Na/K ratios and fluorine contents of micas from the skarn-type tungsten deposits of the Fujigatani, Kiwada, and Kuga mines, Southwest Japan

Yasuhiro SHIBUE

Geological Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, Japan

Abstract

Chemical compositions of micas from the Fujigatani, Kiwada, and Kuga tungsten mines, Yamaguchi Prefecture, Southwest Japan are obtained, and are compared with those from the vein-type tungsten deposits of the Kaneuchi, Ohtani, and Takatori mines.

Activity ratios of NaCl/KCl in hydrothermal solutions for the formation of the Fujigatani, Kiwada, and Kuga deposits are estimated from Na/K atomic ratios of muscovites. The ratios range from 5.5 to 2.9 at 400°C during the formation of muscovites. Na/K atomic ratios in muscovites from the Fujigatani, Kiwada, and Kuga mines are similar to those in muscovites from the Kaneuchi, Ohtani, and Takatori mines. Fluorine contents of muscovites from the studied tungsten mines are above 0.1 wt%, and those of biotites from the Kuga mine are above 3 wt%. These values are comparable to those in muscovites from the vein-type tungsten deposits of the Kaneuchi and Ohtani mines. Fluorine contents of micas from the three mines are higher than those from several porphyry copper deposits. High fluorine contents of micas are characteristic features of skarn-type tungsten deposits as well as vein-type tungsten deposits.

Introduction

The Fujigatani, Kiwada, and Kuga mines are located in the Kuga district, Yamaguchi Prefecture about 50 km southwest of the Hiroshima City, Southwest Japan (Fig. 1).

Geology of this area has been discussed by various workers (*e.g.*, Higashimoto, 1977; Higashimoto *et al.*, 1983). The tungsten deposits in this district occur in the Kuga Group of Triassic to Jurassic age (Higashimoto *et al.*, 1983). The Kuga Group consists mainly of slates, pebbly mudstones (clasts of chert and sandstone in a shale matrix), and decametric to hectometric intercalations of bedded chert, and limestone. The sediments of the Kuga Group were intruded by granitic rocks. Shibata and Ishihara (1974) showed an age of 94.6 ± 2.8 Ma for muscovite in the granitic rock near the Fujigatani mine. K–Ar ages for muscovites from the Fujigatani and Kiwada mines are 92.1 ± 3.7 and 95.8 ± 2.9 Ma, respectively (Shibata and Ishihara, 1974). Therefore, formation of the tungsten deposits are closely associated with the granitic activity. Previous works have been mainly focussed on the skarnization of these mines, espe-

FIG. 1. Locality map of the Fujigatani, Kiwada and Kuga mines.

cially on the zonation of skarn minerals (*e.g.*, Ito, 1962; Sato, 1980; Matsueda and Arai, 1982; Hoshino *et al.*, 1982; Nagahara, 1978; Hiiragi *et al.*, 1984).

In these mines, scheelite occurs both in skarns and in quartz veins which are found in skarn bodies (Sato, 1980; Nagahara, 1978; Higashimoto, 1977). In the Fujigatani mine, ore grade is sometimes higher than 0.3 wt% in quartz veins, whereas that in skarns is generally lower than 0.2 wt% (Kuwahara and Nakamura, 1975). Nagahara (1978) also discussed that mineralization of scheelite in skarn ore bodies of the Kiwada mine is related to the formation of quartz veins. Higashimoto (1977) discussed that ore grade of the Kuga mine is dependent on the abundance of quartz veins. Generally speaking, tungsten ore becomes richer where more quartz veins are found in the skarns. It is important to know the chemistry of hydrothermal solutions during the formation of quartz veins in order to understand the mineralization of scheelite. Major vein minerals are quartz, muscovite, chlorite, fluorite, and calcite. Chalcopyrite, pyrrhotite, and sphalerite are also found in quartz veins. Skarn minerals were altered to hydrous minerals, such as muscovite, during the formation of quartz veins. Chemical compositions of vein minerals have been documented only for the Fujigatani mine (Sato, 1980). Data for the chemical compositions of vein minerals from the Kiwada and Kuga mines have not been published.

Main purposes of this paper are to evaluate the chemistry of hydrothermal solutions for the formation of quartz veins from the chemical compositions of micas, and to compare chemical compositions of micas from the Fujigatani, Kiwada, and Kuga mines with muscovites from the vein-type tungsten deposits of the Kaneuchi, Ohtani, and Takatori mines.

Analytical methods for minerals

Major elements

Major element chemical compositions of micas were determined with electron probe microanalyzers (EPMA) Model JXA-5A and JXA-733A at an accelerating voltage of 15 kV and a sample current of 20 nA.

Fluorine

Fluorine contents in muscovite were determined with use of a Horiba fluoride ion electrode by the method of Kanisawa (1978). To eliminate the interference of aluminum with fluorine, 1 M sodium citrate – 0.2 M potassium nitrate solution was used (Ingram, 1970) in this study. Muscovite grains were separated by hand-picking and then powdered. Using the ultraviolet lamp, fluorite and apatite were carefully removed. The analyzed muscovites were from the Fujigatani, Kaneuchi, Ohtani, and Takatori mines. These muscovites were used for the standards of EPMA analyses of fluorine in micas from the Kiwada and Kuga mines. Measuring conditions are as follows: accelerating voltage, 10 kV; sample current, 20 nA; beam width, 10 μm ; counting time, 30 sec.; and detector crystal, TAP.

H₂O

Water contents in micas were calculated to satisfy the condition: $\text{F} + \text{OH} = 4$ based on 44 anionic charges.

Ferric/ferrous ratio

Some muscovite grains were analyzed for Fe^{2+} by wet analyses. The difference between Fe contents obtained by EPMA and those by wet analyses were assumed to be due to the trivalent iron.

Chemistry of hydrothermal solutions

Shibue (1985) measured homogenization temperatures and salinities of fluid inclusions in scheelite both in quartz veins and skarns of the Fujigatani, Kiwada and Kuga mines. Temperature ranges of hydrothermal solutions for the mineralization of scheelite are from 320° to 400°C for the Fujigatani mine, and from 350° to 450°C for the Kiwada and Kuga mines.

TABLE 1a. Representative analyses of muscovite from the Fujigatani and Kiwada mines.

	1	2	3	4
SiO ₂	46.56	48.16	46.58	47.56
Al ₂ O ₃	35.57	30.26	30.01	31.51
TiO ₂	0.05	0.34	0.12	0.02
FeO*	1.83	2.41	3.58	2.04
MnO	0.00	0.04	0.11	0.10
MgO	0.77	2.96	2.79	2.20
CaO	0.09	0.04	0.91	0.03
Na ₂ O	0.28	0.20	0.21	0.22
K ₂ O	10.86	10.63	10.95	10.77
H ₂ O**	4.43	4.36	4.28	4.38
F	0.38	0.22	0.2	0.14
O=F	0.16	0.09	0.09	0.06
Total	100.58	99.51	98.77	98.90
Numbers of cations based on O ₂₀ (OH, F) ₄				
Si	6.17	6.47	6.37	6.42
Al	5.55	4.79	4.84	5.01
Ti	0.01	0.03	0.01	0.00
Fe	0.20	0.27	0.41	0.23
Mn	0.00	0.00	0.01	0.01
Mg	0.15	0.59	0.57	0.44
Ca	0.01	0.01	0.00	0.00
Na	0.07	0.05	0.06	0.06
K	1.84	1.82	1.91	1.85
Numbers of OH and F based on OH + F = 4				
OH	3.81	3.91	3.91	3.94
F	0.19	0.09	0.09	0.06

1: Muscovite in a quartz vein of the -40 m level of the Akemidani No. 1 ore deposit of the Fujigatani mine. 2: Muscovite in clinopyroxene skarn of the -20 m level of the Akemidani No. 5 ore deposit of the Fujigatani mine. 3, 4: Muscovite in a quartz vein of No. 11 ore body of the Kiwada mine. *: Total iron as FeO. **: Calculated from fluorine contents.

The close association of muscovite and biotite with scheelite suggests that they were formed at the same stage with scheelite in quartz veins. Chemistry of micas reflects the chemical compositions of hydrothermal solutions for the formation of scheelite. Chemical compositions of muscovites and biotites from the Fujigatani, Kiwada, and Kuga mines are listed in Table 1. Na/K atomic ratios and fluorine contents of micas are used for the evaluation of the chemistry of hydrothermal solutions.

NaCl/KCl activity ratios in hydrothermal solutions

Na and K are major cations in most of hydrothermal solutions. Takenouchi and

TABLE 1b. Representative analyses of muscovite and biotite from the Kuga mine.

	1	2	3	4	5	6	7
SiO ₂	47.01	43.82	48.69	47.69	44.46	47.88	47.02
Al ₂ O ₃	32.30	10.83	28.20	32.52	9.12	33.30	28.73
TiO ₂	1.05	0.09	2.83	0.07	0.14	0.13	0.38
FeO*	1.53	9.41	2.83	1.51	9.46	1.35	3.11
MnO	0.08	0.43	0.03	0.29	0.46	0.11	0.20
MgO	1.73	20.64	3.71	1.27	21.18	1.38	4.12
CaO	0.00	0.03	0.05	0.05	0.05	0.00	0.00
Na ₂ O	0.27	0.13	0.09	0.33	0.04	0.25	0.19
K ₂ O	10.93	9.94	10.91	10.78	9.49	10.19	10.47
H ₂ O**	4.15	3.26	4.15	4.25	2.52	4.43	3.92
F	0.68	3.26	0.60	0.45	3.39	0.13	1.00
O=F	0.29	1.37	0.25	0.19	1.43	0.06	0.42
Total	99.44	99.83	99.40	99.01	99.10	99.10	98.71
Numbers of cations based on O ₂₀ (OH, F) ₄							
Si	6.31	6.32	6.58	6.41	6.47	6.39	6.42
Al	5.11	1.85	4.49	5.16	1.56	5.24	4.62
Ti	0.11	0.01	0.10	0.01	0.02	0.01	0.04
Fe	0.17	1.14	0.32	0.17	1.15	0.15	0.36
Mn	0.01	0.05	0.00	0.03	0.05	0.01	0.02
Mg	0.35	4.44	0.75	0.25	4.59	0.28	0.84
Ca	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Na	0.07	0.04	0.02	0.09	0.01	0.06	0.05
K	1.87	1.83	1.88	1.85	1.76	1.74	1.82
Numbers of OH and F based on OH + F = 4							
OH	3.71	2.49	3.74	3.81	2.44	3.95	3.57
F	0.29	1.51	0.26	0.19	1.56	0.05	0.43

1, 2: Muscovite and biotite from the Deai No. 4 ore deposit. 3, 4: Muscovite from the Suo No. 9 ore deposit. 5, 6: Muscovite and biotite from the Idenooku No. 8 ore deposit. 7: Muscovite from the Umenoki No. 5 ore deposit. *: Total iron as FeO. **: Calculated from fluorine contents.

Ichikuni (1982) measured Na and K contents in inclusion fluids in quartz from the Kiwada mine. They discussed that Na/K atomic ratio is below 1.0 and that the low Na/K ratio in inclusion fluids is a characteristic feature for the Kiwada mine compared with other metal-producing deposits. The activity ratios in hydrothermal solutions for the formation of these ore deposits are evaluated from the chemistry of muscovite in the present study. Na/K atomic ratios of muscovites from the Fujigatani, Kiwada, and Kuga mines range from 0.009 to 0.036, from 0.007 to 0.098, and from 0.009 to 0.057, respectively (Fig. 2). Na and K associate with chlorine at supercritical temperatures (Helgeson and Kirkham, 1976). Activity ratios of NaCl/KCl in hydrothermal solution can be estimated from the following equation:

FIG. Na/K atomic ratios of muscovites from the Fujigatani, Kiwada and Kuga mines. (a) Fujigatani mine. Open and cross-hatched area show the data for muscovite in quartz veins of the Akemidani No. 1 and in skarn of the Akemidani No. 5 ore deposits, respectively. (b) Kiwada mine. Muscovite in quartz veins of the No. 11 ore body. (c) Kuga mine. Open and cross-hatched areas show the data from quartz veins of the Suo and Deai ore deposits, respectively. Open and solid circles show the data from quartz veins of the Ideno-oku and Umenoki ore deposits, respectively.

The equilibrium constant for this reaction can be written as,

$$\log K = \log(a_{\text{mus}}/a_{\text{par}})(a_{\text{NaCl}}/a_{\text{KCl}}) \quad (2)$$

where *a* denotes activity and the subscripts mus and par are muscovite and paragonite, respectively. Thermodynamic data for muscovite and paragonite were given by Helgeson *et al.* (1978). Data for NaCl and KCl were given by Frantz *et al.* (1981).

TABLE 2. Equilibrium constants for the reaction (1).

	log K					
	300°C	350°C	400°C	450°C	500°C	550°C
$P_{\text{tot}} = P_{\text{H}_2\text{O}}$						
1 kb	-1.60	-1.46	-1.09	-1.11	-1.12	-1.13
2 kb	-1.63	-1.49	-1.36	-1.25	-1.16	-1.08

TABLE 3. Margules mixing parameter equations for muscovite-paragonite solid solution.

(i) Eugster <i>et al.</i> (1972)	
$W_{\text{paragonite}}$	$= 3082.1 + 0.1698 T(\text{K}) + 0.0822 P(\text{bar})$
$W_{\text{muscovite}}$	$= 4163.9 + 0.3954 T(\text{K}) + 0.1259 P(\text{bar})$
(ii) Chatterjee and Froese (1975)	
$W_{\text{paragonite}}$	$= 2923.1 + 0.1698 T(\text{K}) + 0.1590 P(\text{bar})$
$W_{\text{muscovite}}$	$= 4650.1 + 0.3954 T(\text{K}) - 0.1090 P(\text{bar})$
$RT \ln \gamma_{\text{mus}}$	$= X_{\text{par}} (W_{\text{mus}} + 2X_{\text{mus}} (W_{\text{par}} - W_{\text{mus}}))$
$RT \ln \gamma_{\text{par}}$	$= X_{\text{mus}} (W_{\text{par}} + 2X_{\text{par}} (W_{\text{mus}} - W_{\text{par}}))$

Calculated activity coefficients at 1 kb and 400°C

X_{par}	0.05		0.10	
Parameters	(i)	(ii)	(i)	(ii)
γ_{mus}	1.00	1.07	1.15	1.02
γ_{par}	9.96	10.86	1.02	10.67

Calculated equilibrium constants are listed in Table 2. Activities of end members in the muscovite-paragonite solid solution are calculated based on the regular solution model (Thompson, 1967), using the Margules mixing parameter equation (Table 3). Activity coefficients do not differ significantly between those calculated by the equation given by Eugster *et al.* (1972) and those by Chatterjee and Froese (1975). Pressures of hydrothermal solutions for the formation of the Fujigatani, Kiwada, and Kuga deposits are assumed to be 1 kbars based on the pressure estimate for the Kiwada deposits (Shimizu and Shimazaki, 1981). Table 4 lists the calculated activity ratios from the chemical compositions of muscovite associated with scheelite. Present results show that Na/K ratios are above 1.0, assuming that the activity coefficients of NaCl and KCl are unity (Helgeson *et al.*, 1981). In the measurement of inclusion fluids by Takenouchi and Ichikuni (1982), primary fluid inclusions could not be separated from secondary inclusions. It is possible that the measured value is a weighted average of primary and secondary fluid inclusions. Although there is an ambiguity on the present evaluation owing to the extrapolation of the Margules mixing parameters derived by experiments, Na/K ratios in hydrothermal solutions are possibly above 1.0 during the formation of quartz veins.

TABLE 4. Calculated activity ratios of NaCl/KCl in hydrothermal solutions during the formation of muscovite based on the equations given by Eugster *et al.* (1972). Average values of X_{par} are used in the calculations.

	$a_{\text{NaCl}}/a_{\text{KCl}}$		
	350°C (1 kb)	400°C (1 kb)	450°C (1 kb)
(A) Fujigatani mine			
(1) $X_{\text{par}} = 0.036$	12.9	4.82	
(2) $X_{\text{par}} = 0.031$	11.2	4.25	
(B) Kiwada mine			
(3) $X_{\text{par}} = 0.045$	15.6	5.52	4.98
(C) Kuga mine			
(4) $X_{\text{par}} = 0.022$	8.40	2.94	2.66
(5) $X_{\text{par}} = 0.034$	12.6	4.44	4.02
(6) $X_{\text{par}} = 0.039$	14.3	5.04	4.57
(7) $X_{\text{par}} = 0.030$	11.2	3.94	3.58

(1): Muscovite in a quartz vein of the Akemidani No. 1 ore deposit. (2): Muscovite in clinopyroxene skarn of the Akemidani No. 5 ore deposit. (3): Muscovite in a quartz vein of No. 11 ore body. (4): Muscovite in a quartz vein of the Deai No. 4 ore deposit. (5): Muscovite in a quartz vein of the Suo No. 9 ore deposit. (6): Muscovite in a quartz vein of the Idenooku No. 8 ore deposit. (7): Muscovite in a quartz vein of the Umenoki No. 5 ore deposit.

Fluorine contents of micas

A generalized reaction for fluorine-hydroxyl exchange of mica with hydrothermal solutions can be written as follows:

where subscript soln denotes solution. If OH and F mix ideally on the hydroxyl site, then the equilibrium constant for the reaction (3) is:

$$\log K = \log (X_{\text{F}}/X_{\text{OH}}) + \log (f_{\text{H}_2\text{O}}/f_{\text{HF}}) \quad (4)$$

where X denotes mole fraction and f denotes fugacity. Gunow *et al.* (1980) showed that

$$\log K = 2100/T(\text{K}) + 1.523X_{\text{Mg}} + 0.416X_{\text{Fe}} - 0.11X_{\text{Al}} \quad (5)$$

for muscovite, where X denotes octahedral site occupancy. Munoz (1984) showed that the equilibrium constant for the reaction (3) can be written as follows:

$$\log K = 2100/T(K) + 1.523X_{\text{phl}} + 0.416X_{\text{ann}} + 0.20X_{\text{sid}} \quad (6)$$

for biotite, where X denotes the molecular proportion of phlogopite (phl), annite (ann), and siderophyllite (sid). End members of biotite are calculated as follows (Gunow *et al.*, 1980):

$$X_{\text{phl}} = \text{Mg}/\text{total of octahedral cation} \quad (7)$$

$$X_{\text{sid}} = ((3\text{-Si}/\text{Al}) \cdot 1.75) \cdot (1 - X_{\text{phl}}) \quad (8)$$

and

$$X_{\text{ann}} = 1 - X_{\text{phl}} - X_{\text{sid}}. \quad (9)$$

The similarity of ionic radii between Fe and Mn (Shannon and Prewitt, 1969) leads to the assumption that the occupancy of Mn is included in X_{Fe} . Ferric/ferrous ratio does not affect significantly to the preference of fluorine in kaersutite (Aoki and Kanisawa, 1970) nor in biotite (Munoz and Luddington, 1974).

Munoz (1984) defined the fluorine intercept value, $\text{IV}(\text{F})$, for muscovite which is as follows:

$$\text{IV}(\text{F}) = -\log(X_{\text{F}}/X_{\text{OH}}) + 1.523X_{\text{Mg}} + 0.416X_{\text{Fe}} - 0.11X_{\text{Al}}. \quad (10)$$

Fluorine intercept value, $\text{IV}(\text{F})$, for biotite can be written as follows:

$$\text{IV}(\text{F}) = -\log(X_{\text{F}}/X_{\text{OH}}) + 1.523X_{\text{phl}} + 0.416X_{\text{ann}} + 0.20X_{\text{sid}}.$$

It is apparent that

$$\text{IV}(\text{F}) = \log(f_{\text{H}_2\text{O}}/f_{\text{HF}}) - 2100/T, \quad (11)$$

which shows that $\text{IV}(\text{F})$ is equal to the log of the fugacity ratio of $\text{H}_2\text{O}/\text{HF}$ at infinite temperature ($1/T = 0$). It can be used as a measure of the fluorine contents of micas which has been corrected for solid solution and temperature effects. Equation (11) shows that smaller fluorine intercept value is correlated with higher degree of fluorine

enrichment. Fluorine intercept values for muscovite and biotite are shown in Figs. 3 and 4. Fluorine intercept values for muscovite from the Fujigatani mine are lower in quartz veins than those in skarn. Solution compositions were affected by high calcium activity owing to the dissolution of calc-silicate minerals during the late stage hydrothermal alteration. Fluoride concentrations were suppressed by high calcium concentration by the formation of fluorite. These suggest that fluoride concentrations were originally high and were buffered by reacting with calc-silicate minerals. The values for muscovite in quartz veins of No. 11 ore body of the Kiwada mine lie in the region for the skarn of the Fujigatani mine. Fluorine intercept values for biotite from the Suo and Deai ore deposits agree with those for muscovite within 0.3. The ore grade decreases in the following order: Deai–Umenoki–Suo–Idenooku ore deposits (Higashimoto, 1977; Matsueda *et al.*, 1981). Fluorine intercept values from the Ume-

FIG. 3. Fluorine intercept values for micas from the Fujigatani and Kiwada mines. Open areas and large circles show the data from quartz veins of the Akemidani No. 1 ore deposit and clinopyroxene skarn of the Akemidani No. 5 ore deposit of the Fujigatani mine, respectively. Squares show the data from quartz veins of No. 11 ore body of the Kiwada mine.

FIG. 4. Fluorine intercept values for muscovite and biotite from the Kuga mine. Open area, large circles, small circles, and hatched areas show the data from the Idenooku, Suo, Deai and Umenoki ore deposits, respectively. Open circles show the data for muscovite and solid circles for biotite, respectively.

noki and Idenooku ore deposits are lowest and highest, respectively. The ore grade is correlated with fluoride concentrations in solutions.

Comparison of chemical compositions of micas with other tungsten deposits in Japan

Muscovites are associated with tungsten minerals in quartz veins of the vein-type

TABLE 5. Representative analyses of muscovite from the Kaneuchi, Ohtani and Takatori mines.

	1	2	3	4	5	6	7
SiO ₂	46.55	46.03	45.62	46.92	44.49	47.66	47.13
Al ₂ O ₃	35.89	35.48	35.61	30.53	34.15	27.58	28.47
TiO ₂	0.22	0.36	0.35	0.26	0.49	0.17	0.28
FeO	0.73	0.68	0.99	1.00	0.61	2.59	2.59
Fe ₂ O ₃	0.58	0.60	0.32	1.89	0.75	1.79	2.02
MnO	0.06	0.11	0.02	0.18	0.10	0.74	0.67
MgO	0.83	1.31	0.76	3.04	1.66	3.47	2.58
CaO	0.02	0.01	0.00	0.00	0.03	0.00	0.06
Na ₂ O	0.55	0.49	0.54	0.18	0.37	0.19	0.22
K ₂ O	10.18	10.56	11.39	11.11	10.91	10.27	10.70
Li ₂ O	0.01	0.00	0.01	0.19	0.11	0.54	0.44
F	0.23	0.19	0.17	0.95	0.91	3.39	2.51
H ₂ O*	4.38	4.35	4.37	4.01	3.98	2.81	3.22
O=F	0.10	0.08	0.07	0.40	0.37	1.43	1.06
Total	99.27	98.37	99.21	99.85	98.18	99.75	99.83
Numbers of cations based on O ₂₀ (OH, F) ₄							
Si	6.14	6.22	6.07	6.31	6.06	6.45	6.41
Al	5.52	5.36	5.62	4.85	5.48	4.43	4.56
Ti	0.04	0.05	0.03	0.03	0.05	0.02	0.03
Fe ²⁺	0.08	0.08	0.11	0.11	0.07	0.29	0.29
Fe ³⁺	0.07	0.06	0.03	0.19	0.08	0.18	0.21
Mn	0.01	0.01	0.00	0.02	0.01	0.08	0.08
Mg	0.18	0.27	0.15	0.61	0.34	0.70	0.52
Ca	0.00	0.00	0.00	0.00	0.01	0.00	0.01
Na	0.14	0.13	0.14	0.05	0.10	0.05	0.06
K	1.83	1.82	1.96	1.91	1.90	1.78	1.86
Li	0.00	0.00	0.01	0.10	0.06	0.29	0.24
Numbers of OH and F based on OH + F = 4							
OH	3.90	3.92	3.93	3.60	3.61	2.54	2.92
F	0.10	0.08	0.07	0.40	0.39	1.46	1.08

1, 2: Muscovite from the -240 m level of the western vein of the Kaneuchi mine; 3: Muscovite from the -180 m level of the western vein of the Kaneuchi mine. 4: Muscovite from the 200 m level of the No. 4 vein of the Ohtani mine. 5: Muscovite from the 200 m level of the No. 12 vein of the Ohtani mine. 6: Muscovite from the -2 m level of the No. 7 vein of the Takatori mine. 7: Muscovite from the -4 m level of the No. 7 vein of the Takatori mine.

tungsten deposits of the Kaneuchi, Ohtani, and Takatori mines (*e.g.*, Shibue, 1985). Representative analyses of muscovites from the Kaneuchi, Ohtani, and Takatori mines are listed in Table 5. Na/K atomic ratios of muscovites from the Kaneuchi, Ohtani, and Takatori mines are shown in Fig. 5. The ratios of the Kaneuchi mine ranges from 0.01 to 0.23, and most are from 0.01 to 0.11. Muscovite from the Ohtani mine shows the ratios ranging from 0.01 to 0.06. Muscovite from the Takatori mine shows the ratio ranging from 0.00 to 0.10. Muscovites from the Fujigatani, Kiwada, and Kuga

FIG. 5. Na/K atomic ratios of muscovites in quartz veins of the vein-type tungsten deposits. (a) Kaneuchi mine, (b) Ohtani mine, (c) Takatori mine.

mines contain similar amount of sodium to those from the vein-type deposits. Temperatures of hydrothermal solutions for the formation of the Kaneuchi, Ohtani, and Takatori deposits are from 370° to 530°C, 450° to 550°C, and from 450° to 500°C, respectively (Shibue, 1985). Na/K ratios in hydrothermal solutions for the formation of the Kaneuchi, Ohtani, and Takatori deposits are above 7.0, 3.0, and 2.5 at 500°C, respectively. These indicate that Na/K ratios in hydrothermal solutions for the formation of muscovites from the Fujigatani, Kiwada, and Kuga deposits are similar to those for the formation of muscovites from the Kaneuchi, Ohtani, and Takatori deposits. It can be concluded that Na/K ratios in hydrothermal solutions for the studied deposits are above 1.0.

Fluorine intercept values for the Fujigatani, Kiwada, and Kuga mines are comparable to those for the Kaneuchi and Ohtani mines, and are higher than those for the Takatori mine (Fig. 6). Munoz (1984) summarized the fluorine intercept values for several porphyry copper deposits. Porphyry copper deposits are closely associated with granitic activities (*e.g.*, Burnham, 1979). Most of the values range from 1.5 to 2.5. Fluorine intercept values for the studied tungsten deposits are smaller than those from some porphyry copper deposits except that for the Kaneuchi deposit. High fluoride concentrations are characteristic for the hydrothermal solutions responsible for the formation of Japanese skarn-type tungsten deposits as well as the vein-type deposits, compared with porphyry copper deposits.

FIG. 6. Fluorine intercept values for muscovite from the Kaneuchi, Ohtani and Takatori mines.

Conclusions

(1) Muscovite from the Fujigatani, Kiwada, and Kuga mines are often associated with scheelite in quartz veins. Based on the temperature and pressure estimates of hydrothermal solutions (Shibue, 1985; Shimizu and Shimazaki, 1981), NaCl/KCl activity ratios in hydrothermal solutions are estimated to be from 5.5 to 2.9 at 400°C during the formation of muscovites from their Na/K atomic ratios. Na/K atomic ratios in muscovite are similar to those from the vein-type tungsten deposits of the Kaneuchi, Ohtani, and Takatori mines.

(2) Fluorine contents in muscovite in quartz veins are higher than 0.1 wt%. The contents in skarn of the Fujigatani mine are lower than those in quartz veins. Fluorine contents in muscovite from the Deai and Suo ore deposits are higher than those from the Idenooku ore deposits of the Kuga mine. These correspond with the ore grade of tungsten. Measured fluorine contents in micas from the Fujigatani, Kiwada, and Kuga mines are comparable to those from the vein-type tungsten deposits of the Kaneuchi and Ohtani mines, and are higher than those from several porphyry copper ore deposits summarized by Munoz (1984).

Acknowledgments—The author wishes to thank to Professors J. T. Iiyama and H. Shimazaki, Drs. N. Shikazono, A. Takada and M. Tsukui of Geological Institute, University of Tokyo for their valuable suggestions. The author also wishes to thank to the staff members of the Kaneuchi, Ohtani, Takatori, Fujigatani, Kiwada and Kuga mines for their kind support during the author's field survey. The author wishes to express sincere thanks to the staff members of the Ocean Research Institute of University of Tokyo for their kind help in using EPMA Model JXA-733. This work was supported in part by the funds from Cooperative Program (No. 85136) provided by Ocean Research Institute, University of Tokyo.

References

- AOKI, K. & KANISAWA, S. (1979) *Lithos*, **1**, 167-171.
BURNHAM, C. W. (1979) *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. Barnes). John Wiley and Sons, New York.
CHATTERJEE, N. D. & FROESE, E. (1975) *Amer. Miner.*, **60**, 985-993.
EUGSTER, H. P., ALBEE, A. L., BENCE, A. E., THOMPSON, J. D. Jr. & WALDBAUM, D. R. (1972) *Journ. Petrol.*, **13**, 147-179.
FRANTZ, J. D., POPP, R. K. & BOCTOR, N. Z. (1981) *Geochim. Cosmochim. Acta*, **45**, 69-77.
GUNOW, A. J., LUDDINGTON, S. & MUNOZ, J. L. (1980) *Econ. Geol.*, **75**, 1127-1137.
HELGESON, H. C. & KIRKHAM, D. H. (1976) *Amer. Journ. Sci.*, **276**, 96-240.
HELGESON, H. C., DELANY, J. M., NESBITT, H. W. & BIRD, D. K. (1978) *Amer. Journ. Sci.*, **278-A**, 1-229.
HELGESON, H. C., KIRKHAM, D. H. & FLOWERS, G. C. (1981) *Amer. Journ. Sci.*, **281**, 1249-

1516.

- HIGASHIMOTO, S. (1977) *Bull. Geol. Surv., Japan*, **28**, 775-793.
- HIGASHIMOTO, S., NUREKI, T., HARA, I., TSUKUDA, E. & NAKAJIMA, T. (1983) *Quadrangle Series Geol. Surv. Japan*.
- HIIRAGI, N., SHIMA, H. & NAKAMURA, Y. (1984) *Joint meeting of Soc. Mining Geol. Japan, Assoc. Miner. Petrol. Econ. Geol. and Miner. Soc. Jpan*, B-31.
- HOSHINO, K., WATANABE, M. & SOEDA, A. (1982) *Mining Geol.*, **32**, 443-456.
- INGRAM, B. L. (1970) *Anal. Chem.*, **42**, 1825-1827.
- ITO, K. (1962) *Japan Journ. Geol. Geogr.*, **33**, 169-190.
- KANISAWA, S. (1978) *Journ. Japan. Assoc. Miner. Petrol. Econ. Geol.*, **73**, 26-29.
- KUWAHARA, T. & NAKAMURA, M. (1975) *Mining Geol.*, **25**, 123-134.
- MATSUEDA, H., KIKUCHI, Y. & MATSUKUMA, T. (1981) *Joint meeting of Soc. Mining Geol. Japan, Assoc. Miner. Petrol. Econ. Geol. and Miner. Soc. Japan*, B-6.
- MATSUEDA, H. & ARAI, K. (1982) *Mining Geol.*, **32**, 129-140.
- MUNOZ, J. L. (1984) *Micas, Reviews in Mineralogy, Vol. 13* (ed. S. W. Bailey). Miner. Soc. Amer. Virginia.
- MUNOZ, J. L. & LUDDINGTON, S. (1974) *Amer. Journ. Sci.*, **274**, 396-413.
- NAGAHARA, M. (1978) *Mining Geol.*, **28**, 373-384.
- SATO, K. (1980) *Econ. Geol.*, **75**, 1066-1082.
- SHANNON, R. D. & PREWITT, C. T. (1969) *Acta Cryst.*, **B25**, 925-946.
- SHIBATA, K. & ISHIHARA, S. (1974) *Econ. Geol.*, **69**, 1207-1214.
- SHIBUE, Y. (1985) Unpublished PhD thesis, University of Tokyo.
- SHIMIZU, M. & SHIMAZAKI, H. (1981) *Miner. Deposita*, **16**, 45-50.
- TAKENOUCHI, S. & ICHIKUNI, M. (1982) *Journ. Japan. Assoc. Miner. Petrol. Econ. Geol. Spec. Issue*, **3**, 331-340.
- THOMPSON, J. B. Jr. (1967) In *Researches in Geochemistry. Vol. II* (ed. P. H. Abelson). John Wiley and Sons, New York.

Received July 11, 1986; revised October 2, 1986.