

THE COMPOSITION AND STABILITY OF DIGENITE

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ABSTRACT

EPMA and X-ray studies on natural digenites from different localities indicate that a small amount of iron always exists in digenite, and that the metastable digenite-type solid solution of the 5.5a type can occur in nature with digenite.

Experiments on synthetic materials have been carried out to determine the stability field of digenite. The field of the homogeneous single phase with the 5a-type structure extends from 0.4 to 1.6 atomic percent iron and from 36.15 to 36.55 atomic percent sulfur at room temperature. The composition of $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ is nearly at the center of the stability field. Cobalt or nickel could not be used instead of iron to synthesize digenite. This indicates that iron is essential for stability of digenite.

Synthetic digenite with the composition of $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ has the cell edge of $5.5562 \times 5 \text{ \AA}$. The apparent space group of digenite, $Fm\bar{3}m$, is considered to be a result of complex domain textures on the basis of the structural considerations.

Dependence of the cell edges of natural digenites on coexisting minerals confirms the existence in nature of the digenite solid solution established by the synthetic experiments.

INTRODUCTION

Digenite is a relatively common mineral occurring in numerous important ore deposits in association with minerals of the Cu-Fe-S system. Buerger (1942) confirmed that the so-called "high-temperature, blue, or isometric chalcocite" had the composition of Cu_9S_5 and proposed the mineral name digenite. This mineral was considered at that time to be the only intermediate compound in the CuS-Cu₂S system. Donnay *et al.* (1958) studied synthetic crystals of Cu_9S_5 admitting the chemical composition of natural digenite proposed by Buerger. They proposed a crystal structure for the synthetic digenite on the basis of the characteristic twin texture. Morimoto and Kullerud (1960, 1963, 1966) studied crystals of the Cu_9S_5 - Cu_5FeS_4 join and found three polymorphs of Cu_9S_5 .

Soon after the description of djurleite, $\text{Cu}_{1.97}\text{S}$, the second intermediate compound in the CuS-Cu₂S system (Morimoto, 1962; Roseboom, 1962), more studies were made on the Cu-S system. Roseboom (1966) studied the phase relations of the Cu-S system at low temperatures and reported that four phases were stable at room temperature. They were chalcocite (Cu_2S), djurleite ($\text{Cu}_{1.97}\text{S}$), the digenite-type solid solution ($\text{Cu}_{1.765}\text{S}$ - $\text{Cu}_{1.79}\text{S}$),¹ and covellite (CuS). Then anilite was found in nature and was determined to have the composition of Cu_7S_4 (Morimoto,

¹ This corresponds to the digenite solid solution by Roseboom (1966). This phase is, however, different from natural digenite (Morimoto and Koto, 1970).

Koto, and Shimazaki, 1969), which was very close to the sulfur-rich limit of the digenite-type solid solution. Morimoto and Koto (1970) further found that anilite and djurleite were the stable intermediate compounds in the CuS-Cu₂S system at low temperatures, and that the digenite-type solid solution was metastable at low temperatures. In the same paper, they studied natural digenite and suggested that digenite was stable at room temperature only when it contained a small amount of iron. However, the stability field of digenite was not studied in detail.

This investigation was initiated in order to elucidate the stability field of digenite in the Cu-Fe-S system at low temperatures and to understand natural occurrences of this mineral. We shall describe first the results on natural digenite, then of experiments on synthetic materials, and finally on natural assemblages with digenite.

NATURAL DIGENITE

The literature does not report any complete chemical analysis on digenite performed subsequent to its establishment as a mineral species. However, several analyses exist of "blue chalcocite", which Buerger (1941, 1942) showed to be identical with digenite. These analyses (Palache *et al.*, 1944) indicate that natural digenite takes some iron into solid solution and when iron is not present digenite apparently is of, or close to, Cu₇S₄ composition (Berry and Thompson, 1962). Before beginning synthetic work on the stability field of digenite at room temperature, crystallographic and chemical studies on natural digenite were carried out.

In this paper, *digenite*, or *digenite solid solution*, designates a phase which has a very narrow composition range in the Cu-Fe-S system and which is stable at room temperature. This is considered to correspond to the mineral, digenite. However, the *digenite-type solid solution*, or simply *digenite-type phase*, is used for the crystals observed in synthetic experiments over a wide range of composition in the Cu-Fe-S system and is metastable at room temperature. The X-ray patterns of digenite are of the modified 5*a*-type (Morimoto and Kullerud, 1963) and those of the digenite-type solid solution are of the nonintegral type (Morimoto and Nakazawa, 1968; Morimoto and Koto, 1970) changing continuously from the 4*a* type to the 6*a* type with composition (Morimoto and Kullerud, 1966; Morimoto, 1970). Where the distinction between the two phases mentioned above is difficult, or unnecessary, the label of digenite-type phase is generally used for both phases in this paper.

Materials. We examined three different digenite crystals from two localities, two from the Leonard Mine, Butte, Montana, and one from the

Magma Mine, Superior, Arizona. One of the Leonard Mine specimens was obtained from Professor G. Kullerud, Purdue University, and the other from the Smithsonian Institution (No. R 9925). They are called Leonard Mine (K) and Leonard Mine (S), respectively, in this paper. The specimen from the Magma Mine was obtained from Professor R. A. Yund, Brown University.

The crystals of the Leonard Mine (K) have well developed crystal faces, $\{111\}$, with remarkable striations along $[110]$, and are found with bornite and pyrite. The crystals of the Leonard Mine (S) are not euhedral and are of two apparently different types; one contains digenite with small amounts of bornite and the other djurleite with small amounts of digenite and bornite. In this study mainly digenite of the former type was studied. The Magma Mine specimen consists of a digenite-like part and bornite, neither of which minerals are euhedral.

X-ray Studies. The crystals of digenite from the three specimens mentioned above were studied by the X-ray powder and precession methods. The precession photographs show the patterns of the modified $5a$ -type of digenite, in which the superstructure reflections divide the repeat of the main reflections into five equal intervals along the $\{111\}$ directions (Morimoto and Kullerud, 1966, Fig. 3, e). The superstructure reflections do not obey the extra extinction rule observed in the digenite-type phase obtained by quenching of synthetic specimens (Morimoto and Kullerud, 1966, Fig. 3, d).

The precession photograph of the Magma Mine specimen (Figs. 1 and 2), indicates existence of two phases, djurleite and the digenite-type phase, besides digenite. Some weak reflections indicate possible existence of anilite in this specimen. However, we were not successful in confirming anilite in the specimen in this investigation. The digenite-type phase is definitely of nonintegral type because the superstructure reflections show slight displacements from the Bragg positions and give the (5.45 ± 0.004) a type according to the conventional expression for the nonintegral types of structures (Morimoto and Nakazawa, 1968; Morimoto and Koto, 1970). This is the first occurrence of the digenite-type phase in nature, and can be compared with the $11C$ type of pyrrhotite, which was also found to be non-integral (Morimoto *et al.*, 1970b). Since the digenite-type solid solution is generally metastable at room temperature (Morimoto and Koto, 1970a), this $5.5a$ type is considered to be metastable. Additional experiments on the natural specimens will be discussed later.

Chemical Composition. Electron-probe analyses on natural crystals of digenite (Table 1) were carried out by Dr. Y. Shimazaki, Geological

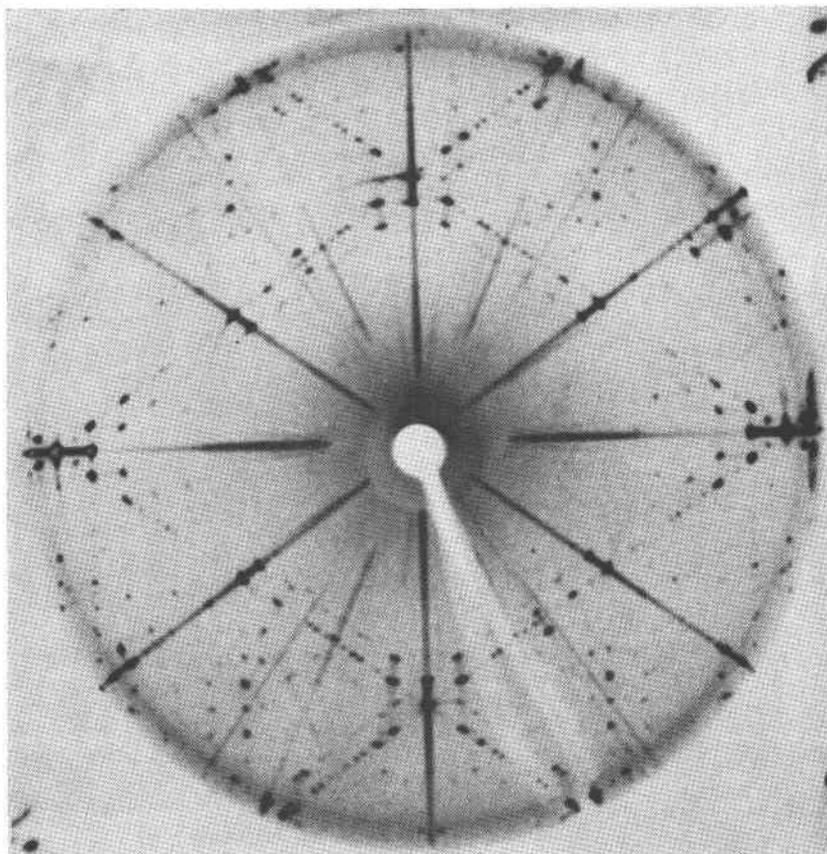


FIG. 1. Precession photograph $(1\bar{1}0)_0^*$ of digenite from Magma Mine, Superior, Arizona. Reflections from djurleite and the digenite-type phase (the $5.5a$ type) are also observed.

Survey of Japan. All the crystals were confirmed by the X-ray single crystal method to consist mainly of digenite before the electron-probe analyses.

When the compositions obtained by the electron-probe analyses are expressed on the basis of four sulfur atoms, the atomic ratio of iron is always near or slightly less than 0.10 for all specimens, though that of copper is rather variable. The specially large values for copper in the Magma Mine specimens are considered due to existence of djurleite and the $5.5a$ -type phase as shown in the X-ray single crystal patterns (Fig. 2).

On the basis of the chemical compositions of natural digenite mentioned above and those obtained from the literature, a possible com-

Table 1. Electron-probe analysis of digenite. (atomic percent)

Locality	No.	Cu	Fe	S	Total	Composition
Leonard Mine (K)	I	78.0	0.95	22.4	101.4	Cu _{7.03} Fe _{0.10} S _{4.00}
	II	79.9	0.88	21.8	102.4	Cu _{7.38} Fe _{0.09} S _{4.00}
	III	78.5	0.88	22.3	101.7	Cu _{7.11} Fe _{0.09} S _{4.00}
Magma Mine	I	81.5	0.85	21.4	103.8	Cu _{7.69} Fe _{0.09} S _{4.00}
	II	79.6	0.85	21.4	101.9	Cu _{7.51} Fe _{0.09} S _{4.00}
Theoretical values	I	76.61	0.98	22.41	100.0	Cu _{6.90} Fe _{0.10} S _{4.00}
	II	77.12	0.96	21.92	100.0	Cu _{7.10} Fe _{0.10} S _{4.00}

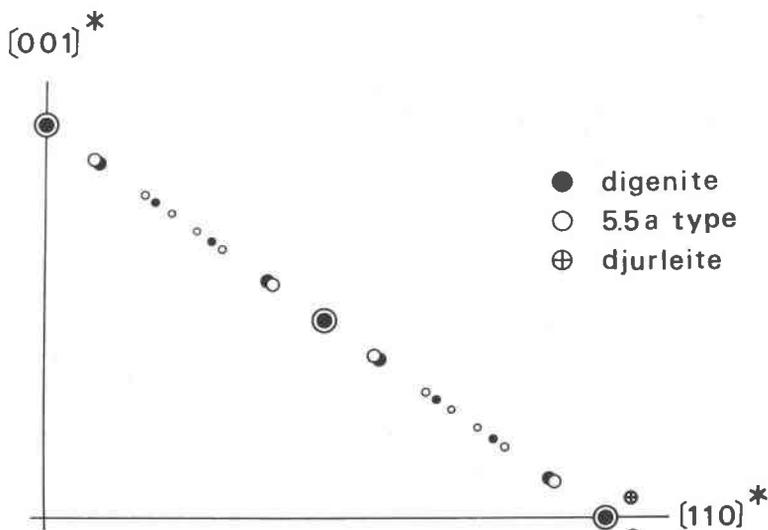


FIG. 2. Precession diagram of Fig. 1. The reflections from digenite, djurleite, and the digenite-type phase are indicated.

position range for digenite was considered to be of $\text{Cu}_{6.90}\text{Fe}_{0.10}\text{S}_{4.0} \sim \text{Cu}_{7.10}\text{Fe}_{0.10}\text{S}_{4.0}$. In order to examine this possibility, preliminary synthetic experiments were carried out with the specimens of $\text{Cu}_{6.90}\text{Fe}_{0.10}\text{S}_{4.0}$ and $\text{Cu}_{7.10}\text{Fe}_{0.10}\text{S}_{4.0}$ compositions. The homogeneous crystals of digenite were obtained by synthesis starting with the mixtures of elements with the former composition, but all attempts to obtain a single phase of digenite from mixtures with the latter composition were unsuccessful. Thus the synthetic experiments to determine the stability field of digenite have been carried out around the composition of $\text{Cu}_{6.90}\text{Fe}_{0.10}\text{S}_{4.0}$.

SYNTHETIC EXPERIMENTS

Synthesis. Except for the natural digenite described above, the samples used in this investigation were synthesized dry from mixture of sulfur, iron, and copper. Copper and iron grains of 99.99 percent purity were obtained from the American Smelting and Refining Co. Sulfur of 99.999 percent purity was also obtained from the same company. Copper and iron were used in the experiments after reduction by hydrogen gas at 600°C.

Most specimens of different compositions were synthesized in the following way. The mixtures of the three elements in appropriate ratios were enclosed in evacuated silica tubes and kept for about 72 hours at 500°C. They were slowly cooled to 300°C with the rate of 15°C/hour and kept 24 hours and again slowly cooled to room temperature at a rate of 15°C/hour. After grinding the products in acetone, they were again sealed in silica tubes. After heating at 500°C for one week, they were cooled to 50°C in four days, kept there for one week and quenched to room temperature, to obtain stable assemblage at low temperature for the compositions of the starting materials. The products were examined soon

after quenching with both microscope and X-rays. Most of the products were kept in desiccators for six months at room temperature and were then studied again to examine possible change at room temperature. The compositions of the synthetic specimens in this investigation are shown (Figs. 3 and 4 and Table 2). Most of the specimens are classified into five groups, in each of which the composition changes along a line in the Cu-Fe-S system when expressed in atomic percent. The five lines (from line 1 to line 5) are also shown in Figure 4.

Identification of Phases. Most synthetic specimens consisted of small single crystals of 0.01~0.1 mm in size. In some specimens, large crystals of about 0.5mm in diameter were occasionally found. All the specimens were examined by the X-ray powder and precession methods using $\text{CuK}\alpha$ (1.5418 Å) and $\text{MoK}\alpha$ (0.7107 Å) radiations. The reflection microscope was also employed to identify existing phases in the samples.

In the range of compositions studied in this investigation (Figs. 3 & 4), most prominent phases are digenite and the digenite-type solid solution. Small amounts of covellite and djurleite were also observed in some specimens. The distinction between digenite and the digenite-type solid solution was based on the N -values obtained from the positions of the superstructure reflections relative to those of the main reflections (Morimoto and Koto, 1970). Because good agreement was obtained between the N -values of the digenite-type solid solution obtained by the X-ray single crystal method and those by the powder method, we decided to proceed as far as possible with the powder method and to use the single crystal method only when the powder method failed. Covellite of the normal type was confirmed by the microscope and djurleite by the X-ray methods. Although bornite was not directly confirmed, its existence was assumed by the existence of the $4a$ type in the X-ray powder patterns as described later. "Blaubleibender" or "blue-remaining" covellite (Moh, 1964) and "abnormal-" or "X-" bornite (Morimoto *et al.*, 1960; Brett and Yund, 1964; Yund and Kullerud, 1966) were not encountered in the present study. The results of the synthetic experiments (Table 2) are listed mostly as five groups along the lines in Figure 4. The results which are not included in the above groups, are given in the last part of the table.

EXPERIMENTAL RESULTS

Microscopic. The microscope examination indicates a possible composition range where covellite appears as one of the stable phases (Fig. 4). The specimens in the sulfur-deficient area of the digenite-type solid solution were microscopically a single phase. Existence of djurleite in these specimens was confirmed by X-ray single crystal and powder methods (Figs. 3 and 4).

Nonintegral N Values. As described previously (Morimoto and Koto, 1970), the superstructure reflections of the digenite-type solid solution in the Cu-S system have the reciprocal coordinates of $(h \pm n\delta t, k \pm n\delta t, l \pm n\delta t)$, where h, k and l are integers and refer to the high-digenite sub-cell, δt represents a nonintegral positive number and n is a small integer such as one, two, or three. The similar nonintegral types were also observed when some iron was added in the specimens. They are also called digenite-type solid solution and their structure type is conventionally

Table 2. Synthetic experiments on the digenite, and the digenite-type solid solutions. The details of the synthesis are given in text. The identification of phases was mainly carried out six months after quenching to room temperature. The standard deviation of the N values is ± 0.05 . The cell edges are represented in Angstrom with a standard deviation of ± 0.0005 A. The phase with * appeared in very small amounts.

Sample group	No.	Composition (at %)			Digenite-type S.S.		Additional phases	Comments
		Cu	Fe	S	N value	cell edge		
1	S-1	63.64		36.36	5.21	5.5577	cv	
	108	63.54	0.10		5.19	5.5570	cv	
	S-2	63.44	0.20		5.12	5.5555	cv	
	110	63.34	0.30		5.14	5.5548	cv	
	S-3	63.24	0.40		5.01	5.5541	cv	
	S-4	63.04	0.60		5.00	5.5550		
	S-6	62.64	1.00		4.98	5.5565		
	S-7	62.44	1.20		4.99	5.5575		
	S-8	62.24	1.40		5.00	5.5583		
	83	62.12	1.52		4.99	5.5580		
	S-9	62.04	1.60		5.00	5.5605		
S-10	61.84	1.80		4.97	5.5598			
S-11	61.64	2.00		4.95	5.5600	4a(bn)		
2	118	61.90	1.30	36.80	4.96	5.5440	id(?)	
	119	62.00	1.40	36.60	4.95	5.5460	bn(?)	
	83	62.12	1.52	36.36	4.99	5.5580		
	121	62.20	1.60	36.20	5.00	5.5618		
3	123	62.40	0.80	36.80	5.05	5.5489	cv	
	124	62.50	0.90	36.60	5.05	5.5489	cv	
	125	62.60	1.00	36.40	5.02	5.5550		
	126	62.70	1.10	36.20	5.05	5.5615		
	127	62.80	1.20	36.00	5.20	5.5665		
	128	62.90	1.30	35.80	5.51	5.5688	dj	
4	130	63.00	0.20	36.80	5.24	5.5560	cv	
	131	63.10	0.30	36.60	5.13	5.5555	cv	
	132	63.20	0.40	36.40	5.00	5.5530	cv	
	133	63.30	0.50	36.20	5.17	5.5580		
	134	63.40	0.60	36.00	5.53	5.5640		
5	62	64.01	0.20	35.79	5.85	5.5660	dj	
	65	63.73	0.40	35.87	5.87	5.5663	dj	
					5.00*			
	84	63.26	0.72	36.02	5.45	5.5635		
	126	62.70	1.10	36.20	5.06	5.5615		
	85	62.34	1.36	36.30	5.01	5.5590		
	83	62.12	1.52	36.36	4.99	5.5580		
	86	61.94	1.64	36.42	5.00	5.5576		
Others	39	61.90	1.50	36.60	4.77		4a(bn)	quenched from 300°C
	49	62.44	1.04	36.52	5.00	5.5515	cv	
	69	62.27	1.00	36.73	5.00	5.5484	cv	
	100	63.32	0.84	35.84	5.78		dj	
	102	63.71	0.18	36.11	5.52	5.5595		
	103	63.46	0.36	36.18	5.33	5.5579		
	104	63.06	0.90	36.04	5.17	5.5568		
					6.00*			
	105	63.39	0.90	35.71	5.89	5.5694	dj	
					5.09*			

expressed by the value of the apparent cell edge, Na , in terms of the high-digenite subcell, where N is equal to $1/\delta t$.

The values of N were obtained by measuring the positions of the superstructure reflection with 2θ near 41° and the main reflection with 2θ near 54° . They correspond to (991) and (15.5.5) for the $5a$ -type structure,

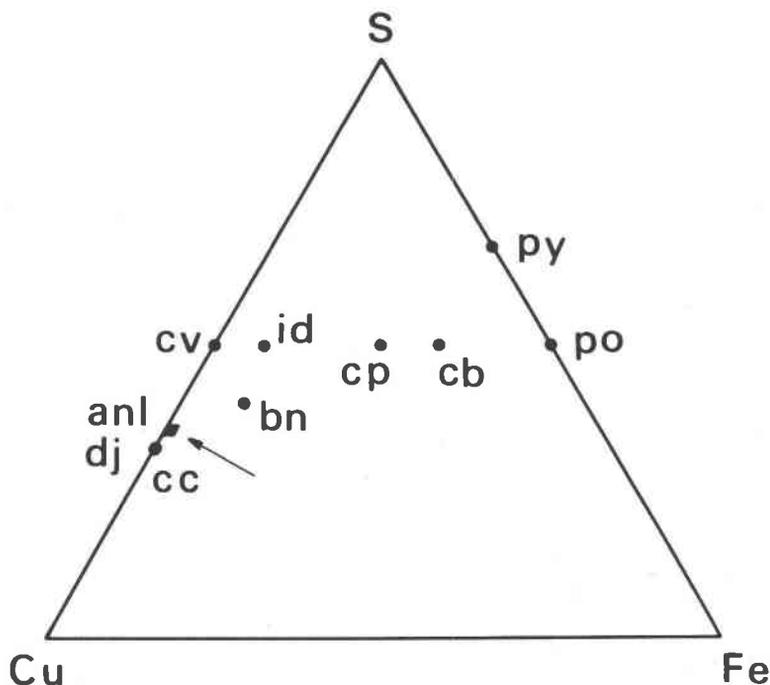


FIG. 3. The area studied in the present study (Fig. 4) is indicated by arrow in the Cu-Fe-S ternary system.

respectively (Morimoto and Kullerud, 1963, Fig. 5). The measured d value of the superstructure reflection was used to obtain the N value on the basis of the a value obtained from the main reflection.

The N values in the region studied in this experiment were given (Table 2), along the lines representing composition changes (Fig. 4). The changes of the N values are graphically shown in Figures 5, 6, 7, 8, and 9. These values and some others obtained from specimens not belonging along the lines are summarized and graphically shown (Fig. 4). These results clearly indicate that the N -value is exactly five in the region studied when the atomic ratio of metal to sulfur is equal to or less than seven to four but it becomes nonintegral when the ratio increases. The digenite-type solid solution, which shows the nonintegral type of structure, is considered to be metastable at low temperature as in the Cu-S system (Morimoto and Koto, 1970). Only in the area where the N -value is exactly five, as for natural digenite, and no other phase than digenite is observed, is digenite considered to be stable. For the specimens with less sulfur than digenite, two or three phases with different

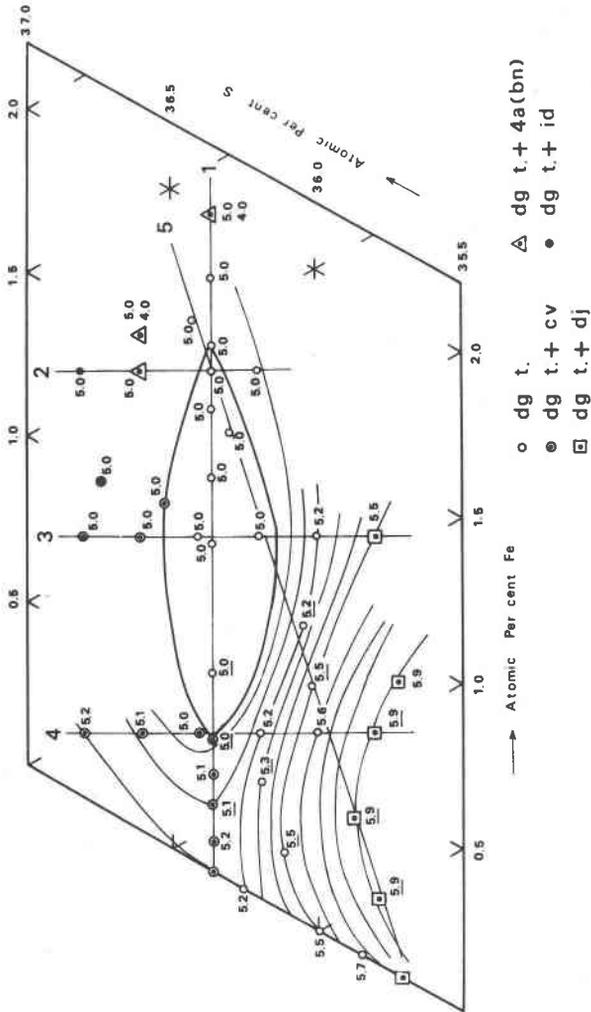


FIG. 4. Diagram of the synthetic digenite-type solid solution at low temperatures in a portion of the Cu-Fe-S system (Fig. 3). The open points represent a homogeneous phase with the digenite or the digenite-type solid solution. The solid points represent two phase regions. The number of each point represents the N -value of the digenite-type phase in each specimen. The underlined N -values represent the phase examined by the X-ray single crystal method. The area of the open points with the N -value of 5.0 represents the possible stable field of digenite. The relations between the 4a-type and bornite are described in text. *dg*: digenite-type solid solution, *cv*: covellite, *dj*: djurleite, *bn*: bornite, *id*: idaite.

N values were occasionally observed by the single crystal method. For example, No. 104 (Table 2) showed the 5.2a type with a small amount of

additional phase of 6.0*a* type, and No. 105 (Table 2) the 5.9*a* type with small amounts of 5.1*a* type and djurleite. The latter specimen can be compared with the natural one from the Magma Mine.

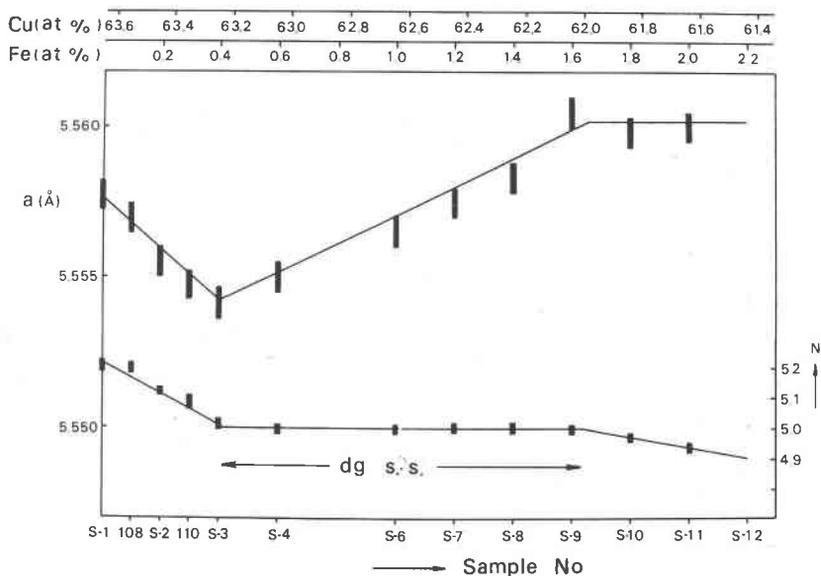


FIG. 5. Cell edges and the *N*-values of the digenite-type solid solution plotted against composition (atomic percent) along the line 1 (Fig. 4). The upper curve represents the cell edges, and the lower the *N*-values. The possible range of the digenite solid solution (*dg s.s.*) is indicated. The procedures to determine the cell edges and the *N*-values are described in text.

For No. S-11, 119, and 39, a small amount of the 4*a* type was confirmed with the 5*a*-type in the X-ray powder patterns. The experiment on the $\text{Cu}_7\text{S}_4\text{-Cu}_5\text{FeS}_4$ join (Morimoto and Gyobu, unpublished) indicates that the 4*a*-type finally decomposes to bornite and digenite. In Figure 4, these specimens are represented in the area where digenite and bornite coexist, though the change of the 4*a* type to bornite within the 5*a* type has not been confirmed in this study.

Cell Dimensions. To obtain the stability field of digenite in more detail, the cell dimensions of the digenite-type phase, including those of digenite, were accurately measured by the powder method assuming cubic symmetry. Silicon was used as standard material and three main peaks, 10.0.0, 10.10.0, and 15.5.5, were measured to obtain the cell dimensions.

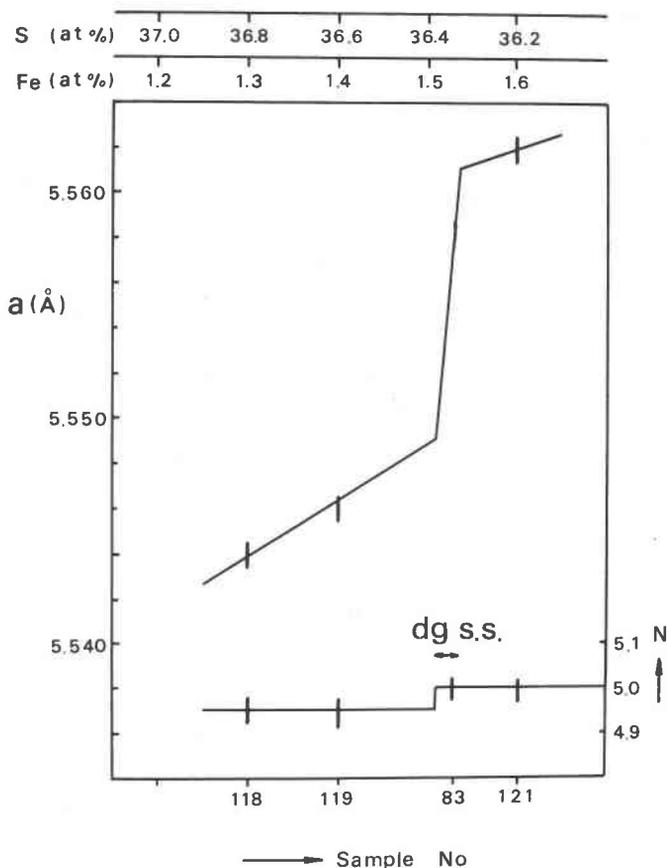


FIG. 6. Cell edges and the N -values of the digenite-type solid solution plotted against composition (atomic percent) along the line 2 (Fig. 4). The upper curve represents the cell edges, and the lower the N -values. The possible range of the digenite solid solution is indicated.

The differences among the cell dimensions obtained from different peaks for each specimen are regular and are slightly greater than the possible standard deviation of each cell dimension, 0.0005 \AA . This supports the conclusion that the digenite, or the digenite-type solid solution is not really cubic, which will be explained later in more detail from the structural viewpoint. For simplicity, however, apparent cell dimensions were obtained from the values of $15.5.5$ on the assumption of cubic symmetry. (Table 2). The changes of the cell dimensions are shown along the lines passing through the digenite solid solution and are compared with the changes of the N values (Figs. 5, 6, 7, 8, and 9). The values for the

fundamental subcell are used for simplicity in the table and figures. The boundaries between the digenite solid solution and the digenite-type solid solution were obtained clearly by discontinuous changes of the cell dimensions. These changes of the cell dimensions are in good agreement with those of the N values and indicate a possible field of digenite solid solution. The range of the digenite solid solution (not the digenite-type solid solution) and the change of the cell dimensions in the solid solution are shown in Figure 10, where some cell dimensions for the digenite-type phase surrounding the digenite solid solution are also added. The values for the digenite-type phase along the Cu-S system in the figure, are taken from Roseboom (1966). The stability field of the digenite solid solution

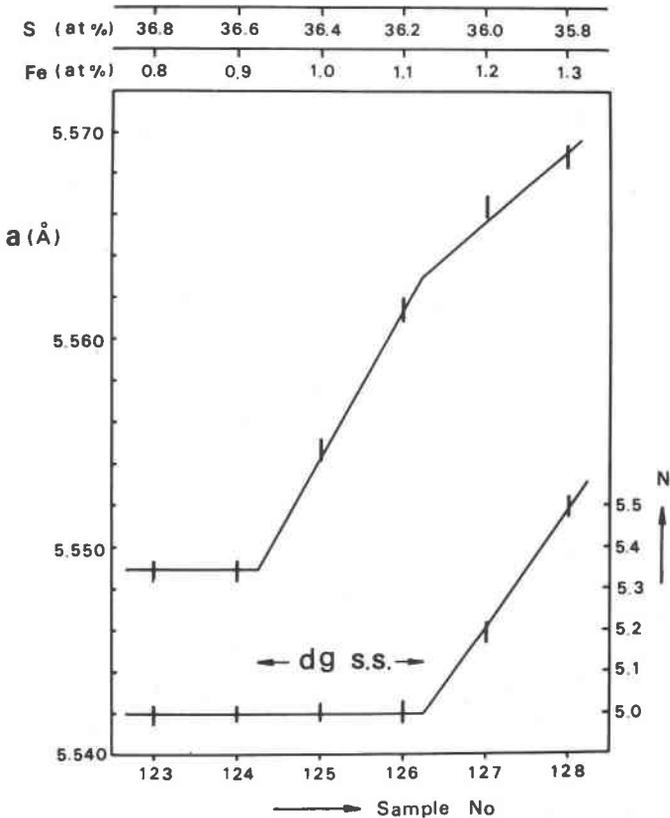


FIG. 7. Cell edges and the N -values of the digenite-type solid solution plotted against composition (atomic percent) along the line 3 (Fig. 4). The upper curve represents the cell edges, and the lower the N -values. The possible range of the digenite solid solution is indicated.

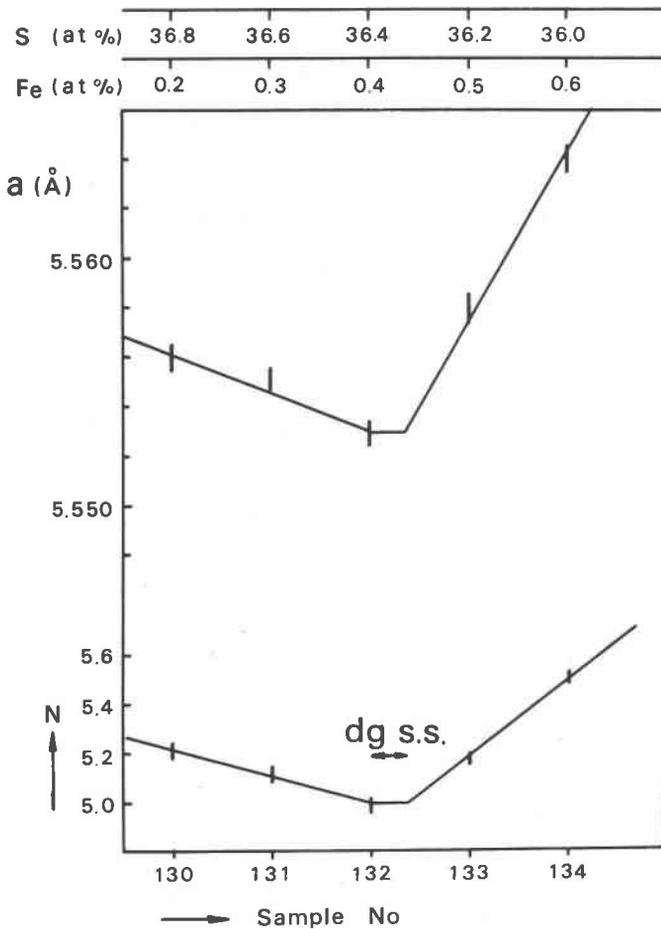


FIG. 8. Cell edges and the N -values of the digenite-type solid solution plotted against composition (atomic percent) along the line 4 (Fig. 4). The upper curve represents the cell edges, and the lower the N -values. The possible range of the digenite solid solution is indicated.

covers an area around the composition $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ (Fig. 10), which was suspected to be the ideal composition of digenite from the EPMA data on natural digenite.

Effect of cobalt and nickel. In order to investigate whether iron is really an essential element for the stability of digenite, syntheses of digenite were carried out by using cobalt and nickel instead of iron. Nickel and cobalt of 99.999 and 99.99 percent purity, respectively, were used in the synthesis. The mixture of sulfur, copper and nickel (or cobalt) in the ratio

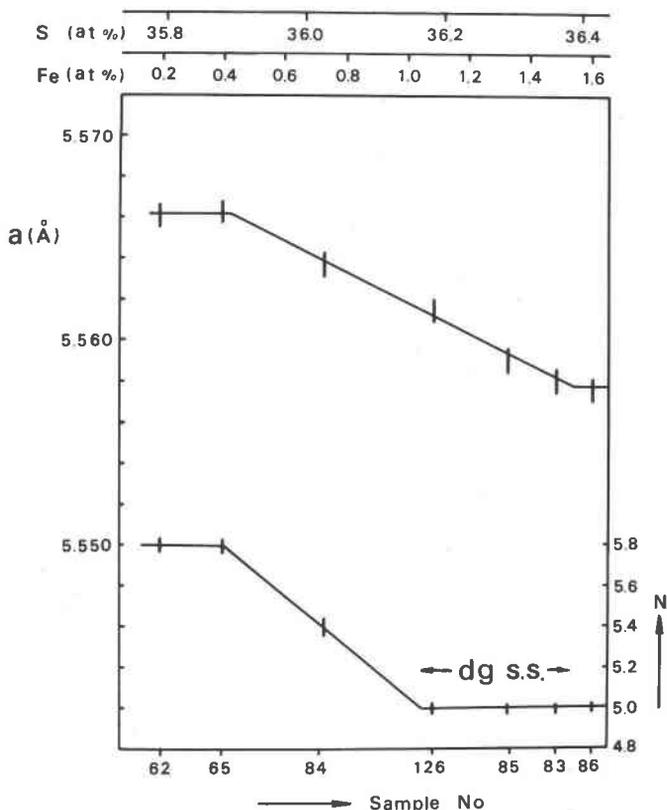


FIG. 9. Cell edges and the N -values of the digenite-type solid solution plotted against composition (atomic percent) along the line 5 (Fig. 5). The upper curve represents the cell edges, and the lower the N -values. The possible range of the digenite solid solution is indicated.

of 4.0:6.9:0.1 were used as starting materials. The procedure was the same as for digenite with iron described above.

The product with the composition of $\text{Cu}_{6.9}\text{Co}_{0.1}\text{S}_{4.0}$ was the digenite-type solid solution of $5.8a$ type with a small amount of Co_3S_4 . Digenite with the $5a$ type structure was not observed. The similar result was obtained with the specimen of $\text{Cu}_{6.9}\text{Ni}_{0.1}\text{S}_{4.0}$ resulting in only the digenite-type solid solution of $5.8a$ -type and Ni_3S_4 . These results support the conclusion above that iron is essential for digenite, though we can not neglect the possibility that solid solutions of cobalt- or nickel-digenite corresponding to real digenite with small amount of iron might be synthesized by keeping appropriate specimens at higher temperatures for longer time.

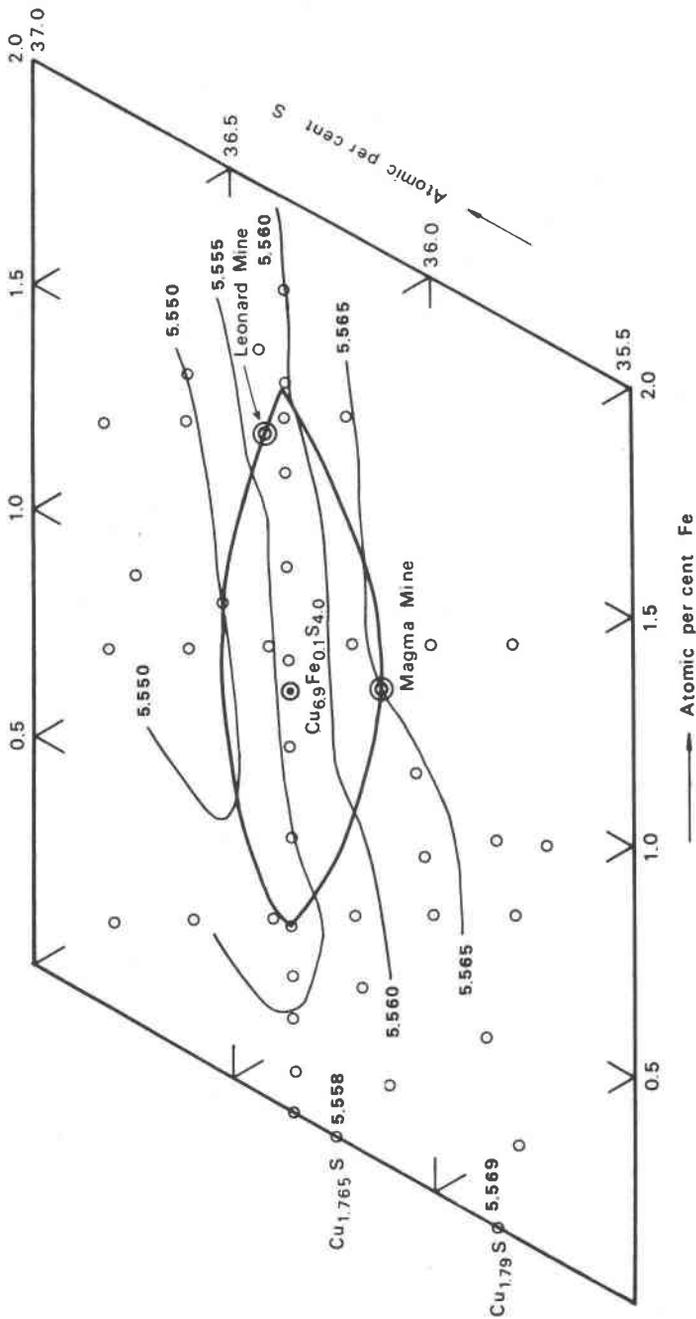


FIG. 10. Cell edges in the digenite solid solution obtained from the synthetic specimens. The cell edges for the digenite-type phase surrounding the digenite solid solution are added. Data points are shown by the open points. The values for the digenite-type phase along the Cu-S system are taken from Roseboom (1966). The cell edges of the two natural digenites are plotted by considering the coexisting minerals.

DISCUSSION

Stability Field of Digenite. The stability field of digenite was determined to be an area of homogeneous $5a$ -type structure based on the synthetic specimens. The field extends from 0.4 to 1.6 atomic percent in iron and from 36.15 to 36.55 atomic percent in sulfur (Fig. 10). The composition of $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ is nearly at the center of the stability field.

This stability field of digenite was based on the synthetic specimens annealed at 50°C for about one week and kept at room temperature for about a half year as described above. When the specimens were examined soon after the annealing, however, the stability field was slightly wider, compared with the field finally obtained in Figure 10. After keeping the specimens at room temperature for nearly three months, the stability field was found to be somewhat reduced. However, no appreciable change was observed after further three months at room temperature. This might mean that the stability field of digenite is much smaller in nature and that the composition of natural digenite is strictly $\text{Cu}_{6.90}\text{Fe}_{0.1}\text{S}_{4.0}$. However, further study of natural digenite indicates existence of a small area of solid solution for digenite as described later.

Many attempts have been made to clarify the relationship between anilite and digenite. The specimens with the compositions between the two compounds were synthesized and examined by the powder and single crystal methods. No trace of anilite was found. Three phases appeared in specimen No. 65; digenite, the digenite-type phase ($5.9a$ type), and djurleite. After keeping the specimen at room temperature for one year, it was reexamined for anilite, but so far no anilite has been confirmed.

Composition and Crystal Structure. The X-ray studies of single crystals of synthetic digenite indicate modified $5a$ -type structure with apparent cubic symmetry in a week at room temperature after quenching (Morimoto and Kullerud, 1963). The space group is apparently $Fm\bar{3}m$.¹ The cell dimension of synthetic digenite with the composition of $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ is $a = 5.5562 \text{ \AA} \times 5$ (Fig. 9) from the d -values of 15.5.5.

Based on space group and cell dimensions, digenite should have 125 of the chemical unit, $\text{Cu}_{6.9}\text{Fe}_{0.1}\text{S}_{4.0}$ in the unit cell. In order to accommodate an integral number of atoms in the cell, the cell content is likely to be $\text{Cu}_{864}\text{Fe}_{12}\text{S}_{500}$. Because the high-temperature digenite (Morimoto and Kullerud, 1963) has a wide composition range of solid solution and has a cubic cell with $a = 5.57 \text{ \AA}$, copper and iron atoms are considered to be

¹ The apparent space group of digenite, or the low-temperature digenite, was erroneously assigned to be $Fd\bar{3}m$ by Morimoto and Kullerud (1963).

randomly arranged in the structure. Because iron is essential for the stability of digenite, or the low-temperature digenite, iron atoms are considered to be orderly arranged in the structure.

To satisfy the space group and the cell content for low-temperature digenite, or low-digenite, however, special position must be occupied by twelve iron atoms, resulting in an arrangement where the iron atoms occupy the centers of octahedra of sulfur atoms. Because the X-ray patterns of the high-digenite and those of the low-digenite are alike, such configurations of iron atoms as in the sulfur octahedra are unlikely. To avoid this difficulty, we must assume that the apparent space group of low-digenite is a result of complex textures, such as domain structures or very fine twinning. The real space group of the low-digenite is, therefore, considered to be much lower than cubic. As described above, the cell dimensions estimated from the d -values of different peaks in the powder patterns also suggest lower symmetry than cubic.

NATURAL ASSEMBLAGES OF DIGENITE

Natural Digenite. According to the results of the synthetic experiments described above, digenite can have a small area of solid solution and have slightly different compositions depending on coexisting minerals. In order to confirm the solid solution range in nature, the cell dimensions of natural digenite crystals were accurately measured. The procedures used in measurements of the cell dimensions of the synthetic specimens were followed for natural specimens, and the apparent cell dimensions were obtained from the d -values of 15.5.5 on the assumptions of cubic symmetry.

The observed dimensions for the subcell of digenite from the Magma Mine are within the value of $5.565 \pm 0.001 \text{ \AA}$, while those observed from Leonard Mine (K) and Leonard Mine (S) are $5.5575 \pm 0.0005 \text{ \AA}$ (Fig. 10). The difference between the cell dimensions of natural digenites indicates the existence of a solid solution, and can be explained by a difference in composition. On the basis of the X-ray and microscopic examinations, digenite used for these measurements of cell dimensions occurs with bornite and pyrite in the Leonard Mine (K) specimen, with bornite in the Leonard Mine (S) specimen. The possible compositions for the natural digenites were, therefore, determined as shown in Figure 10, assuming that the digenite solid solution determined by the experiments on synthetic materials also exists in nature.

Heating Experiments. Heating experiments on natural specimens of digenite were carried out to investigate possible phase changes at high temperatures. The natural specimens were heated in silica tubes at various temperature for 24 hours and quenched to room temperature. The products were examined by the X-ray single crystal methods.

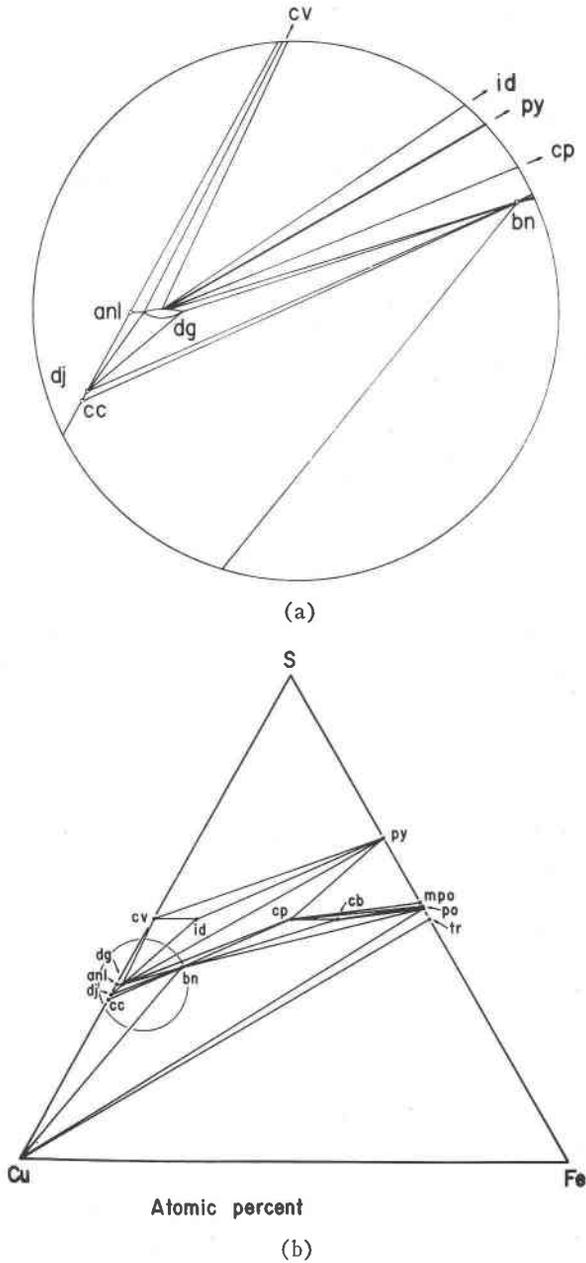


FIG. 11. Possible phase relations in a portion (a) of the Cu-Fe-S system (b) at room temperature. "Blaubleibender covellite" and "abnormal bornite" have been omitted. Many of the tie lines are taken from Kullerud and Yund (1966).

Digenite from the Leonard Mine (K) showed the digenite-type solid solution with the 4.5*a*-type structure after heating at 300°C and became the 4*a* type after heating at 350°C. Because the digenite crystal included a small amount of bornite, some bornite probably dissolved in digenite on heating resulting in the 4*a* type as described by Morimoto, and Kullerud (1966).

The specimen from the Magma Mine, which consisted of digenite, djurleite, the 5.5*a* type, and/or bornite, changed to the 5.7*a* type after heating at 90°C and to the 6*a* type after heating at 275°C. Existence of four phases, especially that of the 5.5*a* type, in the specimen from the Magma Mine obviously indicates lack of equilibrium. This assemblage is considered to be produced as follows: the high-temperature digenite, or high-digenite, with some iron, partly decomposed to the three phases, digenite, djurleite and bornite, in the cooling process. However, the remaining high-digenite changed to the metastable 5.5*a* type by rapid cooling or for other reasons. On heating the specimen, the metastable 5.5*a* type and digenite transformed to high-digenite, and djurleite dissolved into the high-digenite at 90°C changing the composition of the high-digenite. Finally the high-digenite transformed to the 5.7*a* type by quenching. Complete solution of djurleite in the high-digenite changed the composition of the high-digenite and the quenched product was the 6*a* type. This 6*a* type was examined after three months at room temperature following the quenching, but no change was observed.

Stable Assemblages. It is certain from the data presented above that digenite is a discrete mineral in the Cu-Fe-S system. The relationship of digenite to other minerals in the Cu-Fe-S system is shown (Fig. 11). The "blaubender covellite" and "abnormal bornite" are omitted, because we have not succeeded in synthesizing them.

Most combinations of the minerals in Figure 11 were described by Roseboom (1966) and Yund and Kullerud (1966). However, the natural specimens, with both anilite and digenite have not been confirmed. Digenite does not change its structure by grinding but stays as the modified 5*a* type. However, anilite usually changes to a mixture of covellite and the 5.2*a* type by grinding to a powder (Morimoto, Koto, and Shimazaki, 1969). This 5.2*a* type can be easily identified by the powder method, based on the positions of the superstructure reflections relative to those of the main reflections corresponding to the high-temperature digenite subcell. Thus digenite and anilite can be distinguished by the powder method when they exist separately. However, it seems difficult to identify the two phases when they occur together, because superstructure reflections of both phases overlap. Only application of the single crystal method on natural specimens may disclose combinations of anilite and digenite.

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