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Stable isotope studies of quartz-vein type tungsten deposits in Dajishan Mine, Jiangxi Province, Southeast China

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Abstract—The Dajishan tungsten deposits belong to the wolframite-quartz vein type. These occur as fissure-fillings in the contact zone between the Jurassic Yenshanian granites and Cambrian metasandstones and slates. Quartz, beryl, muscovite, wolframite, scheelite, and sulfides are the major minerals formed in the main stage of mineralization. Late-stage minerals include calcite, dolomite, quartz, fluorite, and scheelite (replacing wolframite). No granitic rocks are exposed at the surface, but drilling has revealed hidden granitic bodies ranging in composition from biotite granite and two-mica granite to muscovite granite and pegmatite. These may represent a differentiation series from a common magma. Exceedingly uniform $\delta^{18}O$ values are found in the minerals from the main-stage veins: quartz = 11.1–12.7 (n = 27), muscovite = 8.4–10.0 (n = 22), wolframite = 4.1–5.3 (n = 15), scheelite = 4.2–5.5 (n = 4), suggesting that isotopic equilibrium apparently has attained and that relatively constant physico-chemical conditions prevailed throughout the main-stage of mineralization. Oxygen isotope fractionations for quartz-wolframite, quartz-scheelite, and quartz-muscovite pairs give concordant isotopic temperatures of 320–390°C, consistent with results from fluid inclusion studies. $\delta^{18}O$ values for the mineralizing solution were calculated to be 6.1 to 9.0; δD values of H_2O as determined from fluid inclusions in quartz and calculated from δD of muscovite range from −51 to −85. Both are typical values for magmatic waters. The $\delta^{18}O$ values for minerals in the late stage are: quartz = 6.4 and 6.9 (n = 2), scheelite = −7.6, calcite = 4.3–12.1 ($\delta^{13}C$ = −7.6 to −11.9, n = 8). Quartz-scheelite oxygen isotope fractionation yields 140°C for the temperature of mineralization. The isotopic compositions of the fluid in the late stage were calculated to be −9.8 for $\delta^{18}O$ and −43 for δD, within the range displayed by local meteoric waters. The granitoid rocks have uniform $\delta^{18}O$ values in quartz (11.1–12.8, n = 13) and muscovite (7.9–9.3, n = 6), but more variable $\delta^{18}O$ values in the feldspars (5.2–10.5, n = 14) and biotite (3.9–6.5, n = 3). The $\delta^{18}O$ values of quartz and muscovite in the granitoids are practically identical to those in the wolframite-quartz veins, suggesting that the hydrothermal fluid from which the ore veins precipitated was derived from the granitoids. The large variation of $\Delta_{q\text{-}f}$ (1.8–5.9) suggests that oxygen isotope exchange has occurred between the feldspars and the meteoric water-dominant hydrothermal fluid in the late stage. The primary $\delta^{18}O$ values of the granitic magmas are estimated to be 10.1–11.8, similar to the values observed in many S-type granitoids in S.E. China.

INTRODUCTION

THE DAJISHAN TUNGSTEN MINE, located in southern Jiangxi Province, belongs to the wolframite-quartz vein type deposits which are the most widespread and economically the most important type of tungsten deposits in southeast China. The wolframite-quartz veins occur as fissure-fillings in the contact zones between the Jurassic Yenshanian granite and the Cambrian metasandstones and slates.

Because of their economic importance and relatively simple geologic occurrences, many wolframite-quartz vein deposits in the world have been subjected to detailed geologic and geochemical studies. These include the Pasto Bueno deposit, Peru (LANDIS and RYE, 1974), Carrock Fells deposit, Cumbria (SHEPHERD *et al.*, 1976), Panasquiera deposit, Portugal (KELLY and RYE, 1979), Tungsten Queen deposit, North Carolina, U.S.A. (CASADEVALL and RYE, 1980), Grey River deposit, Newfoundland, Canada (HIGGINS and KERRICH, 1982), San Cristobal deposit, Peru (CAMPBELL *et al.*, 1984), Dae Hwa and Weolag deposits, Korea (SO *et al.*, 1983; SHELTON *et al.*, 1987), and a number of deposits in southeast China (*e.g.*, XU and HU, 1981; GU, 1981; LIU, 1981; MU *et al.*, 1981; ZHANG *et al.*, 1982; RYE *et al.*, 1986; GIULIANI *et al.*, 1988). These studies have given rise to a generalized genetic model that involves an early stage magmatic fluid followed by influx of meteoric water during the late stage of mineralization.

In this paper, we present the results of detailed oxygen, carbon, and hydrogen isotope studies on the Dajishan tungsten deposits. The concealed granitoid bodies, identified and sampled through drilling, have also been studied. Emphasis is placed on elucidating the origin and evolution of the hydrothermal fluid and the genetic relationships between the ore deposits and the granitoids.

GEOLOGIC SETTING

A simplified geologic map of the Dajishan Mine is shown in Fig. 1. A N–S cross section is shown in Fig. 2. More than 90 wolframite-quartz veins have been discovered in the mining district. They range from a few cm to tens of cm in thickness and extend some 600–800 m in both horizontal and vertical directions. The veins occur in fracture zones that trend approximately NW–SE between two major faults in low-grade metasandstones and slates of Cambrian age. No granitic rocks are exposed in the vicinity of the ore veins, but numerous drill holes in the mine area reveal hidden granitic bodies ranging in composition from biotite granite and two mica granite to muscovite granite and pegmatite. The muscovite granite is genetically related to tungsten mineralization in that it contains disseminated wolframites and is commonly crosscut by quartz veins.

K-Ar age for the biotite granite was determined to be *ca.* 180 Ma and that for the muscovite in the wolframite quartz veins *ca.* 167 Ma (Wu and Mei, 1982).

The mineralization can be subdivided into two stages:

1) main stage—beryl, muscovite, quartz, wolframite, scheelite, molybdenite, chalcopyrite, pyrrhotite, sphalerite, pyrite;

2) late stage—calcite, dolomite, quartz, fluorite, scheelite.

Note that scheelite occurs in the main as well as the late stages. In the latter case, it usually replaces wolframite.

EXPERIMENTAL PROCEDURES

To determine the isotopic variation of vein minerals in the area, samples were systematically collected from the ore veins in the north, central, and south groups (Fig. 1) at levels 467, 517, 567, and 601 (Fig. 2). The sampling of the granitoids is less regular; representative samples were collected from four rock types: biotite granite, two-mica granite, muscovite granite, and pegmatite.

Mineral separations were performed by hand-picking and by standard heavy liquid and Frantz magnetic separator techniques. Quartz was purified from the quartz-calcite and quartz-feldspar mixtures by dissolution of calcite or feldspar with HCl or HF acid, respectively. Isotopic analyses were performed using standard techniques and expressed in the δ-notation in per mil relative to SMOW for O and H and PDB for C. The silicate reference sample NBS-28 was routinely included in the analysis and an average $\delta^{18}O$ value of +9.6 was obtained.

RESULTS AND DISCUSSION

The granitoids

From major and trace element studies (Fonteilles *et al.,* 1987), all the granitoids in the Dajishan mine are comagmatic; they represent a continuous differentiation sequence emplaced at successively higher levels (Fig. 2). The oxygen isotope data are consistent with this view. As can be seen from Table 1 and Fig. 3, the $\delta^{18}O$ values of quartz and muscovite in the granitoids show a very restricted range (quartz = 11.1–12.8; muscovite = 7.9–9.1), regardless of rock types. These values are probably close to the original magmatic values. On the other hand, the $\delta^{18}O$ values of the feldspar and biotite are more variable (feldspar = 5.2–10.5; biotite = 3.9–6.5). They most likely reflect the effects of hydrothermal alteration at moderate temperatures (>300°C). Both from experimental studies and from natural samples, it has been shown that among the common rock-forming minerals quartz is the most resistant and feldspar is the least resistant to oxygen isotope exchange with aqueous fluids. The alteration effects are readily seen in the abnormally large quartz-feldspar oxygen isotope fractionations ($\Delta_{Q\text{-}F}$), which range from 1.8 to 5.9 per mil. At magmatic temperatures, $\Delta_{Q\text{-}F}$ values normally range from 1–2 per mil. The measured whole-rock $\delta^{18}O$-values of the granitoids, which range from 8.6 to 10.9, therefore cannot be used as a petrogenetic indicator of granitic magma genesis in this study. The original $\delta^{18}O$ value of the granitoid, however, can be estimated from the $\delta^{18}O$ value of quartz and from its modal abundance, assuming $\Delta_{Q\text{-}F} = 1.5$. The calculated $\delta^{18}O$ values range from 10.1 to 11.8; these are typical values for most "S" type granitoids in southeast China (Zhang *et al.,* 1982). These granitoids also possess many geochemical features such as peraluminous character and high alkali element concentrations (see Table 2), suggesting their derivation from pelitic metasedimentary rocks.

Country rocks and mafic dikes

The main rock types into which the ore veins were emplaced include the Cambrian metasand-

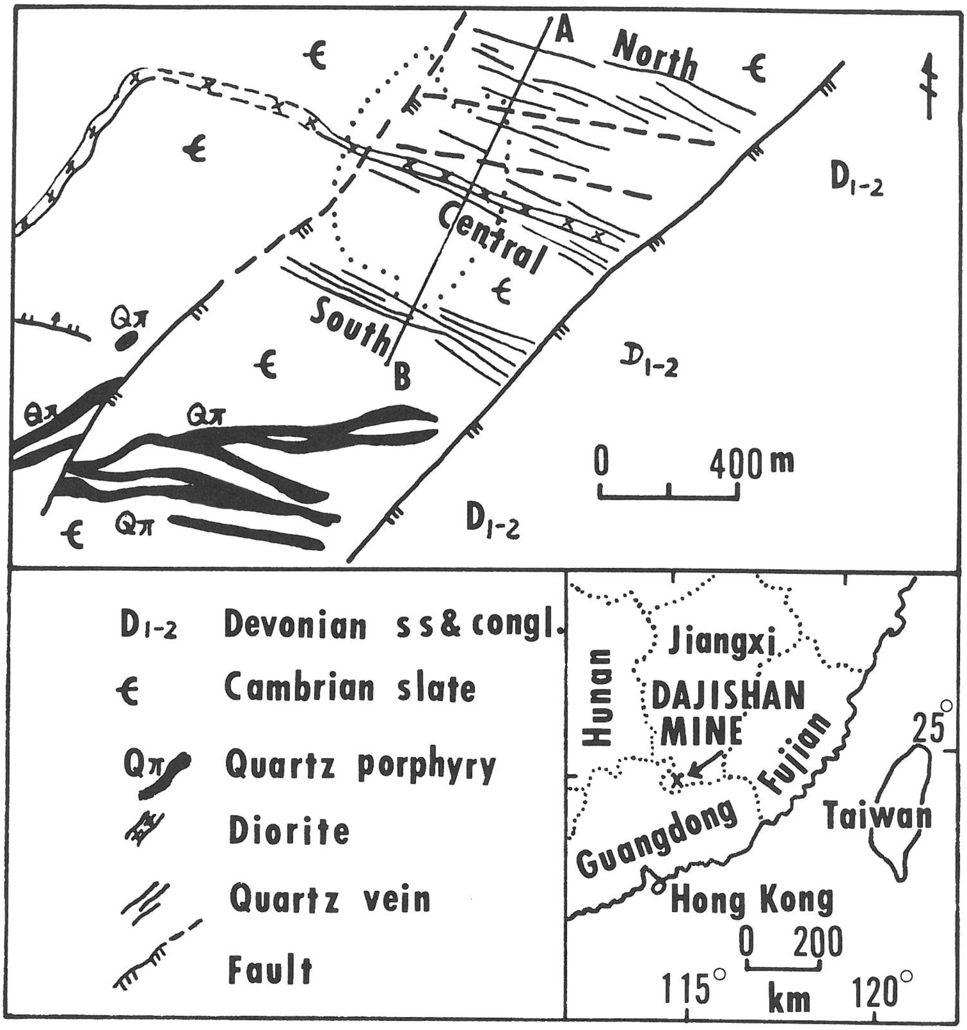

FIG. 1. Simplified geologic map of the Dajishan mining district, Jiangxi province, southeast China. Dotted line indicates concealed granitic intrusions. Cross-section along AB is shown in Fig. 2.

stones and silty slate. In addition, many dikes (diorite and quartz porphyry) can also be seen to crosscut the country rocks and the granitoids. Table 2 lists some representative chemical and isotopic analyses. The country rocks have SiO_2-contents (wt.%) that range from 65.5% for slate to 81.2% for metasandstone and to 85.0% for silicified sandstone. A corresponding increase of $\delta^{18}O$ is observed, from 8.1 to 10.8 to 11.3, respectively, for the above rock types.

Southeast China is an area of W geochemical anomaly. The average W contents in the strata are: Pre-Sinian 14.0 ppm, Sinian 6.7 ppm, Cambrian 6.1 ppm, Devonian 3.5 ppm, Carboniferous 6.0 ppm (YEN, 1981). These are potential source rocks for the granitoids and the oxygen isotope data are in support of this view.

Tungsten-bearing quartz veins (main-stage mineralization)

Quartz, muscovite, wolframite, and scheelite are the predominant gangue and ore minerals that occur in the main stage of mineralization. As can be seen in Table 3, each mineral shows exceedingly uniform $\delta^{18}O$: quartz = 11.1–12.7 (n = 27); muscovite = 8.4–10.0 (n = 22); wolframite = 4.1–5.3 (n = 15); scheelite = 4.2–5.5 (n = 4). To determine if there is any isotopic compositional variation within a single quartz vein, we have plotted the $\delta^{18}O$

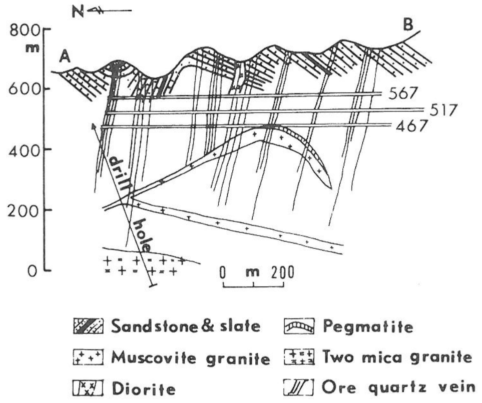

FIG. 2. Geologic cross-section of the Dajishan mining district, showing spatial relationship between the wolframite-quartz veins and the granitic intrusions. Also shown are three horizontal adits at levels 567, 517, and 467 m (above sea-level).

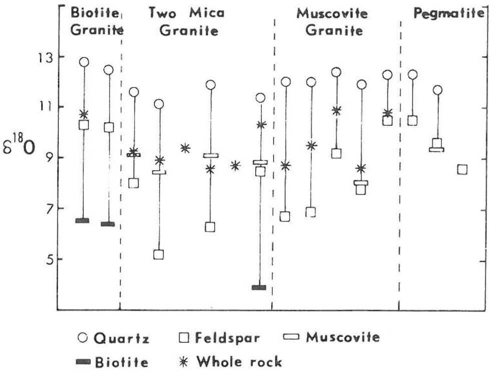

FIG. 3. Plot of $^{18}O/^{16}O$ ratios of whole rock and coexisting minerals in the granitic rocks. The feldspars are a mixture of microcline and Na-plagioclase separated by hand-picking.

of the minerals in four quartz veins as a function of depth (Fig. 4). No significant isotopic variation was detected. The isotopic uniformity is observed in all 12 quartz veins we analyzed as shown in the histograms (Fig. 5). This implies that there is little change in either the temperature or the oxygen isotope composition of the hydrothermal fluid during the main stage of formation of the tungsten-bearing quartz veins.

To determine if there is any regional variation, we have also arranged the $\delta^{18}O$ of the minerals into north, central, and south groups (Fig. 6). There is a slight increase of $\delta^{18}O$ from north to south, *e.g.*, quartz from 11.7 to 12.2 and muscovite from 8.8 to 9.3. The $\delta^{18}O$ values of quartz and muscovite of the granitoids are also shown for comparison. The $\delta^{18}O$ values of the minerals in the ore veins and the granitoids are the same, suggesting that the hydrothermal fluids that precipitated the quartz veins were either derived from or were in isotopic equilibrium with the granitoids. This inference is sup-

Table 1. Oxygen isotope compositions of whole rock and mineral phases in granitic rocks from Dajishan Mine

			$\delta^{18}O$					$\Delta^{18}O$		
Rock type	Sample No.	Locality	WR	Q	F	B	M	Q-F	Q-B	Q-M
Biotite granite	D-23-1	North outcrop	10.7	12.8	10.3	6.5		2.5	6.3	
	D-23-2	North outcrop		12.5	9.9	6.4		2.6	6.1	
Two-mica granite	84-D-82	CK307, 350 m	10.3	11.4	8.5	3.9	8.8	2.9	7.5	2.6
	84-D-85	CK307, 360 m	8.7							
	84-D-73	CK307, 472 m	8.6	11.9	6.3		9.1	5.6		2.8
	84-D-74	CK307, 474 m	9.4							
	84-D-75	CK307, 475 m	8.9	11.1	5.2		8.4	5.9		2.7
	84-D-76	CK307, 478 m	9.2	11.6	8.0		9.1	3.6		2.5
Muscovite granite	D-12-1	C, L517, No. 6	10.7	12.3	10.5			2.2		
	D-31	C, Body 69, 11W	8.6	11.9	7.8		7.9	4.1		4.0
	D-32-1	C, L467, W6H	8.7	12.0	6.7			5.3		
	D-32-2	C, L467, W6H	9.5	12.0	6.9			5.1		
	D-32-6	C, L467, W6H	10.9	12.4	9.2			3.2		
Pegmatite	D-12	C, L517, No. 6		12.3	10.5			1.8		
	D-10-1	C, L517, No. 6		11.7	9.6		9.3	2.1		2.4
	D-48	C, L467			8.6					

WR = Whole rock, Q = Quartz, F = Feldspar, B = Biotite, M = Muscovite.

Locality codes: CK307 = Shaft No., 350 m = 350 m below surface, C = Central group, L = Level, No. 6 = Vein No. 6.

Table 2. Representative chemical and oxygen isotope compositions of igneous intrusions and country rocks

	D-23 Biotite granite	84-D-82 Two-mica granite	D-31-1 Muscovite granite	D-5-1 Diorite dike	D-9-2 Diorite porphyry	D-34-2 Siliceous sandstone	D-26-1 Meta-sandstone	D-19-1 Slate
SiO_2	66.30	76.81	74.10	47.53	44.72	85.03	81.21	65.55
TiO_2	0.60	0.02	0.04	2.72	1.38	0.30	0.31	0.76
Al_2O_3	14.05	12.14	14.74	13.42	11.17	6.42	8.11	15.53
Fe_2O_3	1.13	0.33	0.32	2.68	3.62	0.69	0.57	0.95
FeO	2.61	0.75	0.32	10.83	5.33	2.28	3.04	5.61
MnO	0.05	0.19	0.06	0.15	0.10	0.03	0.06	0.05
MgO	1.85	0.11	0.13	5.77	9.60	0.90	1.59	0.37
CaO	3.45	0.36	0.34	10.50	11.86	0.80	0.25	2.71
Na_2O	2.77	3.64	4.88	2.92	1.40	1.07	0.53	0.51
K_2O	4.43	4.17	3.60	1.04	2.51	2.00	2.28	4.44
H_2O^+	0.59	1.03	0.64	0.94	3.46	0.43	1.42	2.39
H_2O^-	0.13	0.16	0.42	0.23	1.22	0.09	0.13	0.41
P_2O_5	0.25	n.d.	n.d.	0.19	1.01	0.08	0.15	0.14
CO_2	—	—	—	—	3.46	—	—	—
S	0.06	—	—	0.18	—	—	—	0.06
Total	98.27	99.70	99.59	99.10	100.84	100.12	99.65	99.48
$\delta^{18}O$	10.7	10.3	8.6	6.9	6.8	11.3	10.8	8.1

Chemical analyses by D. H. Chen and T. S. Ye, Institute of Geochemistry, Academia Sinica, Guiyang.

Table 3. Oxygen isotope compositions of mineral phases in the main-stage ore veins and the calculated isotopic temperatures

Sample No.	Locality	$\delta^{18}O$				Q-M		Q-Wf		Q-Sch	
		Q	M	Wf	Sch	Δ	T °C	Δ	T °C	Δ	T °C
84-D-34	C, L517, No. 6			4.0							
84-D-35	C, L517, No. 6			4.8							
84-D-23	C, L467, No. 12			4.4							
D-38	S, L567, No. 20	11.4	8.4	4.5		3.0	358	6.9	382		
D-40	S, L567, No. 13	11.7	9.0			2.7	400				
D-7-2	S, L517, No. 20	12.0	8.9	4.7		3.1	346	7.3	367		
D-8-1	S, L517, No. 19	11.3		4.2				7.1	373		
D-9-4	S, L517, No. 13	12.5	9.2			3.3	324				
D-24	S, L467, No. 20	11.1	8.7			2.4	451				
D-25-1	S, L467, No. 20	11.4	8.5			2.9	371				
D-29-1	S, L467, No. 13	12.2	8.6			3.6	294				
D-30	S, L467, No. 13	11.9									
D-1	C, L601, No. 7	11.1	8.8			2.3	470				
D-2-1	C, L601, No. 7	12.3	9.1	5.3	4.8	3.2	334	7.0	378	7.5	356
D-4-2	C, L601, No. 10	12.0	9.1	5.2		2.9	371	6.8	386		
D-6	C, L601, No. 11	11.2	8.8	4.5		2.4	451	6.7	391		
D-41	C, L567, No. 11	11.9	8.9	4.4		3.0	358	7.5	336		
D-44-1	C, L567, No. 6	12.4	9.3	4.1		3.1	346	8.3	317		
D-13-2	C, L517, No. 6	11.3	9.0	4.2		2.3	470	7.1	373		
D-14	C, L517, No. 8	11.4									
D-20	C, L517, No. 1	12.2			4.2					8.0	327
D-35	C, L467, No. 6	11.8	9.8	4.2		2.0	541	7.6	351		
D-3-1	N, L601, No. 27	12.4	8.7			3.7	285				
D-45-1	N, L567, No. 23	12.3	9.3	4.6		3.0	358	7.7	346		
D-46-1	N, L567, No. 23	12.1			4.8					7.3	369
D-47	N, L567, No. 23	12.6	10.0		5.5	2.6	415			7.1	383
D-16-1	N, L517, No. 23	12.7									
D-18-2	N, L517, No. 23	11.3	9.3	4.5		2.0	541	6.8	386		
D-36	N, L467, No. 23	12.0	9.6			2.4	451				
D-37	N, L467, No. 23	12.1	9.1			3.0	358				

Q = Quartz, M = Muscovite, Wf = Wolframite, Sch = Scheelite.
Locality codes: N = North, C = Central, S = South, L = Level, No. = Vein number.

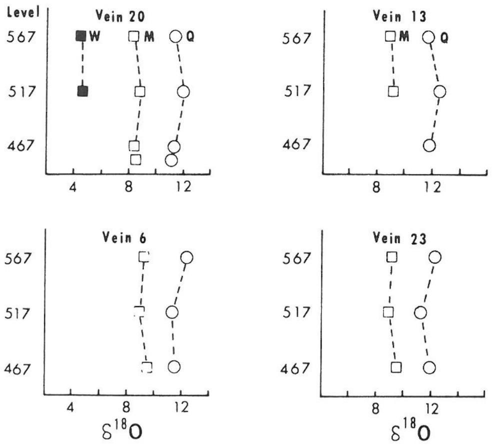

FIG. 4. Variation of $\delta^{18}O$ values in quartz (Q), muscovite (M), and wolframite (W) in individual ore veins as a function of depth at levels 567, 517, and 467.

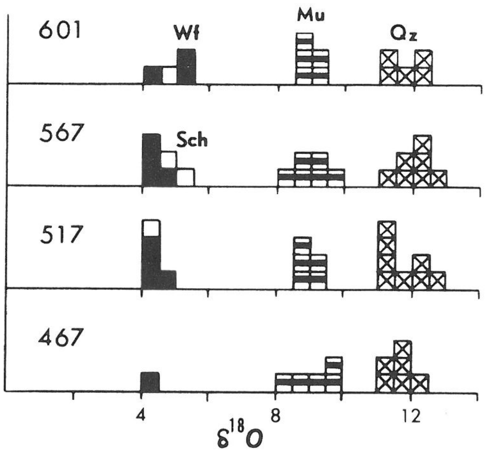

FIG. 5. Histogram showing the frequency distribution of $\delta^{18}O$ values in quartz (Qz), muscovite (Mu), wolframite (Wf), and scheelite (Sch) at levels 601, 567, 517, and 467.

ported by the uniform oxygen isotope fractionations among the co-existing minerals, as discussed below.

Oxygen isotope geothermometry

Table 3 lists the oxygen isotope fractionations among quartz, muscovite, wolframite, and scheelite from the main stage of mineralization. The rather constant isotopic fractionations for quartz-muscovite ($\Delta = 2.0$–3.7) and quartz-wolframite ($\Delta = 6.7$–8.3) over the entire mining district suggest that isotopic equilibrium was probably attained. Quartz-H_2O and muscovite-H_2O oxygen isotope fractionation curves have been calibrated as a function of temperature in the laboratory (CLAYTON *et al.*, 1972; MATSUHISA *et al.*, 1979; O'NEIL and TAYLOR, 1969). However, because of the small isotopic fractionation between quartz and muscovite, uncertainty in temperatures resulting from experimental errors will be large. On the other hand, oxygen isotope fractionations in quartz-wolframite and quartz-scheelite pairs are large and would offer much more sensitive geothermometers. Recently, L. G. ZHANG (1990, pers. comm.) experimentally determined the following wolframite-H_2O equilibrium isotopic fractionation curves:

$$250\text{–}370°\mathrm{C} \quad 1000 \ln \alpha_{\mathrm{wf\text{-}H_2O}} = 1.03 \times 10^6 T^{-2} - 4.96 \quad (1)$$

$$370\text{–}420°\mathrm{C} \quad 1000 \ln \alpha_{\mathrm{wf\text{-}H_2O}} = 0.21 \times 10^6 T^{-2} - 2.91 \quad (2)$$

When combined with the quartz-water fractionation equation of CLAYTON *et al.* (1972), the following equations are obtained:

$$250\text{–}370°\mathrm{C} \quad 1000 \ln \alpha_{\mathrm{q\text{-}wf}} = 2.35 \times 10^6 T^{-2} + 1.56 \quad (3)$$

$$370\text{–}420°\mathrm{C} \quad 1000 \ln \alpha_{\mathrm{q\text{-}wf}} = 3.17 \times 10^6 T^{-2} - 0.49. \quad (4)$$

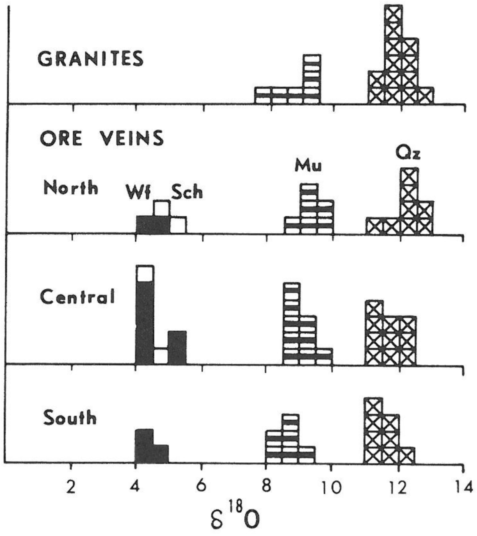

FIG. 6. Histogram showing the regional variation (north, central, south) of $\delta^{18}O$ values of quartz (Qz), muscovite (Mu), wolframite (Wf), and scheelite (Sch) in the ore veins as compared with those in the granitoids.

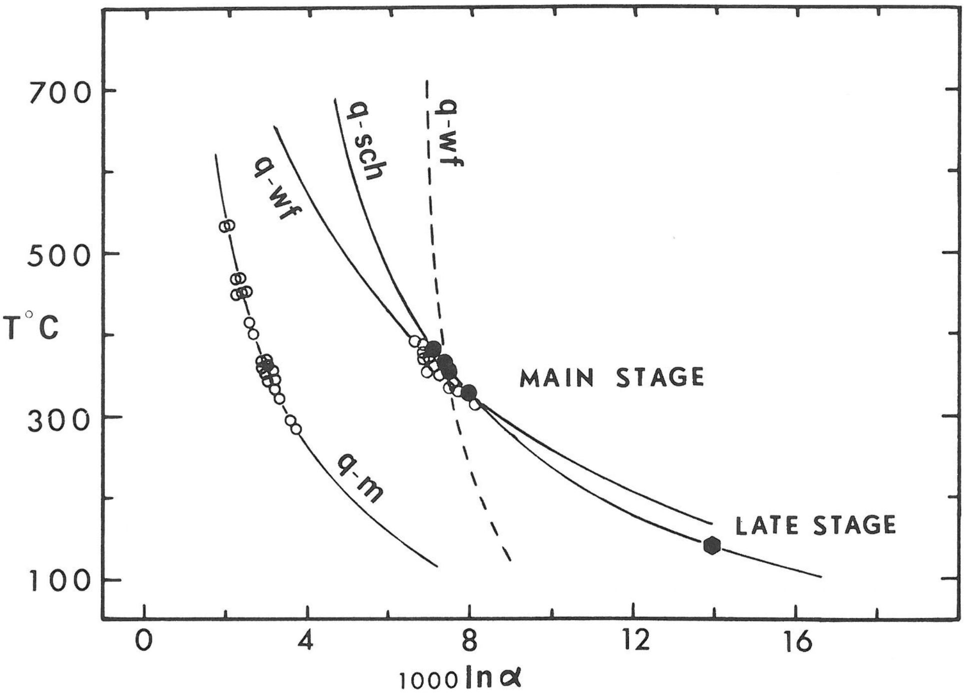

FIG. 7. Oxygen isotopic temperatures obtained from quartz-muscovite, quartz-wolframite, and quartz-scheelite fractionation curves for samples from the main- and late-stage ore veins. Fractionation equations used: quartz-H_2O (CLAYTON *et al.*, 1972); muscovite-H_2O (O'NEIL and TAYLOR, 1969); wolframite-H_2O (L. G. ZHANG, 1990, pers. comm.); scheelite-H_2O (WESOLOWSKI and OHMOTO, 1986). The dashed quartz-wolframite curve is from LANDIS and RYE (1974).

The quartz-wolframite oxygen isotope fractionations of 6.7 to 8.3 observed in Dajishan would yield temperatures of 391–317°C according to Eqns. (3) and (4). When the empirical wolframite-H_2O fractionation curve of LANDIS and RYE (1974) is used, unrealistic high temperatures (>1000°C) are obtained. WESOLOWSKI and OHMOTO (1986), using an analogy based on that between $CaSO_4$ and $CaWO_4$, derived the following scheelite-H_2O fractionation equation:

$$1000 \ln \alpha_{\text{sch-H}_2\text{O}} = 1.39 \times 10^6 T^{-2} - 5.87. \quad (5)$$

When this is combined with the quartz-H_2O fractionation equation of CLAYTON *et al.* (1972), the following quartz-scheelite fractionation equation is obtained:

$$1000 \ln \alpha_{\text{q-sch}} = 1.99 \times 10^6 T^{-2} + 2.47. \quad (6)$$

In Dajishan, $\Delta_{\text{q-sch}} = 7.1\text{–}8.0$ would yield $T = 383\text{–}327$°C, similar to the quartz-wolframite temperatures obtained from Eqns. (3) and (4).

The quartz-muscovite oxygen isotope fractionations correspond to temperatures of 541–285°C. However, the majority of samples fall between 400 and 300°C, consistent with temperatures obtained from quartz-wolframite and quartz-scheelite pairs (see Fig. 7).

LU *et al.* (1974) measured the fluid inclusion homogenization temperatures in quartz which range from 287–260°C, slightly lower than the oxygen isotope temperatures discussed above.

Scheelite in the late (carbonate) stage mineralization

Characteristic of many quartz-vein type tungsten deposits (as cited in the Introduction) is the occurrence of carbonate minerals in the late stage of mineralization. In the Dajishan deposit, large euhedral crystals of wolframite occur in the carbonate veins. Under the microscope, aggregates of scheelite replacing wolframite, mostly along grain boundaries and cleavage planes, can usually be seen. Did the wolframite and scheelite form in the main stage or in the late stage? Oxygen isotope determination of the minerals has given a definite answer to this question (ZHANG and SHIEH, 1989). Because of the intimate intergrowth of scheelite and wolframite, it

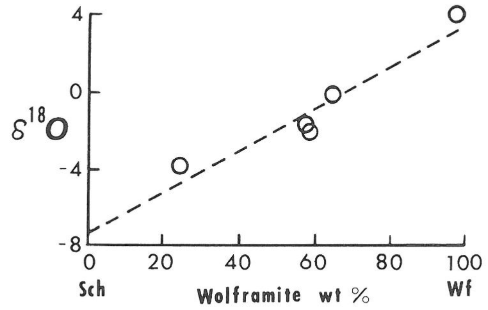

FIG. 8. Plot of $\delta^{18}O$ values of wolframite-scheelite intergrowth samples in the carbonate veins as a function of wt. % of wolframite. Extrapolation to 0% wolframite gives the $\delta^{18}O$ value for the late-stage scheelite, which equals −7.6

is not feasible to physically separate the two minerals for oxygen isotope analyses. We have obtained the $\delta^{18}O$ values of the pure end-members by analyzing the $\delta^{18}O$ of several scheelite-wolframite mixtures of various proportions and by extrapolating to 0 and 100% wolframite, as shown in Fig. 8. The extrapolation gives $\delta^{18}O_{wf} = +3.6$ and $\delta^{18}O_{sch} = -7.6$. The isotopic data clearly suggest that the wolframite was formed in the main stage and the scheelite was formed in the late stage by replacement of the wolframite:

$$\underset{\text{wolframite}}{FeWO_4} + Ca^{2+} \rightarrow \underset{\text{scheelite}}{CaWO_4} + Fe^{2+}.$$

This reaction would be favored under the alkaline conditions suggested by the presence of calcite in the late stage. In addition, some fine-grained quartz crystals are associated with the calcite and scheelite in the carbonate veins. The $\delta^{18}O$ values of quartz range from 6.4 to 6.9, distinctly different from those occurring in the main stage. The quartz-scheelite oxygen isotope geothermometer (Eqn. 6) gives temperatures of equilibration at 134–142°C, comparable to the calcite fluid inclusion homogenization temperature of 129°C as determined by LU *et al.* (1974).

Oxygen and carbon isotope compositions of carbonates

Calcite occurs as fine-granular aggregates and as fine-laminations in the carbonate veins. Oxygen and carbon isotope compositions in the calcite are shown in Table 4. The variations of $\delta^{18}O$ (4.3 to 12.1) and $\delta^{13}C$ (−7.6 to −11.9) are large, particularly for oxygen, reflecting large changes in temperature and in isotopic composition of the hydrothermal fluid during precipitation of the calcite. Within a distance of 1 cm, the laminated calcite can vary in $\delta^{18}O$ from 4.3 to 5.3 and in $\delta^{13}C$ from −11.4 to −10.7. The $\delta^{13}C$ values of the carbonates in Dajishan are distinctly different from those occurring in the nearby Xihuashan mine, which range from +4.4 to −9.0 (MU *et al.,* 1981). The carbon isotope compositions in the carbonates are probably controlled by the dissolved carbonate and bicarbonate ions in groundwaters.

Evolution of the hydrothermal fluids

The $\delta^{18}O$ and δD values of the hydrothermal fluid that would have been in equilibration with the granites and the wolframite-quartz veins are shown in Table 5. The $\delta^{18}O$ values of H_2O were calculated

Table 4. Oxygen and carbon isotope compositions of minerals in the late-stage carbonate veins

Sample No.	Locality	Mineral	$\delta^{18}O$	$\delta^{13}C$
D-16-1A	N, L517, No. 23	Calcite	4.3	−11.4
D-16-1B	Same	Calcite	5.4	−10.7
D-29-1	S, L467, No. 20	Calcite	8.1	−11.9
		Quartz	6.9	
		Wolframite[a]	3.1	
D-39-1	S, L567, No. 13	Calcite	5.5	−7.6
		Quartz	6.4	
		Wolframite[a]	4.1	
		Scheelite	−7.6[b]	
II-4	S, L567, No. 13	Calcite	4.9	−8.1
II-6	S, L467, No. 13	Calcite	7.2	−9.9
II-7-1	S, L467, No. 12	Calcite	8.2	−10.4
II-7-2	Same	Calcite	12.1	−9.5

[a] Formed in the main stage.
[b] Estimated from Fig. 8.

Table 5. Oxygen and hydrogen isotope compositions of waters coexisting with the granites and wolframite-quartz veins

Sample No.	Mineral	T °C[a]	δD[b]	$\delta^{18}O$	δD_{H_2O} Calculated	δD_{H_2O} Measured[b]	$\delta^{18}O_{H_2O}$ (calculated)
Granites							
D-31	Feldspar	526		7.8		−70	6.7
	Quartz	526		11.9		−70	9.9
	Muscovite	526	−82	7.9	−66		8.1
D-32-4	Microcline	503		9.2		−70	7.8
Ore veins							
D-36-1	Quartz	451		12.0		−59	9.0
D-9-4	Quartz	324		12.5		−59	6.4
D-1-2	Quartz	470		11.1		−22	8.4
D-2-1	Muscovite	378	−70	9.1	−57		7.4
D-6	Quartz	391		11.2		−70	6.9
D-40-2	Muscovite	400	−81	9.0	−68		7.6
D-41-2	Muscovite	336	−80	8.9	−67		6.4
D-44-2	Quartz	317		12.4		−51	6.1
D-35-1	Quartz	351		11.8		−60	6.5
	Muscovite	351	−98	9.8	−85		7.6

[a] Temperatures in the granites are the fluid inclusion homogenization temperatures (from LU *et al.*, 1974). Temperatures in the wolframite-quartz veins are oxygen isotope temperatures (from Table 3).

[b] Hydrogen isotope analyses by Fuji Yu, Institute of Geochemistry, Academia Sinica, Guiyang.

from the $\delta^{18}O$ of minerals and fluid inclusion homogenization temperatures (for granites) or oxygen isotope temperatures (for ore veins). The δD values of H_2O were obtained from analysis of fluid inclusions in quartz or feldspar and by calculation from δD in muscovite.

Thus, the $\delta^{18}O$ values of the hydrothermal fluid in the main ore-forming stage range from 6.1 to 9.0 and δD from −51 to −85 (except for sample D-1-2 which shows abnormally high δD = −22). The late-stage hydrothermal fluid has $\delta^{18}O$ = −9.8 to −10.1 (calculated from quartz-scheelite oxygen isotope fractionation) and δD = −43 (from analysis of fluid inclusions in calcite), distinctly different from those in the early stage.

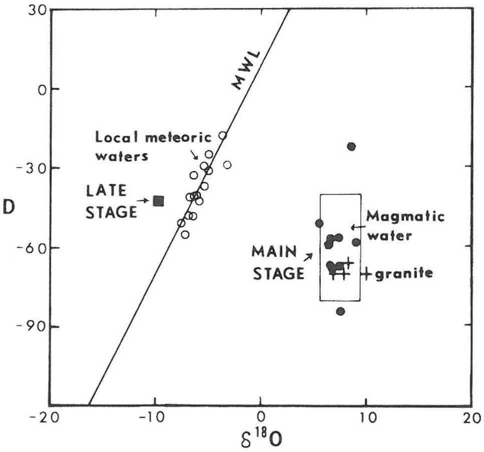

FIG. 9. Plot of $\delta^{18}O$ and δD values of aqueous fluids associated with the granitoids (crosses) and the ore-veins in the main-stage (dots) and late-stage (large square). Also shown are isotopic compositions of local meteoric waters (open circles) and the world meteoric water line (MWL).

The evolution of the hydrothermal fluid during the formation of tungsten deposit in Dajishan is illustrated in Fig. 9. In the main stage, the hydrothermal fluids have isotopic compositions that fall within or very close to the "magmatic-water box." The hydrothermal fluids, regardless of their ultimate origins, have been isotopically equilibrated with the granitic magmas at very low water/rock ratio, *i.e.*, the isotopic compositions of the fluids were buffered by the granites. In the late stage, the system was subjected to a sudden influx of large amount of meteoric water so that the isotopic compositions lie very close to the cluster displayed by the local meteoric waters (Fig. 9).

CONCLUSIONS

1. The Dajishan tungsten deposits possess several geologic and geochemical characteristics that are similar to most wolframite-quartz vein type deposits around the world. The ore deposits appear to be genetically related to the underlying granitoids.

2. The granitoid rocks, consisting of biotite granite, two-mica granite, muscovite granite, and

pegmatite, possess many petrological and geochemical features of "S" type granitoids. The Dajishan granitoids are most likely the product of anatexis of Precambrian and Paleozoic sedimentary rocks that are widespread in the region; most of these show W geochemical anomalies ranging from 4 to 14 ppm.

3. The $\delta^{18}O$ value of quartz in the granitoids is exceedingly uniform (11.1–12.8); this probably represents the primary magmatic oxygen isotopic value. In contrast, the feldspars show more variable $\delta^{18}O$ values (5.2–10.5), reflecting the effects of hydrothermal alteration at subsolidus temperatures (300–400°C).

4. The oxygen isotope compositions of quartz, muscovite, wolframite, and scheelite formed in the main stage of mineralization show very restricted range; these minerals most likely formed in isotopic equilibrium with a hydrothermal fluid that had a relatively constant isotopic composition and temperature. The oxygen isotope temperatures for quartz-wolframite and quartz-scheelite pairs are concordant at 320–390°C, and the coexisting aqueous fluids have calculated $\delta^{18}O$ of 6.1 to 9.1 and calculated δD of -51 to -85, clearly within the range shown by the magmatic waters in isotopic equilibrium with the granitoids.

5. The minerals formed in the late stage of mineralization, including calcite, quartz, and scheelite, all have lower $\delta^{18}O$ values, reflecting the influx of large amounts of meteoric waters into the hydrothermal system.

6. Scheelite can form in the late as well as in the main stage of mineralization. In the late stage, small crystals of scheelite are commonly found replacing wolframite along grain boundaries and cleavage planes. The late-stage scheelite has a very low $\delta^{18}O$ value (-7.6) and formed at low temperature (140°C) from a meteoric water-dominant hydrothermal fluid ($\delta^{18}O \approx -10$). In contrast, all of the wolframite crystals, including those found in association with calcite, were formed in the main stage.

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