

## FIRST TERRESTRIAL OCCURRENCE OF TITANIUM-RICH PYRRHOTITE, MARCASITE AND PYRITE IN A FENITIZED XENOLITH FROM THE Khibina ALKALINE COMPLEX, RUSSIA

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### ABSTRACT

The first terrestrial titanium-rich sulfides, the first natural niobium-rich sulfide  $\text{FeNb}_3\text{S}_6$ , fluorine-rich (ca. 6 wt.% F) end-member phlogopite ( $\leq 0.04$  wt.% FeO) and ferroan alabandite occur locally in a heterogeneous xenolith, enclosed within nepheline syenite in the Khibina alkaline complex, Kola Peninsula, northwestern Russia. This assemblage is exclusively associated with an alkali-feldspar-rich rock, probably fenite. Associated minerals include corundum, Nb-Zr-bearing rutile and monazite. The maximum Ti content reaches 3.9 wt.% in pyrrhotite and 2 wt.% in marcasite and pyrite, which represent products of replacement of the pyrrhotite. Titanium is distributed rather homogeneously within single grains of the pyrrhotite; however, a strong grain-to-grain variation is observed. The Ti-rich sulfides invariably contain an elevated level of vanadium (0.2–0.4 wt.%). The results indicate that both Ti and V enter into solid solution in the sulfides. Presumably, there is an environmental similarity between the occurrences of Ti-bearing sulfides in Khibina and in meteorites (enstatite chondrites), where Ti-bearing troilite occurs. As in the meteorites, strongly reducing conditions probably existed locally at the time of crystallization. Concentration of Mg via a fluid phase accounts for the formation of the Mg-rich phlogopite, associated with the relatively Mg-poor rock.

**Keywords:** Ti-bearing sulfides, V-bearing sulfides, Nb-rich sulfide, end-member phlogopite, alabandite, fenite, xenolith, Khibina alkaline complex, Russia, Fennoscandian Shield.

### SOMMAIRE

Nous présentons une description du premier exemple terrestre de sulfures enrichis en titane et du premier exemple naturel d'un sulfure contenant du niobium,  $\text{FeNb}_3\text{S}_6$ , en association avec une phlogopite fluorée (environ 6% de F, en poids) et à faible teneur en fer ( $\leq 0.04\%$  FeO) + alabandite ferreuse. Cette association est développée dans une enclave dans une syénite néphélinique dans le complexe alcalin de Khibina, péninsule de Kola, secteur nord-ouest de la Russie; l'enclave serait une fénite enrichie en feldspath alcalin. Parmi les minéraux associés sont corindon, rutile enrichi en Nb et Zr, et monazite. La pyrrhotite contient jusqu'à 3.9% de Ti, et la marcasite et la pyrite, qui remplacent la pyrrhotite, en contiennent environ 2%. Le Ti y est réparti de façon assez homogène dans chaque cristal, mais montre une grande variabilité parmi les grains. Les sulfures riches en Ti sont aussi enrichis en vanadium (0.2–0.4%). D'après nos résultats, Ti et V sont incorporés dans la structure des sulfures de cette enclave. Il y a probablement un ressemblance dans le milieu de formation de ces sulfures riches en Ti à Khibina et dans les météorites (chondrites à enstatite), dans lesquelles on peut trouver une troilite riche en Ti. Dans les deux cas, les conditions semblent avoir été fortement réductrices. La concentration du Mg dans une phase fluide pourrait expliquer la formation de phlogopite très magnésienne dans un milieu relativement pauvre en Mg.

(Traduit par la Rédaction)

**Mots-clés:** sulfures riches en Ti, sulfures riches en V, sulfure de Nb, phlogopite, mica riche en F, alabandite, fénite, xénolithe, complexe alcalin de Khibina, Russie, bouclier fennoscandien.

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## INTRODUCTION

In the course of a detailed mineralogical study of one of the contact metamorphic rock xenoliths in the Khibina alkaline complex, northwestern Russia, a unique occurrence of titanium-rich pyrrhotite, marcasite and pyrite, a niobium-rich sulfide and end-member phlogopite was recorded. It is well known that pyrrhotite, pyrite and marcasite are abundant in a wide variety of geological environments (*e.g.*, Deer *et al.* 1992). These minerals have been the subject of numerous studies; however, Ti-enriched terrestrial examples were not previously known. The Khibina pyrrhotite, reported in this paper, contains up to 3.9 wt.% Ti, being considerably richer in Ti than troilite from enstatite chondrites (up to 1.0 wt.% Ti), the only other Ti-bearing sulfide so far known in nature (Keil & Andersen 1965, Keil 1968). In addition, the base-metal sulfide minerals are reported here to contain remarkable concentrations of vanadium (up to 0.4 wt.% V in the pyrrhotite). The presence of the Nb-rich sulfide and a nearly iron-free, fluorine-rich phlogopite, occurring in the rather Mg-poor environment, is also of particular interest.

## OCCURRENCE

The unique mineral assemblage occurs in the Khibina alkaline complex (Kola Peninsula, NW Russia: 67°43'N; 33°47'E), one of the largest (about 1330 km<sup>2</sup>) and most well-known alkaline complexes in the world. As noted in Kogarko *et al.* (1995), only the Guli alkaline ultrabasic complex in Siberia may be somewhat larger (1500–1600 km<sup>2</sup>). The Khibina complex is located at the contact between Archean granite gneisses and Proterozoic volcanic–sedimentary complexes. Kramm *et al.* (1993) have recently reported a very narrow range of Rb–Sr ages, from 361.7 to 377.3 Ma (*i.e.*, late Middle Devonian to Upper Devonian), for igneous activity in the Kola–Finnish alkaline province, including that of the Khibina complex. This complex is composed of various alkaline rocks, predominantly (from the periphery to the center) alkaline syenite, nepheline syenite, khibinite, rischorrite, ijolite, urtite, apatite–nepheline rocks, melteigite, nepheline syenite and carbonatite; it is surrounded by abundant fenites and hornfels (*e.g.*, Gerasimovsky *et al.* 1974, Galakhov 1975, Kostyleva–Labuntsova *et al.* 1978). The geology, petrography and mineralogy of the Khibina complex have been described in numerous publications (*e.g.*, Kupletsky 1928, Eliseev *et al.* 1939, Zak *et al.* 1972, Gerasimovsky *et al.* 1974, Galakhov 1975, Kostyleva–Labuntsova *et al.* 1978, Shlyukova 1986). However, in spite of a large number of publications, only Kupletsky (1932) and Men'shikov (1978) have addressed the geological and mineralogical features of heterogeneous xenolithic hornfels and fenite bodies, which are located within alkaline rocks in the central part of the complex. It is important to emphasize that xenoliths are widespread over a large area in Khibina. Men'shikov (1978) reported a zone of the corundum-bearing xenolithic bodies of over 20 km in length and described

the typical assemblages of minerals. The xenoliths are present as numerous isolated bodies having wide variations in their size (from <5 m up to approximately 0.5 km across) and mineral assemblages. The mineralogy of some xenoliths is exceptionally diverse.

The assemblage described here was identified in a relatively small xenolith (<0.2 km in the longest dimension) surrounded by nepheline syenite (foyaite). The xenolith is extremely heterogeneous texturally and mineralogically, and seems to be composed of various contact metamorphic rocks, accidentally incorporated into foyaitic magma. The rocks tend to be fine grained; however, medium- to coarse-grained rocks and pegmatitic facies locally also are common in the occurrence. It is noteworthy that, in general, the rocks in the xenolith show an essential enrichment in titanium, and an abundance of Ti–(Fe) oxide occurs at the contact with the host nepheline syenite.

Alkali feldspar, nepheline, sodalite, analcime, mica, corundum, rutile, titanite, ilmenite and topaz occur in places as the chief or essential minerals in the xenolith. It is of interest to note that rare mineral species freudenbergite, representing the first Fennoscandian occurrence, and members of the crichtonite–loveringite–landauite solid-solution series were found to occur in a close association with other oxides in the xenolith (Barkov *et al.*, in prep.). Zircon and minute grains of uraninite (?) (≤10 μm) also were observed. Base-metal sulfide mineralization is rather abundant in places.

Within the xenolith, the unusual assemblage is intimately associated with a medium- to coarse-grained rock consisting predominantly of alkali feldspar (bulk composition  $Ab_{55.9-69.3}Or_{27.0-41.6}An_{1.1-3.7}$ ), the modal abundance of which is not uniform, but seems to exceed 75–80% on the whole. This rock may be regarded as an alkali-feldspar-rich variety of fenite. Platy phlogopite, subhedral to euhedral corundum, pyrrhotite (up to *ca.* 3–4 vol.%) and rutile are present in varying proportions. Monazite is a widespread accessory mineral. It is noteworthy that a graphite-like mineral (identified by X-ray powder diffraction) occurs in the xenolith, relatively close to the Ti-rich sulfide occurrence, as small spherules of less than 0.5 mm in diameter. This fenite xenolith may be an example of “contact fenite”, which may consist of almost monomineralic feldspar rock. Examples of the latter are known in the fenitized xenoliths in the Oldoinyo Lengai carbonatitic lavas (Morogan & Martin 1985).

The occurrence of titanium-rich sulfides seems to be a local feature of the Khibina xenolith. Electron-microprobe analyses of pyrrhotite and chalcopyrite from a related fine-grained nepheline-rich rock in the same xenolithic body do not show detectable concentrations of Ti and V.

## ELECTRON-MICROPROBE ANALYSES

Mineral compositions were determined using both wavelength-dispersion technique (WDS) and energy-dispersion technique (EDS). The WDS analyses

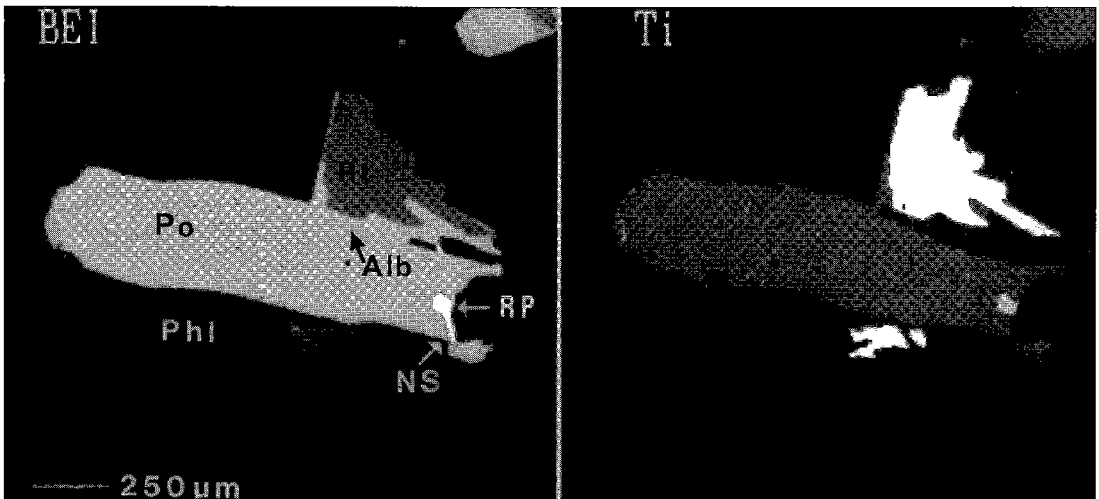


FIG. 1. Left: back-scattered electron image (BEI) showing a grain of the Ti-rich pyrrhotite (Po) associated with rutile (Rt), albandite (Alb), a REE phosphate (probably monazite) (RP), and the Nb-rich sulfide (NS). Phl: the host phlogopite. Right: X-ray scanning micrograph showing distribution of titanium in the pyrrhotite. Note that a bright spot at the margin of the pyrrhotite grain is due to interference between Ti and La in the REE phosphate. Scale bar: 250  $\mu\text{m}$ .

were carried out with a JEOL 733 Superprobe at the Institute of Electron Optics, University of Oulu, Finland, and a Cameca MS-46 electron microprobe at the Kola Science Centre, Russian Academy of Sciences, Apatity. Operating conditions at Oulu were 15 kV and 15 nA. The following X-ray lines and standards were used:  $SK\alpha$  (pyrite),  $VK\alpha$ ,  $FeK\alpha$ ,  $CrK\alpha$ ,  $NiK\alpha$ ,  $CoK\alpha$ ,  $MnK\alpha$ ,  $NbL\alpha$  (pure elements),  $TiK\alpha$  (rutile),  $SiK\alpha$ ,  $CaK\alpha$  (wollastonite),  $MgK\alpha$  (periclase),  $KK\alpha$  (orthoclase),  $NaK\alpha$  (jadeite),  $AlK\alpha$  (synthetic  $Al_2O_3$ ),  $FK\alpha$ ,  $BaL\alpha$  (synthetic  $BaF_2$ ) and  $ClK\alpha$  (synthetic KCl). At Apatity, analyses were made using an accelerating voltage of 22 kV and a beam current of 20 nA (for S, Ti, Fe, Si and Ba), 15 nA (for V, Co and Mn) and 40 nA for the other elements sought. The following lines and standards were used:  $SK\alpha$  (synthetic  $Fe_{10}S_{11}$  for base-metal sulfides; pyrite for Nb-rich sulfide),  $VK\alpha_1$ ,  $MnK\alpha_1$ ,  $NbL\alpha$  (pure elements),  $TiK\alpha_1$  (rutile or lorenzenite or both),  $FeK\alpha_1$  ( $Fe_{10}S_{11}$ ),  $SiK\alpha$  (diopside),  $MgK\alpha$  (forsterite),  $KK\alpha$  (wadeite),  $NaK\alpha$  (lorenzenite),  $AlK\alpha$  (pyrope) and  $BaL\alpha_1$  (barite). The raw data were ZAF-corrected.

For the Ti-V-bearing sulfides, interferences between  $TiK\beta$  and  $VK\alpha$  emission lines are taken into account, but the required corrections were found to be virtually insignificant, much lower than the minimum detection-limit for V.

The quantitative EDS analyses of the sulfides were carried out at the Institute of Electron Optics, University of Oulu, using a JEOL JSM-6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer. The analytical conditions were 15 kV and 1.2 nA; the K line was used in the analyses. Pyrite and pure metals were used as standards. The most finely focused

beam was applied. Counting periods were 100 seconds. The spectra were processed with an on-line Link ISIS (version 3.00) program. Standard deviations in the EDS analyses for both Ti and V are  $<0.1$  wt. %.

#### TITANIUM-BEARING SULFIDES

##### Pyrrhotite

Pyrrhotite forms relatively large (up to 4 mm in length) anhedral to subhedral discrete crystals, which may be associated closely with alkali feldspar, phlogopite (e.g., Fig. 1) and a hydrous (?) Na-Ca aluminosilicate. Since the Ti-bearing pyrrhotite commonly occurs as single, well-formed crystals (e.g., Fig. 2), that do not exhibit any replacement relations with a precursor mineral(s), it appears to represent the primary phase. Small ( $<0.1$  mm across) irregular grains of pyrrhotite, inhomogeneously distributed in the rock, also are not uncommon.

Initial electron-microprobe analyses showed that Ti could be an essential constituent of the Khibina pyrrhotite. The possible presence of Ti in impurities, e.g., as a result of submicroscopic inclusions of rutile, was taken into account, and a number of the grains in polished sections were carefully examined in reflected light, with back-scattered electron imaging and scanning-electron microscopy (at magnifications as high as 10,000 $\times$ ), but inclusions were not found. To test the analytical data with respect to Ti and V, pyrrhotite from the Salmagorsky alkaline ultramafic complex, Kola Peninsula, and from Sudbury, Ontario, was analyzed using the same analytical procedure. Both Ti and V contents of these samples were below the electron-microprobe detection limits. An

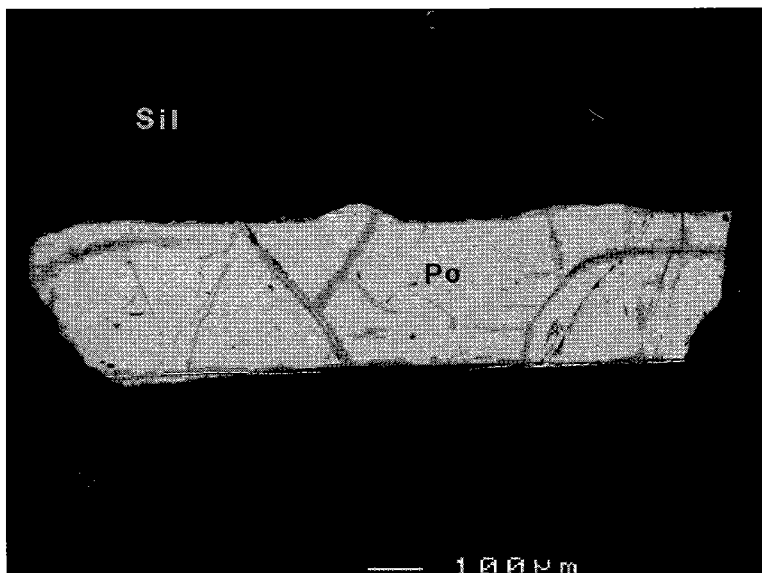


FIG. 2. A subhedral crystal of Ti-bearing pyrrhotite (Po) hosted by silicate (Sil). Back-scattered electron image. Scale bar: 100  $\mu$ m.

X-ray map showing the distribution of Ti in a large grain of pyrrhotite (Fig. 1) indicates homogeneity throughout the grain. More than fifteen individual grains of pyrrhotite, varying in shape (subhedral to irregular) and in size (from less than 0.1 mm to more than 1 mm in the longest dimension), were analyzed to characterize compositional variations. Depending on the grain size, from three to twelve point-analyses were performed for each grain. The results reveal that the individual grains are relatively homogeneous

TABLE 1. REPRESENTATIVE RESULTS OF (WDS) ELECTRON-MICROPROBE ANALYSES OF TITANIUM-RICH PYRRHOTITE FROM Khibina

	WEIGHT %					ATOMIC PROPORTIONS (S = 1)			
	Fe	Ti	V	S	SUM	Fe	Ti	V	$\Sigma M$
1*	57.43	1.80	0.32	38.34	97.89	0.860	0.031	0.005	0.896
2*	58.45	1.89	0.28	39.78	100.40	0.844	0.032	0.004	0.880
3*	58.32	1.93	0.25	38.90	99.40	0.861	0.033	0.004	0.898
4*	58.70	2.10	0.32	38.51	99.63	0.875	0.037	0.005	0.917
5*	56.75	2.93	0.33	39.54	99.55	0.824	0.050	0.005	0.879
6**	56.36	3.01	0.34	40.33	100.04	0.802	0.050	0.005	0.857
7*	56.59	3.08	0.37	40.69	100.73	0.799	0.051	0.006	0.856
8*	56.05	3.15	0.32	40.25	99.77	0.800	0.052	0.005	0.857
9*	56.11	3.28	0.24	40.34	99.97	0.799	0.054	0.004	0.857
10*	55.57	3.89	0.32	40.30	100.08	0.792	0.065	0.005	0.862

\* Analyses are listed in order of increasing Ti content; Ni, Co and Mn  $\leq$  0.1 wt. %.

\* JEOL - 733 electron microprobe; \*\* Cameca MS - 46 electron microprobe.

See text for analytical conditions.

with respect to Ti (and V), whereas there is an essential grain-to-grain variation in Ti, even on the scale of a polished section (Tables 1, 2). Results of the WDS and EDS electron-microprobe analyses are in agreement with each other. The maximum Ti content reaches as much as 3.9 wt.%. In addition to Ti, all the grains also exhibit remarkable

concentrations of vanadium, ranging from 0.2 to 0.4 wt.%. Within the rock sample with Ti-bearing pyrrhotite, neither Ti- nor V-free pyrrhotite grains were found. No correlation between Ti and V concentrations in the pyrrhotite was found. Figure 3 illustrates that the sum of Ti (+ V) has a rather strong negative correlation with Fe (correlation coefficient  $R = -0.86$ ,  $n = 63$ ). A stronger correlation can hardly be expected because of the variable stoichiometry of pyrrhotite. All these findings lead to the conclusion that Ti and V occur in solid solution in the Khibina pyrrhotite. Fe versus Ti (+ V) data for eight selected WDS data-sets define a regression line of  $y = -2.13x + 0.93$  for the Ti-bearing pyrrhotite.

TABLE 2. REPRESENTATIVE RESULTS OF (EDS) ELECTRON-MICROPROBE ANALYSES OF TITANIUM-RICH PYRRHOTITE FROM Khibina

	WEIGHT %				ATOMIC PROPORTIONS (S = 1)				
	Fe	Ti	V	S	SUM	Fe	Ti	V	$\Sigma M$
1	59.16	0.94	0.28	38.65	99.03	0.879	0.016	0.005	0.900
2	59.89	1.02	0.35	38.81	100.07	0.886	0.018	0.006	0.910
3	59.01	1.17	0.38	39.26	99.82	0.863	0.020	0.006	0.889
4	58.70	1.24	0.35	38.78	99.07	0.869	0.021	0.006	0.896
5	59.16	1.41	0.36	38.73	99.66	0.877	0.024	0.006	0.907
6	58.70	1.52	0.23	38.58	99.03	0.874	0.026	0.004	0.904
7	58.09	2.17	0.25	38.78	99.29	0.860	0.037	0.004	0.901
8	58.21	2.31	0.26	38.80	99.58	0.861	0.040	0.004	0.905
9	57.77	2.51	0.30	38.72	99.30	0.857	0.043	0.005	0.905
10	57.37	2.62	0.21	39.06	99.26	0.843	0.045	0.003	0.891
11	57.53	2.71	0.39	38.74	99.37	0.853	0.047	0.006	0.906
12	57.70	2.83	0.25	39.35	100.13	0.842	0.048	0.004	0.894
13	57.19	2.91	0.24	39.40	99.74	0.833	0.049	0.004	0.886
14	56.92	2.98	0.30	39.51	99.71	0.827	0.051	0.005	0.883
15	56.05	3.17	0.30	38.78	98.30	0.830	0.055	0.005	0.890

\* Analyses are listed in order of increasing Ti content. See text for analytical conditions.

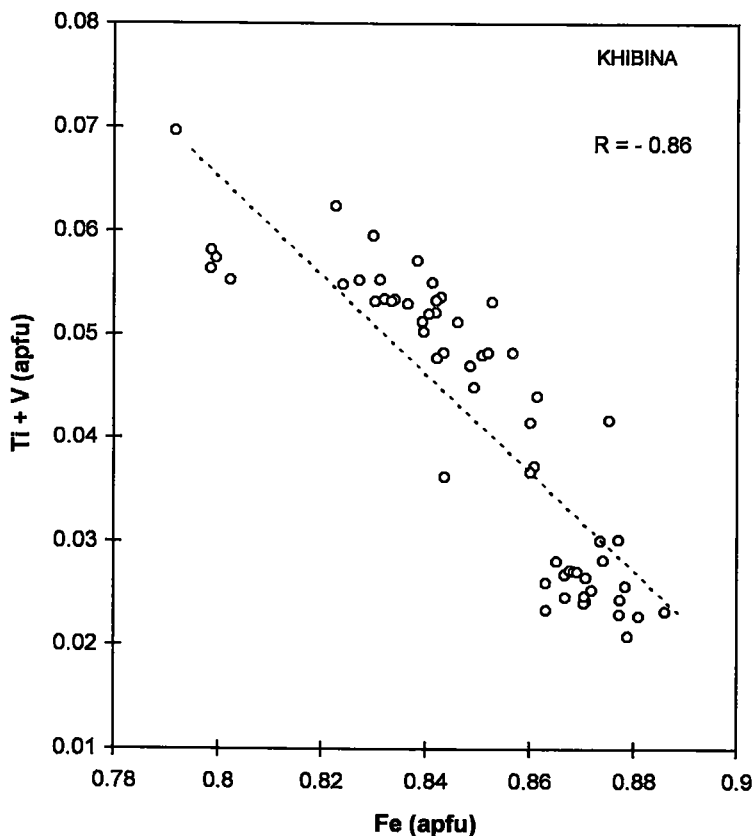


FIG. 3. A plot of concentrations of Fe versus Ti + V (atoms per formula unit, apfu; S = 1) for the Ti-(V)-bearing pyrrhotite from Khibina.

In view of a low Fe + Ti + V content (*ca.* 46 atom.%), the monoclinic structural form is considered likely for the metal-deficient Ti-bearing pyrrhotite from Khibina. Results of an X-ray powder-diffraction study of one of the pyrrhotite samples confirmed that it is monoclinic. It is of interest to note that Kissin & Scott (1972) reported a narrow range of compositions (46.5–47.0 atom.% Fe) for synthetic monoclinic pyrrhotite crystallized under hydrothermal conditions at 115°C. The titanium-bearing pyrrhotite with slightly higher  $\Sigma$ Met. contents (*ca.* 48 atom.%; Tables 1, 2) may represent a low-temperature polytype of (hexagonal?) pyrrhotite; this possibility should be tested with an X-ray study.

#### *Marcasite and pyrite*

An X-ray powder-diffraction study revealed that an alteration product of the Ti-bearing pyrrhotite contains mixtures of marcasite and pyrite. The individual veinlets are typically up to 0.05 mm across, but some pyrrhotite grains are extensively replaced by the marcasite–pyrite aggregate. The X-ray identification is consistent with the

electron-microprobe results and optical observations, showing a distinct anisotropy of some of the FeS<sub>2</sub> veinlets. However, the latter characteristic itself does not necessarily indicate marcasite, since anomalous anisotropy is known in pyrite. An example of the marcasite–pyrite veinlets cutting pyrrhotite is shown in Figure 4. In addition, some pyrrhotite grains have partly been replaced by marcasite and pyrite along the grain boundaries.

Results of electron-microprobe analyses (Table 3) indicate that marcasite and pyrite contain both Ti and V, similar to the host pyrrhotite. Several veinlets and grains, analyzed using the WDS and EDS methods, gave comparable concentrations of Ti (1.61–2.25 wt.%) and V (0.2–0.3 wt.%).

#### ASSOCIATED MINERALS

##### *Niobium-rich sulfide*

A new Nb–Fe sulfide mineral (edgarite; approved by the IMA Commission on New Minerals and Mineral Names) was found to be closely associated with Ti-bearing pyrrhotite,

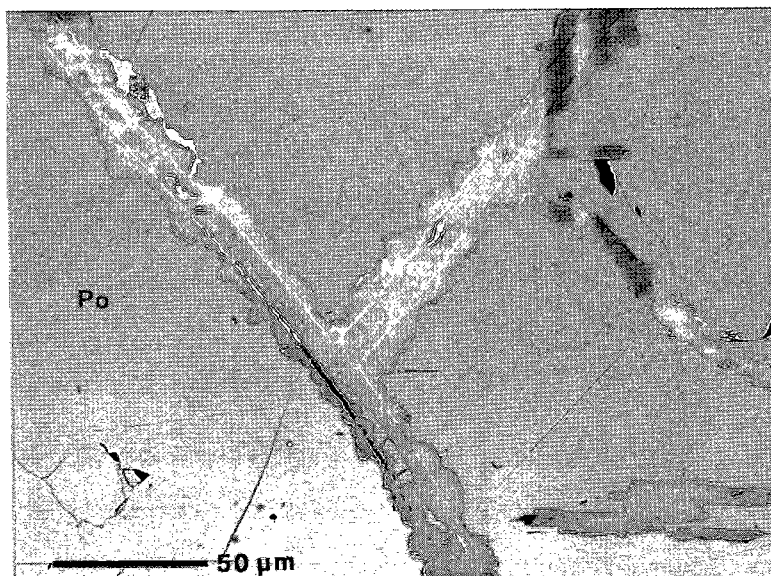


FIG. 4. Veinlets of the Ti-bearing pyrite or marcasite (Mrc) (or both) oriented along fractures in pyrrhotite (Po). Back-scattered electron image. Scale bar: 50  $\mu\text{m}$ . Magnification of a part of Figure 2.

TABLE 3. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF TI-BEARING PYRITE OR MARCASITE (OR BOTH) FROM Khibina

	WEIGHT %				SUM	ATOMIC PROPORTIONS ( $\Sigma \text{atoms} = 3$ )				
	Fe	Ti	V	S		Fe	Ti	V	ZM	S
<i>WDS analyses</i>										
1*	45.80	2.03	0.26	52.70	100.79	0.980	0.051	0.006	1.037	1.963
2*	46.42	1.92	0.20	52.54	101.08	0.992	0.048	0.005	1.045	1.955
3**	44.16	2.25	0.26	50.51	97.18	0.981	0.058	0.006	1.045	1.954
<i>EDS analyses</i>										
4	45.32	1.61	0.30	51.19	98.42	0.995	0.041	0.007	1.043	1.957
5	45.09	2.03	0.20	50.62	97.94	0.996	0.052	0.005	1.053	1.947

\* JEOL-733 electron microprobe; \*\* Cameca MS-46 electron microprobe. Ca, Ni and Mn < 0.1 wt%. See text for analytical conditions.

alabandite and monazite. The mineral forms platy crystals typically located at the margin of the pyrrhotite grains (*e.g.*, Fig. 5) and, more rarely, enclosed within pyrrhotite or alabandite. It has also been observed to fill a fracture in pyrrhotite, indicating relatively late crystallization. In addition, the sulfide was encountered as intergrowths with both alabandite and a rare-earth-element phosphate, probably monazite. The individual crystals of the Nb-rich sulfide typically attain 0.15 mm in length, but masses of plate-like grains may reach more than 0.5 mm across. Results of electron-microprobe analyses of the Nb-Fe sulfide are presented in Table 4. The compositions correspond well to an ideal formula  $\text{FeNb}_3\text{S}_6$ , suggesting that the new mineral represents the natural equivalent of a synthetic  $\text{FeNb}_3\text{S}_6$  phase reported by van den Berg & Cossee (1968). A more detailed description of the Nb-rich sulfide will be given separately.

### Monazite

Relatively large grains (up to 3 mm across) of a member of the monazite group have been identified by X-ray powder diffraction. No detailed electron-microprobe study of monazite was carried out, but some partial WDS and EDS analyses, performed on three grains ( $\leq 0.1$  mm), suggest that this is monazite-(Ce), with significant concentrations of La and Nd.

### Nb-Zr-bearing rutile

Rutile is present as abundant anhedral grains ranging from *ca.* 20  $\mu\text{m}$  to more than 0.5 mm in their longest dimensions. Electron-microprobe data show that rutile is a Nb-bearing phase, but its Nb content is relatively low (up to 2.5 wt.%  $\text{Nb}_2\text{O}_5$ ). For comparison, the  $\text{Nb}_2\text{O}_5$  content of rutile from kimberlite can be up to 20.9 wt.% (Tollo & Haggerty 1987). The sample of rutile analyzed (JEOL 733 microprobe) contains up to *ca.* 1.2 wt.%  $\text{ZrO}_2$ .

### Alabandite

Typically, alabandite appears as relatively rare grains reaching about 0.3 mm in the longest dimension (Fig. 6). Larger grains (>1 mm), identified by X-ray powder diffraction, also are present. Electron-microprobe analyses yield a restricted range of Fe concentrations in the alabandite from Khibina (Table 5). The compositions are characteristically very close to stoichiometric (Mn,Fe)S.

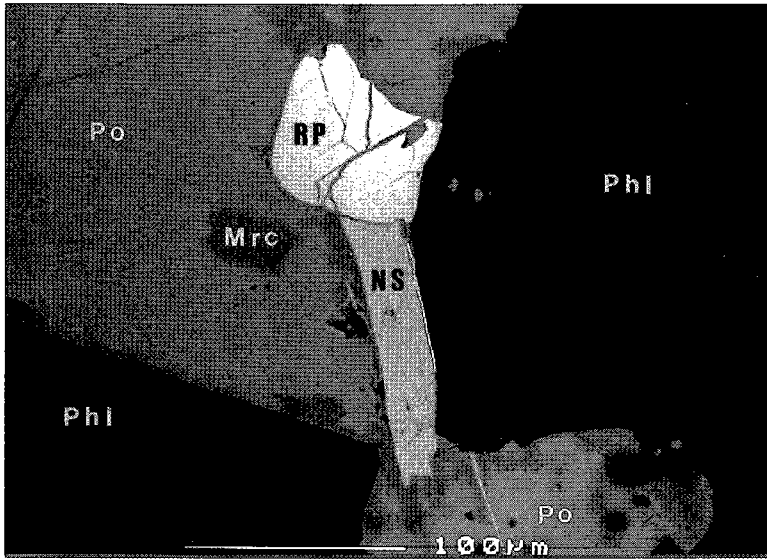


FIG. 5. A platy crystal of the Nb-rich sulfide (NS) intergrown with a REE phosphate (RP) at the boundary between pyrrhotite (Po) and phlogopite (Phi). Mrc: marcasite or pyrite. Back-scattered electron image. Scale bar: 100  $\mu\text{m}$ .

TABLE 4. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF NIOBIUM-RICH SULFIDE FROM Khibina.

	WEIGHT %		FORMULA ( $\Sigma$ atoms = 10)	
	1*	2**	1*	2**
Nb	54.10	52.33	Fe	0.896
Fe	9.48	10.21	V	0.040
V	0.39	0.41	Ti	0.007
Ti	0.06	0.04	Mn	0.008
Mn	0.08	0.13	$\Sigma$	0.951
S	36.30	36.70	Nb	3.074
Total	100.41	99.82	S	5.976

\* JEOL-733 electron microprobe; \*\* JEOL-8600 electron microprobe; courtesy A.D. Edgar and Y. Thibault, University of Western Ontario.

Alabandite was not known to occur in the Kola Peninsula, but was reported from some other localities in the Fennoscandian Shield (Zakrzewski 1980, Törnroos 1982).

#### PHLOGOPITE END-MEMBER

Phlogopite occurs as platelets and subhedral to euhedral platy crystals ranging from <2 to about 4 mm in diameter. Megascopically, the mineral is characteristically greenish blue to blue in color. The unusual composition of this phlogopite is particularly illustrated by its depletion in Fe (*i.e.*, reflecting a strong enrichment in Mg) and high concentrations of fluorine (Table 6). The concentration of Fe was typically at the minimum detection-limit of the microprobe ( $\leq 0.04$  wt.% FeO), but in several point-analyses, Fe was below the detection limit. In addition, the phlogopite is characterized by Si + Al > 8, and rather elevated  $^{VI}Al$

content, expressed by the eastonite end-member. It is poor in TiO<sub>2</sub>, similar to primary phlogopite from peridotite xenoliths and kimberlites (*e.g.*, Carswell 1975, Delaney *et al.* 1980, Arima & Edgar 1981). Another noteworthy compositional feature of the phlogopite in the Khibina samples is its relative enrichment in Ba.

Typically, high-Mg phlogopite reflects the ultramafic nature of its host rocks. Mg-rich members of the phlogopite-annite series are known to occur in various geological environments, including, in addition to peridotite xenoliths and kimberlites, ultramafic cumulates of layered intrusions (*e.g.*, Alapieti 1982), ultramafic rocks associated with the alkaline ultramafic complexes (*e.g.*, Kukharencov *et al.* 1965), lamproites (*e.g.*, Mitchell *et al.* 1987), lamprophyres (*e.g.*, Rock 1991), marbles (*e.g.*, Bol *et al.* 1989), skarns (*e.g.*, Alietti *et al.* 1995), carbonatites (*e.g.*, Gaspar & Wyllie 1987, McCormick & Le Bas 1996) and some sapphirine-bearing rocks (*e.g.*, Williams 1984).

Since the content of Fe in the phlogopite in this suite may be lower than the detection limit of the microprobe, the mica represents the phlogopite end-member. Iron-poor phlogopite (0.11 wt.% FeO), close to the phlogopite end-member, has recently been reported by Chabu (1995) from a Zn-Pb-Cu deposit in the Democratic Republic of Congo. Like the Khibina material, the latter sample and that with 0.3 wt.% FeO cited in Deer *et al.* (1962) are extremely rich in fluorine (5.6 and 6.7 wt.% F, respectively). Very high concentrations of F in the Khibina phlogopite also are comparable with those in phlogopite from lamproite and kamafugite (Edgar & Charbonneau 1991, Edgar *et al.* 1994). Interestingly, phlogopite without Fe was identified in blast-furnace slags (Wearing 1984).

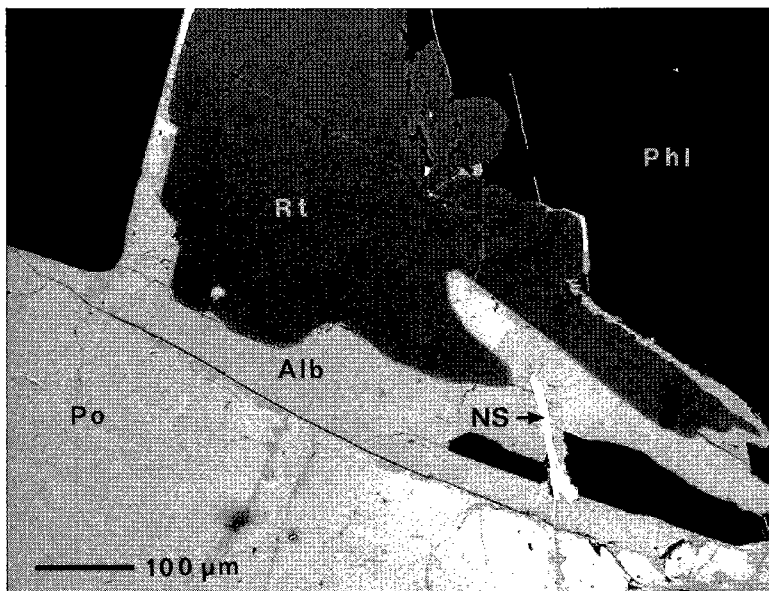


FIG. 6. An irregular grain of alabandite (Alb) associated with pyrrhotite (Po) and rutile (Rt). Note a platelet of the Nb-rich sulfide (NS) enclosed within alabandite. Phl: phlogopite. Back-scattered electron image; see Figure 1 for location. Scale bar: 100  $\mu\text{m}$ .

TABLE 5. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES\* OF ALABANDITE FROM Khibina

	WEIGHT %				FORMULA ( $\Sigma$ atoms = 2)		
	1	2	3		1	2	3
Mn	56.01	55.38	55.24	Mn	0.896	0.889	0.878
Fe	6.42	7.70	7.20	Fe	0.101	0.122	0.113
S	36.61	35.94	37.09	$\Sigma$	0.997	1.011	0.991
SUM	99.04	99.02	99.53	S	1.003	0.989	1.010

\* JEOL-733 electron microprobe. See text for analytical conditions. Mg was sought, but not detected.

## DISCUSSION

As a rule, pyrrhotite contains only small amounts of elements other than Fe and S (*e.g.*, Arnold 1967, Vaughan & Craig 1978, Kelly & Vaughan 1983, Campbell & Ethier 1984, Cabri *et al.* 1984, Stanley *et al.* 1987, Harney & Merkle 1992). These elements are typically Ni, Co, Mn and Cu. According to the maximum minor-element contents cited by Vaughan & Craig (1978), marcasite may contain up to 80 ppm Ti and 200 ppm V, and pyrrhotite may contain up to 1250 ppm V. No titanium was reported in pyrrhotite by these authors. In common with pyrrhotite, typical minor elements in pyrite are Ni and Co. Recently, essential ruthenium (up to 12 wt.% Ru) has been revealed in members of the pyrite-laurite series (Barkov *et al.* 1997).

The results presented in this paper indicate that Ti and, to a lesser extent, V can be incorporated in significant quantities in structures of pyrrhotite, marcasite and pyrite, and the maximum Ti and V concentrations in the pyrrhotite can reach approximately 4 and 0.4 wt.%, respectively.

The presence of both Ti-rich and Ti-free base-metal sulfides in the Khibina xenolith indicates that the Ti-(V)-rich sulfides have formed under particular (local) environmental conditions. No other terrestrial occurrences of Ti-enriched sulfides have so far been reported, and the only related occurrences (*i.e.*, Ti-bearing troilite) are known in meteorites (Keil & Andersen 1965, Keil 1968). Therefore, a certain environmental similarity appears to exist between the Khibina and meteoritic occurrences. In addition to the Ti-bearing sulfides, the probable similarity also is implied by the presence of ferroan alabandite and highly "unusual" sulfides, such as  $\text{FeCr}_2\text{S}_4$  (daubreelite) in chondrites and  $\text{FeNb}_3\text{S}_6$  (edgarite) in the fenite, as well

TABLE 6. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF END-MEMBER PHLOGOPITE FROM Khibina

Wt.%			IONIC FORMULAE: 24 (X, Y, Z)		
$\text{SiO}_2$	38.18	38.91	Si	5.61	5.63
$\text{TiO}_2$	0.68	0.66	Al(IV)	2.39	2.35
$\text{Al}_2\text{O}_3$	15.10	15.17	$\Sigma$	8	8
FeO	0.04	n.d.	Al(VI)	0.22	0.25
MgO	25.83	26.05	Ti(VI)	0.08	0.07
BaO	1.58	1.35	$\text{Fe}^{2+}$	0.005	-
$\text{Na}_2\text{O}$	0.31	0.29	Mg	5.66	5.64
$\text{K}_2\text{O}$	9.71	9.61	$\Sigma$	5.965	5.96
F	5.96	6.30	Ba	0.09	0.08
O = F	2.51	2.65	Na	0.09	0.08
SUM	94.88	95.69	K	1.82	1.78
			$\Sigma$	2.00	1.94
			F	2.77	2.895

JEOL-733 electron microprobe. Ca, Mn, Cr, V, Ni and Cl were sought, but not detected. All Fe is expressed as FeO; n.d.: not detected.



as graphite and the graphite-like phase in the vicinity of the Ti-bearing sulfide occurrence in Khibina.

Meteoritic troilite contains from 0.2 to 1.0 wt. % Ti; in general, the concentrations of Ti are somewhat lower in troilite of type-I than in troilite of type-II enstatite chondrites [see Keil (1968) for details]. However, the observed differences in the average Ti contents are rather minor (type I: 0.38 wt. % Ti versus type II: 0.65 wt. % Ti), whereas the reported ranges are nearly identical (type I: 0.20–0.93 wt. % Ti versus type II: 0.23–1.04 wt. % Ti). Although Keil did not report vanadium in the troilite, this element also is present (S.A. Kissin, pers. comm.). Unlike the Khibina pyrrhotite, meteoritic troilite invariably contains essential chromium (0.5–3.4 wt. % Cr). Keil (1968) suggested that textural and mineralogical differences between the two types of chondrite may have resulted from different cooling histories: type-I chondrites may have cooled quickly to temperatures low enough to prevent extensive solid-state diffusion and recrystallization, whereas type-II chondrites may have cooled more slowly. In the latter case, rates of solid-state diffusion were sufficiently high that extensive recrystallization and equilibration took place. An alternative discussed in Keil (1968) is that type-II enstatite chondrites originated from those of type I by reheating. During reheating, along with other chemical and textural changes, troilite of type-II chondrites may have become relatively enriched in titanium.

The occurrence of Ti in solid solution in the meteoritic troilite, as well as the chalcophile behavior of other typically lithophile elements (Cr, Mn, Mg and Ca), are attributed to highly reducing conditions in the meteorites (Keil & Andersen 1965). It is of interest to note that the chalcophile behavior of Nb, revealed in the Khibina xenolith, is unknown in meteorites.

Apart from the Ti-rich oxide zone, at least locally and in certain stages of crystallization, moderately to highly reducing environments also appear to have existed during recrystallization of the Khibina xenolith. Obviously, similar reducing environments also were characteristic for the other related xenolithic bodies, as native iron is observed as a quite abundant phase within another xenolith in the complex (Men'shikov, unpubl. data). However, the extent of reduction may have varied not only in different bodies, but also through a single xenolith containing Ti-rich sulfide minerals. The highest degree of reduction may well be reflected in the association of the Ti–V-rich sulfides and niobium-rich sulfide (edgarite is not observed in the Ti-poor pyrrhotite occurrence) and in the presence of alabandite. The highly reducing conditions, rather than equilibration at different temperatures or a particular cooling history, could be the most significant factor to explain the Ti-rich sulfides associated with the Nb-rich sulfide in the Khibina complex. This conclusion is supported by the occurrence of vanadium sulfide, patronite (VS<sub>4</sub>) in a bituminous ore deposit in Peru (Baumann 1964).

The mechanism of incorporation of Ti into the structure of the Ti-rich sulfides at Khibina remains unknown. As

Ti in terrestrial minerals is normally tetravalent, the simple heterovalent substitution  $2\text{Fe}^{2+} = \text{Ti}^{4+} (\text{V}^{4+}) + \square$  can be suggested. The very small differences, if any, between ionic radii of Fe<sup>2+</sup> (0.69 Å), Ti<sup>4+</sup> (0.69 Å) and V<sup>4+</sup> (0.67 Å), considered for the same coordination number (Whittaker & Muntus 1970), are in agreement with the proposal. An alternative is the incorporation of Ti<sup>3+</sup> (and V<sup>3+</sup>):  $3\text{Fe}^{2+} = 2\text{Ti}^{3+}$  (or  $\text{V}^{3+}$ ) +  $\square$ . The relevant radii are: Ti<sup>3+</sup> 0.75 Å, V<sup>3+</sup> 0.72 Å, and Fe<sup>2+</sup> 0.69 Å (Whittaker & Muntus 1970). The presence of Ti<sup>3+</sup> seems to be a viable alternative, as considerable trivalent Ti has been shown to enter Ca-rich pyroxene in a meteorite (Dowty & Clark 1973). A detailed study is required to test one of these possibilities.

On the basis of the experimentally determined upper stability limit of monoclinic pyrrhotite, its primary formation is restricted to temperatures below 254°C (Kissin & Scott 1982). Although the presence of Ti and V may influence this limit to some degree, a relatively low-temperature crystallization can be suggested for the Khibina Ti-rich monoclinic pyrrhotite.

From a genetic point of view, the presence of the phlogopite end-member in the Mg-poor fenite at Khibina is quite unusual. Although petrographic observations do not provide exact data on the timing of phlogopite formation, its early crystallization prior to (or with) the alkali feldspar can hardly be expected. It could be instead a late-crystallizing mineral, formed from a fluid phase, after the associated feldspar. This suggestion is consistent with evidence that phlogopite can be formed at low-temperature hydrothermal conditions (Belkin *et al.* 1988). It is known that the phlogopite chemistry is affected by variations in temperature, pressure, oxygen fugacity, bulk-rock chemistry and fluid composition. Foley (1990) concluded that fluid composition may exert much greater control on chemistry of the phlogopite in lamproitic rocks than do either pressure–temperature variations or bulk composition of the host rock. The Khibina phlogopite is rather poor in Ti and rich in Al (Table 6). In general, Ti in phlogopite increases with decreasing pressure and increasing temperature (Edgar *et al.* 1976, Robert 1976a, Tronnes *et al.* 1985, Foley 1990). Robert (1976b) concluded that the Al content of phlogopite decreases with increasing temperature, and this feature is a peculiar property of phlogopite. In addition, the Al content also depends on the H<sub>2</sub>O concentration in the mineral-forming environment. Mica crystallized in H<sub>2</sub>O-rich experimental environments contains considerably higher levels of Al than mica in experiments with less H<sub>2</sub>O (Foley 1990). The behavior of Al during crystallization of phlogopite appears to be a function of the bulk-rock Al content (Foley 1989). Finally, like the other examples of exceedingly Fe-poor phlogopite in the literature (Deer *et al.* 1962, Chabu 1995), the end-member phlogopite is strongly enriched in fluorine (Table 6) at Khibina. These examples are in good agreement with the corollary of the so-called Fe–F avoidance rule.

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