic data for molybdenite from the Yaogangxian tungsten deposit, South China

Sample	Type	Sample (g)	Re(±2σ) (ng/g)	^{187}Re(±2σ) (ng/g)	^{187}Os(±2σ) (ng/g)	Age(±2σ) (Ma)
YGX-25	2H	0.401	561.0±15.1	352.6±9.5	0.9184±0.0075	156.1±4.4
YGX-29	2H	0.401	59.48±1.05	37.38±0.66	0.0953±0.0008	152.9±3.0
YGX-31	2H	0.401	69.03±2.94	43.39±1.85	0.1120±0.0010	154.8±6.8
YGX-36	3R	0.401	10.16±0.20	6.386±0.126	0.01676±0.00019	157.3±3.6
YGX-37-2	2H	0.400	38.38±0.99	24.13±0.62	0.06483±0.00059	161.1±4.5
YGX-39	3R	0.400	1665±60	1047±38	2.725±0.020	156.1±5.8
YGX-40	2H	0.200	2618±57	1645±36	4.172±0.031	152.0±3.5
YGX-43	2H	0.400	767.8±18.6	482.6±11.7	1.268±0.010	157.5±4.1

Uncertainty for the calculated ages is 1.02% at the 95% confidence level

Table 2 $^{40}Ar/^{39}Ar$ analytical data for phlogopite from sample YGX-20 of the Yaogangxian tungsten deposit, South China

H.S.	*T* (°C)	$(^{40}Ar/^{39}Ar)_m$	$(^{36}Ar/^{39}Ar)_m$	$(^{37}Ar/^{39}Ar)_m$	$(^{38}Ar/^{39}Ar)_m$	$^{39}Ar_k$ (10^{-12} mol)	$^{40}Ar^*/^{39}Ar_k$ (1σ)	$^{39}Ar_k$ (%)	Apparent age [Ma (1σ)]
1	300	7.1451	0.00208	0.00284	0.0371	0.1625	6.52±0.28	0.66	154.2±1.5
2	500	7.0080	0.00173	0.00198	0.0179	0.7412	6.49±0.08	3.01	153.5±1.5
3	650	6.9179	0.00155	0.00203	0.0122	2.0783	6.45±0.02	8.44	152.6±1.5
4	750	7.0257	0.00186	0.00291	0.0108	3.3169	6.47±0.01	13.47	153.0±1.5
5	850	7.0308	0.00180	0.00313	0.0092	4.3634	6.49±0.01	17.72	153.5±1.5
6	920	6.9527	0.00160	0.00377	0.0137	3.9177	6.47±0.02	15.91	153.1±1.5
7	1,000	6.9224	0.00154	0.00328	0.0121	4.8830	6.46±0.01	19.83	152.8±1.5
8	1,080	6.9438	0.00165	0.00656	0.0304	2.5634	6.45±0.02	10.41	152.5±1.5
9	1,150	6.9881	0.00184	0.01158	0.0305	1.3839	6.44±0.06	5.62	152.3±1.5
10	1,220	7.0090	0.00180	0.01190	0.0232	1.0096	6.47±0.10	4.10	153.0±1.5
11	1,300	7.1303	0.00214	0.04067	0.0836	0.2044	6.49±0.97	0.83	182.1±1.8

Sample weight=0.102 g, *J*=0.013682, cooling time=101 days
H.S. Heating step

Discussion

Age of the Yaogangxian deposit

In the Yaogangxian mining district, homogenization temperatures (T_h) for quartz from quartz–wolframite ore veins range from 252 to 323°C (RGNTD 1985) or from 220 to 340°C (Ni 1994), and the decrepitation temperatures (T_d) for wolframite from the same veins range from 150 to 305°C (Ni 1994). These temperatures are obviously lower than the closure temperatures of the Re–Os molybdenite and Ar–Ar mica chronometers. The closure temperature for the Re–Os isotope system in molybdenite is estimated at about 500°C (Suzuki et al. 1996), and the closure temperature for the K–Ar isotope system in phlogopite is 400–510°C according to Giletti and Tullis (1977) or about 450°C according to Dodson (1979). The K–Ar closure temperature for muscovite is less certain, somewhere in the range of 350–640°C (Hames and Bowing 1994). Therefore, we can assume that both the Re–Os system for molybdenite and the K–Ar system for phlogopite and muscovite remained closed after mineral precipitation, and thus, the Re–Os and Ar–Ar dates reported in this study are taken as the age of ore formation in the Yaogangxian tungsten deposit.

Therefore, the absolute timing of tungsten mineralization in Yaogangxian is about 154 Ma, obviously younger than K–Ar dates for magmatic biotite and muscovite in the granite (173~178 Ma, Institute of Geochemistry 1972; HBGMR 1988), which coincides with the field fact that the ore veins cut the granite and that granitic breccias occur in molybdenite-bearing quartz veins (Lin et al. 1986).

Timing of the regional W–Sn mineralization

Recent studies reveal that tungsten and tin mineralization in the central Nanling region took place at 150–161 Ma. The Re–Os date of molybdenite from the Shizhuyuan deposit is 151.0±3.5 Ma (Li et al. 1996), whereas the Sm–Nd isochron age of skarn minerals from the same deposit is 160.8±2.4 Ma (Liu et al. 1997) or 149±2 Ma (Li et al.

Table 3 $^{40}Ar/^{39}Ar$ analytical data for muscovite from sample YGX-52 of the Yaogangxian tungsten deposit, South China

H.S.	*T* (°C)	$(^{40}Ar/^{39}Ar)_m$	$(^{36}Ar/^{39}Ar)_m$	$(^{37}Ar/^{39}Ar)_m$	$(^{38}Ar/^{39}Ar)_m$	$^{39}Ar_k$ (10^{-12} mol)	$^{40}Ar^*/^{39}Ar_k$ (1σ)	$^{39}Ar_k$ (%)	Apparent age [(Ma (1σ)]
1	300	7.4242	0.00266	0.00538	0.03844	0.2691	6.63±0.17	0.88	156.3±1.5
2	500	7.2439	0.00237	0.00497	0.02676	0.8777	6.54±0.07	2.87	154.3±1.5
3	650	7.2374	0.00217	0.03604	0.01310	2.3824	6.59±0.02	7.79	155.5±1.5
4	750	7.1570	0.00197	0.03083	0.00939	4.1470	6.57±0.01	13.56	155.0±1.5
5	850	7.1443	0.00187	0.03727	0.00840	4.8963	6.59±0.01	16.01	155.4±1.5
6	920	7.0724	0.00171	0.03771	0.01127	4.4528	6.56±0.01	14.56	154.8±1.5
7	1,000	7.0584	0.00173	0.02782	0.00786	6.6609	6.54±0.01	21.78	154.3±1.5
8	1,080	7.0954	0.00169	0.05666	0.02015	3.3672	6.59±0.02	11.01	155.5±1.5
9	1,150	7.0495	0.00169	0.07795	0.02173	2.0399	6.55±0.04	6.67	154.5±1.5
10	1,220	7.1042	0.00177	0.12367	0.02021	1.2050	6.58±0.08	3.94	155.3±1.5
11	1,300	7.1888	0.00224	0.32475	0.08540	0.2844	6.55±0.70	0.93	183.6±1.8

Sample weight=0.0934 g, *J*=0.013658, cooling time=102 days
H.S. Heating step

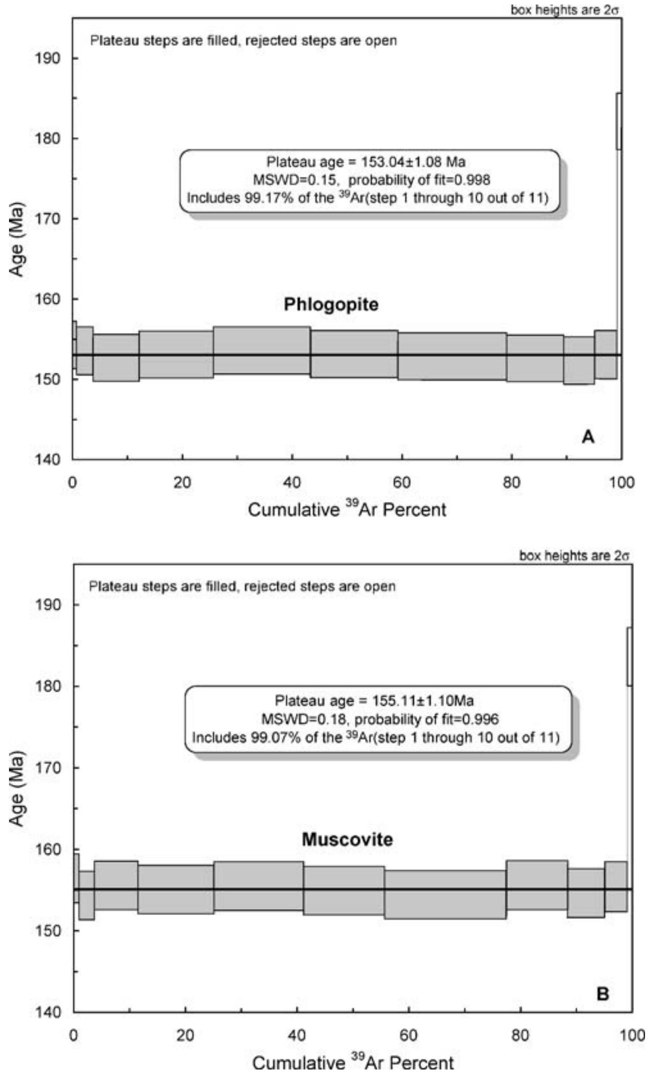

Fig. 5 $^{40}Ar/^{39}Ar$ age spectrum for phlogopite (**a**) and muscovite (**b**) from the Yaogangxian deposit, South China

2004). This deposit also has a $^{40}Ar/^{39}Ar$ mica date of 153.4± 0.2 Ma (Mao et al. 2004a) or 148.2±1.1 Ma (Peng et al., unpublished data). Two hydrothermal muscovite samples from the Furong tin mining district have plateau ages of 159.9±0.5 and 154.8±0.6 Ma, and three hydrothermal phlogopite samples yielded $^{40}Ar/^{39}Ar$ plateau ages of 150.8± 0.8, 154.7±1.1, and 157.3±0.6 Ma (Peng et al. 2006, submitted for publication). Hydrothermal hornblende from the same deposit gave a $^{40}Ar/^{39}Ar$ plateau age of 156.9± 1.1 Ma. Analyses for muscovite from the Furong ore field have yielded similar $^{40}Ar/^{39}Ar$ plateau ages of 156.1±0.4 and 160.1±0.9 Ma (Mao et al. 2004b). In the Xingtianling scheelite deposit, the $^{40}Ar/^{39}Ar$ plateau age of a zinnwaldite sample from skarn is 157.1± 0.3 Ma (Mao et al. 2004a). Three hydrothermal muscovite samples from the Xianghualing mining district have $^{40}Ar/^{39}Ar$ plateau ages of 154.4±1.1, 158.7±1.2, and 161.3±1.1 Ma (Yuan et al. 2006, submitted for publication). Thus, the age of tungsten mineralization in Yaogangxian coincides closely with that of tungsten–tin mineralization elsewhere in the central Nanling region. This large-scale mineralization event at about 154 Ma was probably associated with Mesozoic lithospheric extension in South China (Hu et al. 2004; Mao et al. 2004a; Li et al. 2006). Recent studies have identified several granite belts in South China with low T_{DM} values and relatively high $\varepsilon_{Nd}(t)$ values (−4.0 to −8.0), which are considered to result from crust–mantle interaction during lithospheric extension (Gilder et al. 1996; Chen and Jahn 1998; Hong et al. 1998; Zhu et al. 2003). Lithospheric extension in this region is supported by the presence of numerous Mesozoic basic dikes and some A-type granites in the central Nanling region (Zhao et al. 2000; Zheng and Jia 2001; Fu et al. 2005; Bo et al. 2005).

Conclusions

The Re–Os mineral ages and isochron age of molybdenite coincide well with $^{40}Ar/^{39}Ar$ plateau ages of hydrothermal phlogopite and muscovite from the Yaogangxian tungsten deposit. The results constrain the absolute timing of mineralization in this deposit at about 154 Ma, further documenting a Late Jurassic regional tungsten–tin mineralization event in the central Nanling region.

Acknowledgments This research was financially supported by the Important Program of Knowledge Innovation from the Chinese Academy of Sciences (Grant KZCX3-SW-125) and the Natural Science Foundation of China (Grant 40472053). We thank the geologists of the Yaogangxian Mine for their help during our field investigations. Special thanks are due to Mr. Dai Tongmo for his help with the argon analyses and Prof. Li Jianwei for reading an early draft. We express our gratitude to Prof. Bernd Lehmann for his invaluable suggestions that helped to improve an early draft of this paper.

References

Bo DY, Chen JC, Ma TQ, Wang XH (2005) Geochemical characteristic and tectonic setting of Qitianling A-type granitic pluton in Southern Hunan (in Chinese with English abstract). Acta Petrologica et Mineralogica 24:255–272

Cheilletz A, Féraud G, Giuliani G, Ruffet G (1993) Emerald dating through $^{40}Ar/^{39}Ar$ step-heating and laser spot analysis of syngenetic phlogopite. Earth Planet Sci Lett 120:473–485

Che QJ, Li JD, Wei SL, Wu GY (2005) Discussion on the tectonic background of deposit-concentrated Qianlishan–Qitianling area in Hunan (in Chinese with English abstract). Geotectonica et Metallogenia 29:204–214

Chen JF, Jahn BM (1998) Crustal evolution of southeastern China: Nd and Sr isotopic evidence. Tectonophysics 284:101–133

Chen YR (1981) Geological features and ore-prospecting indications in the Yaogangxian vein-type tungsten deposit (in Chinese with English abstract). Geology and Prospecting 17(2):25–30

Dodson MH (1979) The theory of cooling ages. In: Jäger E, Hunziger JC (eds) Lectures in isotope geology. Springer, Berlin Heidelberg New York, pp194–202

Du AD, Wu SQ, Sun DZ, Wang SX, Qu WJ, Markey RJ, Stein HJ, Morgan JW, Malinovskiy D (2004) Preparation and certification of Re–Os dating reference materials: molybdenite HLP and JDC. Geostandard and Geoanalytical Research 28:41–52

Fu JM, Ma CQ, Xie CF, Zhang YM, Peng SB (2004) Zircon SHIMP dating of the Cailing granite on the eastern margin of the Qitianling granite and its significance (in Chinese with English abstract). Geology of China 31:96–100

Fu JM, Ma CQ, Xie CF, Zhang YM, Peng SB (2005) Ascertainment of the Jinjiling aluminous A-type granite, Hunan Province and its tectonic settings (in Chinese with English abstract). Geochimica 34:215–226

Garnier V, Giuliani G, Maluski H, Ohnenstetter D, Trong TP, Quang VH, Van LP, Van TV, Schwarz D (2002) Ar–Ar ages in phlogopites from marble-hosted ruby deposits in northern Vietnam: evidence for Cenozoic ruby formation. Chem Geol 188:33–49

Gilder SA, Gill J, Coe RS, Zhao XX, Liu ZW, Wang GX, Yuan KR, Liu WL, Kuang GD, Wu HR (1996) Isotopic and paleomagnetic constraints on the Mesozoic tectonic evolution of South China. J Geophys Res (B) 101:16137–16155

Giletti BJ, Tullis J (1977) Studies in diffusion: pressure dependence of Ar diffusion in phlogopite mica. Earth Planet Sci Lett 35:180–183

Hames WE, Bowing SA (1994) An empirical evaluation of the argon diffusion geometry in muscovite. Earth Planet Sci Lett 124:161–167

HBGMR (Hunan Bureau of Geology & Mineral Resources) (1988) Regional geology of Hunan Province, China. Geological Publishing House, Beijing, pp 374–465

Hintenberger W, Herr W, Voshage H (1954) Radiogenic osmium from rhenium-containing molybdenite. Phys Rev 95:1690–1694

Hong DW, Xie XL, Zhang JS (1998) Isotopic geochemistry of granitoids in South China and their metallogeny. Resour Geol 48:251–263

Hsu KC (1943) Tungsten deposits of southern Kiangsi, China. Econ Geol 38:431–474

Hu RZ, Bi XW, Su WC, Peng JT, Li CY (2004) The relationship between uranium metallogenesis and crustal extension during the Cretaceous–Tertiary in South China (in Chinese with English abstract). Earth Sci Frontiers 11:153–160

Huang DH, Wu CY, Du AD, He HL (1994) Re–Os isotope ages of molybdenum deposits in East Qinling and their significance (in Chinese with English abstract). Mineral Deposits 19:221–230

Huang GF, Zeng QW, Wen SL, Xu YM, Hou MS, Kang WQ (2001) Geological characteristics and ore-controlling factors of the Furong orefield, Qitianling, Hunan (in Chinese with English abstract). Chinese Geology 28:30–34

Huang GF, Gong SQ, Jiang XW, Tan SX, Li CB, Liu DH (2003) Exploration on the ore-forming regularities of the tin deposits in Qitianling area, southern Hunan (in Chinese with English abstract). Geological Bulletin of China 22:445–451

Institute of Geochemistry (1972) Study on the isotopic ages for granites in the Nanling and its adjacent region (in Chinese). Geochimica 1:119–134

Institute of Geochemistry (1979) Geochemistry of granite in South China (in Chinese). Scientific Publishing House, Beijing, pp 1–160

Kohút M, Stein H (2005) Re–Os molybdenite dating of granite-related Sn–W–Mo mineralisation at Hnilec, Gemeric Superunit, Slovakia. Miner Petrol 85:117–129

Li HY, Mao JW, Sun YL, Zou XQ, He HL, Du AD (1996) Re–Os isotopic chronometry of molybdenite in the Shizhuyuan polymetallic tungsten deposit, Southern Hunan (in Chinese with English abstract). Geol Rev 42:261–267

Li XH, Liu DY, Sun M, Li WX, Liang XR, Liu Y (2004) Precise Sm–Nd and U–Pb isotopic dating of the supergiant Shizhuyuan polymetallic deposit and its host granite, SE China. Geol Mag 141: 225–231

Li JD, Bai DY, Wu GY, Che QL, Liu YR, Ma TQ (2005) Zircon SHRIMP dating of the Qitianling granite, Chenzhou, Southern Hunan and its geological significance (in Chinese with English abstract). Geological Bulletin of China 24:411–414

Li ZL, Hu RZ, Peng JT, Bi XW, Li XM (2006) Helium isotopic geochemistry of ore-forming fluids tin deposit in Hunan Province, China. Resour Geol 56:9–16

Lin XD, Zhang DH, Zhang CL (1986) A discussion on the characteristics of ore-forming fluid in wolframite–quartz ore veins in the Yaogangxian deposit, Yizhang County, Hunan (in Chinese with English abstract). Earth Sci (Journal of Wuhan College of Geology) 11:153–156

Liu YM, Dai TM, Lu HZ, Xu YZ, Wang CL, Kang WQ (1997) ^{40}Ar–Ar^{39} and Sm–Nd isotopic ages for formation and mineralization of the Qilishan granite (in Chinese with English abstract). Sci China Ser D 27:425–430

Lu HZ (1986) Origin of tungsten mineral deposit in South China (in Chinese with English abstract). Publishing House of Chongqing, Chongqing, pp 1–232

Lu HZ, Liu YM, Wang CL, Xu YZ, Li HQ (2003) Mineralization and fluid inclusion study of the Shizhuyuan W–Sn–Bi–Mo–F skarn deposit, Hunan Province, China. Econ Geol 98:955–974

Luck JM, Allègre CJ (1982) The study of molybdenite through the ^{187}Re–^{187}Os chronometer. Earth Planet Sci Lett 61:291–296

Ludwig KR (2004) Isoplot/Ex, version 3.0:a geochronological tool kit for Microsoft Excel. Berkeley Geochronology Center, Berkeley, CA

Mao JW, Zhang ZC, Zhang ZH, Du AD (1999) Re–Os isotopic dating of molybdenite in the Xiaoliugou W (Mo) deposit in the northern Qilian mountain and its geological significance. Geochim Cosmochim Acta 63:1815–1818

Mao JW, Du AD, Seltmann R, Yu JJ (2003) Re–Os ages for the Shameika porphyry Mo deposit and the Lipovy Log rare metal pegmatite, central Urals, Russia. Miner Depos 38:251–257

Mao JW, Xie GQ, Li XF, Zhang CQ, Mei YX (2004a) Mesozoic large scale mineralization and multiple lithospheric extension in South China (in Chinese with English abstract). Earth Sci Frontiers 11:45–55

Mao JW, Li XF, Lehmann B, Chen W, Lan XM, Wei SL (2004b) $^{40}Ar/^{39}Ar$ dating of tin ores and related granite in Furong tin orefield, Hunan Province, and its geodynamic significance (in Chinese with English abstract). Miner Depos 23:164–175

Marsh TM, Einaudi MT, McWilliams M (1997) $^{40}Ar/^{39}Ar$ geochronology of Cu–Au and Au–Ag mineralization in the Potrerillos District, Chile. Econ Geol 92:784–905

McCandless TE, Ruiz J (1993) Rhenium–osmium evidence for regional mineralization in Southwestern North America. Science 261:1282–1286

Mello EF, Xavier RP, McNaughton NJ, Hagemann SG, Fletcher I, Snee L (2006) Age constraints on felsic intrusions, metamorphism and gold mineralisation in the Palaeoproterozoic Rio Itapicuru greenstone belt, NE Bahia State, Brazil. Miner Depos 40:849–866

Mo SZ, Ye BD, Pang WZ, Wan SN (1980) Granitoid geology in the Nanling region. Geological Publishing House, Beijing, pp 115–180

Ni JW (1994) Research on fluid inclusion and ore-forming liquid features of the Yaogangxian tungsten deposit (in Chinese with English abstract). Journal of Zhejiang University 28:73–81

Reynolds P, Ravenhurst C, Zentilli M, Lindsay D (1998) High-precision $^{40}Ar/^{39}Ar$ dating of two consecutive hydrothermal events in the Chuquicamata porphyry copper system, Chile. Chem Geol 148:45–60

RGNTD (Research Group for Nanling Tungsten Deposits, Chinese Ministry of Metallurgy) (1985) Tungsten deposits in South China (in Chinese with English abstract). Publishing House of Metallurgical Industry, Beijing, pp 1–496

Selby D, Creaser BR, Hart CJR, Rombach CS, Thompson JFH, Smith MT, Bakke AA, Goldfarb RJ (2002) Absolute timing of sulfide and gold mineralization: a comparison of Re–Os molybdenite and Ar–Ar mica methods from the Tintina Gold Belt, Alaska. Geology 30:791–794

Shirey SB, Walker RJ (1995) Carius tube digestion for low-blank rhenium–osmium analysis. Anal Chem 67:2136–2141

Smoliar MI, Walker RJ, Morgan JW (1996) Re–Os ages of group IIA, IIIB, IVA, IVB iron meteorites. Science 271:1099–1102

Snee LW, Sutter JF, Kelly WC (1988) Thermochronology of economic mineral deposits: dating the stages of mineralization at Panasqueira, Portugal, by high-precision $^{40}Ar/^{39}Ar$ age spectrum techniques on muscovite. Econ Geol 83:335–354

Stein HJ, Markey RJ, Morgan JW, Du A, Sun Y (1997) Highly precise and accurate Re–Os ages for molybdenite from the East Qinling molybdenum belt, Shanxi Province, China. Econ Geol 92:827–835

Stein HJ, Sundblad K, Markey RJ, Morgan JW, Motuza G (1998) Re–Os ages for Archean molybdenite and pyrite, Kuittila–Kivisuo, Finland and Proterozoic molybdenite, Kabeliai, Lithuania: testing the chronometer in a metamorphic and metasomatic setting. Miner Depos 33:329–345

Suzuki K, Qi L, Shimizu H, Masuda A (1993) Reliable Re–Os age for molybdenite. Geochim Cosmochim Acta 57:1625–1628

Suzuki K, Shimizu H, Masuda A (1996) Re–Os dating of molybdenite from ore deposits in Japan: implication for the closure temperature of the Re–Os system for molybdenite and cooling history of molybdenite ore deposits. Geochim Cosmochim Acta 60:3151–3159

USGS (2006) U.S. Geological Survey Mineral Commodity Summaries. Tungsten, pp 182–183

Xiong XL, Rao B, Chen FR, Zhu JC, Zhao ZH (2002) Crystallization and melting experiments of a fluorine-rich leucogranite from the Xianghualing Pluton, South China, at 150 MPa and H_2O-saturated conditions. J Asia Earth Sci 21:175–188

Yao JM, Hua RM, Lin JF (2005) Zircon LA-ICP-MS U–Pb dating on the Huangshaping granite in Southeastern Hunan and its petrochemical characteristics (in Chinese with English abstract). Acta Petrologica Sinica 21:688–696

York D (1969) Least-squares fitting of a straight line with correlated errors. Earth Planet Sci Lett 5:320–324

Zhang LC, Xiao WJ, Qin KZ, Qu WJ, Du AD (2005) Re–Os isotopic dating molybdenite and pyrite in the Baishan Mo–Re deposit, eastern Tianshan, NW China, and its geological significance. Miner Depos 39:960–969

Zhao ZH, Bao ZW, Zhang BY, Xiong XL (2000) Crust–mantle interaction background of the ore formation in the giant Shizhuyuan tin polymetallic deposit (in Chinese with English abstract). Sci China Ser D 30(Suppl 1):161–168

Zheng JJ, Jia BH (2001) Geological characteristics and related tin–polymetallic mineralization of the Qitianling granite complex in Southern Hunan (in Chinese with English abstract). Geology and Mineral Resources of South China 9(4):50–57

Zhu JC, Huang GF, Zhang PH, Li FC, Rao B (2003) On the emplacement age and material sources for the granites of Cailing superunit, Qitianling pluton, South Hunan Province (in Chinese with English abstract). Geol Rev 49:245–252

Zhu X (1999) The China situation of mineral resources (in Chinese), vol 2. Scientific Publishing House, Beijing, pp 448–449