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Scheelite Sm-Nd dating and quartz Ar-Ar dating for Woxi Au-Sb-W deposit, western Hunan

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Abstract **Scheelite Sm-Nd and quartz Ar-Ar dating were accomplished for the Woxi Au-Sb-W deposit in western hunan. The results show that the Sm and Nd concentrations of scheelite are relatively high, and Sm/Nd ratios are usually high and variable. In the ^{147}Sm/^{144}Nd vs. ^{143}Nd/^{144}Nd diagram, the disseminated scheelites show a good linear array, which corresponds to an isochron age of 402 ± 6 Ma and an initial ^{143}Nd/^{144}Nd ratio of 0.510544 ± 9 (2σ) with a $\varepsilon_{Nd}(t)$ value of –30.7. The Ar-Ar age spectra for 2 quartz samples display the saddle shape. The minimum apparent age, plateau age and isochron age of each quartz sample generally overlap within errors; and both the minimum apparent ages of 420 ± 20 and 414 ± 19 Ma coincide well with the scheelite Sm-Nd age. Both Sm-Nd and Ar-Ar dating results reveal that the Au-Sb-W mineralization at Woxi district took place in the Late Caledonian. This is in good agreement with the tectonic evolution of the Xuefengshan district and with some geochronological data available for Au, Sb and W deposits in this area. The low initial Nd isotope ratio of scheelites suggests that the fluid responsible for Au-Sb-W mineralization at the Woxi is of deep crustal origin and probably originated from the underlying Archaean continental basement rather than the host Proterozoic strata in western Hunan. The constraints on the mineralization time and on the fluid source provide insight into the genesis of the Woxi deposit.**

Keywords: Sm-Nd isotope dating, scheelites, Ar-Ar isotope dating, Au-Sb-W deposit, West Hunan.

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Since Fryer et al.[1] (1984) first dated the hydrothermal deposit using the Sm-Nd isotope method, this isotope systematics has been widely applied in the geochronological study for hydrothermal mineralization. In recent years, many hydrothermal minerals such as fluorite[2—7], tourmaline[8,9], wolframite[5,10,11] and calcite[12,13] have been successfully dated using the Sm-Nd geochronometer. Scheelite is one of Ca-bearing minerals, and rare earth elements (REE) are incorporated in scheelite by substitution at Ca^{2+} structural sties in mineral lattices; moreover, scheelite is usually formed coevally with native gold in many gold deposits, and the W abundance in ores show a positive correlation with the Au concentration in ores[14—17]. Therefore, since the late 1980s, Sm-Nd isotope systematics of scheelites from some foreign gold deposits was studied in order to constrain the precise time of gold mineralization and its ore genesis[8,18—21]. However, the studied deposits are mainly restricted within Archaean-Early Proterozoic greenstone belt gold deposits. Scheelite is widespread in many Chinese tungsten and gold deposits, in spite of that, no attempt using scheelite for isotope dating has been made.

The Woxi Au-Sb-W deposit was located at the middle part of the Xuefengshan gold-antimony metallogenic province. The gold production of the Au-Sb-W deposit ranks first among all gold deposits in the Jiangnan Old Land, South China, and the Au and Sb reserves for the Woxi deposit respectively amount to those of the large-scaled deposit. Due to the characteristic element association and the lasting mining history (more than 130 years), the Woxi deposit is famous in China and attracts a lot of geologists. However, due to the lack of suitable minerals for conventional radiometric methods, the metallogenic epoch of the Woxi deposit is still poorly constrained and remains controversial, and the inferred ages span the Xuefeng Period (about 800 Ma) through the Yenshanian Period (about 213—65 Ma). Before the 1990s, the Woxi deposit was considered to be closely associated with the Xuefeng regional metamorphism based on the strata-bound signature and on lead model ages of ores, and the mineralization time was estimated at about 800 Ma[22—25]. However, since the 1990s, a few geologists disagreed that[26—28]. Instead, they insisted that there is no connection between the Au mineralization and the metamorphic event in this area, and that the Au mineralization took place during the Indosinian-Yenshanian Period[26] or Yenshanian Period[27,28]. Notwithstanding this, due to the lack of reliable age data at present, many Chinese geologists are still ready to accept the viewpoint of Proterozoic Au mineralization at the Woxi deposit[29—31]. The objectives of this contribution are to date scheelite by the Sm-Nd method and date quartz by the Ar-Ar method from this deposit, provide some constraints on the mineralizing time and the fluid source, and lay some foundations for the further understandings of the ore deposit origin.

1 Geological setting

The Woxi Au-Sb-W deposit is located in western hunan, about 200 km west away from Changsha, the capital of Hunan Province. Tectonically, the Woxi deposit was situated in the Xuefengshan arc uplift belt, which consists of the southwestern part of the Jiangnan Old Land. Exactly speaking, the Woxi deposit occurs in the transition part of the Xuefengshan uplift where the northeast strike bends to east-west.

The strata exposed in this area consist mainly of Mesoproterozoic Lengjiaxi Group (Pt_2lj) and Neoproterozoic Banxi Group (Pt_3bn). The former is a series of flysch formation consisting of marine clastic rocks intercalated with volcanic lava; and the latter, which is a series of flyschoid consisting of slate and phyllite interbedded with local volcanic materials, can be subdivided into the Madiyi Formation (Pt_3bnm) and the Wuqiangxi Formation (Pt_3bnw). Orebodies in the Woxi deposit are strictly restricted within the amaranth Ca-bearing sericitic slate in the middle Madiyi Formation, and controlled by interlay faults. Magmatic activities are generally weak in western Hunan, and no igneous rocks outcrop within or around the Woxi mining district.

By appearance, orebodies can be divided into bedded vein, stockwork and joint vein (or veinlet). Economically, the bedded veins rank the most important, which contribute about 70% to the metal accumulations in this deposit[22]. There are 4 ore-bearing bedded veins together in the deposit, each of which is composed of several haricot-shaped ore-bearing quartz veins. The bedded veins with east-west strike are gentle dipping (about 20°—30°). The total thickness of ore-hosting horizons in this deposit is estimated at about 120—350 m. The ore types are predominated by scheelite-quartz, stibnite-native gold-quartz, scheelite-stibnite-native gold-quartz, pyrite-native gold-quartz and scheelite (wolframite)-native gold-quartz. The metallic minerals are predominated by native gold, stibnite, scheelite, wolframite, pyrite, and with minor arsenopyrite, sphalerite and galena; the gangue minerals include quartz, and minor amounts of sericite, calcite and chlorite. The alterations of wall rocks are predominated by decolorization, silicification, pyritization, carbonatization and sericitization.

2 Sampling and analytical methods

Scheelite samples were collected from underground exposures of No. 4 orebody in the Shiliupenggong mining district; the detailed locations are presented in Table 1. No. 4 orebody occurs in the upmost of the ore-bearing bedded veins and ranks first in scale among all bedded veins; its single ore vein, with an average thickness of 0.52 m, extends about 50—350 m in strike and 590—2280 m in dip[30]. The average ore grade for No. 4 orebody is 10.13 μg/g Au, 5.55% Sb and 0.75% WO_3[30]. In the Woxi Mine, the W and Au contents of No. 4 orebody are highest; and there exists the distinct spatial separation of metal mineralization. The tungsten mineralization mainly occurs in the shallow part of the mining district and gradually becomes weak downwards; in contrast, gold and antimony mineralization usually increases downwards from the surface. Scheelite in No. 4 orebody usually appears in 2 forms: anhedral grain or massive aggregate; the irregular fine-grained scheelite is disseminated in the quartz vein, the latter is usually cut by quartz veinlets. Scheelite in this study is usually milky white, grease luster, and shows shamrock or lightly blue fluorescence color under the ultraviolet light.

Based on field investigation and microscopic observations, scheelite samples were selected. Scheelite chips were cut from hand specimens and lightly crushed to 40—60 meshes in size, scheelite separates were prepared using the standard heavy liquid method, and final purification was achieved by handpicking under a binocular microscope with the aid of an ultraviolet light. The cleaned fractions with a purity of more than 99% were powdered to 200 meshes in an agate mortar. Sm and Nd isotope measurements were finished at Tianjin Institute of Geology & Mineral Resources, the Chinese Ministry of Land and Resources.

The Sm and Nd concentrations and Nd isotopic ratios were separately determined. Abundances of Sm and Nd were determined by the isotope dilution method; present-day $^{143}Nd/^{144}Nd$ ratios were measured from unspiked dissolutions of pre-concentrated samples. Samples were taken into solutions in bombs using a mixture of HF and $HClO_4$; the sealed bombs were kept at about 70℃ for at least 72 h, after which the solution was slowly evaporated to dryness until white fume disappeared. 5 mol/L HCl was added into the bomb to attack the sample; the solution was removed and kept. The residue was leached with 5 mol/L HCl again and kept at a hot plate for about 24 h, and then the solution was cooled and removed. The residue was attacked again with 5 mol/L HCl at a moderate temperature, and the solution was removed again. The above procedure was repeated for 3—4 times until the scheelite samples were completely dissolved. All solutions were well mixed and then dried, and re-dissolved in 2 mol/L HCl. Sm and Nd were separated by a reversed phase extraction technique with HDEHP.

The Sm and Nd abundances and $^{143}Nd/^{144}Nd$ ratios were measured on a MAT-261 mass spectrometer. Nd isotopic ratios are normalized to $^{146}Nd/^{144}Nd = 0.7219$ using power law fractionation correction. The analytical results obtained on the Chinese first-rank standard GBS04419 during the course of this work are: [Sm] =3.02 μg/g, [Nd] =10.07 μg/g, $^{143}Nd/^{144}Nd = 0.512739 \pm 5$ (2σ). Concentrations for BCR-1 determined during this study are 6.57 μg/g Sm, 28.75 μg/g Nd, and the $^{143}Nd/^{144}Nd$ value of BCR-1 is 0.512644±5 (2σ). The JMC Nd standard gives a $^{143}Nd/^{144}Nd$ value of 0.511132±5 (2σ). Blanks during the course of this study are 30 pg for Sm and 54 pg for Nd. The precision for the Sm, Nd concentration at the 2σ level is less than 0.5% of the quoted values; and the analytical error (2σ) of $^{147}Sm/^{144}Nd$ falls in a range of ±0.5%. The Sm-Nd isochron age is calculated by using the Program ISOPLOT. In this study, the decay constant λ for ^{147}Sm is 6.54×10^{-12}/a, the $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ values of chondritic uniform reservoir (CHUR) used for $\varepsilon_{Nd}(t)$ calculation are 0.1967 and 0.512636, respectively.

All quartz samples in this study were collected from the main bedded orebodies in the Woxi deposit. The sample WX-17 was collected from the same orebody like the scheelite samples in the Shiliupenggong mining district; the quartz sample, characterized by the grease luster, is milky white, compact massive and intergrown with Coarse-grained tabular stibnite; a few disseminated pyrite and native gold are also found in sample WX-17. Sample YRS-30, collected from the underground exposures of No.1 orebody in the Yu'ershan mining district, is compact massive, slightly yellowish-pink, obscure luster and intergrown with fine-grained massive stibnite.

Based on field investigation and microscopic observations, quartz chips were cut from hand specimens and crushed to 60 meshes in size, and then quartz were hand-picked to the purity of 99% under a binocular microscope. The ^{40}Ar-^{39}Ar analyses for quartz were made using the fast-neutron irradiation method described by Sang et al.[32]. First the samples were put in reaction pile for fast-neutron irradiation at the Chinese Academy of Atom-Energy Science, which took 62 h with an integrated neutron flux of $1.45\times10^{18}/cm^2$. Then the irradiated samples were put in RGA-10 gas-source mass spectrometer integrated with the Ar-separating system for Ar extraction and purification, and the step-heating method was adopted to extract Ar for mass spectrum analysis. Finally, the purified Ar was used for Ar isotope analysis at the RGA-10 mass spectrometer. The sample step-heating, Ar purification and Ar isotope analysis were finished at Institution of Geology & Geophysics, the Chinese Academy of Sciences (CAS). Details were given in ref. [32]. The standard samples, used to supervise the neutron flux in this study, include Chinese hornblende ZBJ and biotite ZBH-25, Australian hornblende 77600 and international standard hornblende BSP-1, which gave the average age of 132.8 ± 1.4, 132.7 ± 1.2, 414.5 ± 3.7 and 2060 ± 8 Ma, respectively. All original data are calibrated to preclude the interference of time zero, mass discrimination, fractionation effect, background blanks, K, Ca, Cl interfering isotope and radiogenic ^{37}Ar. The decay constant λ for ^{40}K is 5.543×10^{-10}/a for the age calculation in this study.

3 Results

(i) Sm-Nd isotope age for scheelite. Sm and Nd concentrations in scheelite samples from the Woxi deposit and its isotope compositions are summarized in Table 1. Sm contents for the disseminated scheelites range between 2.23 and 6.20 μg/g, and its Nd contents vary in the range of 1.86—4.54 μg/g; the Sm and Nd contents for massive scheelite are relatively low. Based on the data available in Table 1, the Sm and Nd concentrations tend to decrease spatially with an increasing elevation. The $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios of disseminated scheelites fall in the range of 0.6409—1.0749 and 0.512229—0.513372, respectively; the massive sample, W-77-1, has a relatively high $^{143}Nd/^{144}Nd$ ratio (0.514194). For all samples, Sm content is higher than that of Nd, and the Sm/Nd ratios are usually high and easily result in the large Nd isotopic fractionation, which is favorable for the Sm-Nd dating.

In the $^{147}Sm/^{144}Nd$-$^{143}Nd/^{144}Nd$ diagram, the disseminated scheelite samples from the Woxi deposit display a good linear array, which yields a slope corresponding to an age of 402 ± 6 Ma and an intercept of 0.510544 ± 9 ($\varepsilon_{Nd}(t)$ = −30.7); the mean square of weighted deviates (MSWD) is 0.3 (Fig. 1). Considering that all samples were collected from the same ore vein and should be regarded as the products of the same hydrothermal event, that no obvious evidence for distribution by late hydrothermal alteration was found for these disseminated scheelites, and that the variation range of the calculated $\varepsilon_{Nd}(t)$ for the disseminated scheelites is relatively small (Table 1), thus the determined isochron age in this study

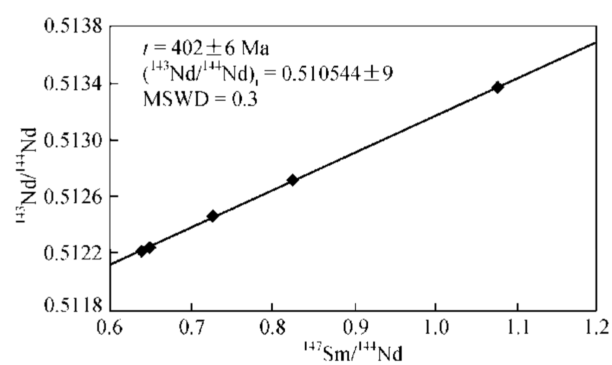

Fig. 1. Sm-Nd isochron for disseminated scheelites from Woxi deposit.

Table 1 Sm-Nd isotope data for scheelites from the Woxi Au-Sb-W deposit[a)]

Locality	Sample No.	Sm/μg • g^{-1}	Nd/μg • g^{-1}	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$ (2σ)	$\varepsilon_{Nd}(t)$
No. 7 level	W-77-1	0.925	0.558	1.0027	0.514194 (7)	−11.00
	W-67	2.23	1.86	0.7267	0.512457 (6)	−30.73
No. 9 level	WX-18	2.31	2.18	0.6409	0.512229 (7)	−30.77
	WX-19	2.86	2.66	0.6492	0.512251 (8)	−30.77
No. 10 level	WX-20	5.73	3.22	1.0749	0.513372 (7)	−30.76
	WX-21	6.20	4.54	0.8260	0.512714 (6)	−30.82

a) Sample W-77-1: Massive scheelite; other samples: disseminated scheelite.

should be interpreted to represent the true time of scheelite precipitation in the Woxi deposit. Noticeably, the massive sample W-77-1 cannot be well fitted in the isochron line, which is probably associated with the overprint of later hydrothermal activity which may reset Sm-Nd isotope system in massive scheelites. Since the quartz veinlets are usually seen to cut through massive scheelite in some hand specimens.

(ii) Ar-Ar isotope age for quartz. The Ar isotope results for quartz samples are presented in Tables 2 and 3. From Tables 2, 3, as well as Fig. 2, it is not difficult to see that the age spectra for 2 samples display a saddle-shape. The minimum apparent age in this saddle-shaped spectrum probably represents the true time for mineral crystallization[33]. Sample WX-17 collected from the same vein like scheelite samples defines a minimum apparent age of 419.8±20.2 Ma, a plateau age of 423.2 ± 1.2 Ma (Fig. 2(a)) and an isochron age of 421.6 ± 4.5 Ma (Fig. 2(b)). The other sample YRS-30 collected from another ore vein yields a minimum apparent age of 414.4 ± 19.2 Ma, a plateau age of 416.2 ± 0.8 Ma (Fig. 2(c)) and an isochron age of 415.1 ± 3.1 Ma (Fig. 2(d)). Obviously, both the minimum apparent ages are in good agreement with our Sm-Nd data in this study. Noticeably, for each quartz sample, its minimum apparent age, plateau age and isochron age generally overlap within errors; this consistency reveals the reliability of our measured Ar-Ar age data in this study[32]. Moreover, the initial $^{40}Ar/^{39}Ar$ ratios corresponding to the 2 isochrones are 295.6 ± 2.88 (Fig. 2(b)) and 295.1 ± 1.98 (Fig. 2(d)), respectively, both data agree well with the Nier value (295.5), which also indicates that the influence of excess Ar on the measured age in this study is negligible, i.e. the minimum apparent age of the measured samples in this study should represent the true time of quartz precipitation.

Table 2 $^{40}Ar/^{39}Ar$ analytical data for sample WX-17 from Woxi deposit[a)]

Stage	T/℃	$(^{40}Ar/^{39}Ar)_m$	$(^{36}Ar/^{39}Ar)_m$	$(^{37}Ar/^{39}Ar)_m$	$(^{38}Ar/^{39}Ar)_m$	$^{39}Ar_k$/mol	$^{40}Ar^*/^{39}Ar_k (1\sigma)$	$^{39}Ar_k$ (%)	Age/Ma(1σ)
1	400	74.00	0.1333	2.780	0.7600	0.8683×10^{-12}	35.13 ± 0.08	8.65	649.5 ± 42.7
2	480	33.54	0.0416	1.523	0.3698	2.224×10^{-12}	21.45 ± 0.04	22.1	423.6 ± 14.7
3	560	40.00	0.0645	1.820	0.5210	1.436×10^{-12}	21.23 ± 0.05	14.3	419.8 ± 20.2
4	650	48.94	0.0941	2.352	0.6918	0.9844×10^{-12}	21.53 ± 0.07	9.81	425.0 ± 27.0
5	760	58.54	0.1266	2.993	0.8449	0.7316×10^{-12}	21.66 ± 0.09	7.29	427.3 ± 33.1
6	880	64.05	0.1370	2.533	0.7479	0.8453×10^{-12}	24.06 ± 0.08	8.42	468.9 ± 31.8
7	1020	73.87	0.1666	2.938	0.8600	0.6945×10^{-12}	25.19 ± 0.09	6.92	488.3 ± 37.8
8	1150	70.76	0.1515	2.801	0.8697	0.7641×10^{-12}	26.53 ± 0.09	7.61	510.9 ± 39.8
9	1300	72.03	0.1351	2.760	0.8189	0.8567×10^{-12}	32.62 ± 0.08	8.54	610.2 ± 43.6
10	1500	98.26	0.1852	3.225	1.1560	0.6250×10^{-12}	44.24 ± 0.12	6.23	785.7 ± 75.6

a) Sample weight w = 0.2214 g; irradiation parameter J = 0.012335.

Table 3 $^{40}Ar/^{39}Ar$ analytical data for sample YRS-30 from Woxi deposit[a)]

Stage	T/℃	$(^{40}Ar/^{39}Ar)_m$	$(^{36}Ar/^{39}Ar)_m$	$(^{37}Ar/^{39}Ar)_m$	$(^{38}Ar/^{39}Ar)_m$	$^{39}Ar_k$/mol	$^{40}Ar^*/^{39}Ar_k (1\sigma)$	$^{39}Ar_k$(%)	Age/Ma (1σ)
1	400	97.56	0.2034	1.545	0.7220	0.6836×10^{-12}	37.95 ± 0.07	6.84	692.8 ± 42.8
2	480	34.32	0.0454	0.991	0.4068	2.040×10^{-12}	21.07 ± 0.04	20.4	416.9 ± 15.9
3	560	37.83	0.0579	1.226	0.4986	1.599×10^{-12}	20.93 ± 0.05	16.0	414.4 ± 19.2
4	660	48.81	0.0952	1.762	0.6857	0.9732×10^{-12}	21.01 ± 0.07	9.74	415.9 ± 26.2
5	780	60.17	0.1333	2.136	0.8867	0.6949×10^{-12}	21.22 ± 0.09	6.95	419.5 ± 34.1
6	900	58.85	0.1242	1.949	0.7547	0.7460×10^{-12}	22.55 ± 0.08	7.46	442.9 ± 30.5
7	1050	61.13	0.1250	2.279	0.8375	0.9265×10^{-12}	24.64 ± 0.09	9.27	478.9 ± 36.2
8	1200	65.53	0.1370	2.335	0.8877	0.8454×10^{-12}	25.54 ± 0.09	8.46	494.1 ± 39.4
9	1350	63.82	0.1316	2.277	0.8763	0.8802×10^{-12}	25.40 ± 0.09	8.80	491.8 ± 38.8
10	1500	83.27	0.1923	2.668	0.8269	0.6020×10^{-12}	27.03 ± 0.08	6.02	519.1 ± 38.4

a) Sample weight w = 0.2243 g; irradiation parameter J = 0.012335.

4 Discussions

The Sm-Nd isotope data defined by the disseminated scheelites and the ^{40}Ar-^{39}Ar data defined by quartz in this study, indicate that the Au-Sb-W mineralization in the Woxi deposit took place in the Late Caledonian. All our data are obviously older than the previous data. Shi et al.[28] obtained an Rb-Sr isochron of 144.8±11.7 Ma by dating fluid inclusions of quartz coevally with stibnite from the Woxi deposit. However, considering the following reasons: (1) the Rb-Sr isochron dating method of fluid inclusions is probably imperfect in theory[34,35]; (2) no other independent isotope data support the Yenshanian mineralization in the Woxi deposit; and (3) no convincing geological evidences lend support for the Yenshanian mineralization event in this district; thus, the data of Shi et al. still remain controversial.

Notably, the isotope ages determined in this study coincide well with the tectonic evolution history in the Xuefengshan district and with the known isotope ages available for gold, antimony and tungsten deposits in this district. In recent years, more and more evidence reveals

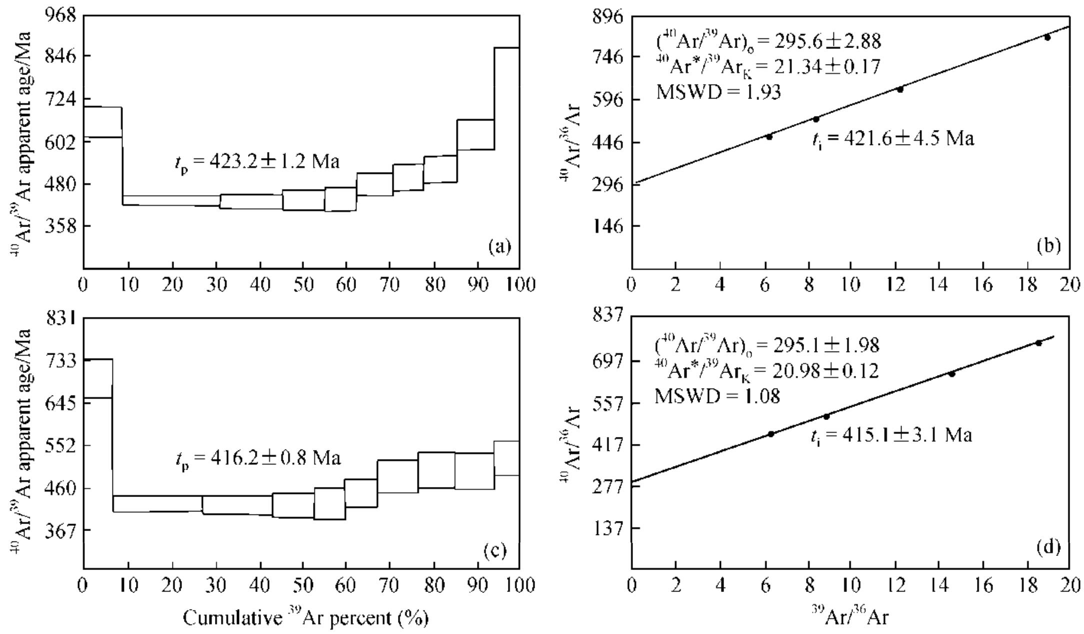

Fig. 2. $^{40}Ar/^{39}Ar$ age spectra, apparent and isochron ages for quartz samples from Woxi deposit. (a) Age spectrum and plateau age for sample WX-17; (b) isochron age for sample WX-17; (c) age spectrum and plateau age for sample YRS-30; (d) isochron age for sample YRS-30.

Table 4 Mineralizing epoch of some gold, antimony and tungsten deposits in Xuefengshan metallogenic province[a)]

District	Mine	Ore-forming element and host strata	Dating target and method	Age/Ma
Western Hunan	Woxi	Au-Sb-W, Pt$_3$*bnm*	scheelite, Sm-Nd isochron method	402±6
			auriferous quartz, ^{40}Ar-^{39}Ar plateau age (minimum apparent age)	423.2±1.2 (419.8±20.2) 416.2±0.8 (414.4±19.2)
	Xi'an	W, Pt$_3$*bnm*	altered slate, K-Ar method	412.2±6.6
	Liulinchai	Au, Pt$_3$*bnw*	potassium feldspar, K-Ar method	412.46
	Banxi	Sb, Pt$_3$*bnw*	quartz, ^{40}Ar-^{39}Ar plateau age (minimum apparent age)	397.4±0.4 (396.4±30.6) 422.2±0.2 (421.6±31.9)
Southwestern Hunan	Pingcha	Au-Sb, Z$_1$*j*	fluid inclusions of auriferous quartz, Rb-Sr isochron method	435±9
	Xiaojia	Au, Pt$_3$*bnw*	fluid inclusions of auriferous quartz, Rb-Sr isochron method	412±33
			altered wallrocks, Rb-Sr isochron method	418±4
	Mobin	Au, Pt$_3$*bnw*	potassium feldspar, K-Ar method	404.2
	Yangwantuan	Au, Pt$_3$*bnw*	auriferous quartz, ^{40}Ar-^{39}Ar plateau age (minimum apparent age)	381.7±0.4 (381.1±19.2)

a) Data sources: Xi'an data from Wan (1986) [41], Liulinchai and Mobin data from Wang et al. (1999) [42], Xiaojia and Pingcha data from Peng and Dai (1998) [43], other data from this study.

that the Late Caledonian tectonism had important influences on the tectonic evolution and metallogeny in the Xuefengshan district[36—40]. This tectonic movement resulted in the formation of many brittle and/or ductile shear zones in western Hunan and eastern Guizhou, and caused the remobilization and enrichment of ore-forming elements including Au, Sb and W in this area. The Xi'an tungsten deposit and the Liulinchai gold deposit, adjacent to the Woxi mining district, were also proven to form during the Caledonian Period[41,42]. For the famous Banxi antimony deposit, the minimum apparent ages of 2 quartz samples coeval with stibnite are 396.4 ± 30.6 Ma and 421.6 ± 31.9 Ma, and the corresponding plateau ages are 397.4 ± 0.4 Ma and 422.2 ± 0.2 Ma (Table 4), which are in good agreement with our determined data for the Woxi deposit. The Caledonian Au mineralization is widespread in southwestern Hunan (Table 4), all age data for the gold deposits in southwestern Hunan fall in the range of 381—435 Ma, which is also consistent with our results for the Woxi deposit.

It is worthwhile to note, the initial Nd isotope composition of scheelites from the Woxi deposit is abnormally low, the corresponding $\varepsilon_{Nd}(t)$ value is −30.7, and this crustal signature that indicates the fluid responsible for the scheelite mineralization is of crust origin. In comparison with the $\varepsilon_{Nd}(t)$ values of the Proterozoic strata outcropped in Hunan Province, the $\varepsilon_{Nd}(t)$ of scheelites is extremely low. The ε_{Nd} data for the host Banxi Group, Mesoproterozoic Lengjiaxi Group and Lower Proterozoic Cangxiyan Group exposed in Hunan, vary in the range of −7.0—−16.1, −7.7—−10.9 and −9.4—−12.3, respectively (our data unpublished), which reveals that Nd in scheelites cannot be simply derived from the host wallrocks, and there is an additional source of Nd except those of Proterozoic strata; the underlying older basement is probably the likely candidate available. This deduction agrees well with the previous results[44,45]. Recently, Yang and Blum[44] confirmed that the Madiyi Formation in this region was not a sourcebed but a geochemical barrier, the background values for Au, Sb and W in the Formation were only 0.0014, 0.42 and 1.9 μg/g, respectively; the ore-forming materials responsible for the Woxi deposit and the high-content ore-forming elements in the host strata were introduced by hydrothermal fluid. Sr isotope geochemistry indicates[45] that the ore-forming fluid responsible for this deposit is characterized by the radiogenic Sr signature, the $^{87}Sr/^{86}Sr$ ratios for scheelites vary between 0.7468 and 0.7500, markedly higher than the measured values of the host Banxi Group and Lengjiaxi Group (less than 0.729); the fluid probably acquired this radiogenic signature from some felsic lithologies of the underlying older continental basement. To our delight, recently more and more geological, geochemical and geophysical data[46—49] also affirmed that, there really exists Neoarchaean even older strata buried in the Xuefengshan district, and the earliest continental crust in South China probably formed before 3.1 Ga[48,50].

5 Conclusions

The Sm-Nd isochron age of 402 ± 6 Ma is obtained for scheelites from the Woxi Au-Sb-W deposit in western Hunan.

The age spectra of quartz samples from the Woxi deposit display the saddle-shape. The minimum apparent age, plateau age and isochron age for each sample generally overlap within errors. Both the minimum apparent ages (420 ± 20 and 414 ± 19 Ma) agree well with the Sm-Nd age determined on scheelite in this study.

Both Sm-Nd and Ar-Ar ages indicate that the mineralization at the Woxi deposit took place in the Late Caledonian, which coincides well with the Caledonian tectonic evolution and with the known geochronological data in the Xuefengshan district.

The $\varepsilon_{Nd}(t)$ for the disseminated scheelites is extremely low, far less than those of the Proterozoic strata in Hunan. The Nd in the ore-forming fluid responsible for the Woxi deposit is likely to originate from the underlying Archaean continental basement rather than the host Proterozoic strata in this area.

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