

THE DISTINCTION BETWEEN ENARGITE AND FAMATINITE (LUZONITE)

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INTRODUCTION

For the past three years the writer has been working on the problem of studying minute samples of ore minerals by a method combining the use of the quartz spectograph and the x -ray powder camera. The method is being developed as an adjunct to the optical study of ore minerals in polished sections; and it is particularly adapted to the study of minerals which occur habitually in fine intergrowths and whose identity and specific properties are in many cases uncertain. The procedure involves excavating minute samples from very small areas in a polished section by means of an improved micro-drill, and utilizing them for powder photographs and spectographic analyses. In this way valuable qualitative structural and chemical data are obtained for comparison with the usual characters observed in polished sections.

THE MICRO-DRILL

The drill used in the present work was patterned after that described by Haycock (1931). This consists of a 1/50 H.P. electric motor connected by means of a flexible cable to a rigidly mounted spindle which holds the drill (Fig. 1). The drill point is simply a No. 7 Sharp needle mounted in a pin vise chuck and supported close to the drilling point by a bearing. The spindle and drill are mounted rigidly in a frame in an inclined position so that the point of the needle is in the center of the field of the microscope when a polished section is in focus. The inclination of the spindle and drill is governed by the focal length and outside diameter of the objective used, leaving sufficient clearance so that the section may be brought into focus when it is lowered out of contact with the drill. In this position, the section may be moved about freely for examination, without danger of scratching the surface. The section is moved by means of a mechanical stage in which the specimen is clamped. Drilling is accomplished by raising the stage of the microscope until the section makes contact with the needle point.

The pin vise chuck, even with a supporting bearing, allowed considerable play because the taper of the needle did not allow an accurate fit. To secure accurate rotation the needle is mounted in V supports and held in place by phosphor bronze springs (Fig. 2). Dispensing with the chuck, the needle is attached to the spindle by means of a crude but

effective universal joint, consisting of a bar forked at each end. One end fits over a tiny bar placed in the eye of the needle; the other over a similar bar in the hollowed end of the spindle. With this arrangement the eccentricity of the needle point depends solely upon the shape of the needle. The needles are remarkably round and straight but their sharp tips are rarely precisely upon their axis of rotation. This is fortunate because it is this slight eccentricity of the needle point which makes an

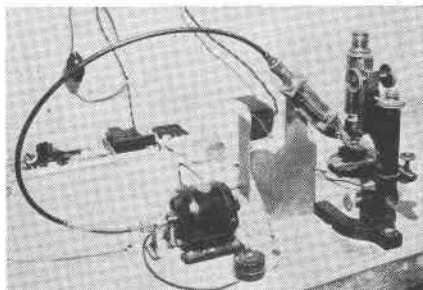


FIG. 1



FIG. 2

ordinary sewing needle a good mineral drill. A few needles in each package are so far from being centered that they are of value only for large grains but the majority fall in the useful range. In operation the eccentricity of the needle point must be small in comparison to the size of the grain being sampled. The best performance which can be secured with the present arrangement is such that an area 0.02 mm. in diameter is affected when the drill is brought into contact with the surface of a mineral. The average mineral grain to be sampled is large in comparison to this minimum, and to secure material sufficient for *x*-ray or spectrographic work the grain and section must be moved about under the drill with the mechanical stage.

PREPARATION OF THE POWDER SAMPLES

The sample provided by the micro-drill accumulates at one side of the needle in a compact pile which may be transferred as a unit to a glass slide by means of a fine splinter of wood. A small drop of solution of collodion in ether is placed upon the sample, the particles of which immediately spread out in the drop and become evenly dispersed. When the drop has dried sufficiently to be handled and yet is still plastic, it is removed from the slide with the aid of a steel needle and rolled between the fingers into a tiny rod about 1/16 inch long. This is placed upon the glass slide again and a second larger drop of collodion-ether is attached to one end of it. When this is partially dry it is rolled again

so as to form a non-diffracting holder for the specimen. When dry the mount is complete and ready to be placed in the camera. As many as 20 such mounts have been prepared in three hours and much of this time was consumed in examining sections and checking minerals and individual grains in order to select a particular grain for sampling.

Powder diffraction patterns are secured with a Debye type of camera of radius 57.5 mm. The sample is mounted in wax and centered by simply pushing sample and wax until the rod-like specimen lies in the axis of rotation of the specimen holder. This procedure is very simple and more satisfactory in all respects than a mechanical chuck. The mount is rotated by a telechron motor. The details of the powder method are fully described in the literature and will not be treated further. The advantages of the application of this method to the opaque minerals were pointed out by Kerr (1924).

SPECTROGRAPHIC ANALYSIS

The spectrographic analyses are carried out with a medium Hilger quartz spectrograph. The logarithmic wedge sector, described by Twyman and Simeon (1929), has been adopted to provide analyses which are semi-quantitative. Excitation is accomplished by a direct current arc drawing 6 amperes from a 110 volt supply. Electrodes are of $\frac{1}{4}$ inch graphite shaped with a pencil sharpener and purified by baking in a stream of chlorine gas at 1000°C. The mineral sample is placed directly into a small cavity drilled in the conical tip of the lower electrode. The minimum size of sample that will give consistent results was studied; a compromise was found necessary between the conflicting objectives of a minimum sample and accurate quantitative measurements. A sample estimated to weigh between 0.002 and 0.0002 mg. was selected as a satisfactory standard.

Quantitative measurements depend upon the fact that the intensity of the spectrum of an element varies with the amount of the element in the sample. The effect of the logarithmic wedge sector, which rotates in front of the slit of the spectrograph, is to give wedge-shaped spectral lines of lengths proportional to the intensity of the radiation which caused them. The difference in the lengths of two lines is proportional to the ratio of their intensities; consequently, other things being equal, this measurement is proportional to the ratio of the amounts of the two elements present in the sample.

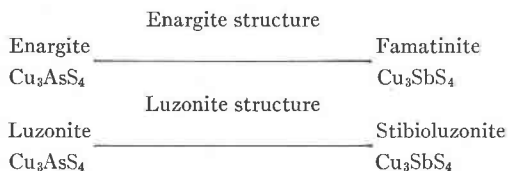
ENARGITE, FAMATINITE AND LUZONITE

Enargite (Cu_3AsS_4) was described by Breithaupt (1820). Doelter (1926) lists thirty-six chemical analyses of enargite ranging from arsenic

19.47%, antimony none to arsenic 11.4%, antimony 6.4%. X-ray powder diffraction patterns of enargite have been studied by Kerr (1924), Frebald (1927), de Jong (1928) and Waldo (1935). A structure of the wurtzite type has been determined by Pauling and Weinbaum (1934). The rarer mineral famatinite (Cu_3SbS_4) was described by Stelzner (1873) from Sierra de Famatina, Argentine. Doelter (1924) lists analyses which range from arsenic 3.23%, antimony 10.9%, to arsenic 10.9%, antimony 21.78%. The mineral luzonite, which occurs only in indistinct crystals at the type locality, was described by Weisbach (1874). It is stated to have the same composition as enargite (Cu_3AsS_4).

Vom Rath (1878) considered famatinite to be isomorphous with enargite; from x-ray powder patterns de Jong (1928) concluded that the two minerals have the same structure, in which opinion he is supported by Schneiderhöhn and Ramdohr (1931) and Waldo (1935), and opposed by Frebald (1927), who obtained unlike powder patterns from famatinite and enargite and concluded furthermore that luzonite is not a distinct species. Moses (1905) regarded luzonite as the same as enargite, on the basis of crystallographic measurements. Schneiderhöhn and Ramdohr (1931) came to the opposite conclusion from x-ray studies. Murdoch (1916), Farnham (1931) and Short (1931) regard luzonite as a variety of enargite on the basis of color difference and the existing crystallographic and chemical evidence. Klockmann (1891), on the other hand considered famatinite and luzonite as isomorphous, and unlike enargite.

Schneiderhöhn and Ramdohr recognize that luzonite has a crystal structure distinct from that of enargite and conclude that two solid solution series exist as follows:



In the first series they do not believe that complete isomorphism exists; in the second series they consider that almost complete miscibility prevails.

It is believed that the confusion in the mineralogy of the enargite group is due primarily to the intimate intergrowth of minerals of the group. Competent investigators have obtained diverse results since chemical analyses, x-ray studies, and observations on polished sections could not be correlated.

Before presenting the results of such a correlation of methods it should

be pointed out that if enargite and famatinite form an isomorphous series, only one representative of the series will occur in a given specimen if equilibrium is attained. If equilibrium is not reached during the formation of the mineral, zoning may result. Dimorphous forms are stable for different ranges of temperature, pressure and concentration, so that one form may replace another as conditions change from one stability range to another.

TABLE 1. SPECTROGRAPHIC DATA ON SPECIMENS OF MINERALS OF THE ENARGITE GROUP

Diffraction pattern No.		Locality	Color	Intensity measurements ¹						
Fig. 3	Fig. 4			Cu	As	Sb	Ag	Sn	Fe	As-Sb
1	1	—	—	Silver						
2	2	Near Santiago, Chile	Grey	11	7	Tr.	—	—	6	7
3		Butte, Mon.	Grey	11	10	5	7	2	7	5
4	3	San Pedro Mine, Argentine	Grey	10	7	4	7	8	6	3
5		San Pedro Mine	Grey	—	—	—	—	—	—	—
6		Butte, Mon.	Grey	9	7	—	6	—	5	7+
7		Butte, Mon.	Grey	11	6	3	—	—	9	3
8		Butte, Mon.	Grey	10	6	1	6	—	6	5
9		Unknown	Grey	10	6	1	4	—	3	5
10		Morococha, Peru	Grey	12	8	5	7	4	3	3
11		San Pedro Mine, Argentine	Grey	12	8	Tr.	8	2	9	8
12	Tintic, Utah	Grey	9	7	4	5	—	—	3	
13	Ouray, Colo.	Grey	—	—	—	—	—	—	—	
14	Butte, Mon.	Grey	8	4	—	—	—	—	4+	
—	Cerro de Pasco, Peru	Grey	10	5	—	8	—	5	5+	
—	Unknown	Grey	9	5	Tr.	—	—	1	5	
15	4	San Pedro Mine, Argentine	Pink	10	6	4	—	4	8	2
16		San Pedro Mine	Pink	—	—	—	—	—	—	—
17		Cerro de Pasco, Peru	Pink	9	6	8	7	4	6	-2
18		Cerro de Pasco, Peru	Pink	12	7	10	9	9	9	-3
19		Loope District, California	Pink	10	6	6	8	4	2	0
—		Morococha, Peru	Pink	8	5	5	7	5	6	0
—	Unknown	Pink	8	1	5	6	2	4	-4	
20	5	Tsumeb, South Africa		Germanite						
21	6	Butte, Mon.		Colusite						
22	7	Burra Burra, South Australia		Sulvanite						
23	8	Magma, Ariz.		Bornite						

¹ The intensity measurements listed above are for the following lines: Cu 2824, As 2780, Sb 2878, Ag 3280, Sn 2839, Fe 3020 Å.

In polished sections of specimens of the enargite group two minerals commonly occur; one is grey in color, the other pink. They occur as a granular intergrowth showing neither zonal relationships nor evidence of replacement. Sections of material labelled enargite contain these two minerals and sections of material rich in antimony and identified as famatinite likewise contain both a grey and a pink mineral as a granular intergrowth. It has been noted that arsenic-rich ores contain only a minor amount of the pink mineral; antimony-rich ores contain a much larger proportion of the pink mineral. The two minerals respond identically to tests in polished section, having the same hardness, etch tests, anisotropism and constituent elements—if qualitative tests are relied upon. Luzonite differs from enargite only in its color, its characteristic lamellar twinning and lack of cleavage.

In figures 3 and 4 and table 1 are summarized the x -ray and spectrographic results of this investigation. In Figure 3 the enargite structure

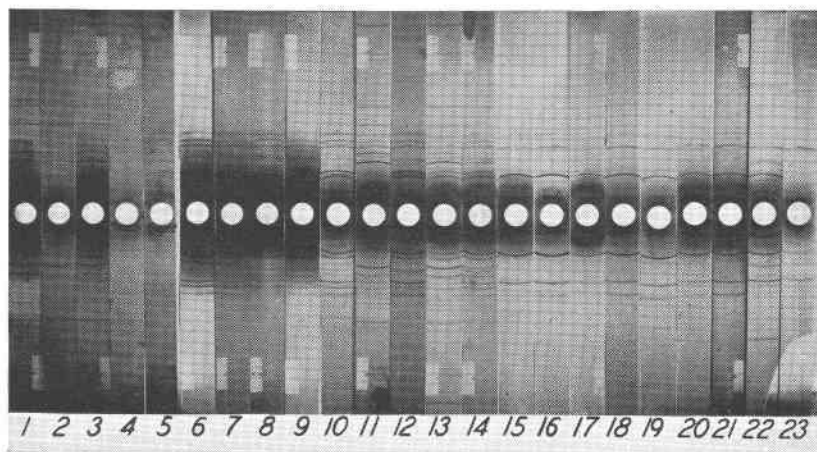


FIG. 3

is represented by the powder diffraction patterns numbered 2 to 14. Patterns 15 to 19 represent the luzonite structure; 20 to 23 represent a few minerals which give patterns similar to the luzonite pattern. Pattern No. 1 is the diffraction pattern of silver; this pattern may be seen in some of the enargite films since silver was added to some of the samples for calibration purposes. In Table 1 the minerals are listed with the corresponding number of the powder patterns of figures 3 and 4, the color of the specimen, location and spectrographic analysis. The numbers under the elements are measurements in millimeters of the length of

selected lines due to Cu, As, Sb, Ag, Sn, and Fe. Each horizontal row contains values taken from a single spectrum and the values are comparable. Since one sample may have been slightly larger than another, or the exposure may have been slightly longer in photographing one spectrum than another, the values in different horizontal rows may not be compared directly. Due to the logarithmic wedge sector, each line increases in length by the same amount as the intensity of the spectrogram increases provided the proportion of the elements in the sample remains constant and conditions are standardized.²

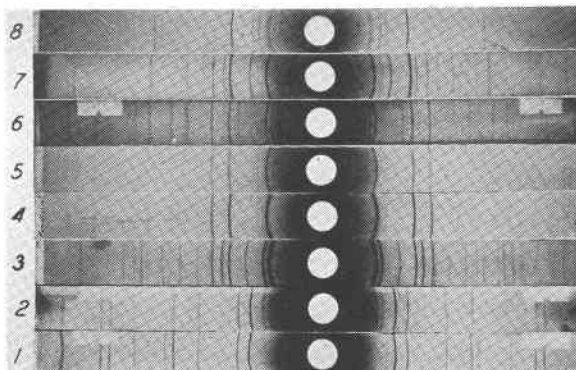


FIG. 4. Diffraction patterns were secured with copper radiation using a nickel filter.

As stated earlier, the difference in the lengths of two lines is proportional to the ratio of their intensities. The relative intensities in turn are dependent upon the relative proportions of the two elements concerned; consequently the figures in the last column of table 1 giving values of As minus Sb give a measurement which is independent of the variations due to the size of sample, exposure, etc., and is determined by the proportion of As and Sb present in the sample analyzed. Exactly what this proportionality is can be established only by preparing artificial mixtures of known composition which duplicate the substances being analyzed over the complete range, plotting the relative intensities secured from these standards against these known proportions, and finally referring the intensity ratios given by the minerals studied to the

² This is true only when precautions are taken: 1, to select spectral lines not subject to erratic variations; 2, to select lines for comparison which lie close to one another in the spectrum; 3, to ensure constant excitation; 4, to ensure accurate alignment of the optical system; 5, to secure rapid rotation of the sector; 6, to ensure photography of a fair sample of the total radiation emitted by the mineral sample; 7, to ensure constant photographic technique.

resulting calibration curve for evaluation. In the present case this has not been done; instead an attempt is made to draw certain conclusions directly from the As-Sb intensity values. A large value for As-Sb indicates high arsenic—low antimony; whereas a low value indicates low arsenic—high antimony.

Now if in this varied collection of minerals of the enargite group there is a fair sample of the range in the ratio of As to Sb which may occur in nature, then there should be a correspondingly representative range in As-Sb intensity values. These values range from 8 to -4 but it is a striking fact that all minerals having the enargite atomic structure range from 8 to 3 and the minerals having the luzonite atomic structure range from 2 to -4. In other words the enargite structures are arsenic-rich, the luzonite structures are antimony-rich; furthermore, the proportions of As to Sb do not overlap for the two groups.

These observations suggest very clearly that there exist two series; that the proportion of antimony in Cu_3AsS_4 may increase only up to a certain amount and still have the enargite crystal structure, and similarly that the proportion of arsenic in Cu_3SbS_4 may increase only up to a certain amount and still have the luzonite structure. The second series will be properly named the famatinitite series, since ideal famatinitite is the pure antimony compound.



While it is recognized that a mineral rich in arsenic having the luzonite structure and one rich in antimony having the enargite structure may eventually be found, the present statistics are much opposed to this possibility. In view of the rather widespread belief, based upon chemical analysis, that luzonite is an arsenic-rich mineral and that there is a mineral having the enargite structure but rich in antimony, one is reluctant to press the indications from the present semi-quantitative determinations; yet the suspicion is strong in the writer's mind that in the chemical analyses of these minerals that have been made too little attention has been given to the possibility of the occurrence of mixtures of two minerals, especially since the microscope reveals that intimate mixtures of enargite and luzonite are so common.

Whatever the final explanation may be, the conclusions to be drawn from the present observations are clear. It is therefore suggested that the relations may be as outlined above and that in the enargite series should be placed only minerals of this general group that have the enargite structure; according to the present study these minerals are all rich in arsenic. Similarly it may be that in the famatinitite series belong

minerals of the group having the structure of the mineral which up to the present time has been called luzonite; as is shown here these minerals are all rich in antimony. If this suggestion is correct, luzonite and famatinite refer to the same mineral series and are therefore synonymous. Since famatinite has date priority and refers to an antimony-rich mineral this name should be retained for the series.

In Figure 4 it will be seen that the diffraction patterns of famatinite (luzonite), germanite and colusite are closely similar not only in the number and position of lines but also in their intensities. Now the structure of germanite has been worked out by de Jong (1930), who found it to be of the sphalerite type with $a_0 = 5.290 \pm 0.005 \text{ \AA}$ or possibly $10.58 \pm 0.01 \text{ \AA}$. Zachariassen (1933) has determined the structure of colusite by oscillation photographs to be of this same sphalerite type, with $a_0 = 5.304 \pm 0.001 \text{ \AA}$. It is thus evident that luzonite belongs to the same structure type. It has the sphalerite type of structure but since it is strongly anisotropic it is not of isometric symmetry.

Pauling and Weinbaum (1934) have pointed out that the structure of enargite is closely related to that of wurtzite, the hexagonal form of ZnS. The structural relations of enargite and famatinite are thus analogous to those of sphalerite and wurtzite.

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