SYNTHETIC FeS_2-CuS_2 SOLID SOLUTION AND FUKUCHILITE-LIKE MINERALS

HIDEHIKO SHIMAZAKI AND L. A. CLARK
Department of Geological Sciences, McGill University, Montreal

ABSTRACT

Various reports of copper-bearing pyrite and other minerals near the FeS_2-CuS_2 join, notably fukuchilite (Cu_3FeS_8), may better be understood in the light of these experiments. Employing hydrothermal synthesis, an extensive solid solution series was found. The cell edge of this solid solution, which has the pyrite structure, varies with composition:

$$a = 5.417 + 0.00403\,x$$

where x is the mol % of CuS_2 substitution. The solid solution limit varies linearly from 82 mol % CuS_2 at 100° C to 67 mol % at 250° C and was determined at 25° C intervals in this range. Above this temperature results were erratic with the solubility limit reduced to approximately 10% CuS_2 at 275° C. Solid solutions heated dry in the presence of sulphur were unchanged after 112 days at 250° C. During the same period some decomposition to covellite plus pyrite occurred at 275° C. A review of the evidence suggests that the solid solutions may be thermodynamically unstable but can form and persist metastably in nature. A new analysis of fukuchilite from the Hanawa Mine, Japan is: Fe 25.6, Cu 25.8, S 48.6 wt. % or $Cu_{0.47}Fe_{0.53}S_{1.75}$. This fukuchilite contains uniformly distributed blebs of pyrite and covellite. This assemblage has possibly formed by decomposition of an earlier phase with Fe 28.9, Cu 23.4, and S 47.7 wt. % (assuming no losses). Evidently fukuchilite can vary considerably from the published composition (Kajiwara 1969).

INTRODUCTION

A number of published analyses show varying small amounts of copper in pyrite. Unfortunately it is difficult to determine what proportions occur in solid solution and as mineralogical impurities. It was concluded in a detailed review by Fleischer (1955) that most, if not all, was due to admixed copper-bearing minerals. The advent of electron microprobe analysis has made it possible to analyze fine-grained mineral aggregates yielding more reliable data on the contents of copper in some natural pyrites. In a general way the copper analyses fall along the composition join FeS_2-CuS_2.

Interest in the copper-iron disulphide phases was sparked when Munson (1966) synthesized a copper end member with pyrite-type structure under very high pressures. To the best of our knowledge the phase relations along the FeS_2-CuS_2 join have not previously been studied experimentally. Accordingly, the results of hydrothermal synthesis of phases along this join are described together with further data on natural fukuchilite (Cu_3FeS_8).

PREVIOUS WORK

Two examples of copper-bearing pyrite were reported recently. In each case the copper was enriched in the core, the rim, or in oriented zones in normal pyrite grains, as confirmed by electron microprobe analysis. Frenzel & Ottemann (1967) reported CuS_2 contents as high as 20 mol % in parts of pyrite aggregates from the Nukundamu deposits, Fiji. The copper enriched portions showed marked anisotropism and weaker reflectivity than the normal pyrite. A unit cell size of 5.42 Å was obtained on a mixture of the copper-bearing and normal pyrite. In a second example from Cerro de Pasco, Perú, Einaudi (1968) found pyrite with crystallographically oriented zones in which copper was enriched up to 3 mol % CuS_2. A cell edge of 5.418 Å was observed, but no variation from ordinary pyrite was observed in colour, reflectivity, or anisotropism.

Villamaninite, the copper-nickel disulphide first described by Schoeller & Powell (1920) from Cármenes District, Spain, was shown by later investigations (for example Thomson 1921) to consist of at least two phases. One phase, to which the name properly applies, lies close to the NiS_2-CuS_2 join, and the other is a ferroan vaesite. Both phases have a pyrite-type structure (Hey 1962). Ypma *et al.* (1968), studying material from the Providencia Mine, Cármenes, Spain, found three cupriferous pyrite-type minerals: cuprian bravoite, nodular villamaninite, and idiomorphic villamaninite. The chemical composition of their idiomorphic villamaninite, based on electron microprobe analysis, lies relatively close to the FeS_2-CuS_2 join. The cell edge for this phase was in the range 5.69 to 5.71 Å. Ypma *et al.* (1968) underlined the solid solubility of CuS_2 in pyrite and bravoite and proposed extension of the name "villamaninite" to all minerals with the pyrite structure containing CuS_2 in the range between 25 and 75 mol %. The occurrence of several disulphide phases with variable cation (Fe, Co, Ni, and Cu) ratios, suggests that extensive solid solution exists, either stably or metastably, in the FeS_2-CoS_2-NiS_2-CuS_2 system.

Recently Kajiwara (1969) reported on a new copper-iron disulphide mineral, termed *fukuchilite*, from the Hanawa Mine, Japan, one of the Kuroko-type deposits. It occurred as a fine-grained aggregate with pyrite and covellite and had a chemical composition near Cu_3FeS_8 based on electron microprobe analysis. From *x*-ray powder diffraction studies of the mineral aggregate, the fukuchilite structure was thought to be similar to that of pyrite but possibly with a lower symmetry. The cubic cell edge was 5.58 Å and when observed with the reflecting microscope, no bireflectance or anisotropism were observed in air or oil.

As mentioned previously, Munson (1966) succeeded in synthesizing a copper disulphide with a pyrite structure under confining pressures of 20 to 65 kilobars. This phase has a cell edge of 5.796 Å, and chemical analysis indicated a composition of $CuS_{1.9}$. Another synthesis under very high pressures was performed by Bither *et al.* (1966) yielding material with a cell edge of 5.790 Å. Chemical analysis of this phase yielded the composition CuS_2. The analytical methods are not indicated in these reports, and so no degree of confidence in the stated compositions may be estimated.

TECHNIQUES OF PRESENT INVESTIGATION

A hydrothermal technique similar to that described by Clark & Barnes (1965) was employed to synthesize phases along the iron-copper disulphide join. The reagents employed were ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4).6H_2O$], cupric sulphate [$CuSO_4.5H_2O$], and ammonium polysulphide [$(NH_4)_2S_x$] in aqueous solution containing about 22 wt. % $(NH_4)_2S$. According to the analysis certificates the largest contaminant in any of these chemicals are 100 ppm manganese and 30 ppm zinc in the ferrous ammonium sulphate.

In preparing the runs, the iron and copper sulphates were weighed in the desired ratio. These were dissolved in approximately 0.3 ml of distilled water in the bottom of a short length of pyrex tubing (4 mm I.D. × 1 mm wall) sealed at one end. Ammonium polysulphide was then added in considerable excess over the amount required, in order to buffer the pH of the solution at about 9 (Clark & Barnes 1965). The tube was then sealed without evacuation, normally leaving a vapour space about equal to the volume of the fluid constituents. Prior to heating, the liquids were thoroughly mixed by vigorous shaking yielding a voluminous black precipitate in the capsule. This apparently amorphous precipitate does not diffract *x*-rays after drying 12 hours under vacuum at 60° C.

At temperatures up to 250° C the capsules were heated in furnaces without external supporting pressure. Runs heated at 275° C were performed in a standard cold seal bomb with an external supporting pressure of water of about 200 bars. In order to investigate the breakdown temperatures of the disulphide phases, dry runs were performed in silica glass capsules employing previously synthesized disulphide phases in the presence of excess sulphur. The runs were heated in electric furnaces in which the temperatures were closely controlled and in the worst instances would be known within ± 3° C. After heating, runs in pyrex capsules were cooled in a few seconds by dropping into a beaker of cold water. The cold seal bomb was immersed in a pail of water and took a couple of minutes to cool.

The products from the hydrothermal runs were filtered and washed with distilled water. After drying, the material was washed again with carbon disulphide to remove excess sulphur. Excess sulphur was removed from the dry runs by the same method. In both instances the products were identified by their optical properties employing a reflecting microscope and by their x-ray powder diffraction patterns. The products encountered were pyrite, covellite, and disulphide phases forming an extensive solid solution along the FeS_2-CuS_2 join. In reflected light the iron-rich disulphide has the brassy yellow colour with high reflectivity characteristic of natural pyrite. With increasing copper substitution the colour changes through light grey to pinkish grey and exhibits a progressively lower reflectivity. The x-ray powder diffraction patterns are all similar to natural pyrite, but the reflections are progressively shifted to lower Bragg angles as a function of copper content. To obtain more precise cell edge values photographs were taken with a 114.59 mm diameter Debye-Scherrer camera, and the results were refined by least squares extrapolation to $\theta = 90°$. Employing this calculation the standard error of the mean cell edge normally was in the 0.0005 to 0.002 Å range.

EXPERIMENTAL RESULTS

Hydrothermal syntheses

Hydrothermal syntheses were conducted at intervals of 25° C from 100° to 275° C. At temperatures of 150° and 225° C extensive solid solution of CuS_2 in FeS_2 was found, the extent being temperature dependent. At other temperatures, copper-rich runs were performed to determine the solid solubility limits.

Results at 100° and 125° C. At these temperatures the products were very fine-grained and included several phases. Even after heating for 35 days, considerable amorphous precipitate remained. The copper-iron disulphide phase together with "pyrite"* and covellite (with normal optical properties) appeared after 17 and 8 days at temperatures of 100° and 125° C respectively. A small amount of chalcopyrite was also present in some cases.

The largest cell values measured for the disulphide phases were 5.749 Å at 100° C and 5.743 Å at 125° C (see Fig. 1). Using the relation between cell edge and composition, as shown later, these values yield compositions of about 82 and 81 mol. % CuS_2 in the disulphide solid solutions and indicate probable limits of the copper content at 100° and 125° C, respectively.

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*In the present paper, "pyrite" set in quotation marks means a pyrite solid solution which, from its brassy yellow colour, appears to be close to FeS_2 in composition. In these instances x-ray measurements were impossible due to its scarcity.

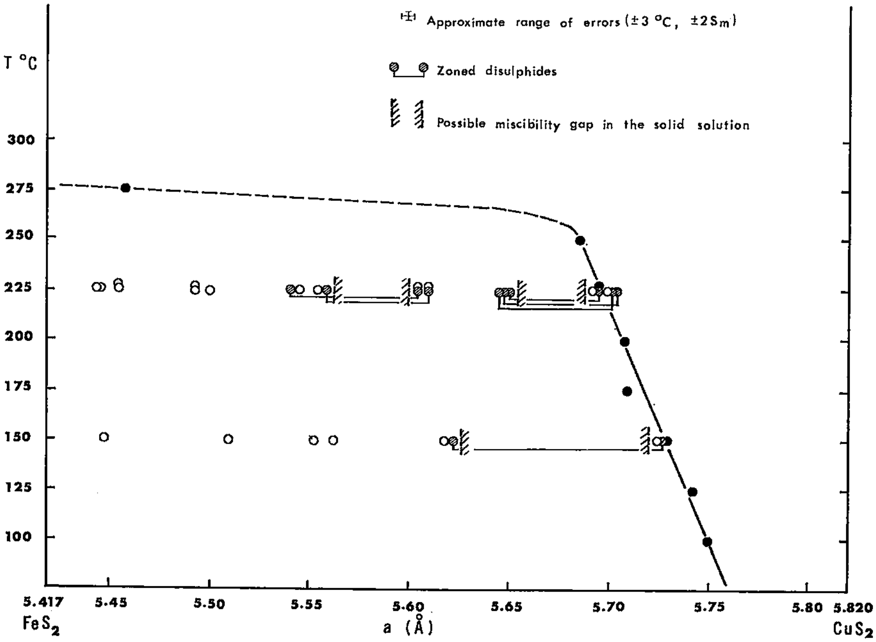

FIG. 1. Cell edges are shown for iron-copper disulphide solid solutions synthesized at various temperatures. (Cell edge is related to composition in Fig. 2.) Open circles: homogeneous phase; hatched circles: two co-existing phases; solid circles: this is the disulphide composition, determined employing Fig. 2, in runs with bulk compositions beyond the CuS_2 solubility limit where covellite appeared as a second crystalline phase. The runs below 150° C also contained minor covellite, "pyrite" and amorphous disulphide solid solution.

Results at 150° C. Runs were performed with various cation ratios at this temperature. The iron-copper disulphide phase was usually present after 1 or 2 days, and about 10 days were enough for the amorphous precipitate to disappear. Iron-rich phases generally crystallized more quickly than copper-rich phases, but their crystallinity was poor. The copper-rich phases formed well developed cubes, and gave sharp *x*-ray powder reflections.

Runs with iron to copper ratios in the initial solutions ranging from 90:10 to 25:75 consisted mainly of the disulphide phase with iron to copper ratios approximating the initial solutions, although trace amounts of "pyrite" and covellite were occasionally observed microscopically. More copper-rich runs, with iron to copper ratios from 20:80 to 10:90, produced disulphide phases with a constant cell edge of 5.729 Å plus covellite in increased amounts. This cell edge, which corresponds to about 77 mol. % CuS_2 in the solid solution, presumably indicates the limit of CuS_2 solid solubility in FeS_2 at this temperature.

As will be shown at 225° C, when the iron to copper ratio of the initial solution was 40:60, it was difficult to obtain a homogeneous disulphide phase. Zoned disulphides resulted with compositions as indicated in Fig. 1.

Results at 175° and 200° C. At temperatures above 175° C, 4 days are sufficient for the disulphide phase to crystallize irrespective of its composition. The largest cell values obtained were 5.712 Å at 175° C and 5.707 Å at 200° C. They correspond to about 73 and 72 mol. % CuS_2, respectively (see Fig. 1).

Results at 225° C. The largest cell edge was 5.704 Å, and suggests that 71 mol. % CuS_2 is the solubility limit at this temperature. Many runs with different iron to copper ratios re-confirmed the extensive solid solution along this join.

However as shown in Fig. 1, a homogeneous disulphide phase was not obtained when iron–copper ratios in the initial solutions were 40:60 and 60:40. Two disulphide solid solutions always grew which were easily distinguished with the reflecting microscope and by *x*-ray powder photographs. With the ratio 60:40, copper-rich grey cores were surrounded by iron-rich yellow rims. On the contrary when the ratio was 40:60 iron-rich cores were overgrown by copper-rich rims. On the *x*-ray powder photograph each reflection was split, and, although very diffuse, two cell values could be determined as shown in Fig. 1. It is unclear whether or not these observations should be interpreted as miscibility gaps.

Results at 250° and 275° C. At 250° C, the largest cell value obtained was 5.685 Å corresponding to 67 mol. % CuS_2. At 275° C, external supporting pressure was employed. Copper-rich runs produced the disulphide phase plus a considerable amount of covellite. Judging from its variable colour under the reflecting microscope, the disulphide phase was variable in composition, on a grain by grain basis, from iron-rich to copper-rich. The cell edge was indeterminate due to weak, broad *x*-ray reflections. Only one experiment with 50:50 initial iron to copper ratio produced covellite and a disulphide phase with a relatively constant composition. Its cell was 5.458 Å indicating only 10 mol. % CuS_2 in this phase.

Because the iron-copper disulphide solid solution seems unstable when heated dry in the presence of excess sulphur at 275° C, as discussed later, hydrothermal synthesis was not attempted at higher temperatures.

Chemical analyses of the disulphide phase

At 225° C, a homogeneous disulphide phase was easily produced from a solution with 50:50 initial iron to copper atomic ratio in a relatively short period (4 days). In order to obtain sufficient product for chemical analysis, many runs were performed under these conditions. When examined under the ore-microscope and by x-ray powder diffraction, the products of 16 runs were free, or bore only traces, of other phases. These products totalled 280 mg, and wet chemical analysis was performed by H. Haramura, University of Tokyo. Electron microprobe analysis was also made on one portion of these products.

Wet chemical analysis gave Fe 24.40, Cu 24.37, S 50.73, total 99.50 wt. %, that is, $Fe_{0.53}Cu_{0.47}S_{1.93}$. Microprobe analysis was made at three points on a polished section using synthetic $CuFeS_2$ as a standard. The results were very similar and the averages are: Fe 23.7 ± 0.6*, Cu 23.8 ± 0.5, S 52.3 ± 0.2 wt. %, that is, $Fe_{0.53}Cu_{0.47}S_{2.04}$.

Both wet and probe analyses give the same iron to copper ratio, 53:47, which is slightly copper-poor as compared with the ratio of the initial solution, 50:50. As shown in a later section, this tendency is probably caused by different solubilities of iron and copper in the aqueous ammonium polysulphide solution which remains after synthesis. Regarding the metal to sulphur ratio, there is a small difference between these analyses, probably due to the uncertainty of sulphur analyses. It can be stated, however, that the metal to sulphur ratio of this phase is very close to two.

Unit cell edge and x-ray powder data

The relation between unit cell edge and chemical composition of the disulphide solid solution is shown in Fig. 2 and Table 1. The data used in this diagram are from runs containing no phases other than the disulphide phase. In each run, except the one where the product was analysed, the composition of the final aqueous solution was checked by atomic absorption analyses. In general, copper remains in the solution in amounts ranging from 10 to 200 ppm. On the other hand, the concentrations of iron in the solution are only 1 to 4 ppm. Considering the relative volumes of the phases, the preferential concentration of copper in the residual liquid has an effect on the copper to iron ratio in the disulphide phase which is minor in terms of other possible errors. Hence the disulphide compositions plotted in Fig. 2 are the same as those in the initial solutions in most cases.

As shown in Fig. 2, the relation between the unit cell value and the chemical composition of the disulphide phase is almost linear and represented by the following equation:

$$a(\text{Å}) = 5.417 + 0.00403x \text{ where } x \text{ is mol. \% } CuS_2.$$

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*Here and elsewhere in the paper errors are given as twice the standard error of the mean yielding 95% confidence.

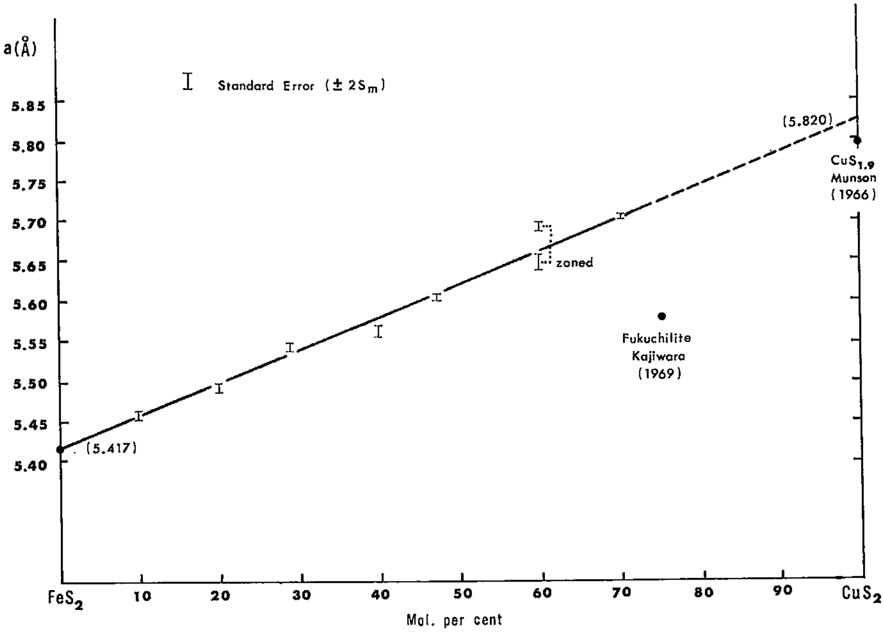

FIG. 2. Cell edge versus composition for the disulphide solid solutions.

TABLE 1. UNIT CELL VALUES FOR VARIOUS COMPOSITIONS OF THE DISULPHIDE SOLID SOLUTION SHOWN PLOTTED IN FIGURE 2

T° C	Cu:Fe mol ratio		a(Å)	Standard error of the mean cell edge
	In original sol.	In precipitate*		
227	10:90	10:90	5.454	0.002
227	20:80	20:80	5.492	0.002
227	30:70	29:71	5.545	0.002
152	40:60	40:60	5.562	0.003
224–228	50:50	47:53**	5.604	0.001
226	60:40	60:40	5.649***	0.003
			5.696***	0.002
226	70:30	70:30	5.701	0.001

* Calculated from atomic absorption data for the residual solution.
** Result of wet chemical and electron microprobe analyses.
*** Two reflections showed almost equal intensities.

Using this equation, to extrapolate to end member CuS_2 composition the cell edge is calculated to be 5.820 ± 0.012 Å. This value is slightly larger than the values 5.796 and 5.790 Å reported by Munson (1966) and Bither *et al.* (1966) for synthetic copper disulphide phase.

X-ray powder diffraction data for synthetic disulphide phases are shown in Table 2 along with data for pyrite, fukuchilite and synthetic

TABLE 2. *X*-RAY POWDER DIFFRACTION DATA FOR VARIOUS Fe AND/OR Cu DISULPHIDE PHASES

hkl	py	*I*	Syn 1	*I*	Syn 2	*I*	Syn 3	*I*	fk	*I*	$CuS_{1.9}$	*I*
110*									3.96	vvw		
111	3.12	2	3.20	m	3.24	m	3.29	m	3.21	s	3.32	m
200	2.70	7	2.77	vs	2.80	vs	2.86	vs	2.789	vs	2.89	vs
210	2.42	6	2.48	m	2.50	m	2.56	m	2.497	w	2.57	ms
211	2.21	5	2.26	m	2.29	m	2.34	m	2.281	m	2.35	ms
220	1.917	4	1.96	m	1.98	m	2.02	s	1.971	w	2.04	s
221	1.803	1/2					1.90	vw			1.92	w
310*											1.86	vw
311	1.632	10	1.67	s	1.69	s	1.73	s	1.685	s	1.73	s
222	1.563	1	1.60	w	1.62	w	1.65	m			1.66	m
320	1.504	2	1.54	w	1.55	w	1.59	m	1.545	w	1.59	m
321	1.448	3	1.48	m	1.50	w	1.53	m			1.54	m
410, 322							1.39	vw			1.40	mw
411							1.35	vw			1.36	w
331	1.243	1	1.27	w	1.29	w	1.31	m			1.325	m
420	1.212	2	1.239	w	1.254	w	1.28	w			1.291	m
421	1.184	2	1.210	w	1.223	w	1.249	w			1.260	m
332	1.156	1	1.181	vw	1.195	w	1.220	vw			1.231	w
422	1.107	3	1.132	m	1.144	m	1.168	m			1.180	mw
430							1.145	vw			1.158	w
431	1.065	1/2					1.123	vw			1.132	w
511, 333	1.044	8	1.067	s	1.079	s	1.102	s			1.112	ms
250, 432	1.007	6	1.030	m	1.041	m	1.064	m			1.073	m
521	0.990	5	1.012	w	1.023	w	1.046	m			1.054	m
440			0.981	s	0.991	s	1.013	s			1.022	m
a(Å)	5.419		5.545		5.604		5.729		5.58		5.796	

py: Pyrite from Leadville, Colorado. Berry & Thompson (1962).
Syn 1–3: Synthetic phases bearing 29, 47, and 77 mol % CuS_2.
fk: Fukuchilite from the Hanawa Mine. Kajiwara (1969).
$CuS_{1.9}$: Synthetic. Munson (1966).
*These reflections, reported by Kajiwara and by Munson respectively, are forbidden by the pyrite space group.

$CuS_{1.9}$ phase. Klemm (1962) recognized a linear change in the x-ray reflection intensity ratio, $I_{(200)}/I_{(210)}$, in proportion to the cobalt and nickel contents in pyrite solid solutions. With copper we find a similar relation. The ratio $I_{(200)}/I_{(210)}$, based on the height of peaks in powder diffraction charts, changes from about 1.4 for Elba pyrite to about 4 for disulphide phase containing about 70 mol % Cu_2S (CuKα radiation). In addition, several reflections such as (221), (322, 410), (411), (430), (431), which in pyrite are always too weak to observe, occur in the Debye-Scherrer photographs for the copper-rich phase indicating a change in the sulphur positions.

Dry experiments

In order to investigate their breakdown temperatures, disulphide phases, previously synthesized by the hydrothermal technique, with various iron to copper ratios, were heated dry in the presence of excess pure sulphur at temperatures above 250° C. At 250° C, after 112 days no change was recognized under the reflecting microscope or by x-ray diffraction. At 275° C, the disulphide phase remained after 38 days, but after 112 days some grains had decomposed to pyrite, covellite, and sulphur liquid. Most of the original disulphide phase remained, and there was no appreciable change in the x-ray diffraction pattern. Even the zoning which was occasionally observed in the disulphide grains was maintained. After 42 days heating at 300° C, the disulphide phase was completely decomposed. Complete decomposition occurs in less than 20 days at temperatures of 320°, 340° and 360° C.

Concerning the composition of the pyrite which occurred as a breakdown product, cell measurements indicated a small copper content (less than 5 mol. % CuS_2). The cell values range from 5.428 to 5.438 Å and tended to be larger when breakdown occurred at lower temperature, from a short period run or from a copper-rich initial phase. Thus it appears that the exsolution of copper from the pyrite structure is sluggish especially at compositions closer to pure FeS_2. For these runs between 250° and 360° C, none of the resultant pyrite can be considered as having a composition in equilibrium with covellite and sulphur liquid due to this sluggishness.

At 400° C the disulphide phase decomposed to pyrite, covellite and sulphur liquid, while at 500° C pyrite, "idaite*" and sulphur liquid were formed. At both temperatures the cell edge of the pyrite was independent of the heating period and original disulphide composition. The cell values

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*Reflections closely similar to data for synthetic Cu_5FeS_6 on Powder Diffraction File card #13–161.

of 5.417 to 5.420 Å are not significantly different than for pure FeS_2. No appreciable amount of copper seems to be dissolved in pyrite in equilibrium with covellite and sulphur liquid at 400° C, and with "idaite" and sulphur liquid at 500° C.

Stability of the iron-copper disulphide phase

The CuS_2 phase with pyrite-type structure was synthesized under very high confining pressures, from 15 kb (400° C) to 65 kb (400° to 1600° C) by Munson (1966) and by Bither *et al.* (1966, 1968). It has not been synthesized under lower pressures. In the pyrite structure the cations are co-ordinated by six anions forming a nearly regular octahedron while the anions are bonded to three cations and another anion. Due to the Jahn-Teller effect of Cu^{2+} placed in an octahedral ligand field* (Orgel 1959), it is reasonable to expect that Cu^{2+} prefers not to enter into the pyrite-type structure (Radcliffe & McSween, 1969).

At very high confining pressure the atoms are forced closer together resulting in broadening of the copper e_g level into a band, and delocalization of the electrons (Bither *et al.* 1968). Hence, CuS_2 is a superconductor (Bither *et al.* 1966; Munson *et al.* 1967). The CuS_2 phase with pyrite-type structure is, therefore, stable only under higher pressures, and probably cannot be synthesized in silica glass capsules where the pressure is less than one atmosphere.

On this basis one must question the stability of the iron-copper disulphide solid solution under the lower pressure conditions employed in the present experiments. Several additional facts also suggest that the iron–copper disulphide phase in question is a metastable phase.

1. Although the disulphide phase was synthesized hydrothermally at 275° C, the results of dry tests indicated that the phase is unstable and decomposes to pyrite, covellite and sulphur at this temperature.

2. Synthesized disulphide phases often show slight compositional zoning in individual grains. And results are sometimes difficult to reproduce.

3. Judging from the results of the dry tests, pyrite cannot dissolve large amounts of CuS_2 at temperatures above 300° C. However, if the iron-copper disulphide solid solution obtained in hydrothermal runs is truly stable, the solubility of CuS_2 in pyrite must increase greatly as the temperature decreases from 300° to 250° C, going from nearly zero to about 70 mol. %. The shape of the solvus for this solid solution seems unusual in our opinion.

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*Due to asymmetrical occupancy of the e_g orbital, Cu^{2+} prefers to occupy an octahedral position elongated along the z-axis, whereas the pyrite structure has rather equidimensional octahedral positions.

4. FeS_2, CoS_2 and NiS_2 prefer the pyrite structure under ordinary conditions and their unit cells increase in this order. These three disulphides are mutually soluble to an appreciable degree at temperatures above 400° C (Klemm 1962; Clark & Kullerud 1963), but the existence of stable solid solutions is doubted at lower temperatures, except for the mineral bravoite which contains approximately equal atomic proportions of FeS_2 and NiS_2 (Clark & Kullerud, 1963). Springer *et al.* (1964) synthesized solid solutions of various compositions in the FeS_2–CoS_2–NiS_2 system below 300° C using a hydrothermal technique, and they believed these synthetic solid solutions and most natural ones to be metastable. The difference between unit cell values of FeS_2 and CuS_2 is about 0.4 Å, which is greater than the differences between any of the other disulphide pairs discussed.

The tentative conclusion follows that the iron-copper disulphide phase synthesized in hydrothermal runs is metastable under the conditions employed. The temperature of 275° C obtained as an apparent upper stability limit of the phase, means that only temperatures above 275° C are sufficient to decompose the metastable phase into the stable assemblage during a relatively short period. Similarly, Springer *et al.* (1964) recognized 300° C as the temperature below which metastable solid solutions occurred during hydrothermal synthesis in the FeS_2–CoS_2–NiS_2 system.

Pyrite-type disulphides in FeS_2–CoS_2–NiS_2–CuS_2 system

The present results show that a probably metastable, pyrite-type, disulphide solid solution can be formed easily under certain hydrothermal conditions along the join FeS_2–CuS_2. While Clark & Kullerud (1963) reported a stable phase with composition close to Fe:Ni = 1:1 below 137° C, Springer *et al.* (1964) found that almost complete solid solution is formed metastably in the FeS_2–CoS_2–NiS_2 system below 300° C. Along the NiS_2–CuS_2 join, Moh & Kullerud (1963, 1964) have synthesized a pyrite-type solid solution with composition close to $CuNi_2S_6$ (500°–300° C, dry) and others from $CuNi_2S_6$ to $CuNiS_4$ (200° C, dry, and 100° C, hydrothermal). This $(Cu,Ni)S_2$ phase seems to be a stable one, especially at higher temperatures. The literature records no experimental results along the CoS_2–CuS_2 join.

These results strongly imply the existence of extensive solid solutions in the quaternary FeS_2–CoS_2–NiS_2–CuS_2 system at lower temperatures, although most of them are probably metastable. Natural occurrence of villamaninite, the pyrite-type disulphide from the Cármenes district, Spain, seems to be an example of these metastable solid solutions. Many investigators have found various ratios of cations, Fe, Co, Ni and Cu, although nickel and copper are predominant (Schoeller & Powell 1920; Hey 1962; Moh & Ottemann 1964; Ypma *et al.* 1968).

Recently, Vaughan (1969) suggested non-stoichiometry (sulphur-deficiency) of bravoites from Maubach. However, he analyzed the metals employing an electron microprobe and derived the sulphur by difference. The results of microprobe analyses for natural villamaninites also showed sulphur-deficiency (Ypma *et al.* 1968). In a later section we will try to explain the inconsistency of unit cell values of natural fukuchilite and synthetic Cu_3FeS_8 phase, partially by the sulphur-deficiency of natural fukuchilite. Because the deficiencies observed are of approximately the same order as the errors when sulphur is determined by electron microprobe analysis, further investigations will be needed to conclusively establish sulphur deficiency in the phases of this quaternary system.

The present experimental results indicate that fukuchilite has a variable cation ratio along the FeS_2–CuS_2 join. Also, 'idiomorphic villamaninite' described by Ypma *et al.* (1968) has a composition $Cu_{0.60}Fe_{0.23}Co_{0.03}Ni_{0.14}S_2$ which is close to that of fukuchilite $Cu_{0.75}Fe_{0.25}S_2$. Clearly a problem in nomenclature exists. Ypma *et al.* (1968) proposed to extend the name villamaninite to minerals with pyrite structure containing more than 25 and less than 75 mol. % CuS_2. But, for a systematic nomenclature the present writers have an alternative suggestion. We suggest that the name *villamaninite* be reserved for minerals with compositions close to the NiS_2–CuS_2 join as proposed originally by Schoeller & Powell (1920), and that the name *fukuchilite* be employed for minerals close to the FeS_2–CuS_2 join.

Fukuchilite from the Hanawa Mine, Japan

This mineral was described in detail by Kajiwara (1969). The composition and unit cell were Cu_3FeS_8 and 5.58 Å. From Fig. 2 of the present investigation a very different cell edge of 5.72 Å would be expected for the Cu_3FeS_8 composition.

In an attempt to resolve this discrepancy, a natural fukuchilite-bearing specimen collected at the type locality was examined. As described by Kajiwara (1969), fukuchilite occurs as a matrix for minute grains of pyrite and covellite in a uniform, almost eutectic-like intergrowth. Large grains of pyrite and covellite are also found with this aggregate and could not be cleanly separated from the aggregate.

X-ray powder diffraction patterns of the fukuchilite-bearing aggregate containing some large pyrite and covellite grains were obtained using Debye-Scherrer and Guinier cameras. Table 3 shows the data from the Debye-Scherrer photographs. The fukuchilite reflections were always weak and broad but gave a cell edge of 5.60 ± 0.01 Å, which is very close

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA FOR THE FUKUCHILITE-BEARING AGGREGATE FROM THE HANAWA MINE, JAPAN

d(Å)	I	Remarks
3.436	vw	Barite (210)
3.204	wb	fk (111), cv $(10\bar{1}1)$
3.114	w	py (111), barite (211)
3.021	m	cv $(10\bar{1}2)$
2.795	sb	fk (200), cv $(10\bar{1}3)$
2.706	s	py (200), cv (0006)
2.484	wb	fk (210)
2.417	m	py (210)
2.307	vw	cv $(10\bar{1}5)$
2.267	vwb	fk (211)
2.204	m	py (211)
2.028	vw	cv (0008)
1.969	wb	fk (220)
1.910	m	py (220)
1.889	m	cv $(11\bar{2}0)$
1.851	vw	
1.753	vw	
1.729	w	cv $(10\bar{1}8)$
1.682	wb	fk (311)
1.629	s	py (311)
1.588	vw	
1.556	wb	py (222), cv $(11\bar{2}6)$
1.500	w	py (230)
1.446	w	py (321)
1.351	vw	cv $(1.0.\bar{1}.11)$
1.279	vwb	fk (331), cv $(20\bar{2}8)$
1.242	vw	py (331)
1.212	w	py (420)
1.183	w	py (421)
1.155	vw	py (332)
1.106	w	py (422)
1.076	vwb	fk (333), (511)
1.043 (α_1)	s	py (333), (511)
1.042 (α_2)	w	py (333), (511)
1.006 (α_1)	m	py (432), (250)
1.006 (α_2)	w	py (432), (250)
0.9893 (α_1)	m	py (521)
0.9892 (α_2)	w	py (521)

Fe*Kα* radiation, λ = 1.9373 Å, 26 kV − 10 mA.
Pyrite py (20 reflections) a = 5.421 Å, standard error of the mean = 0.0013
Fukuchilite fk (8 reflections) a = 5.600 Å, standard error of the mean = 0.005
b = broad reflection. cv = covellite

to the value, 5.58 Å, reported by Kajiwara (1969). Reflection (110) was not observed in the present study. The cell edge of the co-existing pyrite was 5.421 ± 0.003 Å.

Electron microprobe analysis was made of the fukuchilite-bearing aggregate using synthetic chalcopyrite as standard for iron and copper, and pyrite from Elba for sulphur. Unfortunately we could not find an area of fukuchilite large enough (>1 μm) to be analyzed. Therefore the beam diameter was broadened to $\backsim 40$ μm, and the average chemical composition for the fine-grained, three-phase aggregate was obtained. We believe this assumption led to a close approximation of the bulk composition because the pyrite and covellite grains, which average <1 μm diameter, are uniformly distributed in the fukuchilite matrix.

Six replicate analyses were made at each of four points and gave the following result: Fe 28.9 ± 0.1, Cu 23.4 ± 0.2, and S 47.7 ± 0.2 weight per cent. In order to calculate the new chemical composition of fukuchilite, modal analysis was carried out on ten areas on photomicrographs at 1400 and 2800 magnifications. The mode was fukuchilite 47.5 ± 3.0, pyrite 34.6 ± 1.8, and covellite 17.9 ± 1.4 in volume per cent. The small ranges observed confirmed the mineralogical homogeneity of the assemblage analyzed. Using these chemical and modal compositions of the aggregate, the chemical composition and formula of this fukuchilite is: Fe 25.6, Cu 25.8, S 48.6 weight per cent, or $Cu_{0.47}Fe_{0.53}S_{1.75}$.

Since the calculated formula is far from the published value of Cu_3FeS_8, the formula was re-calculated selecting values from the above chemical and modal analyses at the appropriate error limits to maximize sulphur and copper in the formulae, which are respectively: $Cu_{0.43}Fe_{0.57}S_{1.82}$ and $Cu_{0.52}Fe_{0.48}S_{1.69}$. Even these limiting compositions do not approach a sulphur to metal ratio of 2 or a Cu:Fe ratio approaching 3:1. For the above best estimate of the composition the Cu to Fe ratio is almost unity, and the cell edge value of 5.60 Å is very close to that for the ratio of unity in the synthetic solid solutions (see Fig. 2). But under the reflecting microscope, the natural fukuchilite is pinkish grey in colour, and different from the synthetic phase with similar Cu to Fe ratio, the colour of which is light grey in reflected light. The difference probably relates to the different metal to sulphur ratios. In the experiments, a pinkish colour was observed with the more copper-rich phases.

It may be concluded that the fukuchilite investigated in this study is copper-poor and sulphur-deficient compared with that reported by Kajiwara (1969), although sulphur deficiency was suggested in his paper. However this is no reason to question the Cu_3FeS_8 composition he reported because a broad range of compositions can be synthesized sometimes with variations on the scale of a single run.

Kajiwara reported that heating at 200° C for three days in the presence of liquid sulphur causes the partial breakdown of fukuchilite. This behaviour is quite different from that of the synthetic phase which may also suggest the compositional deviation from the metal:sulphur stoichiometry.

As mentioned previously, the fukuchilite-bearing aggregate includes extremely minute inclusions of pyrite and covellite in uniform distribution. This texture is interpreted as a product of the partial breakdown of original fukuchilite grains. Although the exact composition was unobtainable due to minuteness of the inclusions, the reflectivity of pyrite disseminated in fukuchilite is obviously lower than for large-grained pyrite, the composition of which is judged to be FeS_2 from unit cell measurements. No special reflections were obtained for this pyrite even when employing the sensitive Guinier camera. From its reflectivity, this disseminated pyrite would appear to contain a small amount of dissolved copper.

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