ON THE DISCOVERY OF BETEKHTINITE IN THE BULANCAK (GİRESUN, TURKEY) SULPHIDE VEINS

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The investigated area is situated between villages of Küçükdere and Darıköy about 10 km south of Bulancak, between Çamkoza and Büyükgüre streams.

Sulphide veins occur in lower basic series and dacitic series rocks of Eastern Pontid volcanics.

Petrographic study and chemical analyses of the country rocks — despite their hydrothermal alteration — show that they are mainly of calc-alkaline character. Volcanic activity took place from Upper (possibly Lower) Cretaceous to Miocene, as indicated by intrusives dated at 25 million years (Çoğulu, 1970).

The Bulancak Cu-Pb-Zn sulphide veins are the best representatives of their type among the varied deposits of the Eastern Pontus Ore Province. Data based on a study of more than 2500 primary and secondary fluid inclusions have shown that the inclusions were moderately saline, salinity varying within the range 13.2 equivalent wt. % NaCl to almost fresh water indicated by a density change from 0.74 gr/cm^3 in the early vein stage to 0.98 gr/cm^3 at the end of the base metal sulphide stage. Homogenization temperatures ranged from ca. 340°C to 80°C (Akıncı, 1974).

OPTICAL PROPERTIES OF BETEKHTINITE

Betekhtinite has not previously — to the writer's knowledge — been reported, either from this area of anywhere else in Turkey. It has been found only in one location as a major constituent but several veins contain very small amounts.

In polished section betekhtinite has a gray to creamy color, with a pinkish tint, and appears creamy against bornite. Its color appears relatively bright when associated with bornite and digenite and dull when associated with the exsolution lamellae of digenite. It has a weak reflection pleochroism which varies with the orientation of the grains. Polarization colors are dull red or blue, depending on the orientation, whereas with slightly uncrossed polars orange, blue, yellow-green and purple colors may be seen.

Cleavage is seen only when the mineral contains digenite exsolution lamellae and is oriented in three directions in the betekhtinite.

It is found associated with galena, bornite, digenite, fahlerz, pyrite, quartz, dolomite and cerussite. Bornite was seen either forming, rings around a quartz enclosure or in cracks or, in many cases, rimming betekhtinite. Bornite and digenite were also seen veining betekhtinite. Myrmekitic intergrowths of galena-bornite are also enclosed in betekhtinite as well as rare galena-digenite intergrowths (Akıncı, 1974, plates 5, 6, 10b;c,d).

This myrmekitic texture, which is almost identical to that described by Schüller and Wohlman (1955) and Matsukama (1971), has been suggested as representing decomposition or breakdown of betekhtinite.

Betekhtinite replaces galena along quartz-galena boundaries or cleavage planes of galena and is itself replaced by digenite along fractures or the crystal outlines of quartz inclusions. Some galena patches with irregular outlines were observed cutting across the digenite exsolution lamellae in betekhtinite. In places betekhtinite replaces quartz and is seen intergrown with cerussite—possibly altered from pre-existing galena before betekhtinite deposition.

Polishing hardness checks were made against tennantite and bornite when in contact with these minerals and it was found to be harder than bornite. The Vickers microliardness was found to vary from 148.9 to 182 kg/mm^2 with a standard load 100 p (= 100 gr). Most of the measurements fall within the range of 150 kg/mm^2. Tsonev *et al.* (1970) have found the microhardness of betekhtinite as 210-230 kg/mm^2 with a Hohneman-type microhardness meter at a loading of 5 gr.

The optical properties of the Bulancak betekhtinite are similar to those of betekhtinite from Mansfeld and Dzhezkazgan but the intensity of anisotropy varies. It has rather smooth and rounded outlines in contrast to the prismatic, acicular habit reported from the Mansfeld and Dzhezkazgan deposits. The dominant mineral assemblages show almost similar characteristics to the Mt. Lyell occurrences (Markham & Otteman, 1969). Previously reported betekhtinites were confused with chalcocite and wittichinite, and it has similar color and reflectivity characteristics to enargite.

X-RAY DIFFRACTION PATTERN

A needle mounted hand drill was used for powder photography to avoid impurities. In this way material for powder photographs was obtained while the specimen was viewed under the microscope.

A Debye-Scherrer camera (14.6 cm diameter) using the Straumanis film technique was employed with filtered co-radiation to obtain powder photographs as described by Klug and Alexander (1962). Details of various diffraction patterns are given in Table 1 in comparison with other published data.

A computer program DPOW (Hall, 1971) was employed to obtain d-spacings of the diffracted lines which were fed into two programs GENSTRUK and COHEN (Marples & Shaw, 1966) for indexing and calculating the unit cell parameters, respectively.

The cell parameters are in agreement with those given by Dornberger-Shiff and Hohne (1959):

Bulancak, Turkey	*Mansfeld, Germany*
$a = 14.693 \mp 0.006$	14.67 (A°)
$b = 22.720 \mp 0.003$	22.80
$c = 3.861 \mp 0.005$	3.86

Volume = 1288.9 $A^{\circ 3}$. For Z = 4* the density (r) of betekhtinite was found to be 5.68 which is lower than measured value 6.13 by Mukariov *et al.* (1961). However, it was calculated as 5.73 by Dornberger-Schiff and Hohne *(op.cit.),* which is in agreement with the value given above.

Table - 1

X-Ray diffraction data for betekhtinites

Bulancak			*Dzhezkazgan*[1]		*Radka*[2]		*Mansfeld*[3]	
hkl	I/I_0	*d (A°)*	*I*	*d (A°)*	*I*	*d (A°)*	*I*	*d (A°)*
—	—	—	—	—	2	12.3	—	—
—	—	—	—	—	1	11.3	—	—
200	20	7.37	—	—	—	—	—	—
040	50	5.65	—	—	1	5.72	—	—
310	50	4.77	3	4.77	3	4.80	4	4.77
150	20	4.32	1	4.31	2	4.36	1	4.30
330	—	—	—	—	1	4.13	—	—
060,011	—	—	—	—	1	3.82	—	—
400	—	—	—	—	1	3.67	—	—
121	20	3.56	—	—	—	—	—	—
420	20	3.49	—	—	2	3.50	—	—
350	30	3.33	—	—	2	3.34	—	—
—	—	—	—	—	—	—	1	3.27
170,141,231	—	—	—	—	2	3.13	—	—
301,440	80	3.09	7	3.08	8	3.06	8	3.08
051,321	100	2.94	8	2.94	9	2.93	9	2.93
080	—	—	—	—	1	2.83	—	—
530,251,370	30	2.74	—	—	3	2.72	—	—
341,161,280	50	2.68	4	2.67	3	2.68	4	2.67
071,431,190	50	2.52	—	—	2	2.52	—	—
550,071	50	2.48	5	2.48	3	2.47	5	2.46
620	50	2.40	1	2.40	2	2.39	2	2.39
271	70	2.35	6	2.36	5	2.36	6	2.35
451,521	30	2.30	3	2.31	2	2.30	4	2.29
640,390,480	30	2.26	3	2.26	2	2.25	4	2.25
—	—	—	—	—	—	—	1	2.15
091	20	2.11	—	—	1	2.11	—	—
660,471,611	15	2.06	—	—	2	2.06	—	—
730,291	10	2.02	4	2.02	2	2.02	6	2.01
631	10	1.995	—	—	—	—	—	—
561	—	—	—	—	1	1.987	—	—
—	—	—	6	1.952	—	—	7	1.946
4.10.0,002	60	1.934	—	—	6	1.938	—	—
0.12.0,022	10	1.899	—	—	—	—	—	—
651	15	1.888	4	1.894	2	1.892	4	1.894
721,800,042,491	90	1.830	10	1.832	10	1.834	10	1.832
152,770	40	1.762	6	1.766	5	1.769	7	1.766
5.11.0,262	5	1.680	1	1.684	2	1.682	1	1.682
860,172	—	—	4	1.653	3	1.649	—	—
—	—	—	—	—	—	—	4	1.643
—	—	—	—	—	2	1.596	—	—
5.13.0	20	1.506	1	1.510	—	—	1	1.514
—	—	—	1	1.462	1	1.462	3	1.461
—	—	—	—	—	1	1.428	—	—
2.16.0	10	1.399	1	1.409	1	1.405	3	1.406
752,6.14.0	20	1.355	2	1.363	1	1.360	3	1.359
682,6.13.1	20	1.338	2	1.340	1	1.337	3	1.340
10.8.0	20	1.305	4	1.312	2	1.307	5	1.307
103,9.11.0	10	1.283	1	1.287	1	1.285	1	1.287
213,0.18.0	20	1.265	2	1.275	2	1.268	4	1.268

Table - 1 (contd.)

862	15	1.256	1	1.250	—	—	1	1.260
053,792	10	1.239	—	—	1	1.242	4	1.241
882,10.9.1	20	1.206	2	1.212	1	1.214	4	1.208
—	—	—	2	1.192	—	—	4	1.191
10.02	5	1.168	—	—	—	—	—	—
11.11.0	30	1.122	1	1.126	2	1.122	7	1.125
12.71	20	1.099	7	1.103	2	1.101	8	1.103
0.11.3	50	1.093	—	—	—	—	—	—
583	10	1.089	—	—	—	—	—	—
—	—	—	1	1.074	—	—	4	1.074
11.13.0	10	1.0604	1	1.065	—	—	1	1.065
—	10	—	1	1.057	—	—	4	1.056
693	10	1.038	5	1.034	—	—	5	1.034
9.13.2	10	1.0145	5	1.018	—	—	5	1.018
14.80	20	0.984	1	1.005	—	—	—	—
15.30	20	0.970	—	—	—	—	—	—

[1] Mukanov *et al.*, 1961.

[2] Tsonev *et al.*, 1970.

[3] Tsonev *et al.*, 1970.

ELECTRON MICROPROBE ANALYSIS

Instrument employed during this investigation was a Cambridge Scientific Instruments «Geoscan-Mk II» with a take-off angle of 75°. 20 KV accelerating voltage was used. Specimen currents were changed from 0.02 mA to 0.12 mA, depending on the elements and lines excited. Standards and specimens were carbon-coated simultaneously by monitoring carbon film thickness during evaporation.

Raw counts were first corrected for a 4 micro-seconds dead time and drift with the aid of the on-line Varian 620-100 computer, by the program «TIM-3» written by Dr. A. Peckett (Durham University, Geology Department, England). The program corrects for mass-absorption, secondary fluorescence and the atomic number effect (stopping power and electron back-scatter) in the manner described by Sweatman and Long (1969) for K, L, and M lines.

Ag-metal, FeS_2, Cu-metal, PbS, and ZnS were used for Ag, Fe, Cu, Pb and S standards, respectively.

A hand specimen supplied to the writer by Ethem Acar from Harköy Mine, Tirebolu, was found to contain betekhtinite which is confirmed by electron microprobe analysis given in Table 2. Previously only enargite has been described from Harköy Mine (Acar, private communication) possibly due to misidentification of betekhtinite.

Bulancak and Harköy betekhtinites have practically the same chemical composition as the material from the six other localities previously reported (Table 2). Only La Leona (Argentine) betekhtinite differs from all the other analyses listed in Table 2, since it has a very low Pb-content and somewhat higher sulphur, iron and copper contents. Silver was only reported from the Dzhezkazgan deposit specimen.

There is some doubt on the exact formula to be accepted for this mineral. Schüller and Wohlman (1955) have given Cu_{10} (Fe, Pb) S_6, although this formula was corrected as Pb_2 (Cu, Fe) $_{21}S_{15}$ (Dornberger-Schiff & Hohne, 1959). Mukanov *el al.* (1961) suggest (Pb, Ag) (Cu, $Fe)_{11}S_7$. Since the disagreement is on the number of sulphur and copper atoms the formulas derived were calculated on the basis of 1 Pb atom and are given in the bottom part of the Table 2.

Table - 2

Betekhtinite analyses from Bulancak and Harköy in comparison with other occurrences

	Bulancak 1a	*Bulancak* 1b	*Harköy* 2	*Mansfeld* 3	*Mt. Lyell* 4	*La Leona* 5	*Dzhezkazgan* 6	*Bulgaria* 7	*Japan* 8
Cu	59.67	59.34	58.64	59.70	59.00	61.40	58.88	59.07	57.20
Pb	18.71	19.34	18.34	17.33	17.30	12.60	17.47	18.01	18.60
Fe	2.42	2.41	2.65	2.69	2.70	3.50	2.81	1.65	2.50
Ag	N.D.	N.D.	0.14	—	—	—	0.79	—	—
S	19.45	20.19	20.93	20.09	20.60	22.80	20.16	20.77	21.70

1a	$Cu_{10\cdot 40}Fe_{0\cdot 48}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{6\cdot 72}$	(present study)
1b	$Cu_{10\cdot 00}Fe_{0\cdot 46}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{6\cdot 75}$	(present study)
2	$Cu_{10\cdot 43}Fe_{0\cdot 54}Pb_{1\cdot 0}Ag_{0\cdot 01}S_{7\cdot 38}$	(present study)
3	$Cu_{11\cdot 24}Fe_{0\cdot 58}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{7\cdot 50}$	(A. Schüller, 1960).
4	$Cu_{11\cdot 13}Fe_{0\cdot 58}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{7\cdot 70}$	(N.L. Markham, & J. Otteman, 1968).
5	$Cu_{15\cdot 89}Fe_{1\cdot 03}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{11\cdot 70}$	(B.M. Honnorez-Guerstein, 1971).
6	$Cu_{10\cdot 99}Fe_{0\cdot 60}Pb_{1\cdot 0}Ag_{0\cdot 09}S_{7\cdot 50}$	(K.M. Mukanov *et al.*, 1961).
7	$Cu_{10\cdot 70}Fe_{0\cdot 34}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{7\cdot 45}$	(D. Tsonev *et al.* 1970).
8	$Cu_{10\cdot 04}Fe_{0\cdot 49}Pb_{1\cdot 0}Ag_{0\cdot 0}S_{7\cdot 55}$	(T. Matsukama, 1971).

BETEKHTINITE STABILITY

The betekhtinite deposits reported from La Leona, Mansfeld and Dzhezkazgan are from similar geological environments. The betekhtinite from Bulancak, Radka (Bulgaria) and Furotobe Mine (Japan) are, however, representatives of the Kuroko type of volcanic environment in which chalcocite developed at the expense of chalcopyrite with bornite as an intermediate stage preserved as metastable crystals.

In experimental studies Craig and Kullerud (1967, 1968) found no betekhtinite in any of their syntheses which were made at temperatures of 200°C and above. Markham and Otteman (1968) attempted to synthesize betekhtinite at 505°C but they also obtained phase assemblage as Craig and Kullerud did. Slavskaya e*t al.* (1963) found natural betekhtinite decomposed at 150°C to digenite and galena, a mixture that also is stable at room temperature. Decomposition proceeds with decrease in volume. It, therefore, seems that betekhtinite is certainly not stable above 150°C.

Matsukama (1971) suggests that as betekhtinite appears to be the last product of Kuroko deposits, it may indicate a temperature of around 100°C, the stability field being restricted within very narrow limits between those of bornite and chalcocite. The presence of betekhtinite in recrystallized galena in Mt. Lyell deposits as described by Markham and Otteman (1969) suggests that the temperature reached during recrystallization may have coincided with that of the betekhtinite stability field. In contrast, the Mansfeld and Dzhezkazgan betekhtinites show breakdown to galena and copper sulphides. Textural evidence in the Bulancak specimens is not, however, sufficient to indicate in which direction the reaction has occurred in the assemblage betekhtinite, galena and digenite.

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REFERENCES

AKINCI, Ö.T. (1974): The geology and mineralogy of copper, lead, zinc sulphide veins from Bulancak, Turkey. *Unpubl. Ph. D. Thesis, University of Durham,* England.

CRAIG, J.R. & KULLERUD, G. (1967): Phase relations and mineral assemblages in the Ag-Bi-Pb-S system *Mineral Deposits,* 1, 278-306.

————(1968): Phase relations and mineral assemblages in the copper-lead-sulfur system. *Am. Mineralogist,* 53, 145-161.

ÇOĞULU, E. (1970): Gümüşhane ve Rize granitik plutonlarının mukayeseli petrolojik ve jeokronolojik etüdü. *İ.T.Ü. Maden Fakültesi (Doçentlik tezi), İ*stanbul.

DORNBERGER-SCHIFF, V.K. & HÖHNE, E. (1959): Die Kristallostruktur des Betechtinit Pb_2 (Cu, $Fe)_{21}S_{15}$. *Acta Cry st.,* 12, 646-651.

HALL, A.J. (1971): The mineralogy of some synthetic sulphosalts. *Unpubl. Ph. D. Thesis, University of Durham,* England.

HONNOREZ-GUERSTEIN, B.M. (1971): Betekhtinite and bi-sulphosalts from the copper mine of «La Leona» (Argentina). *Mineral Deposita (Berl.), 6,* 111-121.

KLUG, H.P. & ALEXANDER, L.E. (1962): X-ray diffraction procedures. *John Wiley & Sons, Inc.,* 716, p.

MARKHAM, N.L. & OTTEMAN, J. (1968): Betekhtinite from Mt. Lyell, Tasmania. *Mineral Deposita (Berl),* 3, 171-173.

MARPLES, J.A.C. & SHAW, J.L. (1966): Two crystallographic computer programs for lattice parameter refinement and for calculating expected line position. *UKAEA Research Group,* Report AERE-R5210.

MATSUKAMA, T. (1971): Betechtinite from the Kuroko deposits of the Furotobe Mine, Akita Prefecture, Japan. *Mineral Soc. Japan Spec. Paper* 1, 191-195.

MUKANOV, K.M. *et al* (1961): On the occurrence of betekhtinite in the Dzhezkazkan ore deposits. *Dokl. Acad, Sci. USSR, Earth Sci. Sect.,* 130, 133-135.

SCHULLER, A. (1960-1961): Zur Kenntnis des Betechtinit (Cu, $Fe)_{10}$ PbS_6. *Neuesjahrb. Mineral. Monatsh.,* 121-131.

————& WOHLMAN, E. (1955): Betechtinit, ein neues Blei-Kupfer-Sulfid aus den Mansfelder Rücken. *Geologie,* 4, 535-555.

SLAVSKAYA, A.I. *et al.* (1963): O razlozhenii betekhtinita pri nagrevanii. *Journal for Geology of Ore Deposits* (in Russian), 3, 97-100.

SWEATMAN, T.R. & LONG, J.V.P. (1967): Quantitative electron-probe microanalysis of rock-forming minerals. *Jour. Petrology,* 10, 332-379.

TSONEV, D. *et al* (1970): Betekhtinite from the Radka deposit. *Bull Geol Inst. Bulgar. Acad. Sci. Ser. Geochem. Min. Petrogr.,* 19, 167-177.