

ZONED TUNGSTENOAN MOLYBDENITE FROM A FENITIZED MEGAXENOLITH IN THE Khibina ALKALINE COMPLEX, KOLA PENINSULA, RUSSIA

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ABSTRACT

Zoned tungstenoan molybdenite occurs in a fenite (~80 modal % nepheline) within a strongly heterogeneous fenitized megaxenolith (~0.2 km) enclosed by nepheline syenite, in the Khibina alkaline complex, Kola Peninsula, Russia. Molybdenite forms euhedral crystals (~50–60 μm in length), enclosed by pyrrhotite, and abundant veinlets among silicates. The crystals are zoned with respect to tungsten, which is strongly enriched in the central zone. This area is 5–6 μm across and contains up to 5.85 wt.% W (0.05 atoms per formula unit). Tungsten-rich zones of the molybdenite veinlets contain the same concentration of W as the central zone of the euhedral crystals, implying similar conditions of formation. There is thus a substantial solid-solution between molybdenite and tungstenite. We attribute the outward zoning to W-poor molybdenite in terms of increasing fugacity of oxygen and decreasing fugacity of sulfur, apparently in the presence of a reduced H_2S – CH_4 -rich fluid of subalkaline character. The existence of locally reducing conditions in the fenite(s) at Khibina also is implied by the adjacent occurrences of titanium- and niobium-rich sulfides and a graphite-like material.

Keywords: tungsten, molybdenite, molybdenite–tungstenite series, zoning, fenite, xenolith, alkaline complex, Khibina, Kola Peninsula, Russia.

SOMMAIRE

Nous décrivons des cristaux de molybdénite zonés en tungstène provenant d'une fénite (~80% de néphéline) prélevée d'un mégaxénolithe (~0.2 km) fénitisé fortement hétérogène inclus dans une syénite néphélinique du complexe alcalin de Khibina, dans la péninsule de Kola, en Russie. La molybdénite se présente en cristaux idiomorphes (~50–60 μm en longueur) inclus dans la pyrrhotite, et en veinules filamenteuses parmi les silicates. Les cristaux sont zonés par rapport au tungstène, qui est enrichi dans le cœur des cristaux; cette zone, 5–6 μm en largeur, atteint 5.85% W en poids (0.05 atomes par unité formulaire). Les zones riches en tungstène des veinules de molybdénite contiennent la même concentration de W que la zone centrale des cristaux idiomorphes, témoignant ainsi de conditions semblables de formation. Il y a donc une solution solide substantielle entre molybdénite et tungstenite. Nous attribuons le passage à une molybdénite banale sans W en direction de la bordure des grains en termes d'une augmentation de la fugacité d'oxygène et d'une diminution de la fugacité de soufre, apparemment en présence d'une phase fluide subalcaline réductrice contenant H_2S et CH_4 . L'existence de telles conditions réductrices à l'échelle locale dans les fénites de Khibina concorderait avec le développement de sulfures contenant titane et niobium et d'un matériau ressemblant au graphite.

(Traduit par la Rédaction)

Mots-clés: tungstène, molybdénite, série molybdénite–tungstenite, zonation, fénite, xénolithe, complexe alcalin, Khibina, péninsule de Kola, Russie.

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INTRODUCTION

Molybdenite, the most common mineral of molybdenum, is found in many terrestrial environments and in meteorites. Almost invariably, it is very close to the end-member composition, MoS_2 . Significant concentrations of rhenium (up to 11.5 wt.%) have been reported in molybdenite (Kovalenker *et al.* 1974, Bernard *et al.* 1990). On the other hand, tungsten, where present, is incorporated as a trace constituent, regardless of the common coexistence of molybdenite with W-bearing minerals. In this paper, we report an unusual occurrence of tungstenoan molybdenite from the Khibina alkaline complex, Kola Peninsula, northwestern Russia. We attempt to identify the geochemical environment that promoted the structural incorporation of significant quantities of tungsten in molybdenite.

BACKGROUND INFORMATION

Both molybdenum and tungsten exhibit two valence states in the Earth's crust, although the two elements are distinct in their pattern of distribution, as initially recognized by Goldschmidt (1954). Molybdenum exhibits a mixed chalcophile–lithophile character. Molybdenite is by far the main expression of the reduced form (*i.e.*, Mo^{4+}), whereas molybdates and other oxysalts of Mo^{6+} form in zones of secondary oxidation of molybdenite-bearing ore deposits. In addition to rare occurrences of tungstenite (WS_2), W^{4+} also presumably occurs in kiddyckite Cu_6WSnS_8 (Harris *et al.* 1984, Zhang & Zhang 1996), which is the W-rich analogue of hemusite ($\text{Cu}_4\text{Cu}^{2+}_2\text{Mo}^{4+}\text{Sn}^{4+}\text{S}_8$; Terziev 1971, Shimizu *et al.* 1991).

Molybdenite is isotypic with tungstenite, and these sulfides occur as hexagonal and trigonal polytypes, 2H and 3R (*e.g.*, Gait & Mandarino 1970). The strong structural similarities would seem to favor a solid solution between molybdenite and tungstenite. In fact, a complete series between the hexagonal disulfides of Mo and W can be synthesized (Moh & Udubaşa 1976). Yet in spite of a thorough search of the literature, we were unable to find well-documented reports of a solid solution between molybdenite and tungstenite. Only Höll & Weber-Diefenbach (1973) reported the existence of a molybdenite–tungstenite solid solution, as extremely fine ($25 \times 2 \mu\text{m}$) inclusions in scheelite from the Felbertal deposit in Austria. A strong interference from the W-rich host would be expected in analytical work on such minute domains, especially considering the electron-microprobe facility available twenty-five years ago. Furthermore, the minor amounts of tungsten (0.7 wt.% W; Graeser 1964) and titanium (2 wt.% Ti; cited in Newberry 1979) reported in the bulk compositions of molybdenite in the literature could well be due to micro-inclusions of W- or Ti-rich phases.

TUNGSTENOAN MOLYBDENITE IN THE Khibina COMPLEX

The Khibina alkaline complex is a huge (1327 km²) concentrically zoned intrusive body of Devonian age, emplaced into Archean granitic gneiss, at its contact with Proterozoic volcanic and sedimentary complexes (*e.g.*, Arzamastsev 1994, Kogarko *et al.* 1995). It consists of various silica-undersaturated igneous rocks and an aureole of hornfels and fenites. In addition, an extensive zone over 20 km in strike length (Fig. 1) of scattered fenitized xenoliths of variable size and shape has been documented in the central part of the complex (Men'shikov 1978, Barkov *et al.* 2000). These may represent a string of foundered and metasomatized roof-pendants.

The tungstenoan molybdenite occurs in a nepheline- and perthite-rich fenite megaxenolith hosted by nepheline syenite (foyaite). Occurrences of Ti-bearing sulfides and a Nb-rich sulfide, edgarite, have recently been reported from this xenolith (Barkov *et al.* 1997, 2000). The tungstenoan molybdenite characterized in this study occurs in a sample consisting predominantly of fine-grained nepheline (*ca.* 70–80 modal %) that is partly replaced by a member of the sodalite group. Pyrrhotite (Ti–V-free), which is partly replaced by marcasite or pyrite (or both), occurs in subordinate amounts (up to *ca.* 5 modal %); chalcopyrite and galena are very rare. Neighborite, NaMgF_3 , occurs as small (<0.1 mm), typically roundish grains present in the same polished sections, though not in immediate contact with the molybdenite.

The tungstenoan molybdenite is present as (1) euhedral, compositionally zoned crystals 50–60 μm in length, isolated within pyrrhotite or associated with marcasite (or pyrite, or both) (Figs. 2, 3), and (2) veinlets between and across silicate minerals (Fig. 4). The zoning in molybdenite is optically not obvious, and is best recognized by scanning-electron microscopy and electron-microprobe analysis.

ANALYTICAL METHOD

The molybdenite was analyzed by electron microprobe in wavelength-dispersion spectrometry mode (WDS) at McGill University. The analyses were carried out with a fully automated JEOL JXA-8900 electron microprobe, operated at 20 kV and 30 nA. A finely focused beam was used for all the analyses. The following X-ray lines (and standards) were used: $\text{MoL}\beta$ (synthetic CaMoO_4), $\text{WL}\alpha$ (CaWO_4), and $\text{K}\alpha$ for S and Fe (pyrite). Counting times on peaks were 20 to 50 s, and background measurement times above and below peaks were 25 s for W and 10 s for the other elements. The results were processed by a ZAF (JEOL) on-line program. An empirical correction for overlap between the $\text{SK}\alpha$ and $\text{MoL}\alpha$ emission lines was made. The minimum detection limit for W was 0.07 wt.%. The precision of

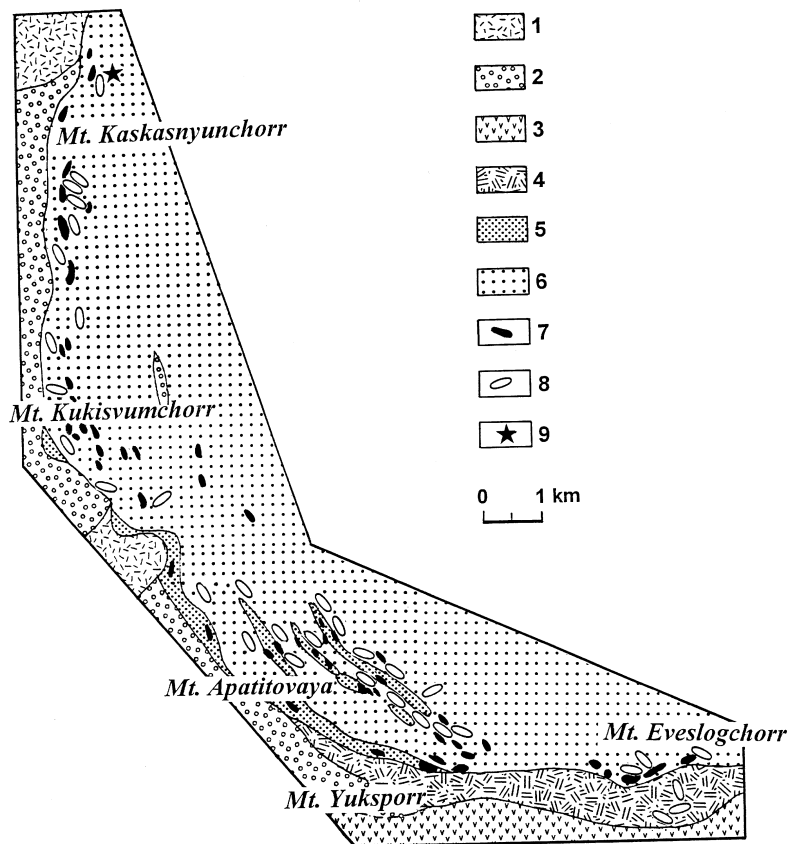


FIG. 1. Schematic geological map showing distribution of fenitized xenolithic bodies in the central part of the Khibina complex (Men'shikov, unpubl. map). 1: massive lyavochorrite, 2: massive rischorrite, 3: foliated rischorrite, 4: foliated and recrystallized nepheline syenite, 5: fine-grained nepheline syenite, 6: albitized trachytic foyaites, 7: fenitized xenoliths, 8: pegmatitic alkaline veins (not to scale), and 9: location of the xenolith containing tungstenoan molybdenite.

the analytical results, listed in Table 1, is ± 0.5 wt.% for Mo, ± 0.1 wt.% for W, and ± 0.25 wt.% for S.

COMPOSITION

The results correspond well to the stoichiometry of tungstenoan molybdenite, $(\text{Mo,W})\text{S}_2$ (Table 1). There is a strong negative correlation between Mo and W (correlation coefficient $R = -0.92$, $n = 25$; Fig. 5), indicating a homovalent substitution involving these elements. In view of the platy habit and small grain-size of the molybdenite, the minor Fe reported (Table 1) may have resulted, at least in part, from interference from nearby pyrrhotite or marcasite. Lower totals observed in some cases may be due to a variable thickness of the grains or their porous surface.

The highest W content (5.85 wt.% W; 0.05 atoms of W per formula unit, *apfu*) is found in the central areas (5–6 μm wide) of the zoned crystals, which, owing to a higher mean atomic number, appear light in back-scattered electron images (Figs. 2a, b). The partly "corroded" shape of the W-rich zone in the center is noteworthy (Fig. 3b). Borders between the W-rich and W-poor zones are characteristically sharp, as illustrated by a detailed electron-microprobe traverse, for example (Fig. 6).

The molybdenite veinlets (Fig. 4a), some of which contain fibrous crystals (Fig. 4b), show exceptionally strong compositional variations. The content of W varies from below the limit of detection to 5.8 wt.% W in the internal zone of a composite veinlet (Fig. 4b; light zone). The adjacent area (Fig. 4b; dark zone) is rela-

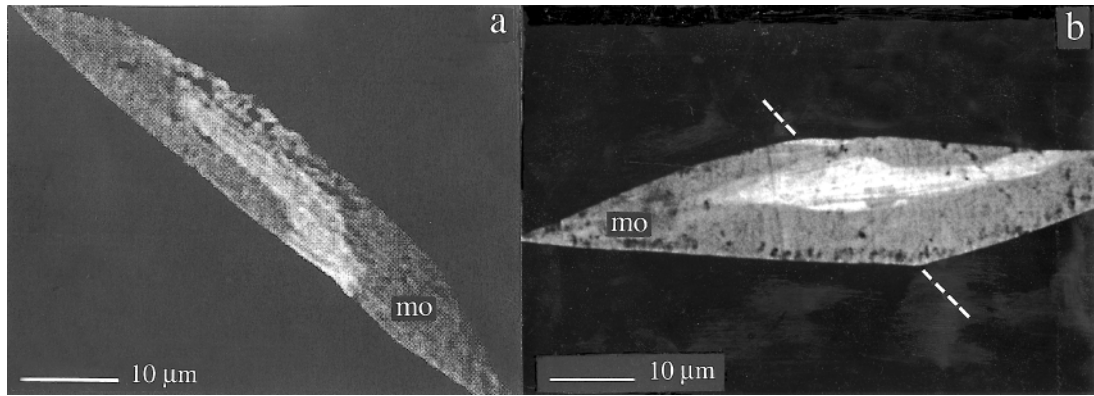


FIG. 2. Crystals of tungstenoan molybdenite (mo), enclosed within secondary marcasite after pyrrhotite (a) and within pyrrhotite (b). Note the W-rich zones (white) within these crystals. Back-scattered electron images. The dashed line across the crystal (shown in Fig. 2b) indicates location of traverse with quantitative electron-microprobe analyses (see Fig. 6).

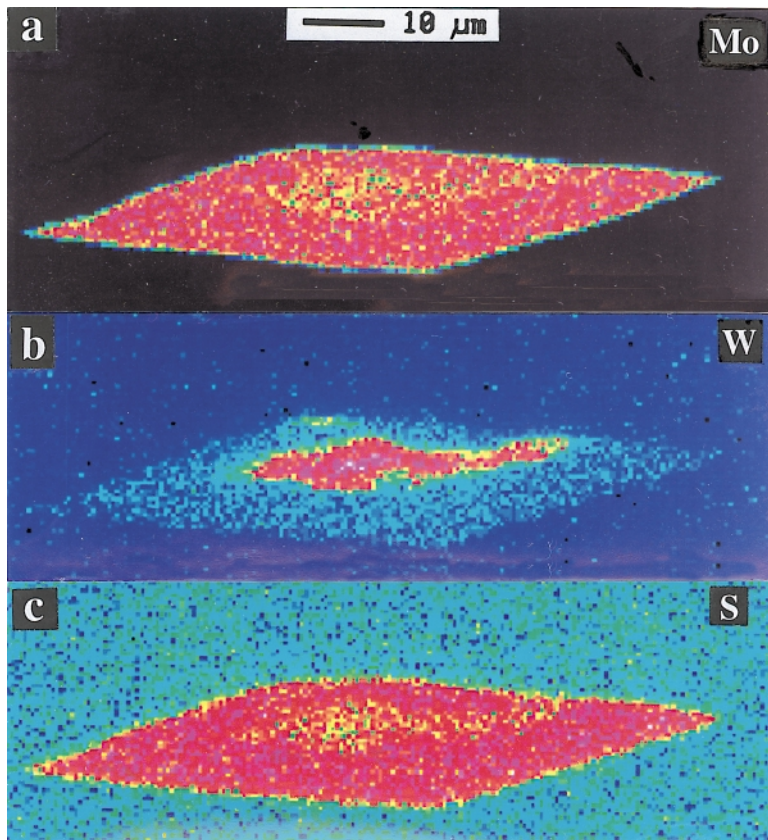


FIG. 3. X-ray maps of the zoned crystal of tungstenoan molybdenite (shown in Fig. 2b) for molybdenum (a), tungsten (b), the W-rich zone being shown in red, and sulfur (c). The thin blue outer zone in (a) is considered an artifact.

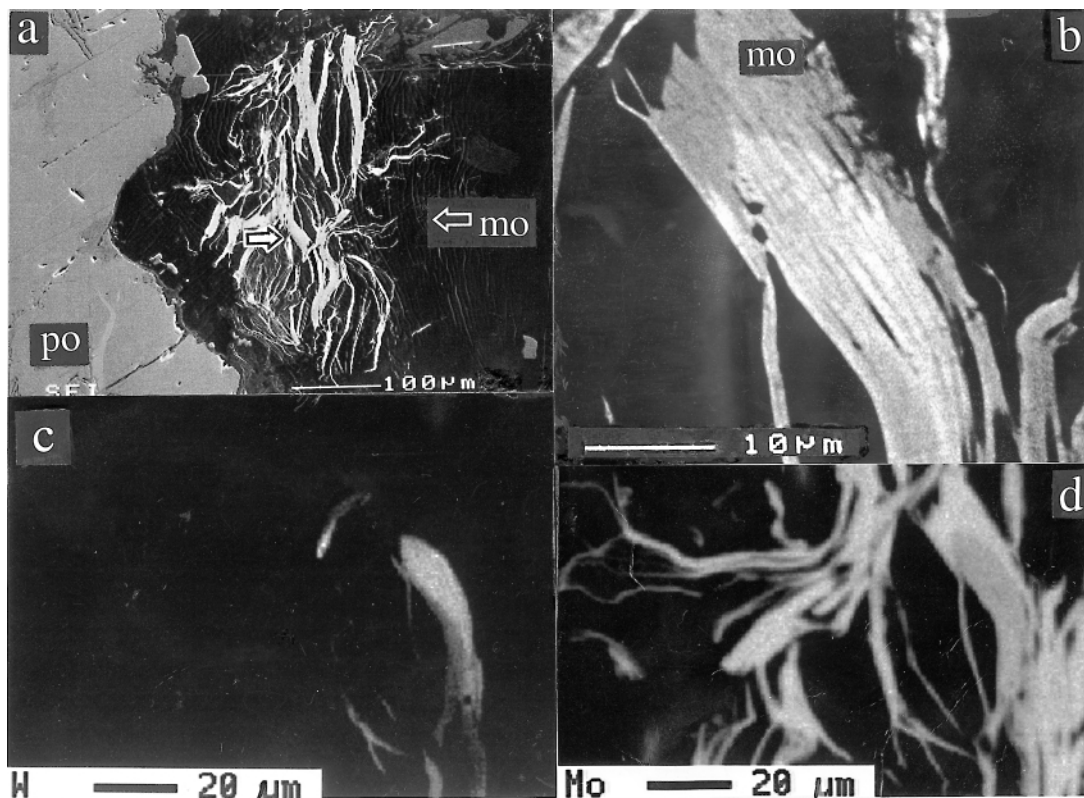


FIG. 4. a) Abundant veinlets of molybdenite (mo) among silicate minerals (black), near a large grain of pyrrhotite (po). Secondary electron image. Arrow in the center shows location of a zoned veinlet (fibrous crystal) of W-bearing molybdenite (mo; Fig. 4b); the W-rich zone is light-colored. Back-scattered electron image. c) and d) Tungsten and molybdenum X-ray maps, respectively, of the zoned veinlet of molybdenite shown in Figure 4b.

tively depleted in W: 1.2 wt.%. In general, the W-rich zones exhibit a veinlet-like morphology, displayed by an X-ray map for W (Fig. 4c). The maximum concentrations of tungsten in the central zone of the zoned crystal (Fig. 2b) and in the W-rich zone of the composite veinlet (Fig. 4b) are identical (5.85 and 5.83 wt.% W, respectively).

The WDS electron-microprobe analysis of the associated neighborite gave Na 23.66, K 0.11, Mg 24.46, F 50.56, sum of 98.79 wt.%; the empirical formula is $(\text{Na}_{1.16}\text{K}_{<0.01})\text{Mg}_{1.13}\text{F}_3$.

DISCUSSION

The apparent lack of W^{4+} in molybdenite in all previously described occurrences, as well as in hemusite, probably results from crystallization in an environment that is too strongly oxidizing, rather than for a structural reason. At Khibina, there are clear signs that a strongly reducing environment existed locally in the fenite. For

example, the highly unusual presence of titanian pyrrhotite and marcasite is noteworthy, in which the titanium could be a mixture of Ti^{3+} and Ti^{4+} (Barkov *et al.* 1997). In addition, the new mineral species edgarite, FeNb_3S_6 , is inferred to contain a mixture of Nb^{3+} and Nb^{4+} (rather than the usual Nb^{5+}), by analogy with structural findings on the synthetic equivalent (Barkov *et al.* 2000). Furthermore, the fenitized xenolith at Khibina contains spherules of a graphite-like phase. The occurrence of ferroan alabandite ($\text{Mn}_{0.87-0.90}\text{Fe}_{0.12-0.09}\text{S}_{1.0}$) and an unusual Mn-(Fe)-rich wurtzite-2H ($\text{Zn}_{0.47}\text{Mn}_{0.27}\text{Fe}_{0.26}\text{S}_{1.0}$; Barkov *et al.* 2000) also is consistent with a reduced environment.

The presence of tungstenoan molybdenite in the core zone of euhedral crystals and veinlets points to an early stage of metasomatism in which $f(\text{O}_2)$ conditions were in the field of stability of the W^{4+} ion. Both molybdenum and tungsten were present in the reducing micro-environment at Khibina as ionic complexes in the fluid phase, which became saturated in molybdenite. We sug-

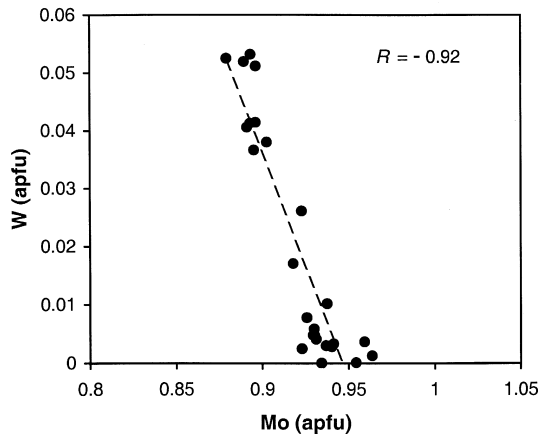


FIG. 5. Compositional variation of tungstenoan molybdenite from a fenite at Khibina. Plot of Mo versus W (atoms per formula unit, *apfu*; Σ atoms = 3).

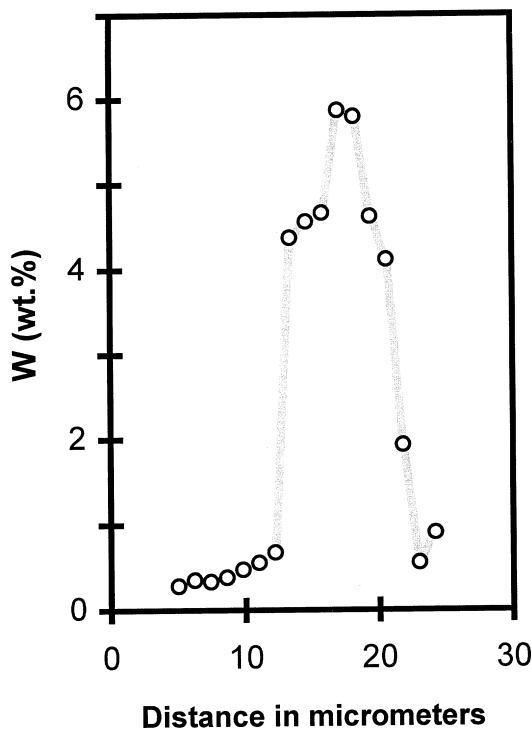


FIG. 6. Electron-microprobe traverse for tungsten (in wt.%) across the zoned crystal of tungstenoan molybdenite (see Fig. 2b for location of this traverse).

TABLE 1. ELECTRON-MICROPROBE DATA ON TUNGSTENOAN MOLYBDENITE FROM THE Khibina COMPLEX

No.	Results of analyses (wt.%)				Proportions of atoms (<i>apfu</i>)				
	Mo	W	Fe	S	Mo	W	Fe	S	
1	51.31	5.85	0.34	39.20	96.70	0.89	0.05	0.01	2.04
2	53.35	5.83	1.05	40.22	100.45	0.90	0.05	0.03	2.02
3	51.88	5.80	1.06	39.50	98.24	0.89	0.05	0.03	2.03
4	52.55	4.66	1.00	39.83	98.04	0.90	0.04	0.03	2.03
5	52.16	4.62	1.14	39.65	97.57	0.89	0.04	0.03	2.03
6	52.23	4.56	0.97	39.94	97.70	0.89	0.04	0.03	2.04
7	54.15	4.37	0.98	40.72	100.22	0.90	0.04	0.03	2.03
8	52.50	4.12	1.19	39.84	97.65	0.90	0.04	0.03	2.03
9	54.61	2.96	0.09	40.49	98.15	0.92	0.03	<0.01	2.05
10	54.18	1.93	1.17	40.05	97.33	0.92	0.02	0.03	2.03
11	56.16	1.17	0.24	40.94	98.51	0.94	0.01	<0.01	2.05
12	55.79	0.67	0.98	40.82	98.26	0.93	0.006	0.03	2.04
13	56.13	0.55	0.98	41.06	98.72	0.93	0.005	0.03	2.04
14	55.93	0.47	1.00	40.86	98.26	0.93	0.004	0.03	2.04
15	58.77	0.43	1.31	40.94	101.45	0.96	0.004	0.04	2.00
16	56.43	0.38	1.02	40.60	98.43	0.94	0.003	0.03	2.03
17	56.83	0.33	1.05	40.95	99.16	0.94	0.003	0.03	2.03
18	58.35	0.14	0.07	41.13	99.69	0.96	0.001	<0.01	2.03

Note: 1 veinlet in silicate, center; 11 the same veinlet, periphery (light and dark zones in Fig. 4b); 2 to 8 euhedral crystal, centre (Fig. 2b, white); 10 and 12 to 17 the same crystal, periphery (Fig. 2b, gray); 9 a veinlet in silicate (center); 18 thin veinlet in silicate. Rhenium was sought, but not detected. The analytical results are listed in order of decreasing content of W. The proportions of atoms are quoted in atoms per formula unit (*apfu*). Σ atoms = 3.

gest that the early formation of molybdenite took place somewhat below the WO_2 - WO_3 buffer (or the WO_2 - $WO_{2.72}$ buffer above $600^\circ C$: Cygan & Chou 1990). Under these conditions, the W^{4+} ion was available for incorporation in the growing crystals of molybdenite. Interestingly, the hydrothermal mobility of tungsten seems significantly enhanced in such a low- $f(O_2)$ environment. Wood & Vlassopoulos (1989) found this to be the case in a study of speciation of tungsten at $500^\circ C$ and 1 kbar, conditions that are probably realistic for the early fenitization of the xenoliths. They found that about three times more tungsten can be held in solution as the tungstenoan complex at this temperature and pressure than would be the case in the field of stability of the tungstenian complex at a fugacity of oxygen above the relevant buffer curve.

To continue with our reconstruction of the events that gave rise to the zoned crystals of molybdenite, we suggest that $f(O_2)$ was generally increasing in the environment of growth. The cores of the euhedral crystals of tungstenoan molybdenite were partly resorbed in the more oxygenated fluid (e.g., Fig. 3b), and the peripheral zones poorer in W formed. As the buffer curve was crossed, molybdenite devoid of tungsten continued to grow, as W^{6+} complexes became predominant in the fluid medium. Presumably, beyond this point, any tungsten-bearing phase likely to form from this fenitizing fluid was a tungstate, or perhaps a peralkaline silicate like khomyakovite or manganokhomyakovite, newly

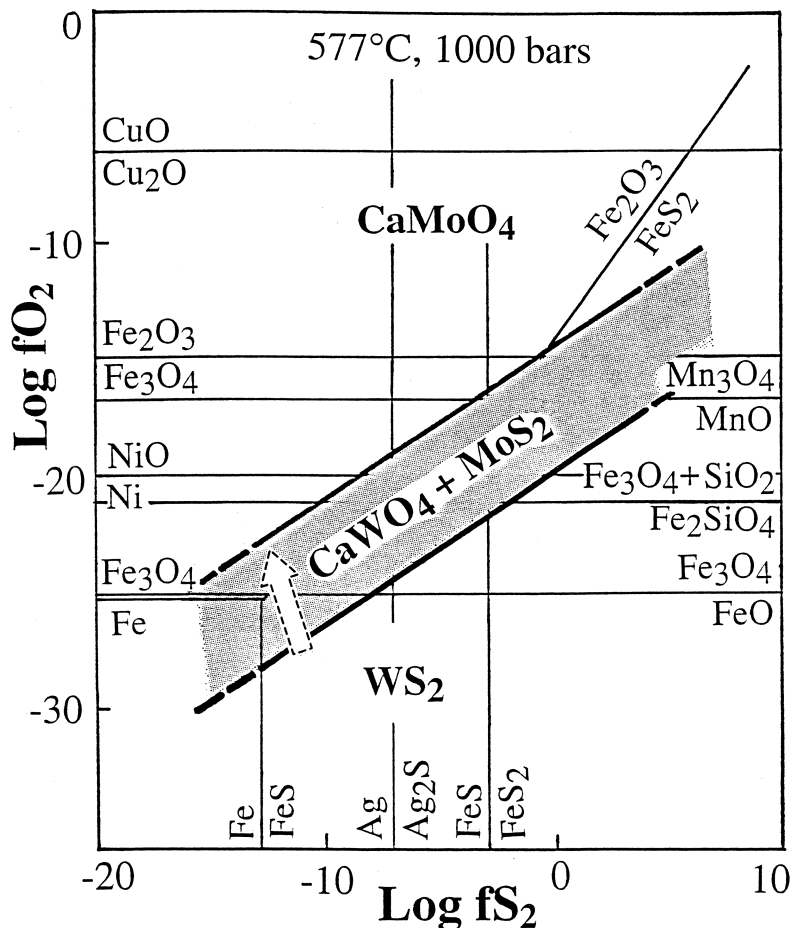


FIG. 7. A plot of $\log f(S_2)$ versus $\log f(O_2)$ showing the stability field of molybdenite and scheelite relative to tungstenite (WS_2) (modified from Hsu 1977).

discovered tungsten-bearing eudialyte-group minerals in which W^{6+} occupies the Nb^{5+} site (Johnsen *et al.* 1999).

In a low- $f(O_2)$ environment, at elevated fugacity of sulfur, elements normally of lithophile character can take on a chalcophile character. This tendency is well displayed in the behavior of Ti, Cr, V, Ca, Mn, and Mg in meteorites (Keil & Andersen 1965, Keil 1968, Keil & Brett 1973, Okada & Keil 1982, Armstrong *et al.* 1985). At the same level of sulfur fugacity, tungstenite, WS_2 , forms at a lower $f(O_2)$ than molybdenite (Hsu 1977). With an increase in $f(O_2)$ and a decrease in $f(S_2)$, the common assemblage molybdenite + scheelite is stabilized at the expense of molybdenite + tungstenite. The likely evolutionary path indicated by the dashed arrow in Figure 7, a plot of $\log f(O_2)$ versus $\log f(S_2)$, is positioned in the field of stability of pyrrhotite, but close to the field of stability of native iron. The presence of native iron has been documented by X-ray diffraction and

electron-microprobe analysis in other samples of fenite from the Khibina complex (Men'shikov, unpubl. data).

Such reducing conditions could well be due to the presence of a hydrocarbon-rich fluid in the environment. Elevated concentrations of hydrocarbons are involved in the formation of secondary minerals at Khibina (Karzhavin 1974). Occurrences of bitumen (Pripachkin *et al.* 1985) and methane inclusions of secondary origin (Potter *et al.* 1998) were reported from the Khibina suite. One way to account for the presence of hydrocarbons is to appeal to the Fischer-Tropsch reaction (*e.g.*, Salvi & Williams-Jones 1997). The graphite-like phase associated with the tungstenian molybdenite may have precipitated from such a fluid by the reaction $CH_4 + CO_2 = 2C + 2H_2O$.

The late increase in $f(O_2)$ in the system is considered to have resulted in the formation of the W-poor molybdenite; this increase could be due to degassing and pref-

erential loss of hydrogen at Khibina, but other hypotheses also are viable. An influx of an external fluid phase could have resulted in a sudden rise in $f(\text{O}_2)$ above the $\text{WO}_2\text{-WO}_3$ buffer into the domain of W^{6+} ; dilution of the earlier fluid and a net loss of alkalis, leading to the development of strongly peraluminous bulk compositions, could also be consequences of this late influx.

In addition, variations in sulfur fugacity may have played a role. According to experimental and thermodynamic data, the formation of WS_2 requires a higher $f(\text{S}_2)$ than the formation of MoS_2 ; the $\text{MoS}_2 - \text{Mo}_2\text{S}_3$ buffer curve is located below the $\text{FeS} - \text{Fe}$ buffer, and the $\text{WS}_2 - \text{W}$ buffer curve is located above the $\text{FeS} - \text{Fe}$ buffer (Štemprok 1971, Fegley & Palme 1985, Palme *et al.* 1994, and references therein). The relative position of these buffers thus suggests that the W-rich molybdenite crystallized at a sulfur fugacity higher than that at which the W-poor molybdenite crystallized. The zoning patterns in the molybdenite at Khibina may thus also reflect a general decrease of $f(\text{S}_2)$ in the fluid (Fig. 7).

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