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polish. Writer needs to be very slow in
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Science Bowl. R.M.T. 10-7570*

A MICROSCOPIC STUDY OF NATURALLY
OCCURRING ARSENIC-ANTIMONY ALLOYS

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submitted by

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Acknowledgments

This report has been prepared from a microscopic study of polished sections of "allemontite" taken from deposits of world wide distribution. The writer wishes to thank Dr. Thompson, who took X-ray photographs and offered helpful advice, and Mr. J. Donnan who helped in the preparation of polished sections.

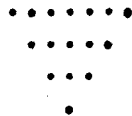


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A MICROSCOPIC STUDY OF NATURALLY
OCCURRING ARSENIC-ANTIMONY ALLOYS

Introduction

The word "allemontite" has long been used in reference to any naturally occurring mixture of arsenic and antimony regardless of the percentages of each present, and regardless of their textured relations. Dana (1932), assigned a composition of $SbAs_3$ to allemontite and suggested that all allemontite is an intergrowth of metallic arsenic and antimony. Walker (1921), studied allemontite from Atlin, British Columbia, and concluded that it is an intergrowth of successive layers of arsenic and antimony which do not form chemical compounds or

isomorphous mixtures. Holmes (1936), studied several specimens of allemontite and decided that it is normally an intergrowth of an arsenic phase which may contain small amounts of antimony (phase "A") and an arsenic-antimony mixture which may be a true chemical compound or a member of a solid solution series (phase "B"). He suggested that the term "allemontite" be restricted to phase "B" but was unable to define its chemical composition or internal structure. More recent investigations by Edwards (1947) have shown that there are three homogeneous alloy phases of arsenic and antimony which he defined as follows: (1) an arsenic-rich phase containing up to five atomic per cent antimony; (2) an antimony-rich phase containing up to five atomic per cent arsenic; and (3) an intermediate phase (stibarsenic) containing about 50 atomic per cent arsenic. On the basis of this, he described three types of allemontite which are: (1) Allemontite I - consisting of a natural intergrowth of the antimony-rich phase and the arsenic-antimony phase; (2) Allemontite II - consisting of the rare, homogeneous arsenic-antimony phase; and (3) Allemontite III - consisting of a natural intergrowth of the arsenic-rich phase and the arsenic-antimony phase. He used the equilibrium diagram of Wretblad (See Edwards, p. 42) to explain the unmixing which occurs at temperatures below 470°C in Allemontites I and III. He felt that Allemontite II is really an alloy phase and not a compound and that it owes its apparent persistent homogeneity simply to the fact that its composition is intermediate between two immiscible phases.

The purpose of this report is to study selected

samples of world wide distribution in order to determine the nature of arsenic-antimony intergrowths, and to see to what extent the conclusions of the above mentioned authors will explain these intergrowths. For convenience, Edward's terminology of the three types of allemontite will be used. In addition, because no other word in common usage will adequately convey the same thought, the word "allemontite" by itself will be used in the popular sense to mean any intergrowth of arsenic and antimony of unknown composition.

Geology of Allemontite Deposits

Allemontite deposits are commonly classed as epithermal, and are probably always hypogene. They are formed under conditions of relatively low temperature and pressure and commonly exhibit botryoidal and colloform structures. Common mineral associates are cobalt-silver-arsenide ores, silver-antimonides and silver-sulpho-antimonides. Calcite, quartz and chalcedony are the usual gangue minerals.

Laboratory Procedure

Polished sections were made from selected specimens and were examined microscopically. In order to become adept at distinguishing between arsenic and antimony which have very similar properties, specimens of native arsenic and of essentially pure antimony were used as test sections. The following differences in etch reactions were apparent:

HNO_3 (Arsenic - slowly effervesces; stains irridescent.
: (Antimony - quickly stains brown or black.

FeCl_3 (Arsenic - quickly stains irridescent to black.
: (Antimony - slowly stains brown or black.

It is realized that these differences are not great and too much importance should not be placed on the results. The tendency of arsenic to tarnish more readily than antimony is used where possible. *how ... to what colours ...*

Detailed Description of Specimens

(1) Varatrask, Sweden

Macroscopic Study

This specimen, about one inch long, contains large, euhedral crystals of allemontite having at least one cleavage well developed. The crystals are silver white in colour. With the aid of a hand lens, a fine structure resembling pillow-lava structure can be seen on the surface. Microscopic examination shows that this is an intergrowth. Associated with the allemontite are crystals of green tourmaline about 1/4 inch across, and some rose quartz.

Microscopic Study

A rather coarse intergrowth of Allemontite I is visible without crossed nicols. Both components are anisotropic. The antimony-rich phase is brighter than galena white in colour and it effervesces instantly and stains brown when etched with HNO_3 . It occurs in oval and polygonal patches up to 150 microns by 250 microns. These patches are all interconnected in at least one corner. The stibarsenic phase is medium grey in colour and does not appear to be etched by HNO_3 . It occurs in curving stringers and bands which almost surround large patches of the antimony-rich phase and which do isolate small patches of the same. (See Photograph no. 1, Appendix). It makes up about 10 per cent of the section. Oriented, elongated pits due to cleavage cut through both minerals indicating that they solidified in a homogeneous phase at first.

The presence of tourmaline and the large size of the

allemontite crystals suggests that cooling occurred slowly at higher than average temperatures. This possibly permitted the nucleation of a small number of large, homogeneous grains which unmixed at lower temperatures to form broad bands of stibarsenic on the boundaries of arsenic-rich grains. At still lower temperatures, the bands of stibarsenic became saturated with antimony and unmixed to form small antimony-rich spots within the bands. It is possible that examination under very high power would show that the large antimony-rich patches also unmixed further at lower temperatures to give a very fine intergrowth of stibarsenic in antimony.

(2) Engineer Mine, British Columbia

Macroscopic Study

Two specimens from the Engineer mine were studied. They show botryoidal structure and indistinct concentric banding. They tarnish almost black but have a silvery lustre on the fresh surface. Both have what appears to be chalcedonic quartz in colloform or rhythmic bands associated with them. The allemontite appears to be essentially homogeneous with the exception of two fractures or rhythmic bands in the large specimen which contains small, irregularly distributed grains of a soft, silvery mineral, and a few grains of a soft, pale yellow mineral somewhat the colour of pyrrhotite. A small amount of ruby silver appears to be present.

Microscopic Study

One section is homogeneous consisting of grains up to 600 microns of essentially pure antimony which show wavy anisotropic extinction with crossed nicols. The composition was

confirmed by X-ray photographs taken by Dr. Thompson.

The other section contains Allemontite III (arsenic-rich), dyscrasite and miargyrite, all of which were confirmed by X-ray photographs. The main mass consists of a very fine intergrowth of small rounded beads less than four microns across of white stibarsenic in a groundmass of a slightly darker arsenic-rich phase. The stibarsenic makes up about 25 per cent of the section. No grain boundaries are visible under crossed nicols.

Dyscrasite, which was confirmed by etching and by its anisotrophism, occurs typically in rod-shaped grains ranging from 20 to 1600 microns in length. (See Photograph no. 2, Appendix) It also occurs in irregular patches up to 1.5 mms across. Miargyrite occurs in isolated, irregularly-shaped patches or in the Allemontite III and in the dyscrasite. It is closely associated with gangue which it appears to replace. (See Photograph no. 3, Appendix)

The miargyrite and dyscrasite occupy what is probably a colloform or rhythmic band, but which may be a fracture, in the Allemontite III. All three appear to be contemporaneous in age, although the miargyrite may be slightly earlier than the dyscrasite.

It is interesting to note that of the two specimens from the Engineer mine studied, one is antimony rich and one arsenic rich. This is probably a condition to be expected in any allemontite deposit.

(3) Unknown locality, British Columbia

Macroscopic Study

Although the locality from which this specimen was taken is not definitely known, it is probably from the Engineer mine. It is a large, massive specimen about 2 1/2 inches square tarnished almost black, but in part having a red stain about the colour of hematite. It has large concentric bands and is bounded by quartz on two sides giving it a vein like appearance.

Microscopic Study

The intergrowth in this section closely resembles the Allemontite III from the Engineer mine. The stibarsenic occurs in rods and elliptical grains having a maximum length of five microns and making up about 10 per cent of the section. When the section is placed over a bottle of nitric acid for two minutes, these spots do not appear to etch, but the main mass, an arsenic-rich phase, is pitted and darkened slightly. Some small, unoriented pits are present. Allemontite III and gangue are the only minerals observed in the section.

(4) Emerald Lead-Zinc Mine, British Columbia

Macroscopic Study

The original mass of allemontite appears to have been brecciated and the fragments cemented with quartz and calcite. It has a bright, metallic lustre and does not tarnish readily. It shows some concentric banding.

Microscopic Study

The intergrowth is Allemontite I as confirmed by X-ray patterns, but is very irregular. There are antimony-rich

rhombs and borders in and around the intergrowth of stibarsenic in antimony. Stibarsenic is not present in all the section, but where it does occur it is in spindle like rods and irregular masses less than 100 microns long.

About four per cent of the section is composed of grains of stibnite which are commonly less than 50 microns across. Some of the grains are twinned. The stibnite is closely associated with and appears to replace the gangue. A few grains of pyrite, up to 100 microns in size, are partially replaced by gangue.

An undetermined mineral about the same colour as stibnite and with anisotropic colours from light to dark grey occurs in isolated, rod-shaped grains up to 100 microns long in the gangue. It appears to be negative to all the standard etch solutions, but the effervescences of calcite obscures the etch reactions to acids. It has a hardness of "B".

The brecciated and subsequent space filling appearance is not as evident in polished section as in hand specimens. On the contrary, the gangue appears to be early and to be replaced by Allemontite I. However, the lack of homogeneity in the Allemontite suggests that either crystallization did not take place under quiescent conditions or there was movement soon after.

(5) Allemont, France

Section No. 1 (Museum no. M9 - E3)

Macroscopic Study

The specimen is about 3/4 of an inch thick and three inches long. Concentric banding, which may be due to a slight κ

change in grain size, is faintly visible. Grains up to two mms. long coat what appears to be fracture planes. These grains show cleavage and tend to be lineated, possibly due to strain or movement. The allemontite has a lead-grey, glittering fracture-surface, and a somewhat tarnished weathered-surface.

Microscopic Study

Etches reactions with nitric acid indicate that the specimen is Allemontite I. About 20 per cent of the section is made up of stibarsenic in grey bent rods averaging 35 to 50 microns in length and reaching a maximum of 180 microns. These longer rods appear to correspond to the elongated crystals observed on the fracture planes. The rods in each of these large grains are straight and markedly lineated. The appearance of the section as a whole under crossed nicols is a mosaic of irregular grains, slightly elongated and up to 100 microns long. The rods of stibarsenic, forming an eutectoid intergrowth, cross these grains and all the rods go into extinction at the same time indicating that the grains were composed of a homogeneous solid solution when they first solidified. This is verified further by the presence in some places of lineated cleavage pits which cross through several grains.

Section No. 2 (Museum no. A9 - E3)

Macroscopic Study

This specimen, about 1/2 inch across, is somewhat similar to section no. 1. It is concentrically banded and appears to be homogeneous except for a slight variation in

grain size. It is predominantly fine grained but a few crystals up to 3 mms across are present and show cleavage.

Microscopic Study

The main groundmass effervesces instantly and stains brownish black with nitric acid indicating that it is Allemnontite I. The stibarsenic in the white, antimony-rich phase occurs in grey rods averaging 80 microns in length. It composes about 35 per cent of the section. For some reason, the antimony-rich phase appears to be more strongly anisotropic than usual. Under crossed nicols, a mosaic of grains up to 75 microns long can be seen. The intergrowth suggests something of the "pillow-lava" type intergrowth observed in the specimen from Varutrask, Sweden, but it is on a much smaller scale and is not as regular.

A few grains of loellingite (for confirmation see under section no. 3 below) occur in grains up to 400 microns long. In one corner of the section, an apparent anomaly seems to consist of antimony replacing gangue.

Section No. 3 (Museum no. M9 - E3)

Macroscopic Study

Two specimens, both somewhat rusty weathering and vuggy, consist mainly of a mineral having the lustre of arsenopyrite, a hardness of 6, and a gravity of about 5. The grains are elongated and somewhat radiating. One specimen contains up to 30 per cent of Allemnontite (?) in short, irregularly distributed crystals having cleavage. Some fractures appear to contain ruby silvers showing radiating structure. Quartz occurs in small, black, twinned and striated crystals.

Some cryptocrystalline quartz or chalcedony is present. The overall mass has a somewhat botryoidal appearance.

Microscopic Study

The main part of one section, and almost all of the other consists of leaf like or blade like, radiating crystals up to 1/2 mm long of loellingite which is strongly anisotropic, the colours ranging from pale brown to grey to pale blue. X-ray photographs indicated that this mineral is safforite (cobalt arsenide) or loellingite (iron arsenide) but micro-chemical tests do not give a positive test for cobalt, so it is assumed that the mineral is loellingite.

The areas of allemontite which, in the presence of loellingite, are enamel-white rather than the usual tin-white, occur in irregularly shaped patches apparently replacing loellingite. These patches consist of a very peculiar intergrowth which is only faintly visible under high power with crossed nicols (because one component is more anisotropic than the other), but which is plainly visible when etched properly. The following etch reactions were observed (those not mentioned being negative):

<u>Reagent</u>	<u>Anisotropic Mineral</u>	<u>Isotropic or weakly Anisotropic mineral</u>
HgCl ₂	Slightly brown	little or no reaction
FeCl ₃	dark brown	irridescent
HNO ₃	reddish-brown (instantly)	etches differentially to show a further intergrowth.

The components occur in oval shaped and polygonal grains, the anisotropic (light to dark grey) grains would

appear to be replaced by the others rather than intergrown with them if it were not for the presence of cleavage pits which extend through both components. These grains are up to 150 microns across. The intergrowth within some of the larger grains brought out by etching with nitric acid consists of small, closely spaced, oval or rounded spots which do not stain as darkly as the ground mass. It does not look like a eutectoid intergrowth. The main intergrowth is difficult to explain. It may possibly be a peculiar intergrowth of the antimony and the arsenic rich phases without an intervening stibarsenic phase. A further study of this section with the use of X-rays would be worth while.

The larger polished section contains some unclassified ruby silver which is fairly strongly anisotropic from grey to blue-grey and which has a deep red internal reflection --- probably miargyrite or pyargyrite. In one place the ruby silver is definitely cut by loellingite but elsewhere it appears to replace loellingite. Gangue cuts or replaces ruby silver.

In the smaller section, there is a small amount of sphalerite confirmed by internal reflection and etch reactions, and a few grains of unclassified ruby silver. These are probably later than the loellingite.

(6) Pzribram, Bohemia

Macroscopic Study

The specimen, about two inches across, is fine to medium grained, shows botryoidal structure, and is inter-banded with calcite. The surface breaks very unevenly. Some

sphalerite and possibly a small amount of ruby silver are present. In addition, a few grains each of a black mineral having a metallic lustre, white streak and hardness equal to 4; and ^{of} a pale yellow, metallic, finely disseminated mineral are present. Calcite shows comb structure and appears to be in part later than and in part contemporaneous with the main mass.

Microscopic Study

The main mass effervesces instantly and stains brown with nitric acid, and slowly stains brownish-black with ferric chloride indicating that it is Allemontite I. It occurs in irregular, concentric bands separated by gangue and stibnite, the bands ranging from a few microns to 2 mms in width. Most of the allemontite appears to be homogeneous and may be just the antimony-rich phase rather than Allemontite I. The grains do not have a wavy extinction pattern as is common with Allemontite I and ^{they} must be very small, possibly less than 10 microns. However, in some areas a definite, but very irregular eutectoid intergrowth is visible. In these places, the lamellae of stibarsenic are less than ten microns long and may compose as much as 40 per cent of the total area. Etching with nitric acid brings out the intergrowth and, in addition, reveals an occasional tiny bead less than four microns across of a very white mineral which is not etched. These spots appear to be negative to other etch reagents also.

In addition to the allemontite, the following minerals are present:

Unknown mineral: It is about as white as allemontite and is fairly strongly anisotropic, the colours ranging from bluish-gray to pinkish-grey to white. It characteristically occurs in diamond-shaped grains ranging from 5 microns to 70 microns across, which are isolated or in narrow veinlets in the gangue. The projection of one end of the diamonds into the gangue gives the veinlet a saw-toothed appearance. The mineral has a hardness of "B". The etch reactions appear to be fairly distinctive. Mercurous chloride stains slightly brown or irridescent near the edge of the drop. Potassium hydroxide etch reveals that the "saw-toothed" veinlets actually consist of diamonds which are stained pale blue to irridescent with the development of etch cleavage, and of a surrounding mineral which is not etched. This surrounding mineral may be the same composition as the small beads appearing in the allemontite. The potassium cyanide etch is similar to the potassium hydroxide etch, but is more positive. Two etch cleavages are developed --- a good one approximately parallel to two sides of the diamond, and a poorer one approximately parallel to the short diagonal of the diamond. Hydrochloric acid, ferric chloride and nitric acid all give negative etch tests.

Stibnite: It makes up about five per cent of the section. It was identified by its strong anisotrophism (blue to pinkish-grey) and by the formation of an orange

residue when etched with potassium hydroxide. It occurs widely distributed in isolated grains, in bands, and in irregular patches. The grains are from sub-microscopic to 50 microns in size. Stibnite is closely associated with the gangue but also occurs isolated in and apparently replaced by allemontite.

Sphalerite: About one per cent of the slide is composed of sphalerite which replaced gangue and possibly stibnite. It is most common where the banding is best developed, and there^{it} tends to occur in thin bands around the gangue.

Galena: A few patches of galena less than 1/2 mm across and showing triangular pits occur in allemontite near gangue-allemontite contacts. It appears to be replaced by allemontite and stibnite.

Ruby Silver: One rod-shaped mass and a few patches up to 1 mm across of ruby silver were observed. They are fairly strongly anisotropic ranging in colour from blue to pale buff to grey, and are blue-grey without crossed nicols. They have a deep red internal reflection. Both gangue and allemontite appear to replace them.

The ruby silver is unclassified but is probably pyargyrite or myargyrite.

No conclusive age relations for the minerals could be determined. For the most part, they appear to be contemporaneous and each was probably deposited during two or more periods when the magma became saturated in the respective

minerals.

Conclusions

Arsenic and antimony form eutectoid intergrowth, the coarseness of which probably depends on the temperature of deposition. Since the solubility of each phase in the other decreases with decreasing temperature, a sub-microscopic intergrowth probably forms in each component after the original exsolution. This, of course, would depend on the rate of cooling which would affect the mobility of the atoms.

The conclusions reached by Edwards seem to be verified by this study. The only possible exception is the intergrowth observed ⁱⁿ section no. 3 from Allemont, France. This intergrowth may be composed of grains of native arsenic and antimony, but this is open to debate.

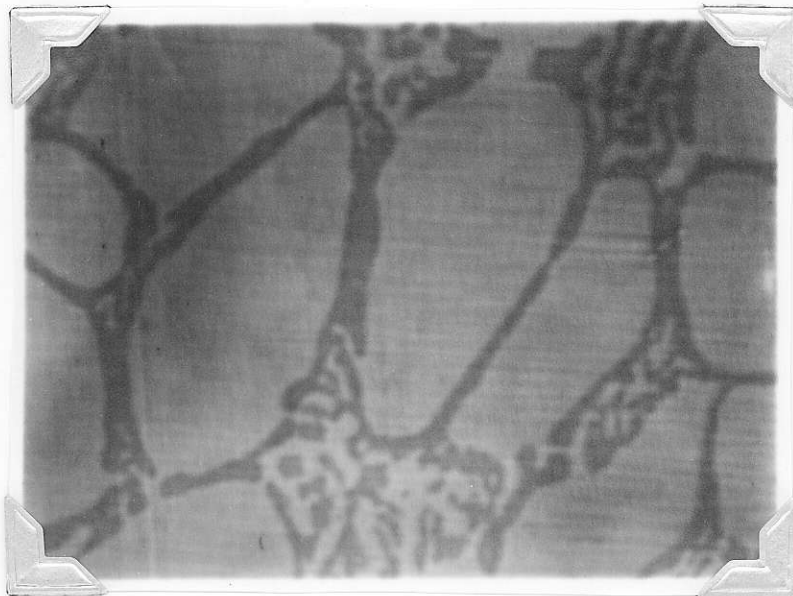
Of the sections studied, the only arsenic-rich ones, were some of those from the Engineer mine. It will be remembered that the intergrown grains of stibarsenic were small and globular rather than long and rod-like as in antimony-rich intergrowth. Artificially prepared intergrowths should be studied to determine the reasons for this difference and to see if the equilibrium diagram is actually as pictured in Edwards.

The writer suggests that the word "allemontite" be retained in the technical language in its present sense meaning any intergrowth of arsenic and antimony. Justification for this is the fact that the nature of the intergrowth cannot be recognized without microscopic study, and some word is required

to describe hand specimens of arsenic-antimony alloys of unknown composition. The word "stibarsenic" suggested by Edwards can be given to the homogeneous solid solution of arsenic and antimony containing about 50 atomic per cent arsenic.

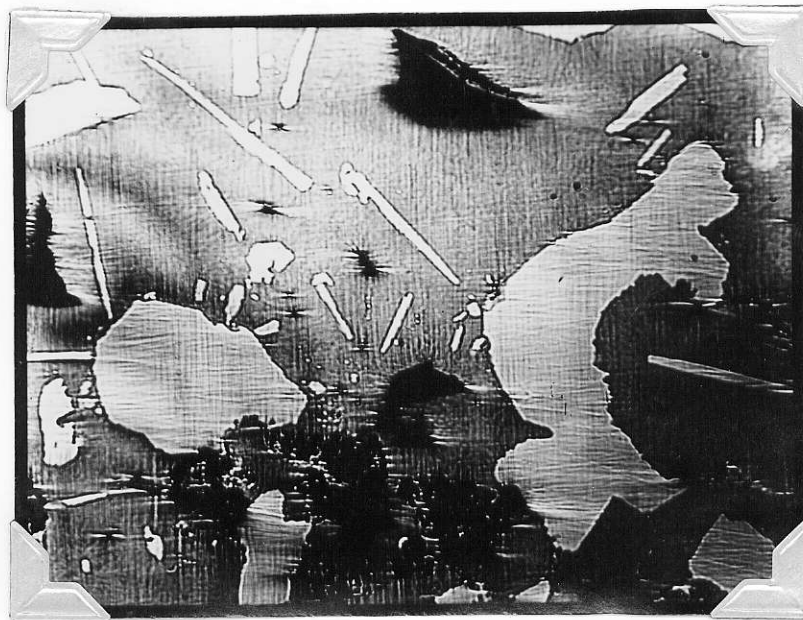
APPENDIX IX

Photographs



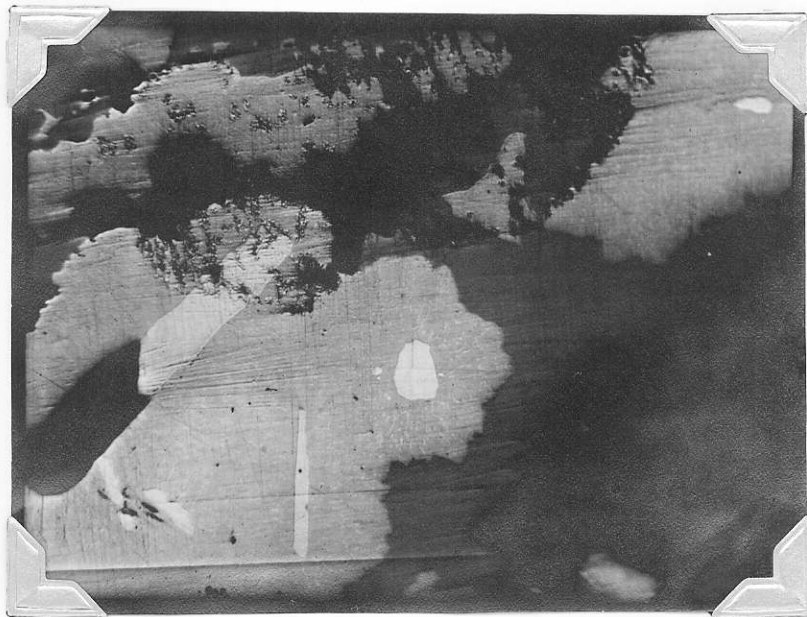
X 168

Photograph No. 1; Allemontite I.
Antimony-rich phase grey; stibarsenic dark grey.



X 75

Photograph No. 2; Dyscrasite white;
Allemontite III grey; gangue black.



x168

Photograph No. 3; Dyscrasite white;
Allemontite III grey; miargyrite dark grey;
gangue black.

Bibliography

- Dana, E.S. (1932): Textbook of Mineralogy; John Wiley and Sons, New York, p. 400.
- Edwards, A.B. (1947): Textures of the Ore Minerals; Australasian Institute of Mining and Metallurgy, Melbourne, Australia.
- Holmes, R.J. (1936): An X-ray Study on Allemontite; Amer. Min., vol. 21, p. 202.
- Walker, T.L. (1921): "Allemontite" From Atlin, B. C.; Amer. Min., vol. 6, p. 98.