BORON MINERALS OF TURKEY: *HYDROBORACITE*

Ali DEMİRCİOĞLU

Mineral Research and Exploration Institute of Turkey

SUMMARY. — The main borate deposits of Turkey are located in the area between Balıkesir and Kütahya Provinces. The chemical analysis of the hydroboracite samples collected from Günevi mine of the Bigadiç-Yolbaşı area and the loss of water recorded at higher temperatures were studied. The samples were further examined under the microscope and by X-ray diffraction methods. Studies carried out to date indicate that no intermediate compounds, containing relatively small amounts of crystal water, compared to the original mineral, were observed as a result of heating the hydroboracite samples to higher temperatures.

Based on the Mohs' scale of hardness, the hardness of hydroboracite mineral discovered in Turkey wes determined to be more than 5 and less than 6. Dana, however, states that the hardness of hydroboracite mineral ranges between 2 to 3.

The DTA curve of the hydroboracite mineral discovered in Yolbaşı reveals the major macro properties of this mineral.

HYDROBORACITE (1)

Hydroboracite has been reported to have the chemical composition $MgO \cdot CaO \cdot 3B_2O_3 \cdot 6H_2O$. Hydroboracite is a magnesium calcium hydrate of boron where one CaO of the colemanite ($2CaO.3B_2O_3.5H_2O$) is displaced by MgO.

Hardness: 2 (crystal), 3 (compact mass)

Crystal system: monoclinic

Specific gravity: 2.167

Theorically it consists of 50.53 % B_2O_3; 13.57 % CaO; 9.75 % MgO and 26.15 % H_2O.

Hydroboracite occurs in small quantities in the various boron deposits of the world. Commercial hydroboracite deposits are found in Inder, a locality in Siberia, U.S.S.R. (2). In Soviet Russia, the primary boron products, namely borax and boric acid, are obtained from this mineral. The B_2O_3 content of the mineral ranges between 25 % to 35 %.

The first discovery of hydroboracite mineral was made in an unknown locality situated somewhere in the Caucasus; later discoveries were also made in the salt deposits of the Stassfurt area; in Ryan, California, associated with colemanite and calcite; and in the vicinity of Inder Lake, West Kazakhstan, U.S.S.R., associated with colemanite, inyoite, ulexite and inderite.

In «Klockmann's Lehrbuch der Mineralogie» (1967) P. Ramdohr and H. Strunz report that hydroboracite has a monoclinic crystal structure and the composition $MgCa\text{-}B_6On\text{-}6H_2O$. The authors further state that the needle-like crystals of hydroboracite mineral were discovered in Stassfurt; in Death Valley, California; and in Kazakhstan. No information on the hardness of this mineral is given in the text. Ny— 1.543 (+).

Table - 1

Chemical analyses of some hydroboracite samples

	1	2	3	4	5	6	7	8
CaO	13.57	13.52	14.06	14.96	13.63	13.86	13.86	14.08
MgO	9.75	10.75	10.14	9.88	9.84	9.93	11.00	10.94
Fe_2O_3	—	—	0.12	0.30	—	—	0.039	0.028
B_2O_3	50.53	49.58	47.71	46.79	49.04	49.22	46.84	46.39
CO_2	—	—	traces	1.37	1.65	—	—	—
H_2O	26.15	26.33	27.37	25.59	25.45	26.59	—	—
Remaining	—	—	0.23	0.58	0.86	0.28	—	—
SiO_2	—	—	—	—	—	—	2.87	4.46

1 - Theoretical hydroboracite; 2 - Sample collected from Caucasus, Hess (1834); 3 - Sample collected from Ryan, California, Boldyreva (1936); 4 - Sample collected from Inder, Siberia, Boldyreva (1936); 5 - Sample collected from Inder, Siberia, Boldyreva (1936); 6 - Sample collected from Inder, Siberia, Boldyreva *in* Godlevsky (1937); 7 - Sample collected from Büyük Günevi-Yolbaşı, Bigadiç, Turkey, A. Demircioğlu (1970); 8 - Sample collected from Büyük Günevi-Yolbaşı, Bigadiç, Turkey, A. Demircioğlu (1971).

Note: Analyses nos. 7 and 8 were made on the samples collected by the author and added to the list.

HYDROBORACITE IN TURKEY

Hydroboracite in Turkey occurs in the Büyük Günevi mine of the Yakal Borasit Ltd. Şti. located near Yolbaşı village, Bigadiç, Balıkesir Province, Western Anatolia. The Bigadiç boron deposits were first discovered by Muharrem Girgin and Dr. Hüsamettin Yakal in the period between 1950 and 1952. During the following years, Dr. Helke and Dr. Heinz Meixner became interested in these deposits. Data furnished by Meixner is the oldest and the most reliable in this respect (3, 4, 5).

Table prepared by Meixner and showing the boron minerals complex of the Bigadiç area (Table 2) was adopted by McMurdock (6), Dr. Ünal Sanıgök (7), and Dr. Işık Özpeker (8) who also studied this area.

Meixner (3), based on the samples submitted by Helke, states that new discoveries of boron deposits were made in the vicinity of Yolbaşı (Faraskdy), Çamköy and İskele villages of the Bigadiç area and that the Ca-borates constitute the main part of these deposits. Meixner correlates these deposits with the bofate deposits of California, U.S.A. He included in his list of minerals colemanite, meyerhofferite, inyoite, pandermite, ginorite, probertite, ulexite, hydroboracite and inderborite. He also gives the theoretic crystal water content of these minerals and their approximate solubility in water.

Meixner (5) also states the presence of pandermite, howlite and hydroboracite minerals associated with the previously determined complex in the vicinity of Yolbaşı (Faraşköy), İskeleköy and Çamköy. Through crystallographic, optical, chemical and weight tests, the presence of the above-referred minerals is established, associated with colemanite, ulexite, meyerhofferite and inyoite.

Based on the data obtained during the works carried out in the borate deposits of the Yolbaşı (Faraşköy) area, some additions were made to the above list:

1. Ulexite is present in the Büyük Kireçlik mine.

2. Terschite was not found in the Kurtpınarı mine.
3. Ulexite is present in the Kurtpınarı mine.
4. Pandermite was not found in the Büyük Kireçlik mine.

Table - 2

Boron mineral complex of Bigadiç, Balıkesir Province [by H. Meixner (5)]

Mine locality	*Colemanite*	*Meyerhofferite*	*Inyoite*	*Priceite*	*Terschite*	*Ulexite*	*Hydroboracite*	*Howlite*
Büyük Kireçlik	+	+	—	+	—	—	—	—
Küçük Kireçlik	+	—	—	—	—	—	—	—
Börekçideresi	+	+	—	—	—	+	—	—
Büyük Günevi	+	+	+	?	—	+	+	—
Küçük Günevi	+	—	—	—	—	—	—	—
Kurtpınarı (right)	+	—	—	—	—	—	—	—
Kurtpınarı (left)	?	—	—	—	+	—	—	—
Acep.	+	+	+	—	—	+	—	—
Beğendikler	+	—	—	—	—	—	—	—
Tulü Değirmen	+	—	—	—	—	—	—	—
Domuz Deresi	+	—	—	—	—	—	—	—

+ = present; — = absent.

Büyük Günevi mine contains the richest mineral complex of the region. Colemanite, ulexite, meyerhofferite, inyoite and hydroboracite occurrences were observed in this area. Furthermore, crude borax is also reported to be present in the area.

Colemanite and howlite were studied by Dr. Hüseyin Gülensoy (10) and ulexite and inyoite by Dr. Ünal Sanıgök (7).

Hydroboracite occurrences of Yolbaşı

The only hydroboracite occurrence of Turkey is located in the Büyük Günevi mine of Yakal Borasit Ltd. Şti.

Meixner reports that the presence of hydroboracite was established through crystallographical, optical, chemical and specific weight tests (5).

During the production activities carried out after 1956, hydroboracite nodules were extracted and readily distinguished because of the peculiar properties of this mineral.

The most important physical property of the mineral is its hardness compared to colemanite. Due to the fact that this mineral causes some undesirable effects during the crushing and grinding stages of colemanite production, miners call it «pistaş», which means bad, undesirable rock.

Hydroboracite occurs in the form of nodules as big as 5-30 cm or more. It is closely associated with colemanite and ulexite and is overlain by a clay layer, which resembles the clay layer observed in the vicinity of colemanite and ulexite occurrence.

The chemical analyses of the hydroboracite mineral discovered in Western Turkey are given in Table 1, columns 7 and 8. Hydroboracite samples of the column 8 were used in our tests.

The general appearance and the macro section of hydroboracite mineral are shown in Figures 1 and 2. The radial structure of the mineral can be readily observed. Figure 3 shows the protuberances, as big as lentils, on the surface of this mineral. Photos 1, 2 and 3 show hydroboracite mineral in natural size. Sections are shown on Photos 2 and 3.

Hardness. — Based on Dana, the hardness of hydroboracite mineral is 2-3. However, the hardness of hydroboracite sample collected from Büyük Günevi mine is measured to be more than 5 and less than 6, according to Mohs' scale of hardness. Since our mineral is harder compared to the associated minerals, the miners gave it the name of «pistaş». The reason of this discrepancy observed between the hardness measured and recorded in the literature needs to be investigated. Is the hardness of hydroboracite samples collected from other sites really 2-3 ? Studies aimed to clarify this problem must be carried out.

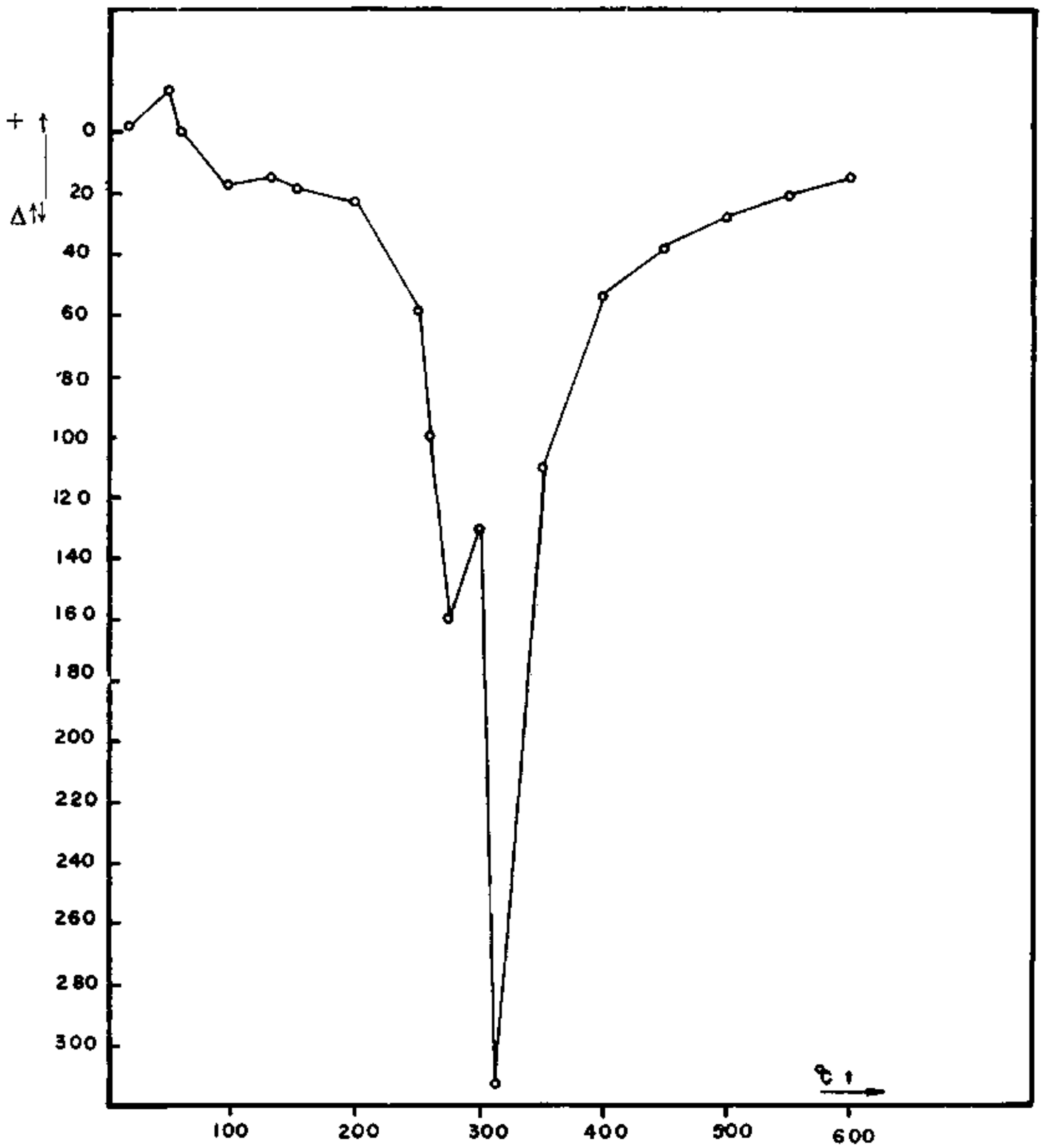
DTA curve. — The DTA curve of the mineral was drawn by Dr. Oktay Orhun, Ceramic Laboratories of Mineral Research and Exploration Institute. The diagram thus obtained (Graph 1), shows that an endothermic peak is formed around 275°C; another endothermic peak, even stronger than the first one, is formed around 320°C.

Loss of water at higher temperatures. — Hydroboracite, like all hydrous boron minerals, loses water when heated to higher temperatures. The loss of water at given temperatures and the B_2O_3-content of the samples after losing their crystal water are given in Table 3. As indicated in the DTA curve, the hydroboracite loses all its crystal water at 500°C and becomes glassy around 700°C.

Table - 3

Loss of water and B_2O_3-content of some hydroboracite samples at various temperatures

	Loss of water (%)	B_2O_3 (%)
Crude	—	46.39
HY-100	0.63	46.72
HY-150	1.73	47.34
HY-200	3.02	48.04
HY-250	5.23	49.16
HY-300	8.56	50.82
HY-350	18.77	57.28
HY-400	22.37	59.92
HY-450	23.21	60.61
HY-500	24.46	61.54
HY-600	25.26	62.19



Graph 1 - DTA curve of natural hydroboracite.

Tests on the loss of water of hydroboracite samples were carried out at the following temperatures: 100°, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500° and 600°C. Tests carried out at 100°, 150° and 200°C were made in ovens. The remaining tests, however, were made by leaving the samples overnight in furnaces adjusted to given temperatures.

The X-ray diffraction graphs of each sample at the above-mentioned temperatures were prepared and their microscopic examinations were made. The results obtained from these tests are given below:

Macroscopic hydroboracite crystals are distinctly concentric (Photos 1, 2, 3).

Photos 4, 5, 6 and 7 (+ N) illustrate the hydroboracite mineral which exhibits rod-like crystal arrangement; Photos 8, 9, 10 and 11 show the hydroboracite mineral which in turn exhibits needle-like crystals of radial structure under the microscope.

The X-ray diffraction graph of the crude hydroboracite is shown in Graph 2.

Microscopic examination of the sample heated to 100°C is illustrated in Photo 12. The X-ray diffraction graph of the sample is given in Graph 3 (HY-100). No structural changes occurred in the sample heated to 100°C.

Sample heated to 150°C is illustrated in Photo 13. The X-ray diffraction graph of the hydroboracite sample is given in Graph 4 (HY-150). No structural changes occurred in the sample heated to 150°.

Photo 14 illustrates the hydroboracite sample heated to 200°C; the X-ray diffraction graph of the sample is given in Graph 5 (HY-200). Peaks recorded in the X-ray diffraction graph of the mineral are relatively smaller.

Photo 15 illustrates the sample heated to 250°C; the X-ray diffraction graph of the same mineral is given in Graph 6 (HY-250). The peaks recorded in the graph are even smaller.

The hydroboracite sample heated to 300°C, is illustrated in Photo 16; the X-ray diffraction graph of the sample is given in Graph 7 (HY-300). Decomposition continues.

The hydroboracite sample heated to 350°C is illustrated in Photos 17 and 18; the X-ray diffraction graph of the same sample is given in Graph 8. It is obvious that the major part of the sample is decomposed.

The hydroboracite sample heated to 400°C is illustrated in Photos 19 and 20 and the X-ray diffraction graph of the same sample is given in Graph 9. The sample is entirely decomposed. Optical isotropes are formed under the microscope.

The hydroboracite samples heated to 450°C, 500°C and 600°C are illustrated in Photos 21, 22 and 23; the X-ray diffraction graphs of the samples are given in Graphs 10 (HY-450), 11 (HY-500) and 12 (HY-600).

At 400°C the thermal decomposition of the mineral was completed.

CONCLUSION

Hydroboracite mineral occurs in the Yolbaşı village, Bigadiç, Balıkesir Province of Turkey.

The chemical analysis of this mineral gave the following average values: B_2O_3 46-47 %; CaO 14%; MgO 11 %, SiO_2 3-4 %.

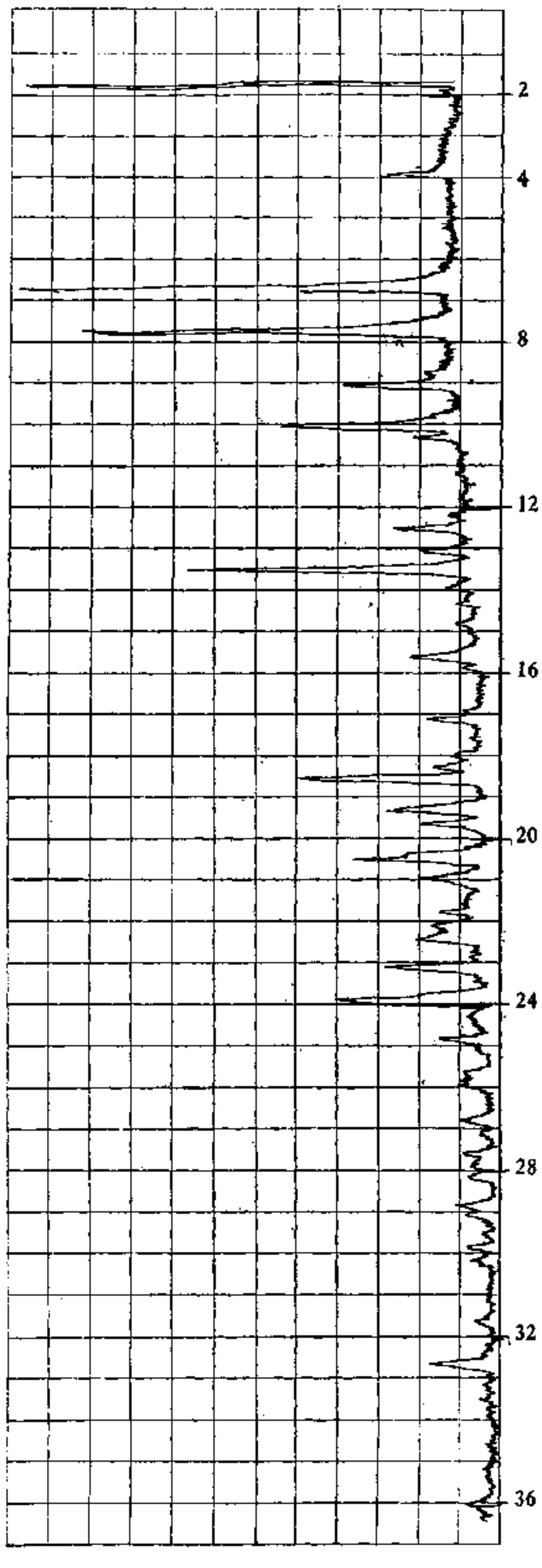
The hardness of this mineral is 5-6 according to the Mohs' scale of hardness.

The changes occurring in the structure of this mineral upon loss of water were investigated. In some types, unstable intermediate compounds were formed as a result of loss of water. Sanıgök states that although a portion of the crystal water was retained in the mineral, no hydrous intermediate compounds were formed on the hydroboracite.

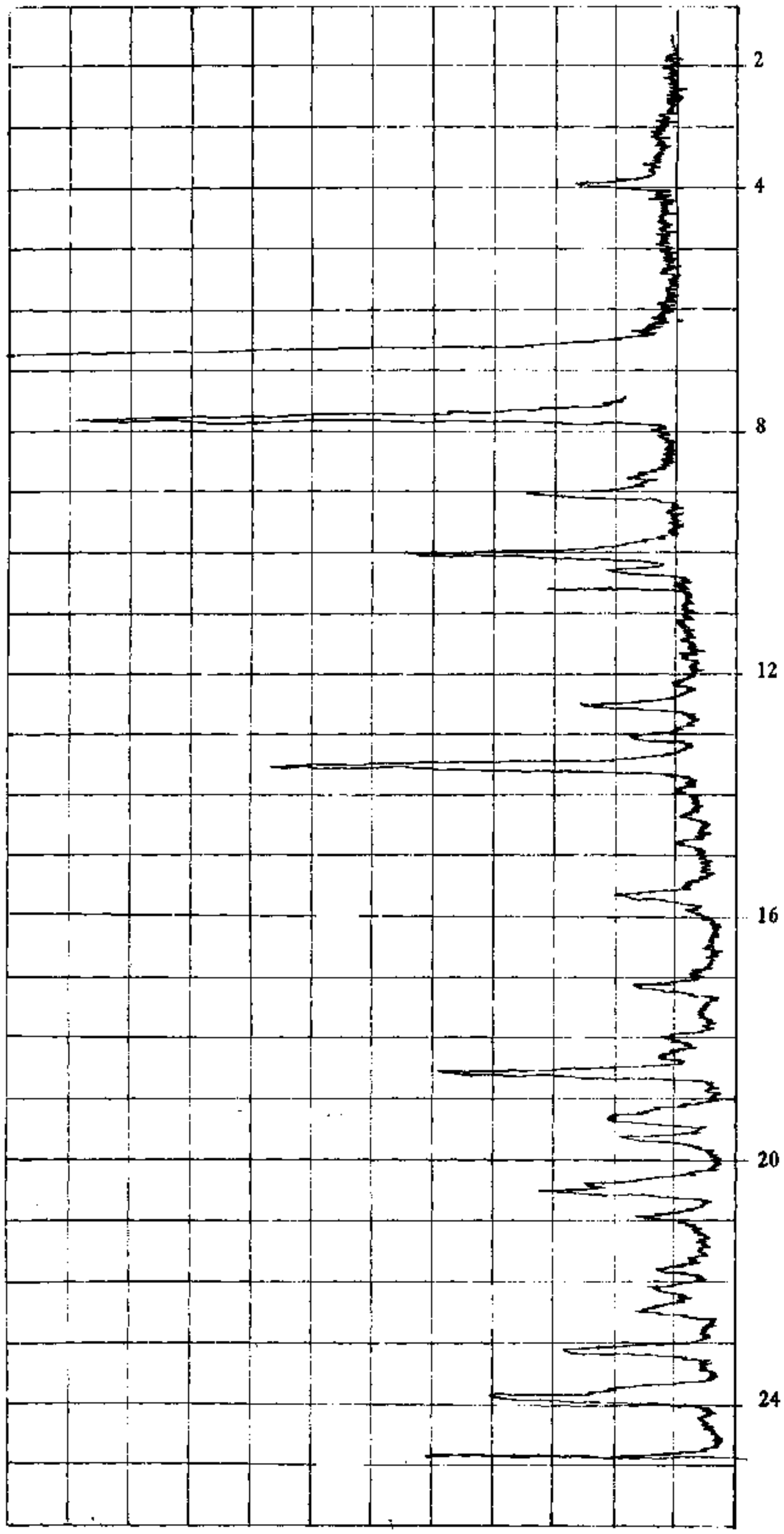
Due to the loss of water and rising temperature, the mineral is inclined to become amorphous.

The nature of the crystal water retained in the structure needs to be investigated further. The solubility of amorphous hydroboracite is 1.5-2.0 times more compared to the crystalline hydroboracite.

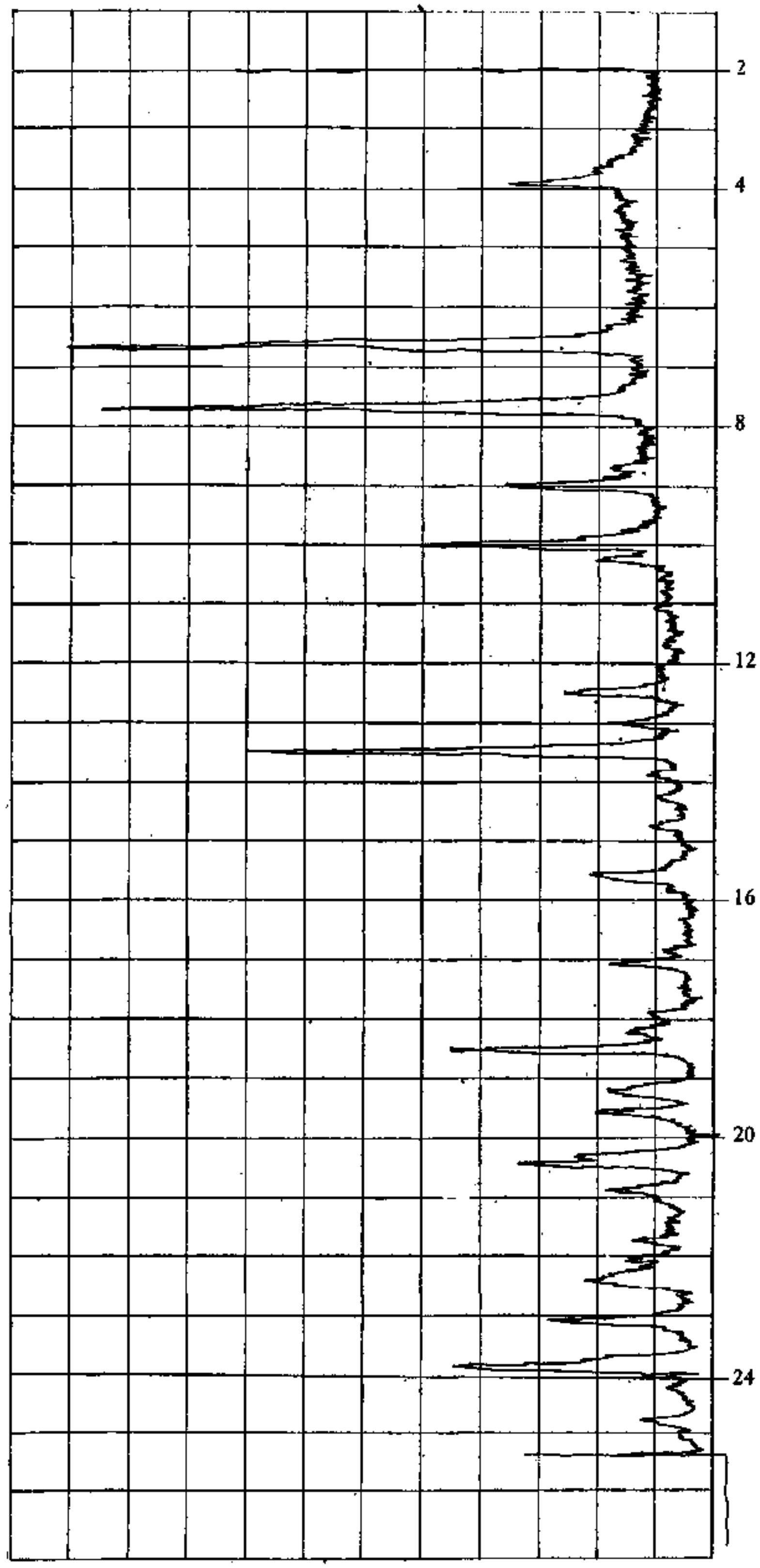
Translated by: Filiz E. DİKMEN *Manuscript received July 27, 1972*



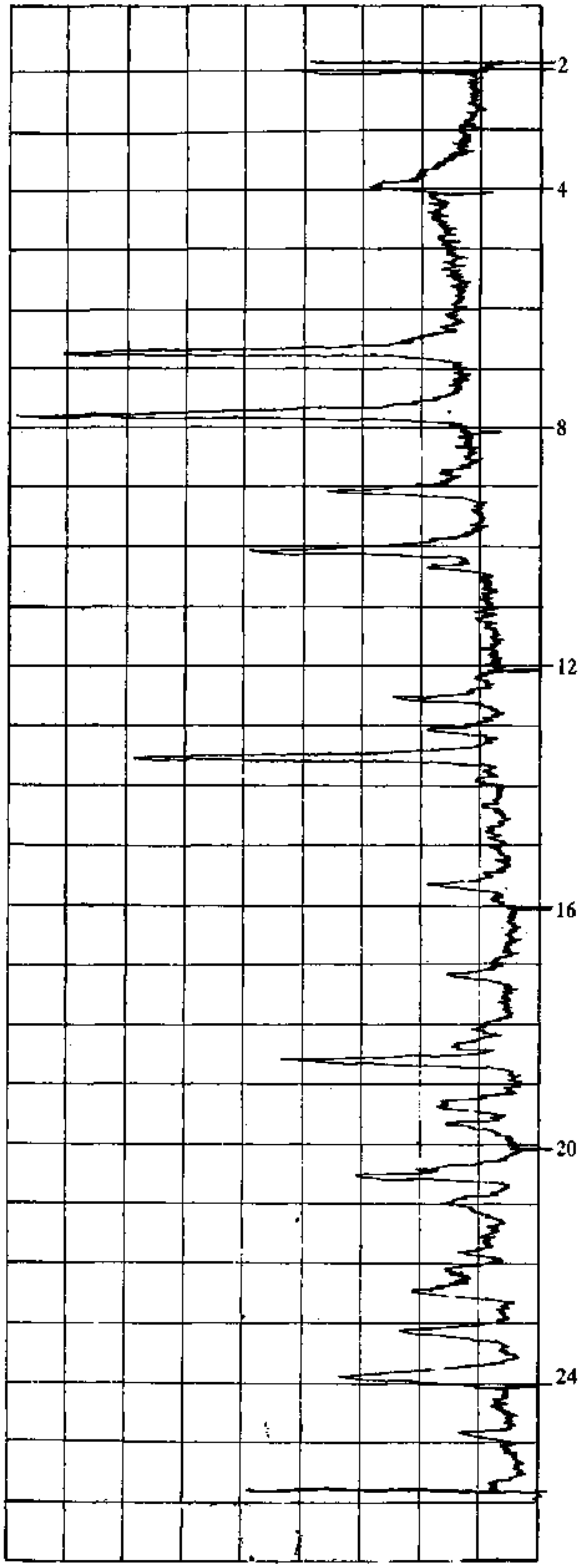
Graph 2 - X-ray diffraction graph of crude hydroboracite (HY-T).



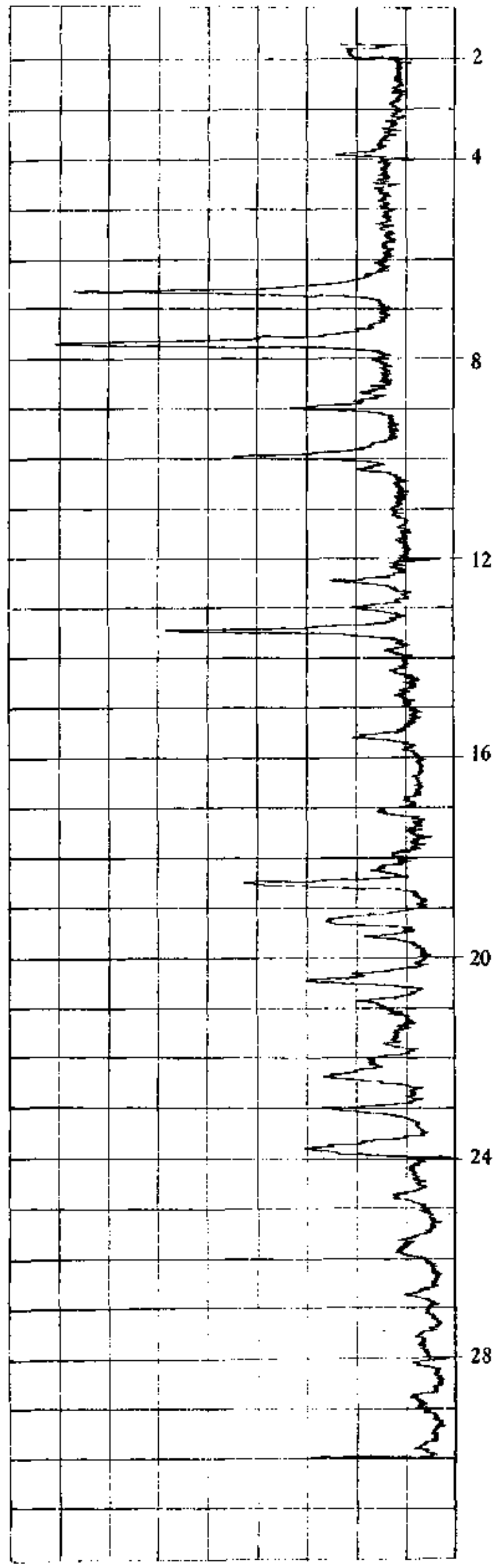
Graph 3 - X-ray diffraction graph of the hydroboracite heated to 100°C. Hydroboracite-100°C (HY-100).



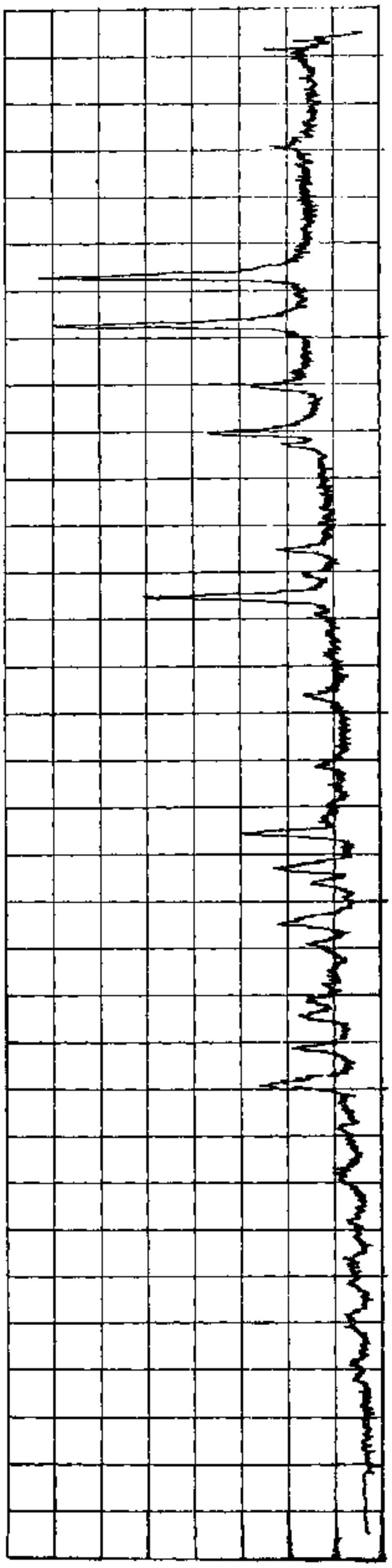
Graph 4 - X-ray diffraction graph of the hydroboracite heated to 150°C. Hydroboracite-150°C (HY - 150).



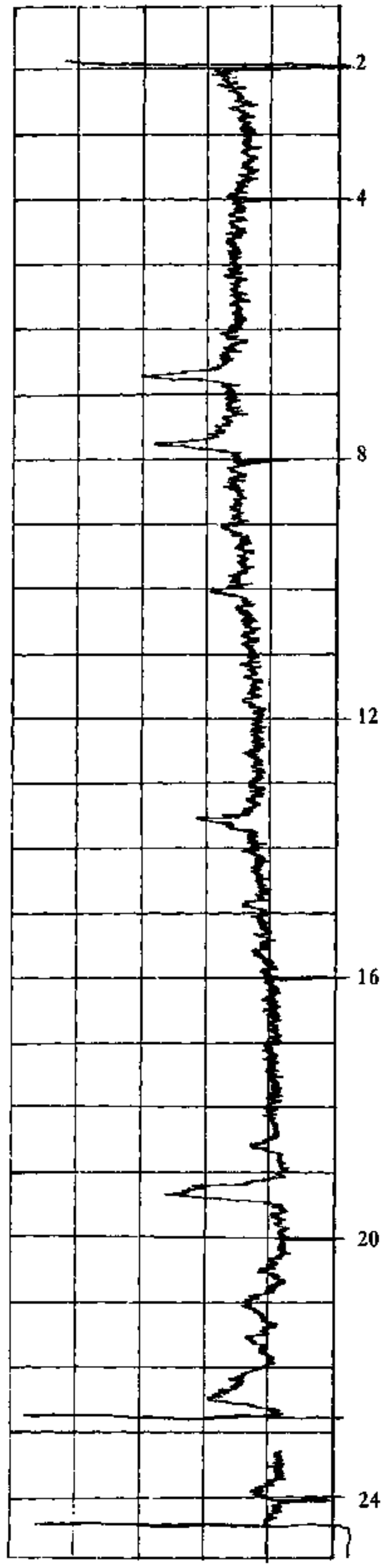
Graph 5 - X-ray diffraction graph of the hydroboracite heated to 200°C. Hydroboracite-200°C (HY-200).



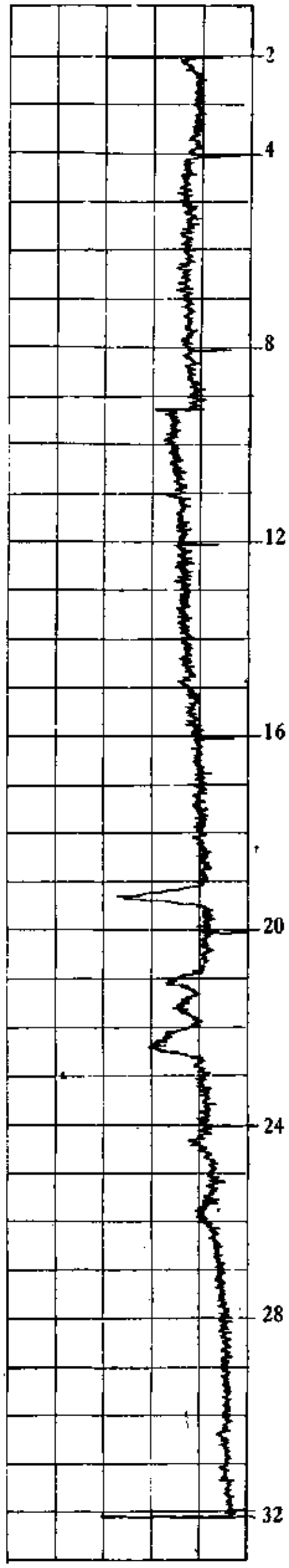
Graph 6 - X-ray diffraction graph of the hydroboracite heated to 250°C. Hydroboracite-250°C (HY - 250).



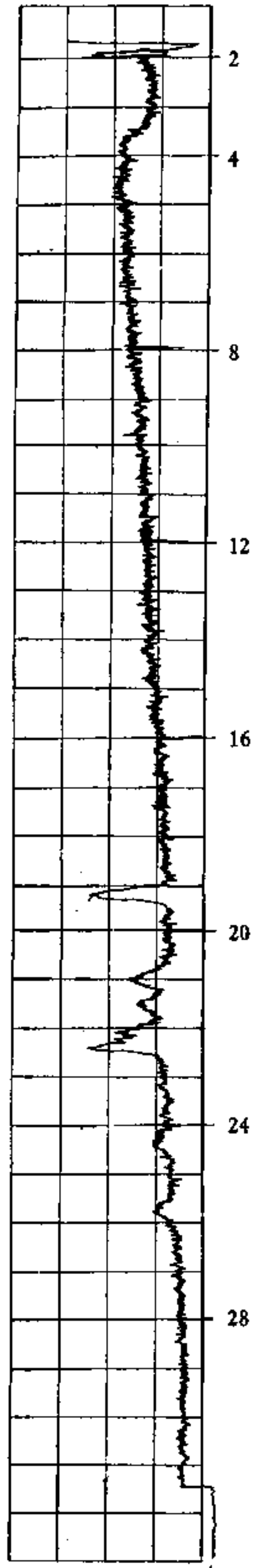
Graph 7 - X-ray diffraction graph of the hydroboracite heated to 300°C. Hydroboracite - 300°C (HY - 300).



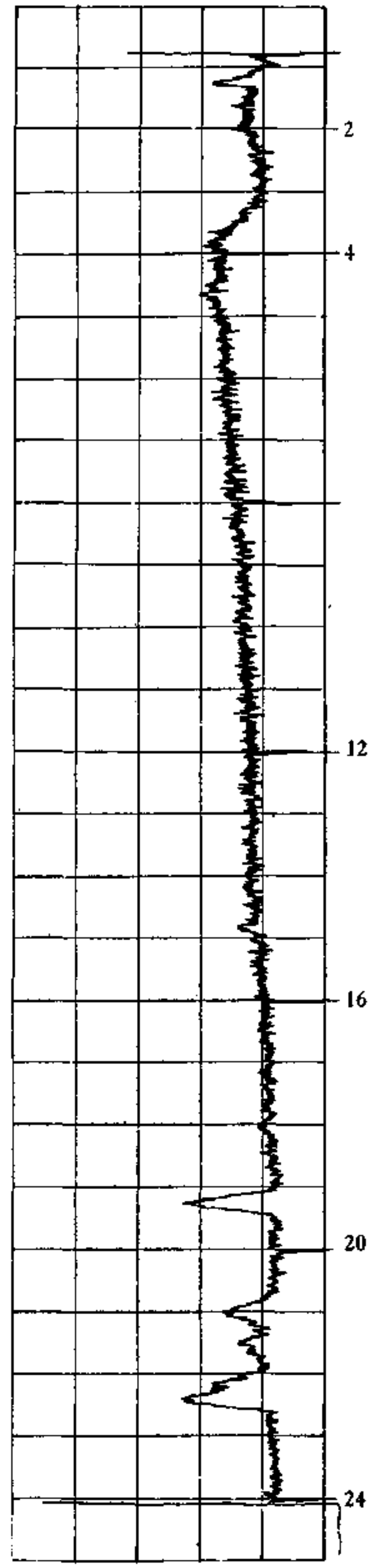
Graph 8 - X-ray diffraction graph of the hydroboracite heated to 350°C. Hydroboracite - 350°C (HY - 350).



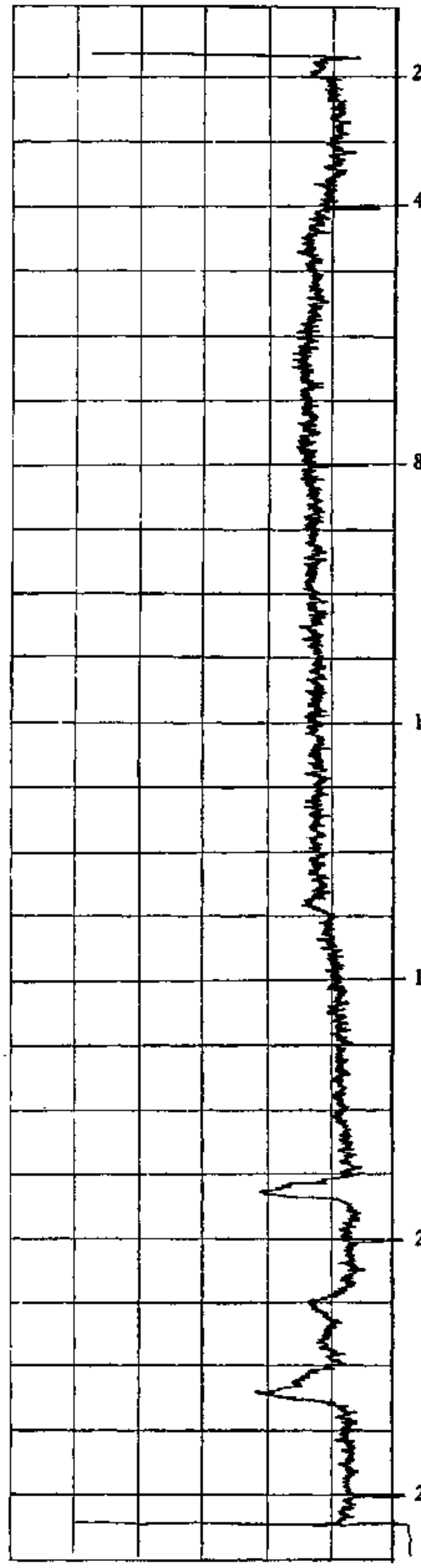
Graph 9 - X-ray diffraction graph of the hydroboracite heated to 400°C. Hydroboracite - 400°C (HY - 400).



Graph 10 - X-ray diffraction graph of the hydroboracite heated to 450°C. Hydroboracite - 450°C (HY - 450).



Graph 11 - X-ray diffraction graph of the hydroboracite heated to 500°C. Hydroboracite - 500°C (HY - 500).



Graph 12 - X-ray diffraction graph of the hydroboracite heated to 600°C. Hydroboracite - 600°C (HY - 600).

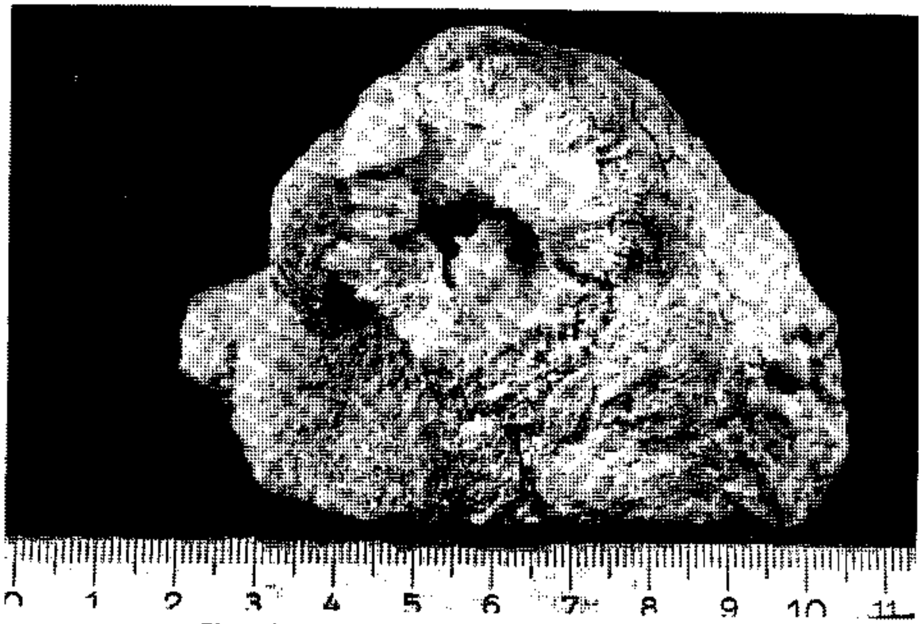


Photo 1 - Original form of hydroboracite (natural size).

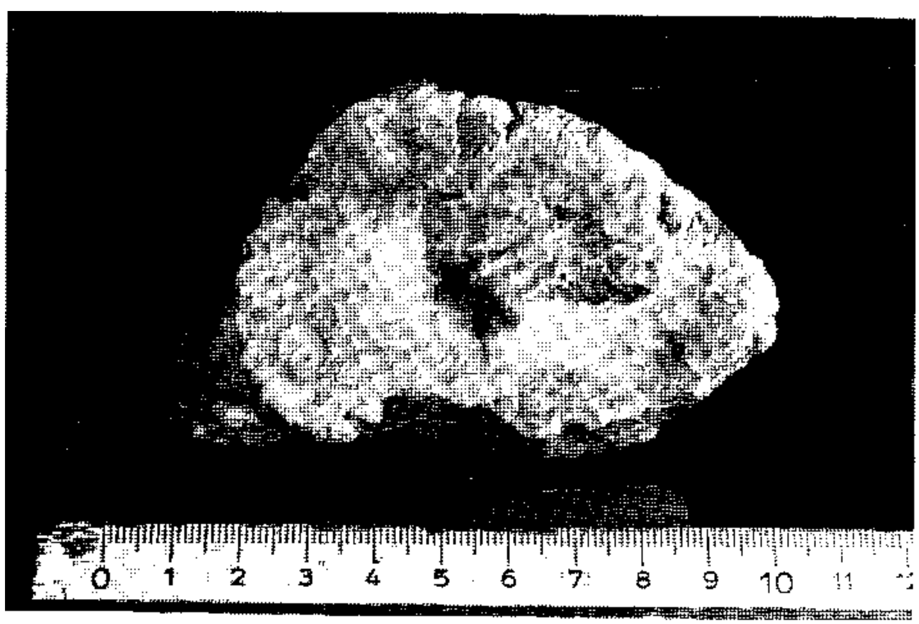


Photo 2 - A cross-section of hydroboracite (natural size).

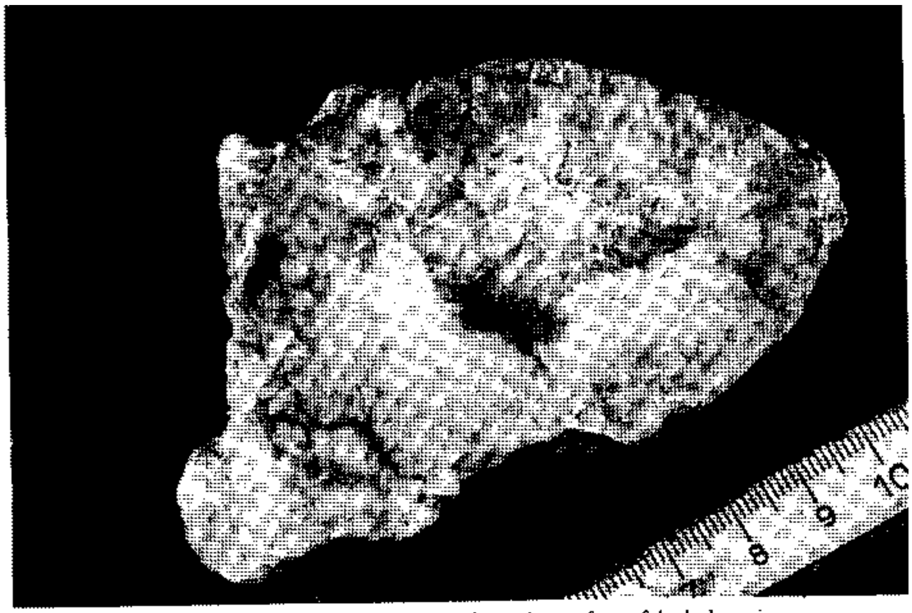


Photo 3 - The nodules observed on the surface of hydroboracite.

Photo 4 - Thin-section of crude hydroboracite (100 ×, + N).

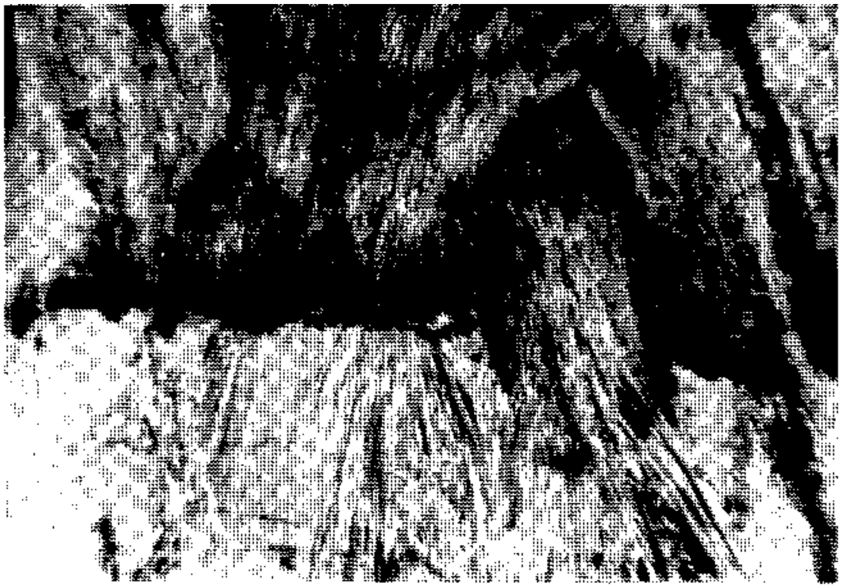


Photo 5 - Thin-section of crude hydroboracite (100 ×, + N).

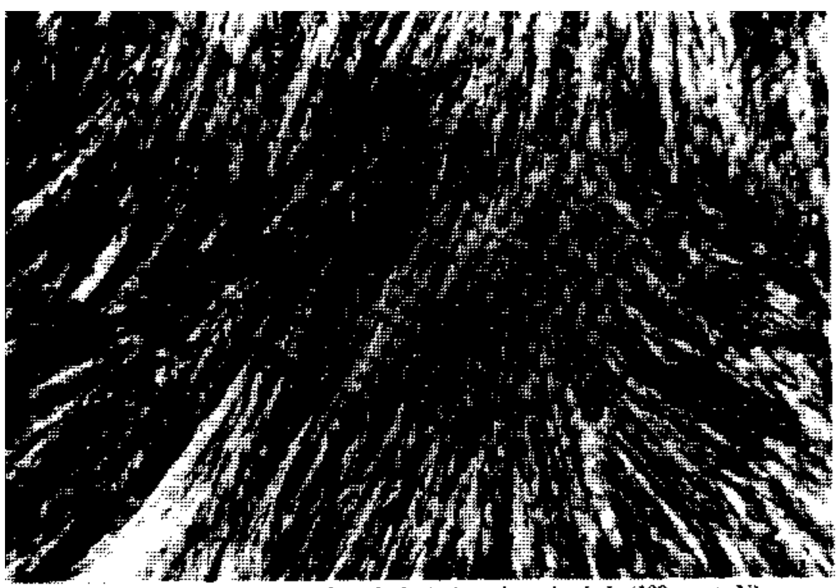


Photo 6 - Radial aggregates of crude hydroboracite microlath (100 ×, + N).

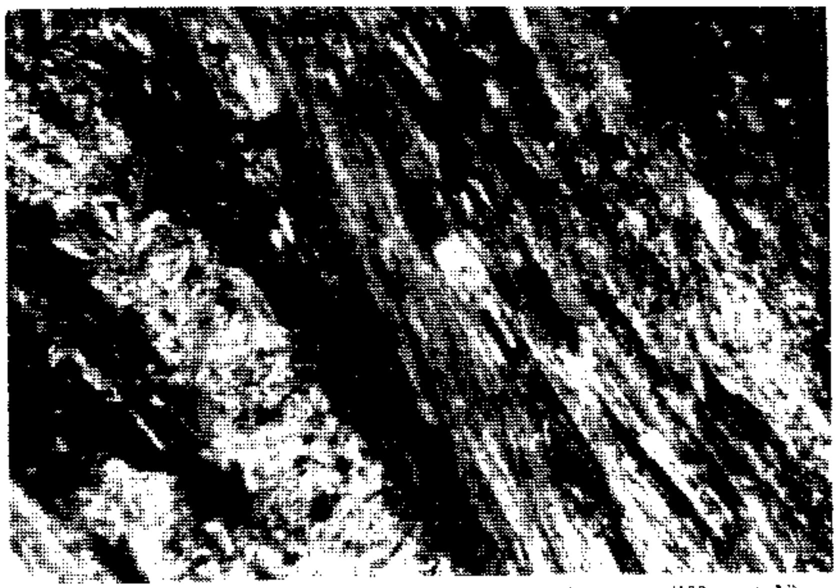


Photo 7 - Another section showing the complex radial structure (100 ×, + N).

Photo 8 - Orientation of hydroboracite crystals, thin section (100 ×, single nicol).

Photo 9 - Another view of crude hydroboracite (100 ×, single nicol).

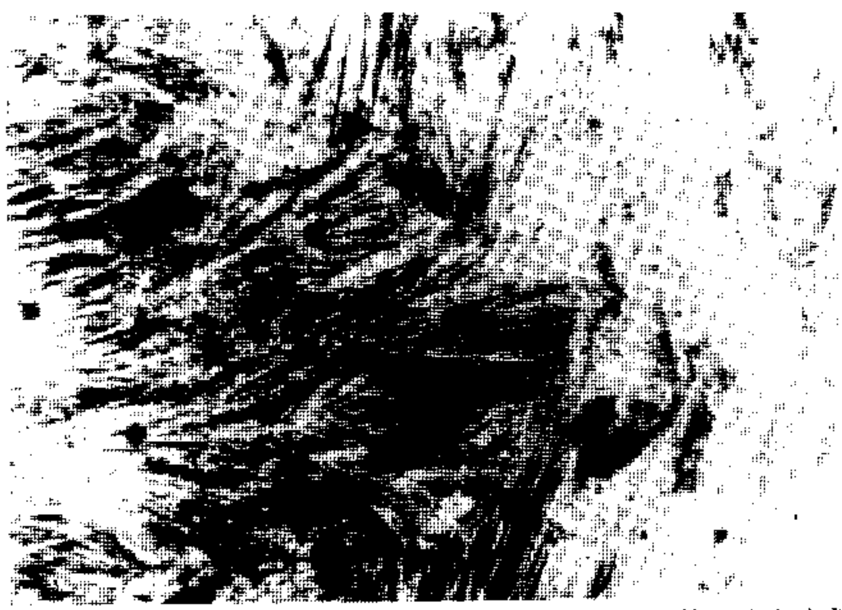


Photo 10 - Section showing the radial structure of crude hydroboracite (100 ×, single nicol).

Photo 11 - Crude hydroboracite (100 ×, single

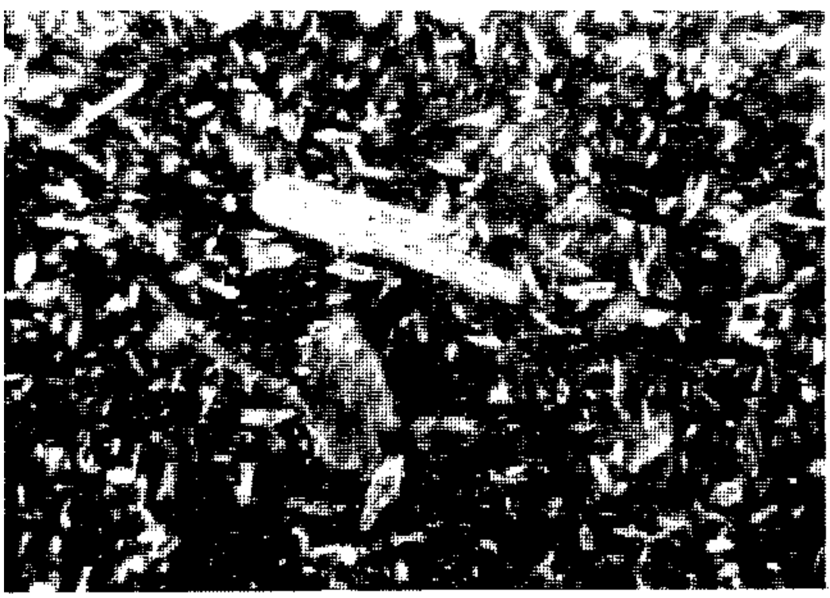


Photo 12 - Hydroboracite heated to 100°C (100 ×, + N).

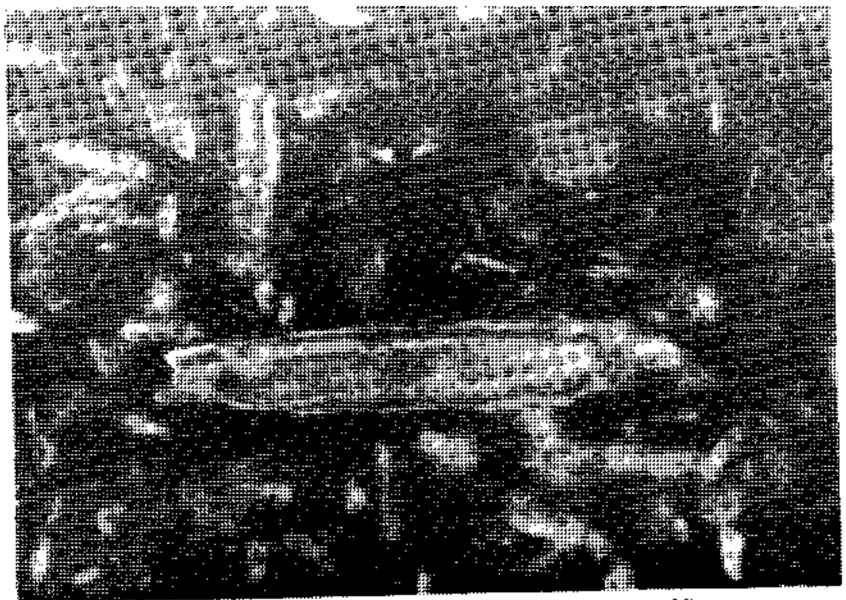


Photo 13 - Hydroboracite heated to 150°C (100 ×, + N).

Photo 14 - Hydroboracite heated to 200°C (250 ×, + N).

Photo 15 - Hydroboracite heated to 250°C (100 ×, + N).

Photo 16 - Hydroboracite heated to 300°C (100 ×, + N).

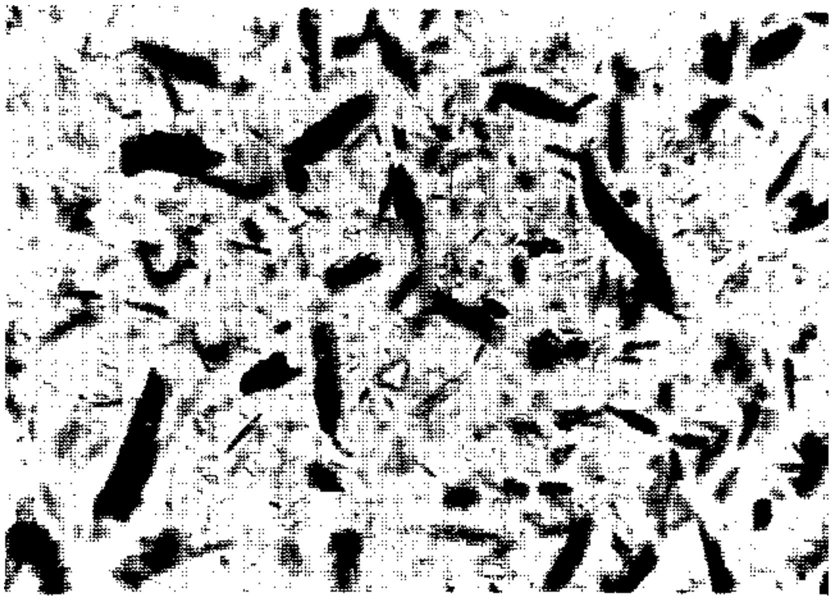


Photo 17 - Hydroboracite heated to 350°C (250 ×, single nicol).

Photo 18 - Hydroboracite heated to 350°C (250 ×, single nicol).

Photo 19 - Hydroboracite heated to 400°C (250 ×, single nicol).

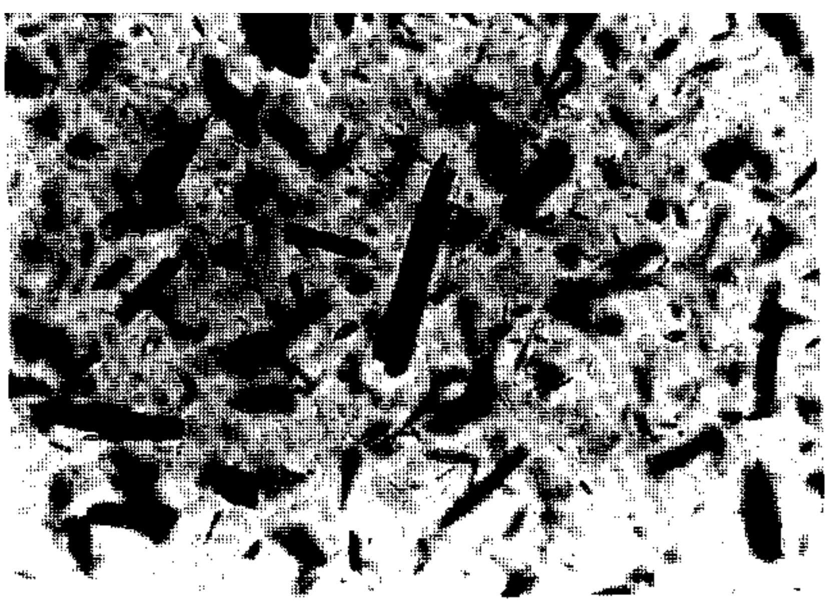


Photo 20 - Hydroboracite heated to 400°C (250 ×, single nicol).


Photo 21 - Hydroboracite heated to 450°C (250 ×, single nicol).

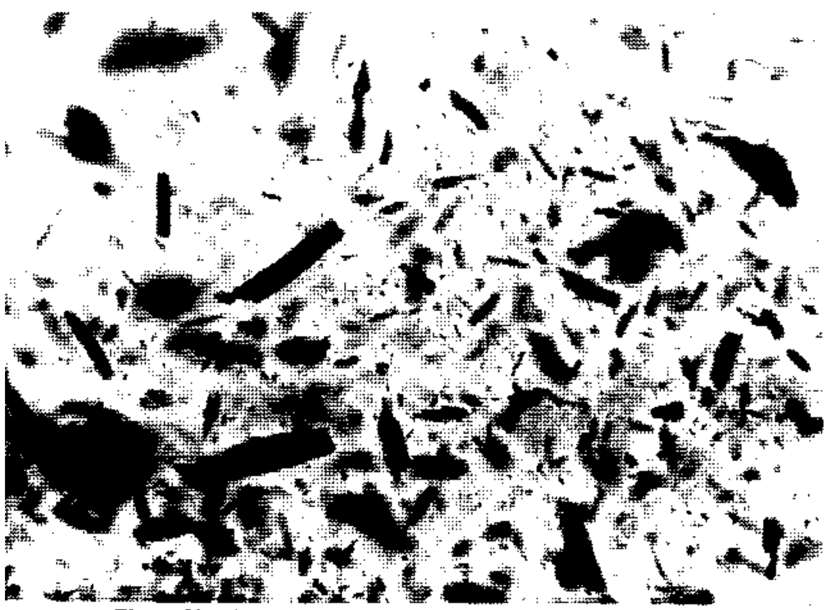


Photo 22 - Hydroboracite heated to 500°C (250 ×, single nicol).

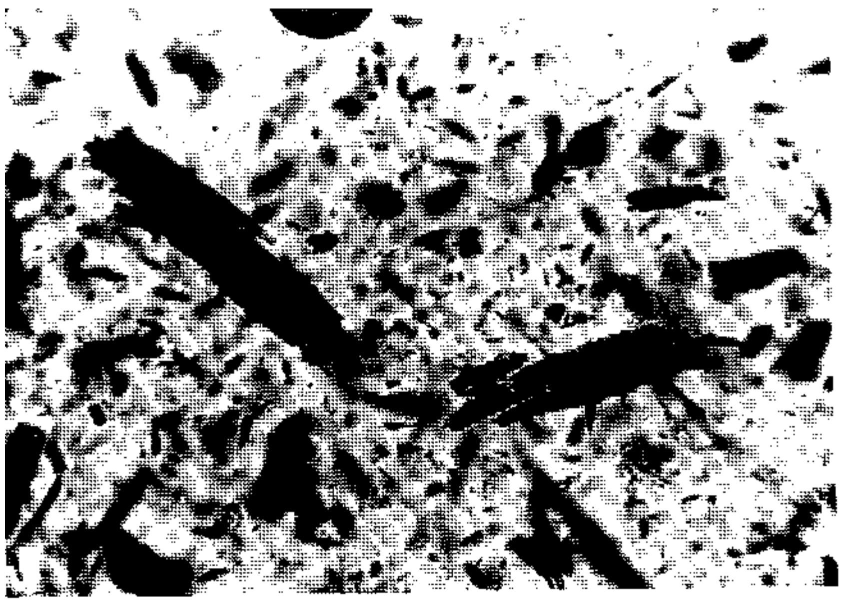


Photo 23 - Hydroboracite heated to 600°C (250 ×, single nicol).

LIST OF REFERENCES

1 —James D. DANA & Salysburry DANA (1960): The system of mineralogy. Seventh ed., vol. II, p. 353.

2 — Gmelins Handbuch der anorganischen Chemie. Bor. Nr. 13, 8. ed (1954).

3 —H. MEIXNER (1952): Über ein wahrscheinlich neues Bor Mineral aus Kleinasien. *Der Karinthin,* 15 Ap., 1952.

4————(1953): Neue türkische Boratlagerstatten. *Berg- und Hüttenmannische Monatshefte,* Band 98, Heft 5, S. 86-92.

5————(1956): Die neu türkische Boratprovinz um İskeleköy bei Bigadiç im Vilayet Balıkesir. *Kali und Steinsalz,* Heft 2, S. 43-47, *Essen-Glückauf Verlag.*

6 —Thomas, G. McMURDOCK (1958): The boron industry in Turkey. *M.T.A. Kütüphane* no. 15855. B.

7 —Ünal SANIGÖK (1964): Türkiye'deki bor minerallerinden üleksit ve inyoit üzerinde araştırmalar. *Şirketi Mürettibiye Basımevi,* İstanbul, s. 4.

8 — Işık ÖZPEKER (1969): Batı Anadolu borat yataklarının mukayeseli jenetik etüdü. *Ak Matbaası,* İstanbul. *İstanbul Teknik Üniversitesi Maden Fakültesi.*

9 —P. RAMDOHR & H. STRUNZ (1967): Klockmann's Lehrbuch der Mineralogie. *Ferdinand Enke Verlag,* Stuttgart, S. 568.

10 —Hüseyin GÜLENSOY (1961): Türkiye'deki bor mineralleri ile bunların dehidrolanmaları, çözünürlükleri ve katı cisim reaksiyonları hakkında. *Şirketi Mürettibiye Basımevi,* İstanbul, s. 12-30.