X-RAY EVIDENCE OF THE EXISTENCE OF THE MINERAL DIGENITE, Cu_9S_5

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Abstract

X-ray studies of the system Cu_2S-CuS have shown the existence of the compound Cu_9S_5 as a separate phase. The diffraction pattern produced by this intermediate compound corresponds with that obtained from a type specimen of digenite, a mineral apparently among *Dana's* discredited species. There is no room for doubt now that the mineral exists, and is indeed the familiar "isometric chalcocite." This is obvious from a comparison of the diffraction pattern of digenite with those obtained by Kerr on three samples of "isometric chalcocite" from Kennecott, Alaska, and by Kurz on the same material; patterns are identical. Since digenite is in fact a rather common mineral occurring with chalcocite and other copper ore minerals, it must be re-established as a species.

In order to investigate the solid phases of the system of Cu_2S-CuS (1), a series of homogenous samples were prepared for *x*-ray study having compositions grading between Cu_2S and CuS. These samples contained the following per cent of CuS by weight: 5, 8, 9, 10, 11, 13, 14, 15, 20, 30, 40, 50, 60, 70, and 80.

Appropriate end-member materials for these mixtures are selected as follows: For the chalcocite end-member, it was known that the Bristol, Connecticut, chalcocite yields an ideal Cu_2S analysis (2, p. 508). Accordingly, a large single crystal of this material was crushed and the fragments examined by several means, including examination of polished sections with the aid of reflected polarized light. All such tests confirmed the preliminary impression that this chalcocite was pure, homogeneous material and would make an ideal Cu_2S end-member. For the CuS end-member, it was at first thought possible to use pure natural crystals. The covellite from the Leonard Mine, Butte, Montana, was selected as the purest material available for this purpose. It was found, however, that it was impossible to hand pick even a small amount of this mineral and obtain a product which was uncontaminated by chalcocite, bornite, and other associated minerals. However, it fortunately proved possible to obtain synthetic CuS of high chemical purity. *X*-ray powder photographs proved this material to be structurally identical with pure natural covellite. This was an extremely important point in facilitating the experimental work, for it provided an easily obtained, pure covellite end-member.

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The samples of this series of mixtures were annealed and homogenized as powder compacts by a method described elsewhere (1, p. 23). Powder photographs of the entire series including the end-members were then made, using a Debye type powder camera and filtered copper radiation supplied from a hot cathode *x*-ray tube. A careful analysis of the powder photographs of this series indicated that they were composites of two of three patterns, namely the two end-members, and another unique pattern which occurred in pure form at a composition about 13 per cent CuS by weight. The field from pure CuS to this composition gave powder photographs which formed a graduated series of mechanical mixtures from CuS to the 13 per cent pattern, the lines of one component decreasing in intensity and finally disappearing as the other is approached. The field from 13 per cent CuS to about 8 per cent CuS gave powder photographs which also formed a graduated series of mechanical mixtures. The solid solution region, from Cu_2S to about 8 per cent CuS, gave the Cu_2S pattern only. It was concluded, therefore, that there were three distinct compounds in this system stable at room temperatures, namely Cu_2S, CuS, and an intermediate compound having a weight composition of 87 per cent Cu_2S, 13 per cent CuS. This compound has an atomic composition of 80 per cent Cu_2S, 20 per cent CuS, and therefore has a formula of $4Cu_2S \cdot CuS$, or Cu_9S_5.

The possibility immediately suggested itself that this hitherto unrecognized compound, Cu_9S_5, might correspond with one or both of the minerals *digenite* (presumably Cu_5S_4) or *carmenite* (presumably Cu_3S_2). It will be recalled that since *Dana* had found visible covellite in carmenite, both of these species have been regarded as discredited. To test the possible identity of the compound Cu_9S_5 with these, powder photographs were made of digenite from Mansfield, Harz, Germany, and of carmenite from the type locality, Carmen Island, Gulf of California, Mexico.

A study of these photographs showed that digenite gave a pattern which was definitely distinct from both Cu_2S and CuS, but which corresponded exactly with the new phase containing 13–14 per cent CuS, i.e., with Cu_9S_5.

Carmenite, however, gave a pattern which was composed of covellite lines, mainly, with some other lines which were probably caused by some other mineral, or minerals.

Digenite, therefore, was established as the third stable mineral (at room temperature) in the system, while carmenite definitely does not belong in the system Cu_2S-CuS.

The data thus obtained seemed to offer certain interesting speculations. Indeed, at this stage in the study, an explanation could be advanced for a point of fact which should always have puzzled economic geologists. In published accounts of chalcocite occurrences one not infrequently finds photographs of polished sections showing mixtures of white orthorhombic chalcocite and "blue isometric chalcocite," intimately associated in a structure which suggests unmixing, or at least contemporaneous growth. If these two minerals are really polymorphous forms of the same composition, it is very difficult to explain this incongruous co-existence, for it would be expected that the unstable isometric form should invert to the stable orthorhombic modification, especially in the presence of an abundance of crystallization nuclei, or "seed crystals" of the orthorhombic form which are present.

Table 1. Comparison of Interplanar Spacings

Index	Cu_9S_5	"Isometric Chalcocite," Kennecott, Alaska	
		Kerr	Kurz
(?)	—	3.93 Å (diffuse)	—
111	3.25 Å	3.22	3.21 Å
200	2.78	2.88	2.78
220 β	2.51	2.41	—
220 α	1.950	1.975	1.96
311	1.665	1.685	1.677
222	1.60	1.516	—
400	1.386	1.445	1.39
133	—	—	—
420	1.315	1.335	1.244
422	1.135	1.140	1.135
511 333	1.070	1.076	1.070
440	.983	.977	.983
531	.943	.938	.940

On the other hand, if "blue chalcocite" is in reality the mineral digenite, a distinct species with not even the composition of chalcocite, but having the composition Cu_9S_5, it is permissible for the two minerals to exist together, and, in view of the similarity of compositions, it is expectable that they *would* exist together and be intimately associated.

Some light is now shed on the seemingly contradictory results of some of the earlier investigators. Barth (3) made powder photographs of chalcocite at 200° C. and obtained an isometric structure, whereas Rahlfs (4) made similar photographs at 170° C. and noted a nonisometric pattern. Rahlfs did, however, get an isometric pattern at 170° C. using material of the composition $Cu_{1.8}S(Cu_9S_5)$. Kurz (5), using orthorhombic chalcocite, observed no inversion to the isometric modification up to 200° C. Barth's

TABLE 2. COMPARISON OF θ VALUES

Line	Indices	$\sum H^2$	1 Cu_9S_5 NWB	2 α-chalcocite Barth	3 "Isometric chalcocite," Jerome, Ariz. Harvard	4 "Isometric chalcocite," Kennecott. Kurz	5 "Isometric chalcocite," Butte, Mont. Kurz	6 "Isometric chalcocite," Khan Mine. Kurz	"Isometric chalcocite," Tsumeb Mine. Kurz
1	111	3	13.9	—	13.9	13.94	13.9	—	13.9
2	200	4	16.1	15.92	16.0	16.04	16.05	16.14	16.01
3	220 β	8	20.9	—	—	20.7	20.63	—	20.83
4	220 α	8	23.2	22.90	23.2	23.15	23.05	23.12	23.16
5	311	11	27.5	27.19	27.5	27.55	27.26	27.69	27.31
6	222	12	28.7	—	—	—	—	—	—
7	400	16	33.7	33.25	33.7	33.54	33.61	33.06	33.51
8	133	19	—	—	—	—	—	—	—
9	420	20	35.8	37.95	—	38.10	38.05	37.98	38.20
10	422 511	24	42.7	42.57	42.9	42.89	42.65	42.83	42.80
11	333	27	46.0	45.57	46.0	45.93	45.96	—	46.11
12	440	32	51.5	51.11	—	51.46	52.21	51.37	50.6
13	531	35	54.7	54.38	—	—	53.79	—	—

results are discussed in another paper (1), but it should be mentioned here that orthorhombic chalcocite does not invert to an isometric form at a high temperature, but rather to a hexagonal modification, while digenite retains its isometric structure at elevated temperatures.

In comparing the various published *x*-ray data on so-called "isometric chalcocite" it is found that in every case the patterns obtained from such material correspond with that obtained from Cu_9S_5, and are not similar in any respect to that of the high temperature form of chalcocite. Table 1 shows the interplanar spacings of Cu_9S_5 compared with those of "isometric chalcocite" from Kennecott, Alaska. It is quite obvious that the materials giving rise to these patterns were the same in each case. In Table 2 a comparison is given between the patterns of Cu_9S_5 and of six so-called "isometric chalcocite" specimens, including the Jerome, Arizona, "fire zone" material.[1] Again there can be no doubt that all of these are identical structures.

In view of this evidence it must be recognized that a mineral having the composition Cu_9S_5 exists, and is in fact the rather common mineral incorrectly called "isometric chalcocite" and "blue chalcocite." It would seem to be highly desirable to reinstate the name *digenite* for this mineral since the powder pattern obtained from a type speciment of digenite from Mansfield, Germany, corresponds with that of Cu_9S_5.

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[1] Dr. Harry Berman of Harvard University kindly supplied the powder photograph of the Jerome material from which the data given in Table 2, column 3, were obtained.