

A STUDY ON THE CHROMIAN TREMOLITE FROM GULEMAN, ELAZIĞ

Işık KUMBASAR

İstanbul Technical University, Mining Faculty

ABSTRACT.— Chemical composition, optical properties, D.T.A. curve, unit cell dimensions and indexed powder diffraction pattern of the chromium-rich tremolite from Guleman District are given.

Chemical composition of this mineral is much more close to the chemical composition of hornblende. It contains 2.97 % Cr_2O_3 .

Optical properties are obtained as:

$g=1.632$, $b=1.623$, $a=1.615$ all + 0.002 $2V=90^\circ$ $ZIC=33^\circ$.

Unit cell dimensions are: $a=9.819 \text{ \AA}$, $b=18.084 \text{ \AA}$, $c=5.200 \text{ \AA}$, $104^\circ 40'$ $V=893.44 \text{ \AA}^3$ c
Dimension of this mineral is smaller than those found in tremolite and other hornblendes.

Exothermic reaction at 830°C found for tremolite is not seen at D.T.A. curve of chromian tremolite from Guleman.

INTRODUCTION

R.Norin (1940) had given the chemical composition and optical properties of a chromium-rich hornblende from Turkey. An occurrence of the chromian hornblende was reported by A. Helke (1962) in the chromite veins of the Soridağ chromium deposits, Guleman District, Turkey. F. Schumacher (1957), in his book about ore deposits, «Maden Yatakları Bilgisinin Esasları», written in Turkish, described a mineral found in the Soridağ chromite deposits. According to him it contains 2.8 % Cr_2O_3 , looks like actinolite, has green color and is essentially a hornblende. Schumacher considered it as a new mineral and called it «Gulemanit». Wijkerslooth (1946), von Kaaden (1959) and Borchert (1961) mentioned in their works the occurrence of chromian tremolite formed during pneumatolytic stage while they were discussing the formation of chromite deposits of Turkey. Chromium-rich tremolite is found quite extensively in chromite deposits of Turkey (*M.T.A. Publ.*, no. 132).

In the present study only the sample taken from Soridağ, Guleman District, has been investigated. Any relationship between this mineral and the other occurrences mentioned as chromian tremolite found in various districts is not established.

CHEMICAL COMPOSITION

The sample which has been studied was obtained from the museum of the İstanbul Technical University. It contained partly chromite grains. For chemical analysis the sample was ground and screened to various sizes.—74m fraction was not considered. 0.210-0.149 mm, 0.149-0.105 mm, 0.105-0.074 mm fractions were treated with tetrabromethane (density: 2.96) to remove any talc coating and then with methyl iodide (density: 3.32) to purify from chromite. The 0.105-0.074 mm fraction was seen the cleanest and this part was also purified once more by hand under the binocular microscope.

The result of chemical analysis is given in Table 1. The number of cations calculated on the basis of 24 (O, OH, F) is also given. During this calculation H₂O(-) was ignored considering it as adsorbed water.

As it is known, monoclinic calcic amphiboles include tremolite-hornblende series and their chemical formula is abbreviated as A₀₋₁X₂Y₅Z₈O₂₂(OH, O, F)₂. Cation coordination numbers are as follows: A=10, X=6-8, Y=6, Z=4. When the A site is unoccupied, the formula will be written as X₂Y₅Z₈O₂₂(OH, O, F)₂, where X=Ca²⁺, Na¹⁺, K¹⁺, Mg²⁺, Fe²⁺; Y=Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Ti³⁺, Mn²⁺, Cr³⁺; Z=Si⁴⁺, Al³⁺. There are various solid solutions between end members. The chemical complexity affects extensively the physical properties of amphiboles.

Table - 1

Chemical composition of chromian tremolite from Guleman

(Analyst: Yılmaz Bürküt, I.T.U. Mining Faculty)

SiO ₂	54.04
TiO ₂	0.88
Al ₂ O ₃	8.54
Fe ₂ O ₃	3.23
FeO.....	1.24
MnO.....	15.02
CaO.....	10.70
Na ₂ O.....	0.76
K ₂ O.....	1.29
P ₂ O ₅	0.01
H ₂ O+.....	2.01
H ₂ O.....	0.12
Cr ₂ O ₃	2.97
F.....	0.02
	<u>100.99</u>
O=F.....	-0.02
	<u>100.97</u>

Numbers of ions on the basis of 24 (O, OH, F) :

Si.....	7.411	
Al.....	0.589	8.00
Al.....	0.791	} 4.769
Ti.....	0.091	
Fe ³⁺	0.333	
Mg.....	3.070	
Fe ²⁺	0.142	
Mn.....	0.019	} 1.846
Cr.....	0.322	
Na.....	0.185	
Ca.....	1.572	1.983
K.....	0.226	
OH.....	1.837	
F.....	0.009	

100 Mg : (Mg+Fe²⁺ + Fe³⁺ + Mn)=91.47

If the chemical composition of chromium-rich tremolite from Guleman is compared with the chemical composition of tremolite, it is seen that the Al^{3+} content is higher and the Mg^{2+} content is lower. Mg^{2+} at the octahedral site is replaced by Fe^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} , Mn^{2+} and Ti^{3+} . Besides, the amount of Na and K is higher than that expected for tremolite. According to the numbers of (Na+K) and $[\text{Al}]^{\text{t}}$ atoms per formula unit the mineral studied is in the hornblende group, but it is very close to the border of tremolite. Also according to the numbers of $([\text{Al}]^{\text{t}} + \text{Fe}^{3+} + \text{Ti})$ and $[\text{Al}]^{\text{t}}$ atoms per formula unit chromian tremolite from Guleman is between hornblende and tremolite. In edenite and pargasite (Na, K) and $[\text{Al}]^{\text{t}}$ is higher and Si is lower.

OPTICAL PROPERTIES

Chromian tremolite from Guleman is light green in color showing very slight pleochroism under the microscope.

y=very pale creamy; a=very pale greenish. The maximum interference colors in thin section are in the lower second order. Optical properties are given in Table 2.

Table - 2
Optical properties of chromian tremolite from Guleman

γ : 1.632	± 0.002
β : 1.623	± 0.002
α : 1.615	± 0.002
ZAC : 33°	$\pm 1^\circ$
$2V_{\text{meas.}} = 90^\circ$	
$r < v$	
1(+)	

Indices of refraction were determined by Abbe refractometry using standard oils. During the measurements sodium light source was used. Axial angle, $2V$, was measured on a universal stage.

The value of the extinction angle is greater than those found for tremolite where it is about 15° - 20° .

DIFFERENTIAL THERMAL ANALYSIS

D.T.A. analysis of chromian tremolite from Guleman was made in air at one atmosphere from room temperature to 1350°C . Thermocouple was Pt-Pt/Rh. The curve obtained is shown in Figure 1.

There is one endothermic peak at 1005°C . This shows the decomposition and recrystallization of the compound. The X-ray powder diffraction pattern of the sample taken right after that temperature does not have any peak of tremolite, instead, it gives the peaks of plagioclase feldspar and augitic pyroxene. Hornblendes having complex chemistry recrystallize at 1100°C and yield polyaugite, plagioclase, hematite and water (Wittels). Calcic and aluminous amphiboles such as pargasite and hastingsite give the same products. Beurger stated that the presence of aluminium proxying for silicon in a silicate increases the disintegration temperature for that silicate. Disintegration

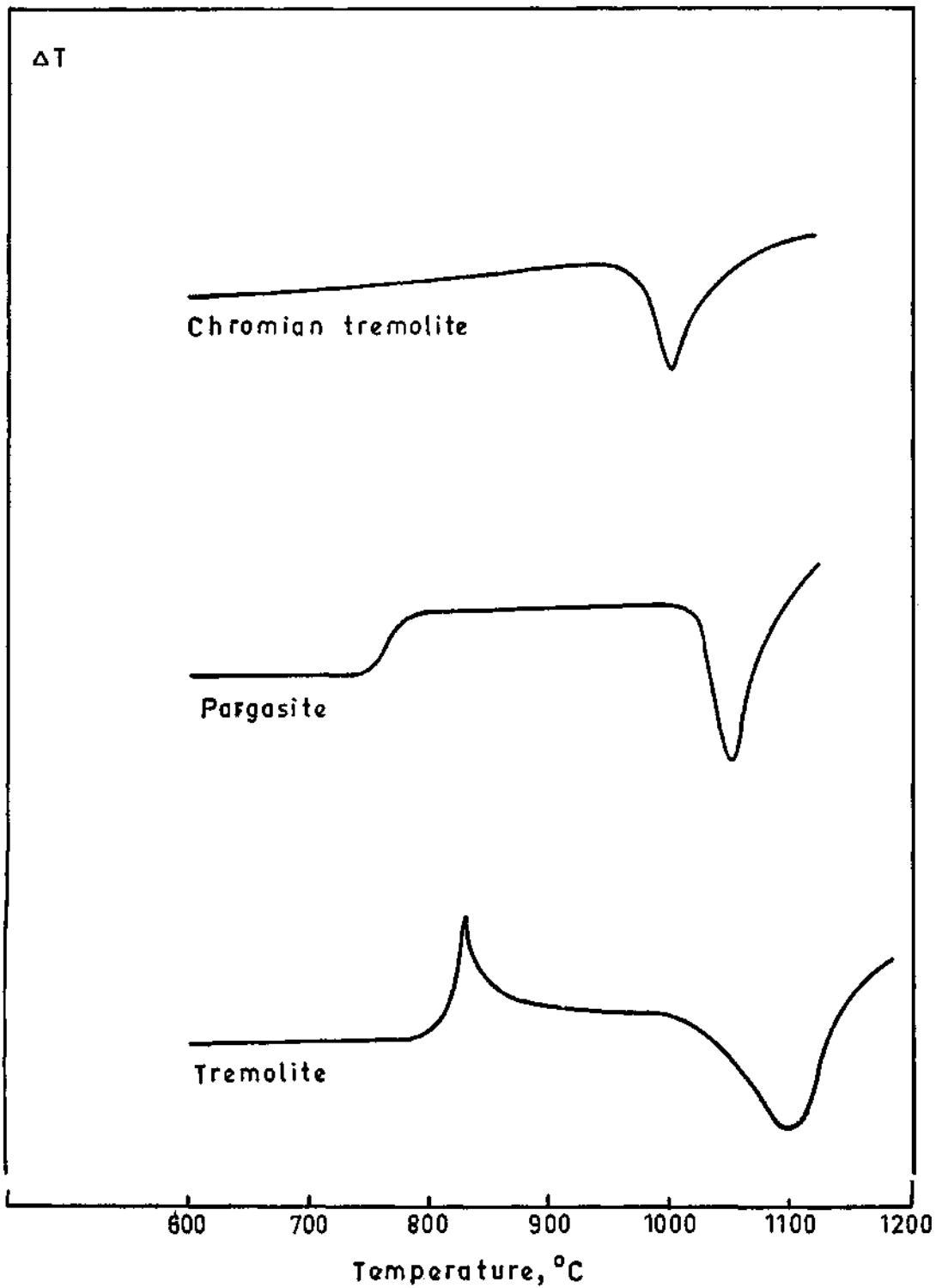


Fig. 1 - D.T.A. curves for chromian tremolite from Guleman (present study), tremolite (Wittels) and pargasite (Wittels).

peak temperature of chromian tremolite from Guleman is about 1000°C. This relation also holds the small amount of four coordinated aluminium found in the structure of the mineral.

D.T.A. patterns for tremolite and pargasite are given in Figure 1. The exothermic peak at about 830°C seen at the curve of tremolite is absent at the pattern of chromian tremolite from Guleman. According to P.P. Glassert, one possible explanation of the 830°C peak is that it represents a polymorphic transition (Wittels, 1951) which, if it occurs, must be rapidly reversible, as high-temperature form of tremolite has not been encountered in other studies. Tremolite recrystallizes at 1000°-1100°C yielding monoclinic pyroxene (Wittels, 1952). Pargasite which contains 11% Al₂O₃ shows an asymmetric exothermic reaction which is not seen at the pattern of chromian tremolite from Guleman. There is very slow exothermic reaction at the chromian tremolite curve beginning at 250°C. This is probably due to the continuing oxidation of Fe²⁺ during the course of the heating.

UNIT CELL CONSTANTS

Experimental Data: X-ray powder diffraction data were obtained with a Philips diffractometer using nickel filtered copper radiation. Scanning speed was 1/2° 2θ per minute. Divergence and scatter slits were 1°. Natural colorless α-quartz was used as internal standard. Powdered sample was mounted in an aluminium holder together with powdered α-quartz. Besides, slight amount of sample with α-quartz was mounted with acetone on a glass slide. Both of them were run three times between 2θ=9°-65°. No notable difference was found due to the mounting. The center of each peak was read at 3/4 of its height. Difference between the values of 2θ measured from different three patterns were about + 0.02°. Some of the reflections were indexed according to the values given in A.S.T.M. card with number 13-437. Unit cell dimensions a, b, c, b and unit cell volume were calculated with 20 values of reflections obtained from the planes given as:

$$20: 020, 110, 200, 040, 220, 240, 310, 1\bar{5}1, 330, 231, 151, 1\bar{1}2, 350, 261, 202, 510, 210\bar{1}, \\ 511, 103, 4\bar{5}1$$

Unit cell constants found were refined on the IBM 1620 computer using the least-square refinement program developed by Nahit Kumbasar. The possible a values were calculated and the indices of some reflections were also found. Unit cell dimensions for chromian tremolite from Guleman are given below:

$$\begin{array}{ll} a = 9.819 \text{ \AA} & \\ b = 18.084 \text{ \AA} & \text{Space Group: C2/m} \\ c = 5.200 \text{ \AA} & \text{Z: 2} \\ b = 104^\circ 40' & \text{Calc. density: 3.079 gr/cm}^3 \\ V = 893.44 \text{ \AA}^3 & \end{array}$$

X-ray powder diffraction data for chromian tremolite from Guleman are shown in Table 3.

As it is well known the M₁, M₂, M₃ octahedral sites at C2/m monoclinic amphibole crystal structure may be filled by Mg, Al, Fe²⁺, Fe³⁺, Cr³⁺, Ti³⁺ and Mn²⁺. M₄ site with six-to eight-fold coordination can be occupied by Ca, Na and Mn²⁺, Fe²⁺, but too small for K. Limited amounts of Mg can be accommodated in M₄ site. A site may be vacant or may contain either or both Na and K. The two tetrahedral sites T₁ and T₂ are occupied by Si or Al. At tremolite structure M₁, M₂, M₃ octahedral sites are filled by Mg, M₄ site by Ca. T₁, T₂ tetrahedral sites contain only Si. The A site is vacant.

Table - 3
X-ray powder diffraction data for chromian tremolite from Guleman
(CuK α = 1.5418 \AA Ni filter)

<i>I</i>	<i>d</i>	<i>d</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>	<i>d</i>	<i>d</i>	<i>h</i>	<i>k</i>	<i>l</i>
<i>obs.</i>	<i>obs.</i>	<i>calc.</i>				<i>obs.</i>	<i>obs.</i>	<i>calc.</i>			
14	9.988	9.042	0	2	0	5	1.864	{ 1.864 1.865	$\bar{1}$	9	1
100	8.409	8.409	1	1	0	7	1.814	1.812	4	6	0
10	5.085	{ 5.090 5.031	1	3	0	4	1.685	{ 1.677 1.677	5	3	0
8	4.906	4.820	$\bar{1}$	1	1	17	1.647	1.647	0	0	3
10	4.758	4.749	2	0	0	7	1.637	{ 1.637 1.638	$\frac{0}{2}$	8	2
15	4.506	4.521	0	4	0	6	1.617	{ 1.616 1.618 1.614 1.611 1.610	2	10	$\bar{1}$
23	4.203	4.205	2	2	0	12	1.587	{ 1.587 1.585 1.584 1.583 1.590	4	8	0
8	3.880	3.849	$\bar{1}$	3	1	6	1.512	{ 1.511 1.514 1.509 1.507	5	1	1
18	3.377	{ 3.380 3.363	1	5	0	13	1.503	{ 1.504 1.504 1.499 1.507	0	3	3
30	3.270	3.275	2	4	0	4	1.469	{ 1.469 1.468 1.465 1.465	5	2	$\frac{1}{3}$
100	3.124	3.119	3	1	0	18	2.159	{ 2.156 2.177	1	4	$\frac{3}{2}$
18	2.936	2.931	$\bar{1}$	5	1	9	2.040	{ 2.041 2.062	3	7	$\frac{2}{3}$
35	2.805	2.803	3	3	0	12	2.014	2.021	3	6	$\frac{2}{3}$
13	2.735	2.746	2	3	1	5	2.003	{ 2.002 2.010	5	8	0
28	2.704	2.695	1	5	1	4	1.961	{ 1.966 1.968	4	4	2
12	2.588	2.574	1	1	2	12	1.893	1.889	4	10	0
13	2.536	{ 2.515 2.500	0	0	2	30	1.439	{ 1.439 1.440 1.436 1.436	4	5	$\frac{0}{3}$
4	2.411	2.387	$\bar{1}$	3	2	6	1.457	{ 1.457 1.459 1.454 1.460	4	7	$\frac{2}{3}$
12	2.381	{ 2.382 2.375	3	5	0	4	1.469	{ 1.469 1.468 1.465 1.465	3	6	$\frac{2}{3}$
17	2.339	2.332	4	0	0	6	1.457	{ 1.457 1.459 1.454 1.460	3	7	$\frac{2}{3}$
14	2.325	2.315	4	2	$\bar{1}$	4	1.469	{ 1.469 1.468 1.465 1.465	5	8	0
8	2.299	{ 2.298 2.297	0	7	0	6	1.457	{ 1.457 1.459 1.454 1.460	4	4	2
5	2.280	2.274	1	1	2	4	1.469	{ 1.469 1.468 1.465 1.465	4	4	2
18	2.159	{ 2.156 2.177	2	6	1	6	1.457	{ 1.457 1.459 1.454 1.460	4	4	2
9	2.040	{ 2.041 2.062	2	8	0	4	1.439	{ 1.439 1.440 1.436 1.436	4	10	0
12	2.014	2.021	2	0	2	30	1.439	{ 1.439 1.440 1.436 1.436	4	5	$\frac{0}{3}$
5	2.003	{ 2.002 2.010	3	7	0	6	1.457	{ 1.457 1.459 1.454 1.460	4	4	2
4	1.961	{ 1.966 1.968	2	8	$\bar{1}$	4	1.469	{ 1.469 1.468 1.465 1.465	4	10	0
12	1.893	1.889	5	1	0	30	1.439	{ 1.439 1.440 1.436 1.436	4	5	$\frac{0}{3}$

In hornblendes the variation in the lattice parameters is controlled by ionic substitution. They are the variations due to the amount of replacement of the constituent ions by larger or smaller ions. The substitution of the larger Fe^{2+} for the smaller Mg^{2+} at the octahedral site would increase the dimensions of a and b, whereas the substitution of the smaller Al^{3+} or Fe^{3+} for the larger Mg^{2+} at the same site would produce opposite effects.

If the values of the unit cell dimensions found for chromian tremolite from Guleman are compared with those for tremolite, pargasite and edenite, Table 4, a slight increase in b dimension and a slight decrease in c dimension are seen.

Table - 4
Lattice parameters of some calcic amphiboles

	a, Å	b, Å	c, Å	β	V, Å ³
Chromian tremolite (present study)	9.819	18.084	5.200	104°40'	893.44
Tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ J. Papike <i>et al.</i>	9.818	18.047	5.275	104°39'	904.2
Fluor tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$ Cameron & Gibbs	9.787	18.004	5.263	104°26'	898.1
Edenite $\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}(\text{OH})_2$ Colville <i>et al.</i>	9.853	18.005	5.236	104°24'	899.8
Paragasite $\text{NaCa}_2\text{Mg}_4\text{AlSi}_2\text{Al}_2\text{O}_{22}(\text{OH})_2$ Colville <i>et al.</i>	9.906	17.986	5.265	105°18'	904.7

The slight increase might be due to the substitution of some Fe^{2+} for Mg^{2+} at the octahedral site. It is difficult to explain the decrease in c dimension. According to Colville *et al.*, variation in c dimension is controlled by the size of cations in M_1 and M_3 sites and by the amount of Al^{3+} at tetrahedral site and the increase in c, as all of the magnesium in M_1 and M_3 sites replaced by iron is about 0.05 Å. The chemical analysis of the chromian tremolite from Guleman shows that there is small amount Al^{3+} at tetrahedral site and this makes increase in c dimension instead of decrease. M_1 and M_3 sites are occupied by Mg^{2+} , Fe^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} . The Fe^{2+} amount is small and the total amount of Al^{3+} , Cr^{3+} , Fe^{3+} is considerable. Atomic radii of Al^{3+} , Cr^{3+} , Fe^{3+} are smaller than the atomic radius of Mg^{2+} . For that reason, a decrease in c dimension might be expected.

The values of the cell parameters given in Table 4 are for the amphibole end members. The variation of the unit cell dimensions with various chemical substitutions for various intermediate solid solutions is not completely obvious because of their combinations in many ways. It is still hard to make a conclusion for the natural amphiboles.

BIBLIOGRAPHY

- BUERGER, M.J. (1948): The role of temperature in mineralogy. *The American Mineralogist*, vol. 33, pp. 101-121.
- BORCHERT, H. (1961): Türkiye krom cevheri yataklarında yapılan etütlerden öğrendiklerimiz. *M.T.A. Derg.*, no. 56, Ankara.
- CAMERON, M. & GIBBS, G.V. (1973): The crystal structure and bonding of fluor-tremolite. *Am. Mineral.*, vol. 58, pp. 879-888.
- COLVILLE, P.A.; ERNST, W.G. & GILBERT, M.C. (1966): Relationships between cell parameters and chemical compositions of monoclinic amphiboles. *Am. Mineral.*, vol. 51, p. 1727.
- DEER, W.A.; HOWIE, R.A. & ZUSSMAN, J. (1963): Rock-forming minerals, vol. 2, *Longmans*.
- ENGİN, T. & ANCOTT, J.W. (1971): A microprobe study of chromites from the Andızlık-Zımparalık area, South-west Turkey. *Min. Mag.*, 38, pp. 76-82.
- ERNST, W.G. (1968): Amphiboles. *Springer Verlag*.
- HELKE, A. (1962): The metallogeny of the chromite deposits of the Guleman District, Turkey. *Econ.Geol.*, vol. 57, no. 6, p. 954.
- KAADEN, G.v.d. (1959): On relationship between the composition of chromites and their tectonic-magmatic position in peridotite bodies in the SW of Turkey. *M.T.A. Bull.*, no. 52, Ankara.
- KLEIN, C. (1964): Cummingtonite-grunerite series: a chemical, optical and X-ray study. *Am. Mineral.*, vol. 49, 963-982.
- M.T.A. INSTITUTE (1966): Chromite deposits of Turkey. *M.T.A. Publ.*, no. 132, Ankara.
- NORIN, R. (1940): Notes on a chrome amphibolite from Turkey. *Geol.F6rd.Fdrh.* Stockholm, vol. 62, p. 98.
- PAPIKE, J. J.; ROSS, M. & CLARK, J.R. (1969): Crystal-chemical characterization of clinoamphiboles based on five new structure refinements. *Mineral. Soc. Amer. Spec. Pap.* 2, 117-136.
- RAYCHAUDHI, B. (1964): Relation of atomic constitution to lattice parameters in some hornblendes from the Black Hills, South Dakota. *Am. Mineral.*, vol. 49, p. 198.
- SCHUMACHER, F. (1957): Maden yatakları bilgisinin esasları. *İ.T.Ü., Maden Fakültesi*, İstanbul.
- WIJKERSLOOTH, p. de (1946): Die Metamorphose des anatolischen Chromerzes und ihre Abhängigkeit von den magmatischen Ereignissen. *M.T.A. Publ.*, no. B. 10, Ankara.
- WITTELS, M. (1951): Structural transformations in amphiboles at elevated temperatures. *Am. Mineral.*, v. 36, p. 851.
- (1952): Structural disintegration of some amphiboles. *Am. Mineral.*, vol. 37, p. 28.