COULD A COMPLETE SOLID SOLUTION BETWEEN AIKINITE AND BISMUTHINITE EXIST ?

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ABSTRACT. — During the study of polymetallic sulphide veins in Bulancak (Giresun, Turkey) the presence of aikinite (Cu Pb BiS3) was identified by means of x-ray diffraction, optical studies, and electron probe microanalysis methods.

Minerals identified as aikinite have compositions which are not in agreement with the theoritical aikinite compositions. They are suggested to be members of the aikinite-bismuthinite solid solution series and are close to the aikinite end member.

As a result of these studies it was shown that every solid solution composition is possible between aikinite and bismuthinite.

INTRODUCTION

The subjects of the authors previous papers were the geology, formation temperatures, salinity and density, of ore - bearing solution giving way to the sulphide veins to the south of Bulancak (Akıncı, 1974; 1975; 1976a; 1976b). During the study of samples collected from five separate sulphide veins the presence of aikinite minerals was identified for the first time in Turkey by the author.

MATERIALS STUDIED

The colour of the aikinite in the studied samples is hardly distinguishable from that of galena. When enclosed in sphalerite and pyrite, aikinite shows greyish or dull colours and weak anisotropy. In contrast, when associated with chalcopyrite and digenite, it appears pinkish and much brighter with a strong anisotropy. Reflection pleochroism is distinct. Cleavage is in one direction and distinctive when digenite and covellite replace the mineral along cleavage planes. Elongated, lath-like, prismatic forms and xenomorphic grains are common.

Under crossed polars polarisation colours change from deep bright blue to bright yellowish-green or yellowish - brown depending on the orientation of the grains and possibly on the bismuth content.

It shows a coarse polycrystalline texture with grains oriented parallel to the prismatic direction and was seen cutting across a twin lamellae of chalcopyrite.

Aikinite grains are commonly found enclosed in chalcopyrite as rounded or elongated forms or as an island in digenite which is enclosed in chalcopyrite (Photo 1).

Digenite always replaces aikinite along cleavage planes or occurs as patches throughout the aikinite grains. Tennantite was fond replacing, veining or surrounding aikinite. It is usually found in association with pyrite and marcasite. It replaces pyrite along grain boundaries and cleavage planes or the replacement may develop from the central part of pyrite crystal along cleavage directions (Photo 2).

Replacement of sphalerite was also observed in one of the samples in which aikinite is in turn replaced by fahlerz. Sometimes aikinite was seen cutting across a quartz- fahlerz boundary in a limonite - digenite intergrowth resulting from the alteration of chalcopyrite which is seen as relics in the limonitic groundmass.

X-RAY DIFFRACTION PATTERN

Unit cell parameters of one of the samples, of which composition was established by electron probe microanalysis, was measured with the powder photography method explained previously (Akıncı, 1976b). The cell parameters as seen in table 1, are in agrement with those of the Berezovsk aikinite given by Peacock (1942).

Table 1 - Unit cell parameters and densities of Bulancak and Berezovsk aikinites

Bulancak (Turkey)	*Berezovsk (Russia)*
a = 11.297 A°	11.30
b = 11.654 A°	11.64
c = 4.061 A°	4.00
Volume = 534.650 A$^{\circ 3}$	p Measured = 7.22
Calculated p = 7.66	p Calculated = 7.08

The details of various diffraction patterns were given in Table 2.

Peacock (1942) noted that «the aikinite from Berezovsk had a spacing at d 2.36 A° which does not correspond with any possible set of planes in the mineral although it does agree with the strongest reflection in the diffraction pattern of gold which is reported to exist together with aikinite». This spacing, however, was found to occur in all aikinites shown in table 2. It therefore seems unlikely to be due to gold; x-ray diffraction pattern suggest that it is due to the 411 plane reflection.

Table 2 - X-Ray diffraction data for aikinites

*hkl**	*Bulancak*	*Berezovsk (Russia)*[1]	*Dzhido (Russia)*[2]	*Gladhammer (Sweden)*[3]
120	5.16	—	5.20	—
—	—	—	—	4.862
—	—	—	4.54	—
220	4.04	4.07	4.07	4.069
101, 011	3.80	3.77	—	3.82
130	3.66	3.67	3.66	3.716
111	—	—	—	3.626
310	3.59	3.58	3.58	3.600
021, 201	3.29	—	—	3.328
121	—	3.18	3.18	3.194
211, 320	3.170	—	—	3.171
040	—	—	—	2.915
221	2.856	2.88	2.85	2.87
140	—	—	—	2.84
410, 301	2.745	2.74	2.73	2.764
313, 330, 311	2.673	2.68	2.68	3.713
240	2.585	2.580	2.590	2.594
420	—	2.56	2.55	2.553
231, 321	2.498	2.510	2.510	2.513

Table 2 - (Çontinued)

*hkl**	*Bulancak*	*Berezovsk*[1]	*Dzhido*[2]	*Gladhammer*[3]
041	—	—	2.40	—
411	2.356	2.36	2.36	2.366
150, 340	2.301	—	2.30	2.314
—	—	2.27	2.27	2.278
510	—	—	—	2.25
241	2.174	2.17	2.190	2.183
250, 421	2.145	2.15	2.16	2.157
440, 051	2.015	2.02	2.03	2.024
431, 151	1.985	1.984	1.99	1.993
501, 151	—	—	—	1.979
530, 112, 511	1.9456	1.947	1.952	1.959
202, 600, 212	1.8778	1.883	1.888	—
441	1.8041	1.805	—	—
312, 351, 132	1.7638	1.766	1.766	—
360	1.7231	—	1.731	—
261	1.670	—	1.680	—
621, 042, 170	1.6369	1.648	1.647	—
270, 710	1.5919	1.593	1.598	—
720	1.5536	—	1.564	—
370, 342	1.5208	1.524	1.525	—
730, 461	1.4867	1.488	1.490	—
560	1.4697	1.475	1.478	—
721	1.4488	—	1.455	—
—	—	—	1.425	—
062	1.4017	1.406	1.417	—
—	—	—	1.395	—
651	1.3758	1.380	1.370	—
471	1.3518	1.354	1.345	—
—	—	1.330	1.323	—
632	1.300	1.302	1.295	—
840, 133	1.2688	1.271	2.265	—
—	—	—	1.241	—
481	1.232	—	1.232	—
413	1.2127	1.216	1.216	—
—	—	—	1.204	—
—	—	—	1.192	—
053, 472	1.1704	1.174	1.170	—
513	1.546	1.158	1.157	—
—	—	—	1.138	—
—	—	1.123	1.125	—
—	—	—	1.120	—
603	1.0983	—	—	—
591	1.0815	1.083	1.084	—
—	—	—	1.078	—
—	—	—	1.069	—
690, 902	1.0661	—	1.0640	—
4.10.1	1.0467	—	1.049	—
—	—	—	1.041	—
—	—	—	1.031	—
—	—	—	1.027	—
723,1.11.1	1.0205	1.020	1.018	—
—	—	—	1.010	—
—	—	—	1.000	—
653	0.9928	—	0.992	—
183	0.9869	0.989	0.986	—
813, 971	0.9725	0.975	—	—
823,6.10.1	0.9613	—	—	—

[1] Peacock, 1942.

[2] Wclin, 1966.

[3] Welin, 1966.

* Few extra lines were taken from other authors and included in the list.

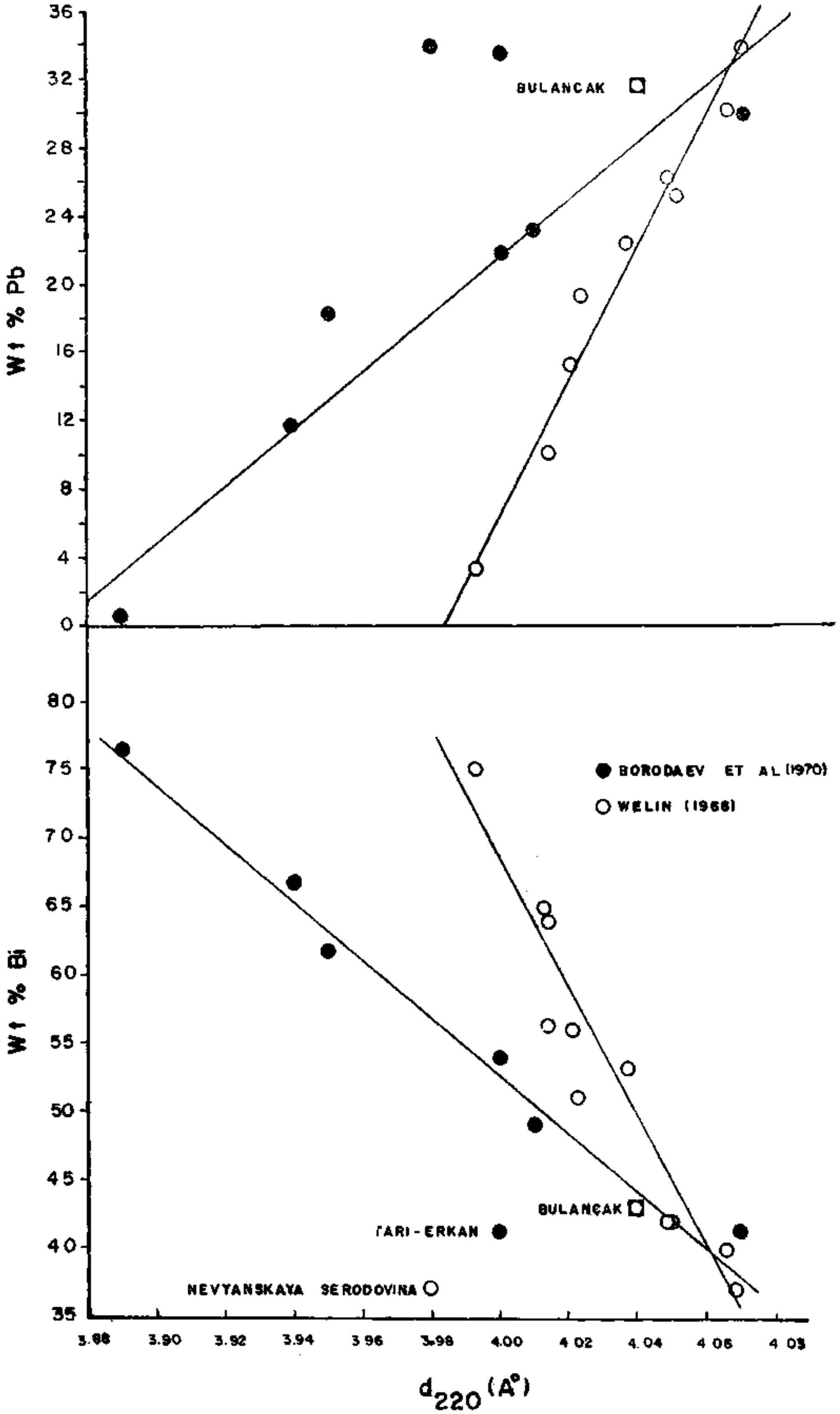

Fig. 1 - The relationship between d_{220} and Bi-Pb contents of aikinite-bismuthinite solid solution minerals.

Welin (1966) has demonstrated a linear relationship between d_{220} of aikinite-bismuthinite minerals and their Pb content. The Pb and Bi contents of these minerals from Gladhammar (Sweden) and Russia (Borodaev *et al.*, 1970) were plotted against d_{220} values together with that of Bulancak aikinite in Fig. 1. A better correlation was obtained, for both elements, from the data given by Borodaev *et* al., *(op. cit.)* in comparison to Welin's (1966) data. The only data given for Tari - Erkan and Newyanska Seredovina aikinites are scattered. Curves obtained from Russian and Swedish aikinites intersect at 4.07 A° (d) for an equivalent of 33.5 % Pb, both curves diverging into bismuthinite field because the given d_{220} values, for bismuthinite of both authors are different.

ELECTRON MICROPROBE ANALYSIS

Since the method of the microprobe analysis of the five aikinite samples was explained in an earlier paper (Akıncı, *1916b)* it will not be repeated.

The aikinite analysis given in table 3 do not exactly correspond to the theoretical aikinite composition but the plot is close to the aikinite end member in the PbS-Bi_2S_3-Cu Pb BiS_3 sub-ternary (Fig. 2).

Table 3 - Electron microprobe analyses of aikinites

	1a	1b	20	25	50	*Theoretical aikinite*
Cu	11.80	10.55	10.22	10.20	10.70	11.00
Pb	35.76	34.40	31.39	32.18	34.45	36.00
Bi	36.00	39.85	42.94	41.95	39.64	36.30
Ag	0.00	0.0	0.0	0.0	0.0	—
S	16.20	15.40	15.75	15.83	16.27	16.70
Total	99.76	100.20	100.30	100.21	101.06	100.00
Ia	$Pb_{1\cdot02}\ Cu_{1\cdot10}\ Bi_{1\cdot02}\ S_3$					
Ib	$Pb_{1\cdot03}\ Cu_{1\cdot19}\ Bi_{1\cdot03}\ S_3$					
20	$Pb_{0\cdot98}\ Cu_{1\cdot25}\ Bi_{0\cdot93}\ S_3$					
25	$Pb_{0\cdot97}\ Cu_{1\cdot22}\ Bi_{0\cdot96}\ S_3$					
50	$Pb_{1\cdot0}\ Cu_{1\cdot10}\ Bi_{0\cdot98}\ S_3$					
Theoretical $PbCuBiS_3$						

DISCUSSION ON THE AIKINITE - BISMUTHINITE SOLID SOLUTION SERIES

Bismuth minerals constitute approximately one - fifth of the known sulphosalts yet have received less attention than other sulphosalt groups. Aikinite was known to Mohs (1804) but has recently assumed increased importance in understanding the crystal chemistry of the bismuth sulphosalts. Its structure has been studied by many workers (Peacock, 1942; Wickman, 1953) and the metal atoms were readily located. Accurate coordinates for the sulphur atoms have, however, only recently been located by Kohatsu and Wuenesch (1971) using a single crystal from Berezovsk, Russia. Other occurrences of aikinite have been reported from Russia (Berezovsk, Dzhido), Sweeden (Gladhammar), Greenland (in Ivigtut cryolite deposit by Karup - Moller, 1973), Greece (Nicolaou & Hakli, 1970) and England (Kingsburry & Hartley, 1953).

Due to the similarity between both the space groups and cell dimensions for aikinite and bismuthinite (Peacock, 1942) Padera (1955) suggested the use of a common name Rezbanyite (Fig. 2) for intermediate aikinite - bismuthinite solid - solution minerals. These include such compositions as Gladite, Pb Cu Bi_5 S_9; Hammarite, Pb_2Cu2Bi_4S9 and Lindstromite, Pb Cu Bi_3S_6. Another intermediate $Pb_3Cu_3Bi_7S_{15}$ was recently described by Welin (1966) who demonstrated the development of superstructures after single crystal x-ray work on these intermediate members from the Gladhammar deposits. Recently Mumme, Welin and Wuench (1976) have shown that this intermediate composition is krupkaite and rezbanyite composition is actually Lindstromite. Welin *(op. fit.)* is also concluded that solid - solution between bismuthinite and aikinite is not continuous but that only discrete compositions are possible. He also suggested a structural classification for this solid - solution series.

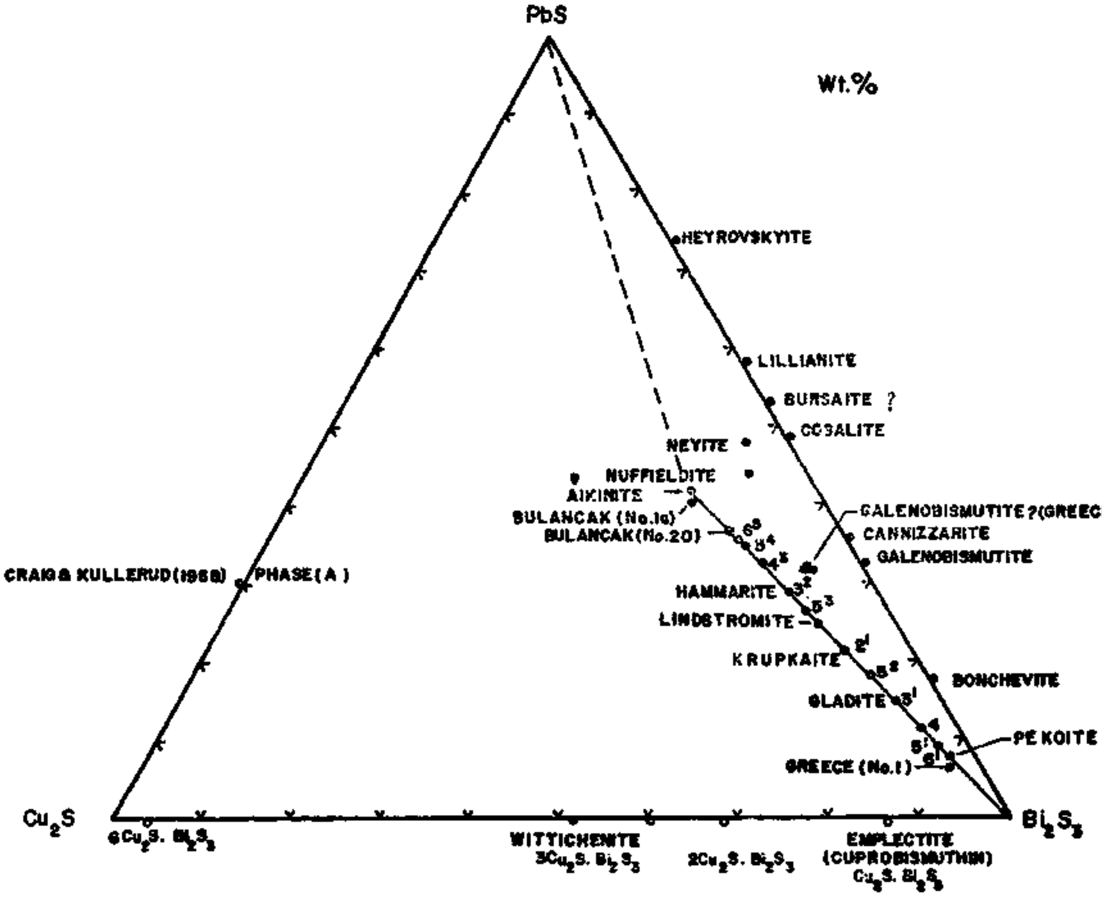

Fig. 2 - The system PbS-Cu_2S-Bi_2 S_3 showing naturally occurring compositions (solid circles) including minerals from the Bulancak area. Numbers represent z^n aikinites according to Moore (1967).

A classification was established by Moore (1967) Table 4. As aikinite is considered to be compositional limit of Pb: Bi substitution there are no extra cavities remaining to accommodate copper. Retaining aikinite as the limit of the series, Moore *(op. fit.)* referred to the intermediate members as Z_n aikinite where n=x/4 is the number of the lead(or copper) atoms in the asymetric unit cell smaller than Z; hence Z=l,x=4, n=l in aikinite Gladite $=3^1$ aikinite, Hammarite 3^2 aikinite.

«Z» is defined, as the integral multiple of the (a) translation in aikinite, without changing (b) and (c) parameters, for the superstructure with 4Z > x restriction in the general cell formula, $Cu_xPb_xBi_8z{-}_xS_{12}z$, for the aikinite derivatives.

The analysis of Bulancak aikinites indicate at least complete solubility between Dzhido aikinite, which is practically the nearest composition together with Berezovsk aikinite to the ideal aikinjte and the 6^5 aikinite composition calculated by "Moore (1967). Specimen, no. 20 has an almost identical composition to 6^5 aikinite (See table 4).

Springer (1971) has demonstrated complete solid solution between bismuthinite and aikinite in the temperature range from 300°C upwards to the melting and breakdown points. The temperature of formation may control the derivation of superstructures. Springer *(op. cit.)* could not, however, detect the superstructures which has been observed by Welin (1966) in natural specimens. This may be due to the rapid cooling under the laboratory conditions.

Table 4 - Compositions of bismuthinite derivatives* recalculated as molecular percent Bi_2S_3, PbS, Cu_2S.

Composition	*Zn*	*Bi_2S_3*	*PbS*	*Cu_2S*	*Mineral*	*Locality*
Bi_2S_3		90.16	6.80	3.25	Bizmuthinite	
$CuPbBi_{11}S_{18}$	6_1	89.90	9.15	3.00	Pekoite	Australia
$CuPbBi_9S_{15}$	5_1	87.85	9.15	3.75	—	Theoretical
$CuPbBi_5S_9$	4_1	85.15	12.95	4.65	Gladite	Russia
		80.10	14.90	5.00	Gladite	Theoretical
		79.33	14.32	5.75	Gladite	Greece
$CuPb_3Bi_3S_6$	2_1	71.30	21.30	7.40	Krupkaite	Australia
		73.82	19.50	7.40	Krupkaite	Russia
$Cu_3Pb_3Bi_4S_{15}$	5_3	66.42	24.83	8.25	Lindstromite	Dobsina
		65.60	25.40	9.00	Lindstromite	Australia
$Cu_2Pb_2Bi_4S_9$	3_2	61.75	28.75	9.50	Hammarite	Russia
		60.27	25.79	9.61	Hammarite	Theoretical
$Cu_3Pb_3Bi_5S_{12}$	4_3	57.35	32.00	10.65	—	Theoretical
$Cu_4Pb_4Bi_6S_{15}$	5_4	54.75	34.00	11.25	—	Theoretical
$Cu_5Pb_5Bi_7S_{18}$	6_5	53.00	35.25	11.75	—	Theoretical
		52.82	35.00	12.77	—	Present Study no.20
		51.60	35.88	12.75	—	Present Study no.25
$Cu_2Pb_2Bi_2S_6$		49.00	38.80	13.20	Aikinite	Present Study no.1b
		48.76	38.41	13.37	Aikinite	Present Study no.50
		44.28	39.87	14.75	Aikinite	Present Study no.1a
		45.15	40.85	14.00	Theoretical	Aikinite Composition
		46.13	38.02	15.25	Aikinite	Dzhido
		41.62	41.58	13.62	Aikinite	Berezovsk

* After Welin (1966), Moore (1967), Mumme (1975) and Mumme, Welin and Wuench (1976).

Recently discovered aikinite - bismuthinite solid solution series in Greece (Nicolaou & Hakli, 1970) range between 6^1 aikinite (analysis no. 1) and 5^3 aikinite (Analysis no. 6). Their galenobismuthinite analysis falls within the range Hammarite and Cannizzarite on the Bi_2S_3- PbS-Cu Pb BiS_3 subternary (Fig. 2). Finally, although Welin (1966) states that in fact every composition in the series bismuthinite - aikinite seems to be possible. Concequently no continuous solid solution series exists» present study ofBulancak natural sulphide specimens shows every solid-solution composition is possible between aikinite and bismuthinite. Mumme, Welin and Wuench (1976) propose that the z^n classification be discontinued.

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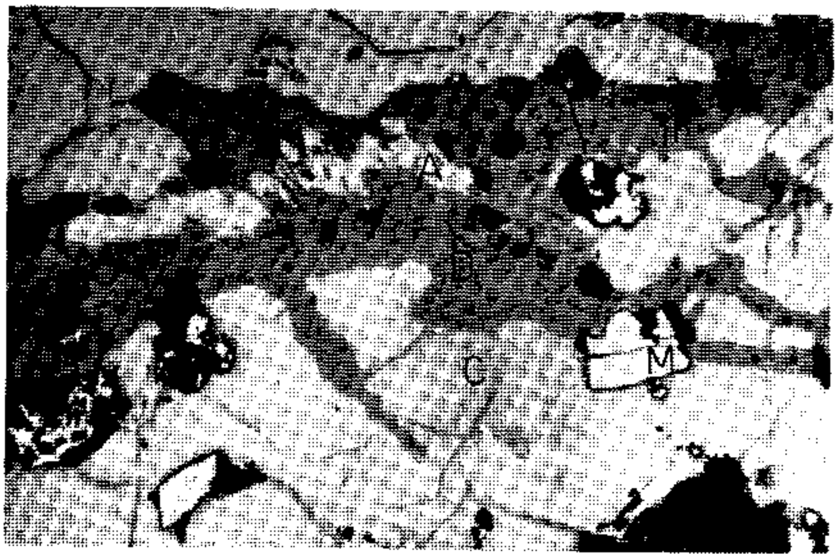

Photo 1 - Chalcopyrite (C) and marcasite (M) relationship withe Aikinite (A) as island in Digenite (D), X 100.

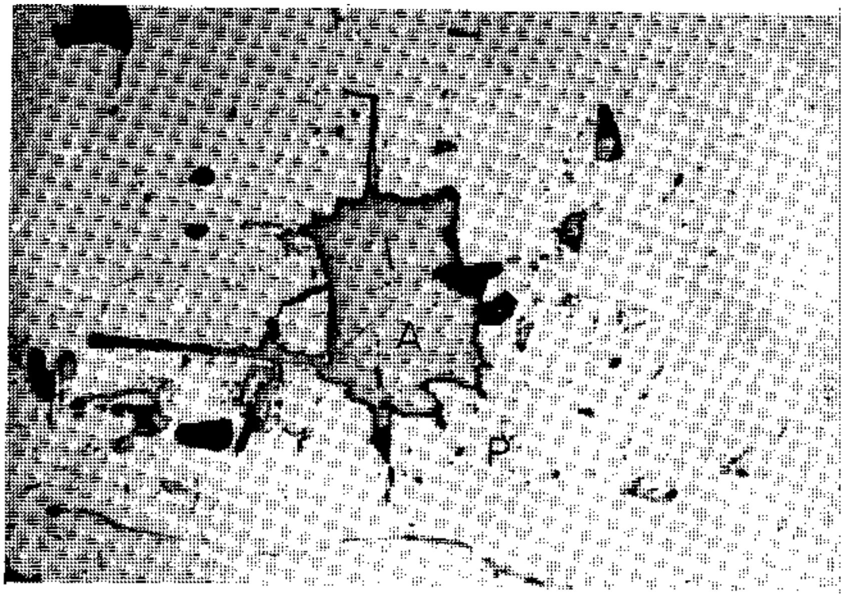

Photo 2 - Aikinite (A) development in pyrite (P) along cleavage Planes. X 100.