FIBROUS FOITITE FROM ŞEBİNKARAHISAR, GİRESUN Pb–Zn–Cu–(U) MINERALIZED AREA, NORTHERN TURKEY

FUAT YAVUZ
İstanbul Teknik Üniversitesi, Maden Fakültesi, Maden Yataklaeri-Jeokimya Anabilim Dalı, 80670, Maslak, İstanbul, Turkey

MUAZZEZ ÇELİK AND NECATİ KARAKAYA
Selçuk Üniversitesi, Mühendislik Mimarlık Fakültesi, Jeoloji Mühendisliği Bölümü, Mineraloji-Petrografi Anabilim Dalı, 42250, Konya, Turkey

ABSTRACT

Fibrous foitite occurs in cavities in quartz veins near Şebinkarahisar town, Giresun mineralized area [Pb–Zn–Cu–(U)], in northern Turkey. Veins of quartz + fibrous tourmaline generally cut monzonitic and syenitic rocks. Acicular and hairlike light gray crystals of foitite have a mean composition of \(\text{Na}_0\text{Ca}_0\text{Si}_0\text{Al}_0\text{Si}_6\text{O}_{18}\text{OH}_3\text{O}_3\text{H}_2\text{O}\). The crystals of this low-temperature tourmaline radiate from irregular patches of schorl in cavities in quartz veins. Each fiber is zoned along its length with respect to Fe, Mn, Mg, Ca, Na, K, and P. The fibrous foitite from the Şebinkarahisar area contains higher Mg, Ca and Na contents than that from southern California and Elba.

Keywords: foitite, tourmaline, fibers, alkali-deficient, cavity, quartz vein, Pb–Zn–Cu–(U) mineralization, Şebinkarahisar, northern Turkey.

Sommaire

On trouve des cristaux fibreux de foitite dans des cavités des veines de quartz près de Şebinkarahisar, zone minéralisée de Giresun [Pb–Zn–Cu–(U)], dans le nord de la Turquie. Les veines de quartz + tourmaline fibreuse recoupent en général des roches monzonitiques ou syénitiques. Les cristaux aciculaires et capillaires gris pâle de foitite ont une composition moyenne de \(\text{Na}_0\text{Ca}_0\text{Si}_0\text{Al}_0\text{Si}_6\text{O}_{18}\text{OH}_3\text{O}_3\text{H}_2\text{O}\). Il s’agit d’une tourmaline de basse température en amas fibro-radiés développés sur des taches irrégulières de schorl le long des parois de cavités dans des veines de quartz. Chaque fibre est zonée le long de la fibre par rapport à sa teneur en Fe, Mn, Mg, Ca, Na, K, et P. Les échantillons de foitite fibreuse provenant de Şebinkarahisar contiennent plus de Mg, Ca et Na que les exemples connus du sud de la Californie et de l’île d’Elbe.

Mots-clés: foitite, tourmaline, fibres, déficit en alcalins, cavité, veine de quartz, minéralisation en Pb–Zn–Cu–(U), Şebinkarahisar, Turquie.

INTRODUCTION

Tourmaline presents a complex chemical spectrum owing to its extensive substitutions at the \(X\), \(Y\), and \(Z\) sites. The general formula of tourmaline is given as \(X\text{Y}_3\text{Z}_6\text{(BO)}_3\text{Si}_6\text{O}_{18}\text{(OH,F,Cl,O)}\), where \(X = \text{Na}^+, \text{Ca}^{2+}, \text{K}^+, \text{Na}_0\text{Ca}_0\), \(Y = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Al}^{3+}, \text{Fe}^{3+}, \text{Mn}^{3+}, \text{Cr}^{3+}, \text{Li}^+, \text{Z} = \text{Al}^{3+}, \text{Mg}^{2+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}\). Alkali-deficient tourmaline is characterized by the predominance of vacancies at the \(X\) site (i.e., \(0 \leq X_{\text{total}} < 0.5\)). It seems that foitite is more common, but less strongly alkali-deficient, in ore-related environments than in pegmatite and aplite dikes (Foit et al. 1989).

Fibrous foitite was first described by Foit et al. (1989) as schorl with dumortierite in hydrothermally altered tuffs at Jack Creek, Jefferson County, Montana. Alkali-deficient tourmaline in this area occurs as irregular fibrous patches and cavity fillings in dumortierite-enriched rocks. MacDonald et al. (1993) described the highly alkali-deficient tourmaline (i.e., \(X_{\text{total}} = 0.26\)) as

E-mail address: yavuz@sariyer.cc.itu.edu.tr
foitite, and proposed the ideal composition \[ \text{Fe}^{2+} \left(\text{Al}, \text{Fe}^{3+}\right) \text{Al}_6 \text{Si}_4 \text{O}_{16} (\text{BO}_3)_4 (\text{OH})_4 \] from an unknown locality in southern California. Pezzotta et al. (1996) defined a second occurrence of fibrous foitite from a complex pegmatite dike at San Piero in Campo, Elba, Italy.

In this study, we report on the occurrence of foitite from Şebinkarahisar, near the Giresun Pb-Zn-Cu-(U) mineralized area, in northern Turkey. The area investigated shows signs of widespread formation of tourmaline, hydrothermal alteration, Pb-Zn-Cu mineralization and, to a lesser extent, high-background radioactive anomalies of up to 40 ppm uranium (Çalapktulu 1982). Foitite from this area occurs as fragile acicular and hairlike crystals in cavities in quartz veins cutting Upper Cretaceous to Paleocene monzonitic plutonic rocks. We document here the mode of occurrence of the fibrous foitite and its compositional variations in relation to environment of mineralization.

**MODE OF OCCURRENCE**

The Asarck plutonic rocks outcrop about 20 km north of the town of Şebinkarahisar, Giresun, in the eastern part of the Pontide metallogenic belt, in northern Turkey. The rocks in the study area range from alkali granite to diorite, but syenite, quartz syenite, monzonite, quartz monzonite, rhyolite, rhyodacite, and trachyandesite are dominant. In the study area, these rocks were separated into two groups, the lower and upper series (Çalapktulu 1982). The upper series is mainly composed of dacite, andesite, basilat and related tuffs and pyroclastic units. The lower series contains calc-alkaline igneous rocks and interbedded sedimentary units. The upper series and part of the lower series are characterized by intensive formation of tourmaline, hydrothermal alteration and Pb-Zn-Cu mineralization. K-Ar age determinations by Oyman et al. (1995) on orthoclase, biotite and hornblende from the Asarck suite and surrounding magmatic rocks indicate a time interval from Upper Cretaceous to Upper Paleocene (i.e., 82.4 to 58.3 Ma). Monzonite, quartz monzonite and quartz syenite is cut by later quartz veins (1 to 15 cm) and aplite dikes up to 5 cm in thickness. These quartz veins contain cavities up to 2 cm across and about 1 cm in depth, especially around the Asarck region. Black schorl, about 0.5 cm thick, rims these cavities. The light gray acicular and hairlike fibrous tourmaline crystals project inward from the schorl rim (Fig. 1). Pezzotta et al. (1996) pointed out that fibrous foitite from Elba only develops as an overgrowth on the analogous end of the tourmaline crystals. According to their study, the analogous end of crystals is composed mainly of coarse-grained schorl-elbaite. In terms of their physical appearance, our samples of fibrous foitite from Şebinkarahisar show a great similarity to that at Elba except for the absence of dark brown analogous schorl-elbaite ends. Figure 2a shows a SEM (scanning electron microscopy) low-magnification view of a miarolitic cavity in a quartz vein. In this figure, the acicular and hairlike crystals radiate from the irregular patches of schorl in the foreground. A higher-magnification view of these acicular and hairlike crystals of fibrous tourmaline is shown in Figures 2b, c. Accessory minerals in the foitite-bearing quartz veins are K-feldspar, chrysoprase and hematite. Hematite is characteristic of an oxidized environment. Its presence may suggest Fe\(^{3+}\) in the structure of the coexisting tourmaline.

**CHEMICAL COMPOSITION**

Fibrous foitite-bearing samples in cavities of quartz veins were first cut into small sections for electron-microprobe determinations. In order to remove the dust and other impurities on fibrous tourmaline crystals, they were placed in an ultrasonic cleaner for a short time and then were carbon-coated for electron-microprobe studies. Microprobe analyses of samples were obtained by wavelength-dispersion spectrometry (WDS) at the laboratory of Metallurgy Engineering, Istanbul Technical University. A JEOL JSM-840 scanning microscope was used at 15 kV accelerating voltage, a beam current of 15 nA, a beam diameter of 5 μm, and a ZAF correction scheme. Representative electron-microprobe chemical data describing the fibrous tourmaline are given in Table 1. The TOURMAL software package (Yavuz 1997) was used for calculation and preparation of diagrams.

The mean chemical composition of the foitite is different than those described by MacDonald et al. (1993) and Pezzotta et al. (1996). The manganese contents of our tourmaline samples are low (0.18–1.32 wt.% MnO),

![Fig. 1. Sketch of fibrous foitite samples in cavities in a quartz vein from Şebinkarahisar, Giresun, northern Turkey.](image)
TABLE 1. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF ALKALI-DEFICIENT TOURMALINE (FOITITE) FROM ŞEKİNBAKARHAŞIR, GİRESUN, NORTHERN TURKEY

<table>
<thead>
<tr>
<th>FOITITE FROM THE GIRESUN MINERALIZED AREA, TURKEY</th>
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<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.64-35.53</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.96-33.30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00-0.08</td>
</tr>
<tr>
<td>FeO</td>
<td>11.96-11.53</td>
</tr>
<tr>
<td>MgO</td>
<td>0.85-0.47</td>
</tr>
<tr>
<td>CaO</td>
<td>0.52-0.32</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.52-1.55</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00-0.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.00-0.00</td>
</tr>
<tr>
<td>Total</td>
<td>85.01-85.15</td>
</tr>
</tbody>
</table>

The chemical composition of foitite fibers is given in Figure 4 in terms of R₁+R₂ versus R₃. This plot indicates that the composition of the tourmaline corresponds to the ideal alkali-deficient substitution proposed by Foit & Rosenberg (1977). The chemical spectrum of foitite samples shows an important resemblance to the tourmaline from the association of several polymetallic and uranium-bearing deposits in volcanic rocks (Fuchs & Maury 1995). The mean composition of other examples of alkali-deficient tourmaline is given on this figure for comparison.
The distribution of foitite compositions on a diagram of Fe versus Mg shows a great similarity in terms of the schorl trend (Fig. 5). The slope of the foitite vector, however, is lower than the schorl trend, possibly because of the lower iron content of foitite. All the chemical data for the foitite fall within the schorl quadrant, with Fe > Mg and Na > Ca (Fig. 6).

**Fig. 2.** Scanning electron microphotographs of foitite from Sebinkarahisar, Giresun. (a) Low-magnification image of several fibrous patches developed in a cavity in a quartz vein. (b, c) High-magnification images of acicular foitite fibers.

**Fig. 3.** Sketch of compositional zoning of a single sample of fibrous foitite.

**Fig. 4.** Plot of electron-microprobe data on the $R_1 + R_2$ versus $R_3$ diagram. Shaded area: fibrous tourmaline composition of Sebinkarahisar area, filled box: mean composition of foitite from southern California (MacDonald et al. 1993), filled diamond: mean composition of fibrous foitite from Filone della Speranza, Elba (Pezzotta et al. 1996), filled triangle: mean composition of alkali-deficient schorl from Jack Creek, Montana (Foit et al. 1989), filled circle: mean composition of alkali-deficient schorl from Ben Lomond, Australia (Foit et al. 1989), cross: mean composition of alkali-deficient tourmaline from Sullivan, British Columbia (Jiang et al. 1997).
The schorl rim surrounding the cavities in the quartz veins has a composition similar to that of the fibrous foitite, except for slightly higher Fe and Ca contents. The chemical composition of a fiber in Figure 3 also is included in Figure 6 to document the compositional trend. It is clear from this figure that the starting composition of the solution was Mg-rich. Depending on the increasing fractionation, ore-related solutions were enriched in iron and thus the chemical composition shifted from the dravite to the schorl end member.

The chemical make-up of the X site is shown in a plot in terms of Na–Ca–☐ (Fig. 7a). The chemical variation is between the Na and vacancy (i.e., ☐), with slight increase toward the Na component. In terms of the Fe–Mg–Al diagram (Henry & Guidotti 1985), the compositions of fibrous tourmaline from the Sebinkarahisar area plot in field 2 (Fig. 7b), and correspond to tourmaline from Li-poor granites and their associated pegmatites and aplites. The compositional variation of
fibrous foitite from the Sheinkarahisar area is very similar to those of the alkali-deficient schorl from Jack Creek, Montana and Ben Lomond, Australia (Foit et al. 1989, Foit 1989).

Using the increasing fractionation versus atomic fraction diagram (Jolliff et al. 1986), we have observed that among the elements Fe, Mg, Mn, and Ti, Fe and Mg are good indicators of progressive crystallization of foitite compositions (Fig. 8). With increasing fractionation, Mn reaches its maximum and then diminishes as the temperature falls during crystallization. This inference is in agreement with the schematic ideal sequence of crystallization proposed by Jolliff et al. (1986). The chemical composition of the foitite fiber in Figure 3 indicates that Mn increases during its crystallization. On the other hand, in a plot of all data on atomic fraction versus Fe + Mg diagram (Fig. 8), Mn does not show a clear trend compared those of the Fe and Mg. It makes a distribution similar to parabola, with a peak corresponding to 2.2 Mg + Fe. The different behavior of Mn from Sheinkarahisar area may be used as an index to the crystallization history of foitite in relation to mineralized systems. This conclusion, however, must be checked in further studies of foitite specifically taken from mineralized environments.

The chemical compositions of the foitite samples from Sheinkarahisar are shown on plots of Na** + Mg** versus □ + Al_y and Ca_x + Mg** versus Na** + Al_y diagrams (Figs. 9a, b), where Mg** = Mg + Fe + Mn, Na** = Na + K, □ = X-site vacancy. These compositions are characterized by approximately negative linear regression lines, showing the major chemical substitutions: Na_x + (Fe,Mg)_y = □_x + Al_y and Ca_x + (Fe,Mg)_y = Na_x + Al_y. These chemical substitutions are of almost identical to those in the alkali-deficient tourmaline from the Sullivan Pb-Zn-Ag deposit, British Columbia, as given by Jiang et al. (1997).

**Discussion**

The study area is located in the eastern part of Pontide metallogenic belt, which includes abundant Pb-Zn-Cu mineralization. The area produced small- to medium-scale polymetallic mineral deposits. The Asarck region (Sheinkarahisar, Giresun) was investigated in detail by several researchers because of high background of radioactive anomalies in the magmatic rocks (Çalapku 1982). The Pb-Zn-Cu mineralized veins in Upper Cretaceous to Upper Paleocene granitic rocks and E-W- and NE-SW-trending normal faults generally control the emplacement of volcanic rocks. Galena, sphalerite, chalcopyrite, pyrite, arsenopyrite,
and tetrahedrite constitute the main ore minerals. The associated gangue minerals are quartz, barite, and calcite (Çalapku 1982). The chemical composition of black tourmaline in the Sebinkarahisar Pb-Zn-Cu mineralized area varies from dravite to schorl end-members. Tourmaline in monzonite and syenite tend to be schorl, whereas black tourmaline associated with Pb-Zn-Cu mineralization in quartz veins approaches dravite (work in progress).

Although the chemical compositions of southern California and Elba foitite samples are similar to ours, their macroscopic appearances and physical properties are different (MacDonald et al. 1993, Pezzotta et al. 1996). The fibrous foitite described here shows a great similarity in terms of rock composition, physical appearance and mode of occurrence to the fibrous foitite described by Pezzotta et al. (1996). Its chemical composition, however, presents an important distinction, especially with respect to the Mn, Mg, Ca, and Na contents. The chemical distinction between the fibrous foitite from Sebinkarahisar and that from Elba possibly resulted from the chemical composition of hydrothermal fluids in the Sebinkarahisar environment of Pb-Zn-Cu mineralization. The behavior of Mn seems to have had an important effect during the crystallization of foitite from the low-temperature ore-bearing solutions.

Mn-rich tourmaline is generally rare. This type of tourmaline is found most commonly in Na-Li-rich granitic pegmatites, with up to 8.86 wt.% MnO contents (Shigley et al. 1986). However, alkali-deficient tourmaline in the foitite compositional range contains high levels of Mn (up to 1.71 wt.% MnO) compared to tourmaline compositions belonging to the dravite–schorl solid-solution series. Jiang et al. (1997) reported unusually high levels of Mn (up to 1.48 wt.% MnO) in alkali-deficient tourmaline from some of the Sullivan Pb-Zn-Ag deposit. They attributed the presence of Mn-rich alkali-deficient tourmaline to the local availability of Mn and the lack of other coexisting minerals that preferentially incorporate Mn into their structures. We have not observed important Mn-bearing minerals in study area that could buffer the chemical composition of foitite. However, the Mn may be supplied by Mn-rich minerals such as silicate, carbonate or oxide compositions during the formation of foitite in cavities of quartz veins.

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REFERENCES


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