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CRYSTAL DATA FOR SYNTHETIC $Cu_{5.5x}Fe_xS_{6.5x}$ (IDAITE)

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A synthetic phase corresponding to the general formula $Cu_{5+x}FeS_{6+x}$ was first reported by Merwin and Lombard (1937). Roseboom and Kullerud (1958) found that this phase has a Cu:Fe ratio of approximately 17:3 when synthesized in equilibrium with liquid sulfur between 434° and 501° C. The latter temperature is the upper stability limit under these experimental conditions. Frenzel (1959) reported the natural occurrence of this phase, based on the similarities of the *x*-ray powder patterns and distinctive optical properties of the natural and synthetic materials, and named the new mineral idaite. He proposed a hexagonal unit cell with $a = 3.90$ Å and $c = 16.95$ Å on the basis of the powder pattern of the synthetic preparation.

The phase $Cu_{5+X}FeS_{6+X}$ was synthesized in this laboratory as part of a study to determine the stable phase assemblages in a portion of the system Cu-Fe-S. High purity elements (>99.999 wt. %) were reacted in evacuated, silica-glass tubes at controlled temperature. A bulk composition of $Cu_{16}Fe_3S_{19}$ was prepared by heating synthetic CuS and FeS at 400° C. for 200 days. The phases present at the end of this period were well crystallized $Cu_{5+X}FeS_{6+X}$ and 1 to 2 volume per cent FeS_2 (pyrite) which was estimated by a microscopic examination of a polished section of the sample. A second preparation with a bulk composition of $Cu_{17}Fe_3S_{20}$ was prepared by reacting the elements at 400° C. for 11 days, then regrinding to promote reaction, and reheating for an additional 11 days. The final product consisted of $Cu_{5+X}FeS_{6+X}$ and 1 to 2 volume per cent CuS (covellite). Assuming negligible weight loss during regrinding, these experiments indicate that the Cu:Fe ratio of $Cu_{5+X}FeS_{6+X}$ is 5.5 ±0.2 and that the (Cu+Fe):S ratio is one or very nearly one under the P-T conditions of the experiments. Although the elemental ratios are approximately known, the formula weight is not known and the number of formula weights per unit cell (Z) cannot be calculated directly. Therefore the more general formula $Cu_{5.5X}Fe_XS_{6.5X}$ is preferred because it does not exclude values of less than one for X. The formula written in this manner is not intended to exclude the possibility of a small variation in the Cu:Fe ratio, although any such variation must be within the limit given above.

The corresponding d values for $Cu_{5.5X}Fe_XS_{6.5X}$ in these preparations are equal within the experimental error, but they are significantly different from the values reported by Frenzel (1959). The observed d values listed in the third column of Table 1 were obtained on a diffractometer with copper radiation, using silicon ($a = 5.4306$ Å) as a standard. Also included in this column are reflections which were only observed with a 114.6 mm camera using either copper or iron radiation. These reflections have been assigned intensities of <2. The two or three most intense reflections of FeS_2 (pyrite) and CuS were also recorded on the films, but they were easily eliminated by comparing the patterns of the two prepa-

TABLE 1. X-RAY POWDER DATA FOR $Cu_{5.5x}Fe_xS_{6.5x}$

This Study Hexagonal $a=3.77_7$ Å $c=11.18$ Å $Cu_{K\alpha}$: $\lambda=1.5418$ Å				Frenzel (1959) Fe_K: $\lambda 1.9373$ Å	
Intensity	hkl	d obs.	d calc.	Intensity[1]	d obs.
3	001	11.17	11.18		
5	002	5.58	5.59		
10	003	3.723	3.727		
				ss	3.45 ($Fe_{K\beta}$ of 101)[2]
25	100	3.265	3.270	s/m	3.27
100	101	3.134	3.139	st	3.14
				ss	3.00 ($Fe_{K\beta}$ of pyrite 200)
80	102	2.818	2.823	st	2.82
60	004	2.792	2.795		
				m	2.70 (pyrite 200)
5	103	2.456	2.458		
				s	2.42 (pyrite 210)
<2	005	2.236	2.236		
				s	2.20 (pyrite 211)
7	104	2.123	2.125	ss	2.13
65	110	1.887	1.888	st	1.89
65	105	1.845	1.846	st	1.85
				ss	1.79 ($Fe_{K\beta}$ of pyrite 311)
				s	1.73 ($Fe_{K\beta}$ of 114)
2	113	1.684	1.684	ss	1.686
<2	200	1.635	1.635		
				s/m	1.630 (pyrite 311)
10	201 106	1.618	1.618 1.619		
<2	007	1.597	1.597		
30	114	1.564	1.565	st	1.564
<2	203	1.497	1.497	ss	1.500
5	107	1.435	1.435	s	1.442
<2	204	1.413	1.412		
10	205	1.320	1.320	m	1.317
				ss	1.275 ($Fe_{K\beta}$ of 109)
5	121 206	1.229	1.229 1.229	s	1.225
3	122	1.207	1.207	s	1.206
				ss	1.188 (pyrite 421)
5	109	1.162	1.161	s/m	1.161
<2	207	1.141	1.143	ss	1.141
<2	124	1.128	1.130		

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[1] ss = very weak, s = weak, m = medium, st = strong.

[2] Suggested explanations for additional reflections reported by Frenzel (1959) are given in parentheses.

TABLE 1.—(*Continued*)

This Study Hexagonal $a=3.77_7$ Å $c=11.18$ Å $\mathrm{Cu}_{K\alpha}$:$\lambda=1.5418$ Å				Frenzel (1959) $\mathrm{Fe_K}$:$\lambda 1.9373$ Å	
Intensity	hkl	d obs.	d calc.	Intensity[1]	d obs.
				ss	1.104 (pyrite 422)
5	300	1.091	1.090	ss/s	1.091
10	125	1.082	1.082	m	1.081
<2	10·10	1.057	1.058	s	1.058
				m	1.043 (pyrite 511)
<2	126	1.030	1.030		
3	304	1.015	1.016	s	1.017
				s	1.006 (pyrite 432)
<2	209	.9895	.9892	s	.987
<2	305 127	.9787	.9799 .9775		
<2	220	.9435	.9441		
<2	20·10	.9224	.9229		
<2	131	.9039	.9041		
<2	224	.8938	.8944		
3	129	.8762	.8762		
<2	20·11 134	.8632	.8632 .8628		
<2	135	.8405	.8405		
<2	401 136	.8151	.8154 .8155		
<2	10·14	.7763	.7758		

rations. The x-ray powder data reported by Frenzel (1959) are included in Table 1 for comparison. The important differences between the new data and those of Frenzel are the three new reflections corresponding to the largest spacings, as well as other new reflections at higher 2 θ, and the absence of 13 reflections reported by Frenzel. It is possible, however, to account for all the additional reflections on his pattern by FeK_β radiation and the stronger pyrite reflections. (See Table 1.)

Synthetic $\mathrm{Cu_{5.5x}Fe_xS_{6.5x}}$ has been reindexed on the basis of the data in Table 1 with a hexagonal unit cell of $a=3.77_7$ Å, $c=11.18$ Å. The good agreement between the observed and calculated d values can be seen in the table.

Appleman (1962) has called to the author's attention that the volume of the unit cell of covellite or chalcopyrite divided by the number of sulfur atoms in the unit cell results in a value of approximately 35 Å^3/sulfur atom for both minerals. The unit cell volume of $\mathrm{Cu_{5.5x}Fe_xS_{6.5x}}$ is about

138 Å^3 and by analogy with covellite and chalcopyrite suggests a formula corresponding to $Cu_{3.38}Fe_{0.62}S_4$ for the unit cell. The density computed on the basis of this formula is 4.54 gm/cm^3. Although the material used for the *x*-ray study was unsuitable for an accurate density determination, a value of 4.2 gm/cm^3 was obtained for a polycrystalline aggregate from the preparation containing a trace of CuS. Thus the proposed formula appears reasonable on the basis of all available evidence.

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ON CRYSTAL DATA FOR IDAITE

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I have noted with satisfaction that the mineral idaite has aroused a good deal of interest. It was only after the acceptance of the relatively common occurrence of idaite by my colleagues that I read Eliseev's (1960) criticism on this subject. Eliseev is of the opinion that this mineral, which he has never seen, is only covellite containing bornite or chalcopyrite. Eliseev comes to this conclusion on grounds of purely theoretical considerations. His nonacceptance of the mineral was not based upon any laboratory investigation and therefore cannot be accepted seriously. Of greater interest, however, is Dr. Yund's letter which I have just received. Dr. Yund is of the opinion that a new hexagonal unit cell with $a=3.77_7$ Å, $c=11.18$ Å (approximately $\frac{2}{3}\times 16.95$) should be given to idaite with $Z=1$, if the composition be expressed by the formula $Cu_{3.38}Fe_{0.62}S_4$. This is in lieu of the hexagonal cell which I published (Frenzel, 1958, 1959) with $a=3.90$ Å, $c=16.95$ Å and $Z=1$, if the compound is Cu_5FeS_6. Dr. Yund is of the opinion that 13 lines of my powder diagram (made with Mn-filter[1] Fe-radiation (FeK_α)) are K_β-lines plus pyrite K_α- and K_β-reflexes. If FeK_β-radiation were to play any role in my diagrams (which is practically impossible because of the set-up of the

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[1] By this the intensities of the $K\beta$ lines are reduced down to 1% of the K_α lines.

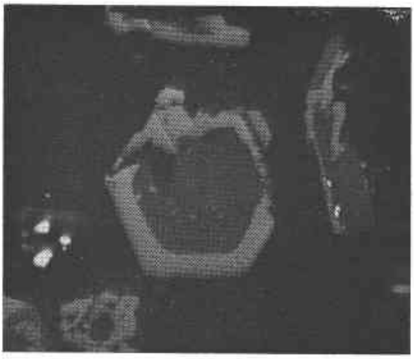

FIG. 1. Cu_5FeS_6 in KCl-LiCl melt. 6 days ∽420° C. Parallel intergrowth between Cu_5FeS_6 (outside) and CuS (inside), 550×, oil immersion (polished section).

apparatus) then the FeK_β-radiation would result in all strong reflexes having a subsidiary K_β-reflex in addition to the ones mentioned by Dr. Yund.

That Dr. Yund believes that the strong pyrite lines occur in his own idaite powder diagrams, in spite of the small amount of 1 to 2 vol. % pyrite and the mass absorption coefficients of Fe and Cu (with copper radiation) is astonishing. I feel it is almost impossible. I can only state that with my camera (57.3 mm diameter), amounts of pyrite up to nearly 10 vol. % do not show up, and definitely not as K_β-lines.

The *x*-ray samples used by me were carefully selected after complete investigation under the microscope on a polished section. Possible impurities such as pyrite were present in the same or greater amounts as in Mr. Yund's substance. These impurities were nearly eliminated.

The "accidental" coincidence of d-values from my idaite-diagram with the mentioned K_α- and K_β-lines of pyrite should not mislead one into ignoring these as irrelevant. For example one could, in the same erroneous way, discover nearly all the strong chalcopyrite lines in idaite or find pyrite lines in covellite and klockmannite[2] etc. It is no surprise in diagrams having so many lines. The unit cell I suggested for idaite accentuates the similarity with covellite and klockmannite. For example, this similarity is also noticable in the oriented intergrowths of idaite and covellite (Fig. 1).

However, as a final point I would like to remark that it is theoretically possible that sheet-structure minerals such as covellite, klockmannite and idaite have varieties of structure with different values for *c*.

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[2] According to Betechtin and Below there are $[S_2]^{2-}$ "double-ions" contained in the covellite structure having the same distance between the S-"ions" (*i.e.* 2.05 Å) as is the case in pyrite.

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FLUOBORITE FROM CRESTMORE, CALIFORNIA

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Introduction

The thermally metamorphosed impure limestones at Crestmore, California, are well known for the wealth of minerals found in them (Murdoch and Webb, 1948). Among specimens collected by one of us (E.R.S.) during an excursion to Crestmore quarries in 1958 was a dolomitic marble containing numerous prismatic crystals up to 5 mm by 1 mm in size. Thin sections of the rock showed the presence of two non-carbonate minerals. One was the new mineral wightmanite (Murdoch, 1962), and the other occurred as somewhat poikiloblastic crystals which were first taken to be scapolite. Some basal sections, however, appeared to be hexagonal rather than tetragonal (Fig. 1), and more detailed optical and *x*-ray examination identified the material as fluoborite. It comprised about one per cent of the rock sample.

Chemical Composition

An analysis of the Crestmore material is given in Table 1. Two samples, each of approximately 0.1 gram, were separated from two apparently identical rock fragments by dissolving the carbonate mineral in 10 per cent hydrochloric acid followed by centrifuging the residue in bromoform, in which the fluoborite just sank.

The first sample was almost completely free from contaminating materials. Fluorine and boron were determined on this at the C.S.I.R.O. Micro-Analytical Laboratory, Melbourne, Australia. The second sample