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THE PYRITE—MARCASITE RELATION

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ABSTRACT

The control of the precipitation of pyrite and marcasite by chemical environment suggests that these two minerals are not a dimorphous pair in the usual sense of the term, but rather that they are chemically distinct compounds. A critical study of all available analyses indicates that pyrite corresponds very closely to ideal FeS_2 , but that marcasite is definitely sulfur-low. Allen and Johnston's precision analyses of these two minerals, using identical procedures on each, also bears out this conclusion. Marcasite is thus a compound somewhat more iron-rich than FeS_2 , just as its isomorphous arsenic analogue, löllingite, is a compound usually somewhat more iron-rich than FeAs_2 . The phase boundary between pyrite and marcasite is, therefore, analogous to a phase boundary in, say, the Cu-Zn (brass) system, with crystal structure a function of chemical composition. At ordinary temperatures, the boundary between marcasite and pyrite is close to the composition FeS_2 , which gives rise to the probable misconception that both are exactly FeS_2 . The excess iron in marcasite and löllingite can be accommodated in the crystal structure in only one simple way out of three possibilities: interstitial solid solution, omission solid solution or proxy solid solution. These three cases are distinguishable by comparing the unit cell densities with the experimentally determined densities. Proof is given that in löllingite and marcasite, the excess iron is due to proxy solid solution, which indicates the corresponding chemical formulas of these minerals to be:



The chemical difference between pyrite and marcasite provides a ready explanation for preferential formation of marcasite in acid solution as against the formation of pyrite in alkaline solution. The function of the hydrogen ion seems to be to remove some of the S from the normal FeS_2 groups to form H_2S and sulfur-deficient- FeS_2 , which is marcasite.

INTRODUCTION

Pyrite and marcasite have long been regarded as two different forms of the same chemical compound, FeS_2 , an opinion which has been largely consolidated by several publications of the Geophysi-

cal Laboratory.^{1,2} In addition to placing pyrite and marcasite definitely in the category of polymorphous pairs, with marcasite as the unstable member under ordinary conditions, investigations of that laboratory have also established the following important fact: Acid solutions and low temperatures favor the precipitation of marcasite, while alkaline solutions and high temperatures, on the other hand, favor the precipitation of pyrite. At a given temperature, the proportion of FeS_2 precipitating as marcasite is an almost linear function of the final acid concentration.

This is held to be an example of the theory that the external chemical environment can affect the nature of the phase precipitated, for Allen, Crenshaw, Johnston, and Larsen³ say, in explanation,

Monotropic forms often crystallize from some particular solvent. . . .

The particular solvent, in this case, differs from the one which precipitates the stable modification by the hydrogen ion contribution of a half per cent, or less, of sulfuric acid, or of a quarter per cent, or less, of hydrochloric acid. Furthermore, the unstable marcasite will precipitate even in the presence of the stable modification, pyrite, provided that the acid concentration is right. In nature, cases are known of the unstable marcasite growing in parallel position on the stable pyrite.⁴

It is natural to entertain the suspicion that this group of conditions contains elements which do not fit into a consistent system. One could understand the situation much more readily if pyrite and marcasite were not polymorphous forms but were actually chemically distinct. It is easy to understand why a slight difference of chemical environment should condition the precipitation of chemically distinct compounds, but it requires a rather elaborate pyramiding of theories and hypotheses to explain why an insignificant change in the chemical environment would change the physical modification of a precipitating compound.

This objection may be summarized semiformaly as follows: There are two propositions:

¹ E. T. Allen, J. L. Crenshaw, John Johnston and Esper S. Larsen, The Mineral Sulphides of Iron: *Am. J. Sc.*, (4) 33, pp. 169-236, 1912.

² E. T. Allen, J. L. Crenshaw, and H. E. Merwin, Effect of Temperature and Acidity in the Formation of Marcasite (FeS_2) and Wurtzite (ZnS); A Contribution to the Genesis of Unstable Forms: *Am. J. Sc.*, (4) 38, pp. 393-431, 1914.

³ Reference 1, p. 190.

⁴ Victor Goldschmidt, Atlas der Krystallformen, Heidelberg, 1920, Vol. 6, figs. 107 and 118.

1. Pyrite and marcasite are polymorphous forms of FeS_2 , of which pyrite is the stable modification under ordinary conditions.
2. Pyrite and marcasite are precipitated together, the proportion of the marcasite present being proportional to the hydrogen ion concentration, the maximum absolute value of which is very low.

One chooses, arbitrarily, let us say, to doubt that these form a consistent body of facts. He is then confronted by three alternatives:

- (a) 1 is in error.
- (b) 2 is in error.
- (c) Both 1 and 2 are in error.

There is no reason to doubt the careful work of the investigators of the Geophysical laboratory with regard to 2. Therefore all alternatives except (a) are eliminated.

The present paper has as its theme, an inquiry into possible support for the proposition that pyrite and marcasite are chemically distinct, and the consequences of the results.

THE COMPOSITION OF PYRITE AND MARCASITE

In considering the possible variations in composition of pyrite and marcasite from the ideal FeS_2 formula, and realizing how impure minerals almost universally are, one might very naturally be lead to look for impurities in one or the other, or at least different impurities in pyrite than in marcasite, in nature, as a possible cause of the difference in modification. It will appear, as a matter of fact, that impurities are a factor in so determining the modification to precipitate. At the present stage of the inquiry, however, the guiding principle must be that as many variables as possible should be eliminated from the problem in order to gain a clue to the fundamentals of the situation. In this connection, it will be recalled that the investigators of the Geophysical Laboratory worked with as pure preparations as laboratory conditions permitted, and still were able to produce pyrite or marcasite at will. As a start then, one only need consider the variations possible in the system iron-sulfur. The writer has therefore studied analyses of pyrite and marcasite which contain only iron and sulfur. Most of the analyses are taken from Doelter's compilations.⁵

⁵ C. Doelter and H. Leitmeier, *Handbuch der Mineralchemie*, IV, Erste Hälfte, 1926, pp. 527-529; pp. 566-567.

TABLE I. ANALYSES OF PURE IRON-SULFUR PYRITE (arranged according to date of publication)

No.	Locality	Source	Remarks	Weight per cent				Atomic per cent		Atomic ratio Fe — S
				Fe	S	Other	Total	Fe	S	
1.	Phillipshoffnung near Siegin	K. Schnabel, through C. F. Rammelsberg, <i>Mineralchem.</i> , 4 , Suppl. 198, 1849. (<i>Doelter</i> , 1 , p. 527)	Massive	46.53	53.39	—	99.92	.833	1.665	1 — 2.000
2.	Heinrichsseen near Müsen	" (<i>Doelter</i> , 2 , p. 527)	Crystals	46.50	53.50	—	100.00	.833	1.669	1 — 2.001
3.	Tuscany	C. v. Hauer, <i>Sitzb. Wie- ner Ak.</i> , 12 , 287, 1854. (<i>Doelter</i> , 14 , p. 528)	Pyritohedrons d = 4.925	45.53	53.37	1.10 (Insoluble)	100.00	.815	1.664	1 — 2.040
4.	Elba	Mène, Pyr. d. fer., 1867, through A. d'Achiardi, <i>Min. Tosc.</i> , 2 , 321, 1873. (<i>Doelter</i> , 17 , p. 528)		43.50	52.20	4.10 (Insoluble)	99.80	.779	1.628	1 — 2.090
5.	Monte Amiata, Tuscany	J. F. Williams, <i>N. Jb. Min., Beil. Bd.</i> , 5 , 430, 1887. (<i>Doelter</i> , 18 , p. 528)		48.78	46.95	—	95.73	.874	1.465	1 — 1.677

TABLE I (continued). ANALYSES OF PURE IRON-SULFUR PYRITE (arranged according to date of publication)

6.	Wattegama, Ceylon	C. Schiffer, <i>Diss. Min- chen</i> , 5, 1900. (<i>Doelter</i> , 20, p. 528)	In the dolomite	44.99	53.79	1.22 (Insoluble)	100.00	.8045	1.676	1 — 2.085
7.	Miniera di Casall, Prov. Grosseto	G. De Angelis d'Ossat. <i>R. Acc. d. Linc.</i> , 11, 548, 1902. (<i>Doelter</i> , 21, p. 528)		47.10	52.97	—	100.07	.843	1.652	1 — 1.960
8.	Paraña, Brasil	C. v. John and C. F. Eichleiter, <i>J. k. k. geol. R. A.</i> , 53, 481, 1903. (<i>Doelter</i> , 24, p. 528)		46.84	51.97	0.52 (SiO ₂)	99.33	.839	1.620	1 — 1.933
9.	Central City-Mine, Gilpin Co., Colo- rado	E. H. Kraus and I. D. Scott, <i>Z. Krist.</i> , 44, 148, 1908. (<i>Doelter</i> , 25, p. 529)	Crystals	46.51	53.26	0.59 (SiO ₂)	100.36	.833	1.661	1 — 1.994
10.	Colorado	E. H. Kraus and I. D. Scott, <i>Z. Krist.</i> , 44, p. 153. (<i>Doelter</i> , 29, p. 529)	Well formed crys- tals free from im- purity; no trace of Ni, Co, As, Sb, or Au.	46.31	53.06	0.54 (SiO ₂)	99.91	.829	1.656	1 — 1.998

TABLE I (continued). ANALYSES OF PURE IRON-SULFUR PYRITE (arranged according to date of publication)

No.	Locality	Source	Remarks	Weight per cent				Atomic per cent		Atomic ratio
				Fe	S	Other	Total	Fe	S	
11.	Colorado	E. H. Kraus and I. D. Scott, <i>Z. Krist.</i> , 44 , 153, 1908. (<i>Doelter</i> , 30 , p. 529)	Well formed crystals free from impurity; no trace of Ni, Co, As, Sb, or Au.	46.39	53.11	0.52 (SiO ₂)	100.02	.830	1.657	Fe — S 1 1.997
12.	Colorado	" (<i>Doelter</i> , 31 , p. 529)	Well formed crystals free from impurity; no trace of Ni, Co, As, Sb, or Au.	46.35	53.08	0.53 (SiO ₂)	99.96	.830	1.656	1 — 1.996
13.	Elba	E. Arbeiter, <i>Diss. Breslau</i> , 1913, 1. (<i>Doelter</i> , 39 , p. 529)		47.00	52.50	—	99.50	.841	1.637	1 — 1.947
14.	Elba	E. T. Allen, J. L. Crenshaw, and J. Johnston. <i>Z. Anorg. Chem.</i> , 76 , 210, 1912. (<i>Doelter</i> , 40 , p. 529)	No impurities	46.49	53.49	0.04 (SiO ₂)	100.02	.832	1.669	1 — 2.003

TABLE I (continued). ANALYSES OF PURE IRON-SULFUR PYRITE (arranged according to date of publication)

15.	Rio Tinto	K. Bornemann and O. Hengstenberg, <i>Metall und Erz</i> , 1920, 344. (Doelter, 41, p. 529)		46.20	52.81	1.00 (Insoluble)	100.01	.8275	1.649	1 1.991
16.	Locality unknown	Carmichael, <i>Univ. Toronto Studies, Geol. Series</i> , No. 22, pp. 29-36, 1926.		46.52	52.70	0.40	99.62	.834	1.644	1 1.970
17.	Elba	Robert Juza and Wilhelm Biltz, <i>Zeit. Anorg. Chem.</i> 205, 273-286, 1932.		46.69	52.97	0.09	99.75	.837	1.651	1 1.973
18.	"	"		46.62	53.14	0.08	99.84	.835	1.657	1 1.985
19.	U. S. A.	"	d=4.978	47.28	52.89	—	100.17	.847	1.652	1 1.950
20.	"	"	"	47.35	52.74	—	100.09	.848	1.645	1 1.940

TABLE II. ANALYSES OF PURE COBALTFEROUS PYRITE (arranged according to date of publication)

No.	Locality	Source	Remarks	Weight per cent				Atomic percent		Atomic ratio
				Fe Co	S	Other	Total	Fe Co	S	
21.	Franklin Furnace, N. J.	E. H. Kraus and I. D. Scott, <i>Z. Krist.</i> , 44 , 148, 1908. (<i>Doelter</i> , 26 , p. 529)	Crystals	45.12 1.19	53.34	0.02 (SiO ₂)	99.67	.8075 .0202 — .8277	1.663	1 — — 2.010
22.	Franklin Furnace, N. J.	" (<i>Doelter</i> , 27 , p. 529)	Crystals	45.28 1.30	53.26	0.03 (SiO ₂)	99.87	.811 .022 — .833	1.661	1 — — 1.994
23.	Franklin Furnace, N. J.	" (<i>Doelter</i> , 28 , p. 529)	Crystals	45.20 1.25	53.30	0.03 (SiO ₂)	99.78	.809 .021 — .830	1.662	1 — — 2.001
24.	Locality unknown, (Probably Franklin Furnace, N. J.)	W. Vernadsky. <i>Centr. Min.</i> 495, 1914.		45.2 1.7	53.3	—	100.2	.809 .029 — .838	1.662	1 — — 1.987

TABLE III. ANALYSES OF PURE IRON-SULFUR MARCASITE (arranged according to date of publication)

No.	Locality	Source	Remarks	Weight per cent				Atomic per cent		Atomic ratio
				Fe	S	Other	Total	Fe	S	
1.	Oxford clay near Hannover	H. Vogel and Reischauer, <i>N. Jb. Min.</i> , 676, 1855 (<i>Doelter</i> , 3, p. 566)		46.90	52.70	—	99.60	.840	1.644	Fe — S 1 — 1.958
2.	Münstertal, Baden	Trapp, <i>Berg-u. hüttl. Z.</i> , 23, 55, 1864. (<i>Doelter</i> , 4, p. 566)		46.93	51.95	—	98.88	.840	1.620	1 — 1.929
3.	Jasper Co., Mo.	E. Arbeiter, <i>Diss. Breslau</i> , 11, 1913. (<i>Doelter</i> , 8, p. 567)	Chicken comb structure, surface greenish yellow, interior silver-grey.	46.55	53.05	As, Trace	99.60	.833	1.656	1 — 1.987
4.	Joplin, Mo.	E. T. Allen, J. L. Crenshaw, and J. Johnston, <i>Z. anorg. Chem.</i> , 76, 210, 1912. (<i>Doelter</i> , 9, p. 567)	Minute trace of Cu, only impurity	46.53	53.30	0.20 (SiO ₂)	100.03	.833	1.663	1 — 1.995

TABLE III (continued). ANALYSES OF PURE IRON-SULFUR MARCASITE (arranged according to date of publication)

5.	Westfalia	Eilfriede Ammermann, <i>Centr. Min.</i> , 577, 1924. (Doelter, 11, p. 567)	Sulfur determi- nation only	(47.38) by diff.	52.62	?	—	.848	1.641	1 — 1.936
6.	Macigno Calafuria, Tuscany	E. Manasse, <i>Atti. della Soc. Tosc. di. Sci. Nat., res. Pisa</i> , 21, 159, 1905; <i>Z. Krist.</i> , 43, 496, 1907. (Doelter, 12, p. 567)		42.69	48.65	As, Trace FeO, 0.71 SO ₃ , 0.83 H ₂ O, 0.58 BaSO ₄ , 6.48	99.94	.764	1.517	1 — 1.985
7.	Hill near Osnabrück	M. Dittrich through Fr. Schöndorf and R. Schröder, <i>2. Jahresber. Niedersächs., geol. Ver.</i> 152, 1909. (Doelter, 13, p. 567)		47.22	52.61	—	99.83	.846	1.641	1 — 1.941
8.	Loughborough Township, Ontario	Carmichael, <i>Univ. Toronto studies, Geol. Ser. No. 22</i> , pp. 29-36, 1926.		46.56	53.40	0.05 (Insoluble)	100.01	.834	1.665	1 — 1.997

To Doelter's have been added those which have been mentioned since.

Table I lists the available analyses of pyrite containing (according to the analyses themselves) only iron and sulfur. Table II gives a set of excellent analyses of pure cobaltiferous pyrite, three of which are surely from Franklin Furnace while the fourth is so nearly identical to these that it may also be reasonably supposed to represent pyrite from the same locality, although the actual locality for this material is not given. Table III gives available analyses for marcasite containing no essential elements other than iron and sulfur.

The analyses have been reduced to iron and sulfur atom ratios, which are given in the last columns of the tables. The analyses may be easily studied by means of the graphical representation of all analyses given in figure 1. Here the analyses are plotted according to indicated iron-sulfur ratio, which should, of course, be 1/2.000 for ideal FeS_2

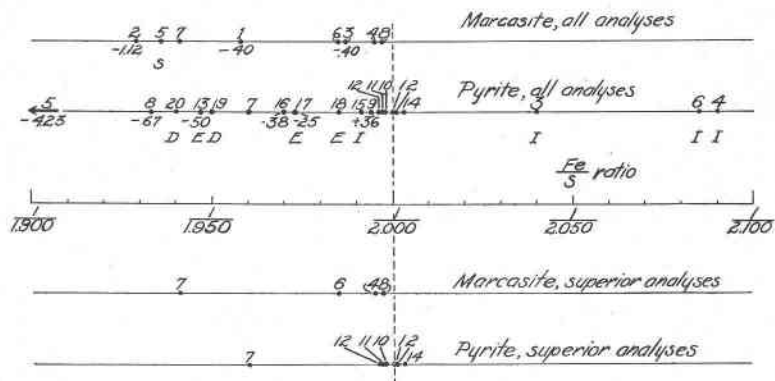


Fig. 1. Graphical representation of iron: sulfur ratios of marcasite and pyrite analyses. The iron content is arbitrarily considered constant while the sulfur content is taken as a variable. The notation beneath individual analyses is explained by the following key:

- E=Elba pyrite, probably contaminated with hematite.
- D=Subnormal density.
- I=Contains insoluble material in excess of 1%.
- S=Sulfur determination alone available, iron by difference.
- .67=Percentage deviation of summation from 100.00%.
(noted only in cases having notable deviation)

PYRITE. One notes that the pyrite analyses cover a considerable spread in iron-sulfur ratio. There is, however, a distinct tendency for the analyses to cluster densely about a value just a trifle lower than $1/2.000$, with the rest of the analyses scattered in a group which also centers approximately here. This very strongly suggests a distribution of error about a correct value. That this is almost certainly the case is indicated by the following critical discussion of the analyses.

5. This analysis adds only to 95.73 and is obviously untrustworthy. In addition, the material for analysis is described as coming in thin leaves. The analysis may be summarily discarded.

8. This analysis is part of a routine report of a number of heterogeneous analyses, made, it would appear, by a firm of commercial analysts. There was no selection of material, but merely an analysis of a "pyrite" sample, which, incidentally, was a concretion. Whether the concretion was actually pyrite or marcasite cannot be ascertained. Newhouse,⁶ as well as Van Horn and Van Horn,⁷ have indicated that concretions may be of either mineral or both. Under any circumstances, this analysis is not one in which sufficient care has been exercised to warrant its inclusion among data to be used in establishing the composition of pyrite.

13, 17, and 18. These analyses represent Elba pyrite. The writer happens to be very familiar with this material from a search for fluid inclusions in pyrite. This particular material contains much hematite occurring as inclusions within single pyrite crystals. The lusters of the two minerals, although very different, blend very well on the conchoidally fractured surface of broken pyrite, which appears as intense yellow highlights and deep shadows. The hematite is therefore easily missed even though a search is made for it. Needless to say, included hematite would raise the apparent iron content of the pyrite. This is evidently just what has happened. Analysis 13 is accompanied by the statement: "with hematite, analysis free from same." The present writer doubts the latter statement. Analyses 17 and 18 are accompanied by the statement that the material "perhaps contains a little oxide," and the authors (chemists evidently), avoided the use of this material supposedly for this reason in their experimental work on the iron-sulfur system (using instead, however, pyrite which is probably just as questionable; see beyond). The list of analyses given in table I contains one by the Allen, Crenshaw and Johnston (No. 14) also of the Elba pyrite. This, if any, should be trustworthy, for it was published by men qualified both mineralogically and chemically to select and analyze minerals. It is noteworthy that this analysis is within the central region of pyrite iron-sulfur ratios. One can, therefore, discard the other Elba pyrite analyses as being very probably contaminated with hematite.

⁶ W. H. Newhouse, Some Forms of Iron Sulphide Occurring in Coal and Other Sedimentary Rocks: *Journ. Geol.*, **35**, 1927, pp. 77 and 83.

⁷ Frank R. Van Horn and Kent R. Van Horn, X-Ray Study of Pyrite or Marcasite Concretions in the Rocks of the Cleveland, Ohio, Quadrangles: *Am. Mineral.*, **18**, pp. 288-294, 1933.

19 and 20. The density of this pyrite, of unknown locality, "U. S. A.," is given as 4.978. In spite of Dana's generous range, this is too low for pyrite which ought to have a density of 5.02, according to Allen, Crenshaw, and Johnston. In view of the fact that the authors were evidently chemists, it seems fair to conclude that the high iron content and low density may not indicate an unusual pyrite (for certainly a higher-than-normal iron content ought to be accompanied by a high density), but rather indicate, say, pyrite plus some limonite-like alteration product, or possibly other contamination. Incidentally, the two (duplicate) analyses show a noteworthy variation of Fe:S of from 1:1.950 to 1:1.940. This is greater than the greatest deviation of any of the analyses of the central compact group of thoroughly trustworthy analyses, from their mean value. This indicates, then, either poor chemical manipulation, which is not very probable, or, irregular contamination of the samples, as from alteration products.

16. Carmichael has contributed a number of analyses of sulfides used in certain ore dressing tests. Analyses of both pyrite (locality unknown) and marcasite are included. (Incidentally, if the labels pyrite and marcasite were transferred on these two analyses, they would fit the groups of superior analyses very well.) As it stands, they form outposts beyond the superior analyses. This may be due, in the case of pyrite, to incomplete analysis, for the summation totals only 99.62%, which is a greater deviation from 100.00% than any unquestionably good analysis retained.

7. No obvious fault can be detected in this analysis.

3, 4, and 6. These three analyses are exceptional in displaying *too great* a sulfur content. They are also exceptional in being the only pyrite analyses containing insoluble matter in excess of 1%, containing, 1.11%, 4.10%, and 1.22% insoluble. In analysis 3, this "insoluble" shows up by lowering the density to 4.925. The material was obviously contaminated in various ways and certainly unsuited to analysis. Numbers 3 and 6, incidentally, add to exactly 100.00, which makes it appear that some additional impurity was suspected and subtracted from the true experimental data.

This leaves a group of what might be termed superior analyses, published by such unimpeachable authorities as Kraus and Scott, and Allen, Crenshaw, and Johnston. There have been included two slightly doubtful analyses: one by Schnabel, which adds to exactly 100.00%, and therefore appears to have had some other original constituents which have been allowed for against the original data, and one by Bornemann and Hengstenberg, which contains the high amount of 1.00% insoluble. If these are omitted, the analyses constitute a consistent group with a maximum deviation of iron:sulfur ratio of less than half a per cent, the center of gravity of the group being just a trifle more iron-high than called for by the formula FeS_2 . If the two analyses mentioned in this paragraph are retained, the group is extended about again as far as the previously-mentioned limit on the iron-high side. Although the theory to be presented by the writer is consistent with

either interpretation of the analyses, it is the writer's opinion that the slightly doubtful analyses be best omitted. This would give pyrite a composition close to, if not actually, FeS_2 , with a possible very slight iron excess.

MARCASITE. There are all too few marcasite analyses available. A glance at Fig. 1, however, will indicate that all of these indicate an Fe:S ratio less than 1:2.000, without exception. Taken as a group, the analyses show less tendency to cluster about some well defined average value. Nevertheless, the group as a whole has an iron content distinctly greater than that of pyrite, the average of the group indicating a value somewhere in the region of 1:1.970, with several analyses clustered in the region of Fe:S=1:1.985.

Analysis 2 does not add to near 100% and may be omitted from the list of superior analyses. Analysis 5, although it shows a significant deficiency of sulfur which should not escape attention, contains no direct determination for iron. Analyses 1 and 3 do not total to within 0.40% of 100%. But in spite of this fact, however, it is significant that if sulfur were added to them to the amount of the deficiency, analysis 1 would still not have enough sulfur to make FeS_2 , and analysis 3 would have only just enough. This same sulfur handicap could be given other analyses of marcasite and still not make FeS_2 .

The analyses by Allen, Crenshaw, and Johnston (No. 4), and the one by Manasse (No. 6) may be distinguished as distinctly superior, and these may be used with confidence in establishing a formula for marcasite. The one by Arbeiter (No. 3) also seems to have been done with some mineralogical responsibility, in spite of its somewhat low summation. These form a system of three good analyses which indicate an iron:sulfur ratio of from 1:1.985 to 1:1.995. These, as well as all the rest (except 2 and 5, which show such obvious internal grounds for rejection) are shown plotted in fig. 1.

COMPOSITIONS OF PYRITE AND MARCASITE. Figure 1 shows graphically that the composition of pyrite is very close to FeS_2 , but may possibly run as low in sulfur as $\text{FeS}_{1.998}$. This conclusion may be subject to some extension with the appearance of further reliable analyses of pyrite. The figure also shows that marcasite runs preferably to a formula $\text{FeS}_{1.990}$, but may possibly vary somewhat, or even vary extensively—the data are not sufficiently numerous to decide on this point with any assurance—, but that

it only approaches the composition FeS_2 . If Carmichael's analysis is excluded—and it seems obvious from her recorded data that an analysis comparable with the best complete mineralogical determination was not attempted for her ore dressing purposes—, one can say that no marcasite analysis has appeared which more than approaches the formula FeS_2 , in some cases even with the handicap that all analytical deficiencies be conceded to be unapprehended sulfur.

This excess of iron in marcasite is quite unorthodox, but need not be regarded with surprise. The other well known member of the marcasite group, löllingite, FeAs_2 , almost always runs to excess iron. Pure FeAs_2 contains 27.16% Fe and 72.84% As. A glance over pages 594, 595 and 596 of *Doelter's Handbuch* will show that the iron content of löllingite is usually higher than this value even making allowances for some of the arsenic being replaced by sulfur. This is well known and customarily explained by saying that the löllingite contains the "leucopyrite molecule," Fe_3As_4 , in solid solution.

PRECISION ANALYSES OF PYRITE AND MARCASITE. Since the analyses just discussed were not originally made with a view to determining a chemical difference between pyrite and marcasite, it would be desirable to have a series of comparable analyses of ideally pure minerals made with extreme care for this particular purpose. Fortunately, just such data are available for one occurrence of pyrite and one occurrence of marcasite. These have been provided by Allen and Johnston⁸ who obtained them for quite a different purpose, namely, for tests of the precision character of iron and sulfur determinations in FeS_2 . Their best determinations are those given as pyrite analysis 14, table I, and marcasite analysis 4, table III, above. The minerals were ideally pure except that the marcasite contained a trace of copper and that both minerals contained a slight admixture of quartz.

Not only does their best result show the marcasite to have a supernormal iron:sulfur ratio, but each of the sulfur determinations, made by different methods, show a lower sulfur content for marcasite than for pyrite. These determinations are as follows:

⁸ E. T. Allen and John Johnston, The exact determination of sulphur in pyrite and marcasite: *Journ. Ind. and Eng. Chem.*, 2, pp. 196-203, 1910.

	<i>Pyrite</i>	<i>Marcasite</i>
Allen and Johnston's method		
Sodium carbonate variation	53.46	53.28
Magnesium oxide variation	53.53%	53.33%
	<hr/>	<hr/>
	53.49 Av.	53.30 Av.
Fresenius's method modified	53.37	53.13
		53.11
		<hr/>
		53.12 Av.
Lunge's method modified	53.18	52.99
		53.07
		<hr/>
		53.03 Av.
Ideal FeS ₂	53.44	

The lower determination of each comparable pair is given in block type. Note that the marcasite is always the lower, and that it is always less than the ideal value. It would appear that the low sulfur content of marcasite called forth the duplicate analyses for this mineral as compared with the single determinations for pyrite in the two last methods. The low sulfur content of marcasite, evidently, then, does not depend on the method of analysis.

Furthermore, the gravimetric determinations of iron gave higher iron for marcasite than for pyrite in each comparable determination. These are as follows, the higher iron content being indicated in block type:

	<i>Pyrite</i>	<i>Marcasite</i>
	46.46%	46.49%
	46.53	46.57
	<hr/>	<hr/>
	46.49 Av.	46.53 Av.
Ideal FeS ₂	46.55%	

The volumetric determinations of iron were as follows:

Pyrite: 46.75, 46.67, 46.66, 46.75, average, 46.72%.

Marcasite: 46.63, 46.49, 46.54, average, 46.55%.

Unfortunately, the volumetric comparison does not tend in the same direction as the gravimetric. The authors, however, accept the gravimetric results as nearer the truth, especially in view of the fact that if the volumetric results were used, the totals would be 100.25% for pyrite and 100.05% for marcasite as against 100.02% for pyrite and 100.03% for marcasite in the gravimetric

determinations. The totals appear to indicate a false iron excess for pyrite in the volumetric determinations.

One may conclude, therefore, that not only does the statistical study of the pyrite and marcasite analyses give practically unanimous support to a higher iron:sulfur ratio in marcasite than in pyrite, but that the most carefully made individual determinations, using identical methods on both minerals, bear out the same thesis.

THE DISTRIBUTION OF EXCESS IRON IN THE MARCASITE GROUP.

LÖLLINGITE. In the discussion of what happens to the excess iron in the marcasite group of minerals, it will be convenient to start with löllingite, for in this mineral the effects are exaggerated and excellent data are available.

Löllingite may be conceived as having a high iron:arsenic ratio in only three simple ways:

1. The structure of the crystal is that of ideal FeAs_2 , with additional iron atoms in the interstices, between other atoms in the normal structure. This may be termed *interstitial solid solution* and may be represented by the formula $\text{FeAs}_{2+n\text{Fe}}$, where n is a small fractional number indicating the iron excess.
2. The structure of the crystal is that of the ideal FeAs_2 with occasional arsenics missing in the structure. This is actually not a solid solution at all, but could not be distinguished from that general class of compounds by its analysis alone. For uniformity, however, this may be designated, *omission solid solution*, and represented by the formula FeAs_{2-m} , where m is a small fractional number indicating the arsenic deficiency.
3. The structure of the crystal is that of the ideal FeAs_2 with some of the arsenic atoms missing but with iron atoms proxying in their places. This may be represented by the formula $\text{Fe} \begin{vmatrix} \text{Fe}_x \\ \text{As}_{2-x} \end{vmatrix}$, where x is a small fractional number indicating

the number of iron atoms occupying the positions normally occupied by arsenic atoms. This condition may be designated *proxy solid solution*.

Complex solutions can also be imagined which involve combinations of the above cases. Case 1 gives rise to a supernormal density, because the unit cell has its normal contents plus additional iron.

Case 2 gives rise to a highly subnormal density because the unit cell has its normal contents less, on the average, a fraction of an arsenic atom. Case 3 gives rise to a slightly subnormal density in the case of löllingite (slightly supernormal in the case of marcasite), because the cell has its normal contents plus the loss in weight (gain in marcasite) accruing from replacing a fraction of an arsenic atom, on the average, by its equivalent in the lighter iron. From the cell dimensions as revealed by *x*-ray diffraction measurements, the known atomic weights of iron and arsenic, and the value of *n*, *m*, and *x*, as calculated from the chemical analysis, it is possible to calculate the mass per unit volume, or the density of the cell, which can then be compared with the actual measured density.

In the case of löllingite, excellent data are available for the use of the above criterion, in the published values of the constants of the Franklin Furnace crystals.^{9,10}

These are as follows:

Chemical Analysis		Weight per cent	atom ratios	atomic per cent
	As		69.80	.933
S		0.21	.007	0.013
Fe		29.40	.530	1.00

Cell, containing 2 formula weights: $a = 2.85\text{\AA}$

$b = 5.25$

$c = 5.92$

Volume = 88.6\AA^3

The iron:arsenic+sulfur ratio is evidently much too high for ideal FeAs_2 , so the excess iron must be allowed for according to either case 1, 2, or 3 above. These give the following results:

$$1. \text{Fe} \left| \begin{array}{c} \text{As}_{2-k} \\ \text{S}_k \end{array} \right| + n\text{Fe}, \text{ where } n \text{ is determined by the condition: } \frac{1+n}{2} = \frac{1.000}{1.773}$$

This gives $n = .0128$

$$\text{Also } \frac{\text{As} + \text{S}}{\text{S}} = \frac{2}{k} = \frac{1.773}{.013}, \text{ which gives } k = .015$$

$$\text{The formula is then } \text{Fe} \left| \begin{array}{c} \text{As } 1.985 \\ \text{S } .015 \end{array} \right| + .128 \text{ Fe.}$$

⁹ L. H. Bauer and H. Berman, Löllingite from Franklin, New Jersey: *Am. Mineral.*, **12**, pp. 39-43, 1927.

¹⁰ M. J. Buerger, The Crystal Structure of Löllingite, FeAs_2 : *Zeit. Krist.*, **82**, pp. 165-187, 1932.

This corresponds to a formula weight of 213.3, which, substituted in the density relation $d = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{2 \times 213.3 \times 1.65 \times 10^{-24}}{88.6 \times 10^{-24}}$ leads to a density of 8.06

2. FeAs_{2-m} , is here, $\text{FeAs}_{1.76} \text{S}_{.013}$, which corresponds to a formula weight of 187.8.

This leads to a density of 6.99

3. $\text{Fe} \begin{vmatrix} \text{Fe}_x \\ \text{As}_q \\ \text{S}_r \end{vmatrix}$, where p, q , and r are determined by the conditions: $\begin{cases} 1+x = 1 \\ (q+r) = 1.773 \\ x+(q+r) = 2 \end{cases}$

This leads to $\begin{cases} x = .079, q \text{ and } r \text{ are then} \\ (q+r) = 1.921 \end{cases}$

determined by $\begin{cases} q+r = 1.921 \\ \frac{q}{r} = \frac{1.760}{.013} \end{cases}$

which gives $\begin{cases} q = 1.91 \\ r = .01 \end{cases}$

The formula is then $\text{Fe} \begin{vmatrix} \text{Fe}_{.08} \\ \text{As}_{1.91} \\ \text{S}_{.01} \end{vmatrix}$

This has a weight of 203.7 and leads to a density of 7.58.

These values are conveniently gathered together in Table IV.

TABLE IV. POSSIBLE CONSTANTS FOR LÖLLINGITE, WITH VARIOUS POSSIBLE DISPOSALS OF THE EXCESS IRON ATOMS

Iron disposal	1. Additional solution	2. Omission solution	3. Proxy solution	4. No excess iron
General formula for löllingite	$\text{Fe} \begin{vmatrix} \text{As}_{2-k} \\ \text{S}_k \end{vmatrix} + n\text{Fe}$	$\text{Fe} \begin{vmatrix} \text{As}_{2-s-m} \\ \text{S}_s \end{vmatrix}$	$\text{Fe} \begin{vmatrix} \text{Fe}_x \\ \text{As}_q \\ \text{S}_r \end{vmatrix}$	FeAs_2
Formula for Franklin löllingite	$\text{Fe} \begin{vmatrix} \text{As}_{1.985} \\ \text{S}_{.015} \end{vmatrix} + .128\text{Fe}$	$\text{Fe} \begin{vmatrix} \text{As}_{1.76} \\ \text{S}_{.013} \end{vmatrix}$	$\text{Fe} \begin{vmatrix} \text{Fe}_{.08} \\ \text{As}_{1.91} \\ \text{S}_{.01} \end{vmatrix}$	
Formula weight for Franklin löllingite	213.3	187.8	203.7	205.8
Density for Franklin löllingite	8.06	6.99	7.58	7.66

The density actually determined by means of a pycnometer was found to be 7.53. This is definitely too low for pure FeAs_2 , but within about half a per cent of the calculated value on the assumption that iron atoms proxy for arsenic atoms in an otherwise normal crystal structure. This agreement is within the limits of experimental error. This criterion thus not only confirms the accuracy of the chemical analysis, in its apparent arsenic deficiency, but it also definitely proves that the iron excess is to be accounted for through the condition of proxy solid solution.

MARCASITE. In the case of marcasite, the available data are not so precise; they have not all been obtained on marcasite from the same locality, and, finally, the effects to be looked for are less pronounced than in löllingite due to the slighter iron excess in marcasite. Nevertheless, it is possible to arrive at valuable conclusions with the scanty and imperfect data at hand.

Cell constants for marcasite have been published by de Jong¹¹ Buerger,¹² and Bannister.¹³ These are as follows:

	<i>de Jong</i>	<i>Buerger</i>	<i>Bannister</i>
<i>a</i>	$\frac{1}{2} \times 3.395$	3.37	3.38Å
<i>b</i>	4.45	4.44	4.44
<i>c</i>	5.42	5.39	5.39
V	81.8	80.6	80.8Å ³

The constants given by Bannister and the writer agree exactly except for the length of the *a* axis. The writer has gone over his original measurements and finds that the length of this axis was determined by averaging the distances of spots appearing in two pairs of layer lines. The average of each pair of layer lines agrees with that of the other within one part on two thousand, so these measurements seem to be trustworthy ones. It will appear in a subsequent publication that the length of the *a* axis shrinks with increasing iron content, without great effect on the other axes, so Bannister's and the writer's data may be considered to be in complete harmony for crystals of slightly different iron content. Since

¹¹ W. F. de Jong, Bepaling van de absolute aslengten van markasiet et daarmee isomorfe mineralen: *Physica*, **6**, pp. 325-332, 1926.

¹² M. J. Buerger, The Crystal Structure of Marcasite: *Am. Mineral.*, **16**, pp. 361-395, 1931.

¹³ F. A. Bannister, The distinction of pyrite from marcasite in nodular growths: *Min. Mag.*, **23**, pp. 179-187, 1932.

a density will be introduced which was measured on the very crystals on which the writer made *x*-ray determinations, his own value of the cell dimensions will be retained. De Jong's results are so different that it appears likely that he made his measurements on crystals containing other than iron and sulfur in their compositions, probably arsenic.

A critical quantitative analysis is not available for the marcasite used by the writer, but a qualitative analysis has ascertained it to be free from the usual impurities to be expected for this mineral. In lieu of the actual iron:sulfur ratio, therefore, it will probably not be far wrong to assume a value of 1:1.985, which is the average value deduced for marcasite. The constitution of the cell may then be studied according to the general cases discussed above. The resulting constants are given in table V. The density actually determined by pycnometer was 4.92, which agrees only with an excess of iron if it is in the structure as a proxy solid solution, as was

TABLE V. POSSIBLE CONSTANTS FOR MARCASITE, WITH VARIOUS POSSIBLE DISPOSALS OF THE EXCESS IRON ATOMS

Iron disposal	1. Addition solution	2. Omission solution	3. Proxy solution	No excess iron
General formula for marcasite	$FeS_2 + nFe$	FeS_{2-m}	$Fe \left[\begin{array}{c} Fe_x \\ S_{2-x} \end{array} \right]$	FeS_2
Formula for marca- site assuming: Fe 1 ----- S 1.985	$FeS_2 + .0755 Fe$	$FeS_{1.985}$	$Fe \left[\begin{array}{c} Fe_{.004} \\ S_{1.996} \end{array} \right]$	
Formula weight for marcasite assuming: Fe 1 ----- S 1.985	124.17	119.45	120.1	119.97
Density of marca- site assuming: Fe 1 ----- S 1.985	5.08 ⁺	4.88	4.92	4.91

the case with löllingite. While this is not a very sensitive criterion for distinguishing pure FeS_2 from a compound containing excess iron, it should be pointed out that the agreement is better with excess iron than without it, which tends to raise confidence that the excess iron indicated by chemical analyses is real and not due to some sort of systematic analytical error.

It should be noted that if Bannister's dimensions for the marcasite cell be used instead of the writer's, the densities calculated in Table V would each be decreased by about 0.01. If the excess iron which appears in the chemical analyses is conceded to be real, it can only be accounted for as proxying for sulfur atoms, regardless of whose values for the marcasite cell are selected. Furthermore, if the iron:sulfur ratio of marcasite is eventually found to be somewhat different than that deduced in the preceding discussion of analyses, or if it is found to be variable, the value of the density which will be least affected by the change is the density calculated on the basis of proxy solution.

In connection with the original data used for the marcasite given above, it should be pointed out also that these figures were a matter of published record¹⁴ before the theory of excess iron in marcasite had been developed, and that they can therefore be relied upon to be unprejudiced by theoretical views. It is necessary to mention this due to the fact that the writer's published density is in excess of any other published for marcasite including that of Allen, Crenshaw, Johnston, and Larsen's¹⁵ figure of 4.89. It is interesting to note that the density of the material used by these investigators rose to 4.91 after heating to about 620°C. and cooling.

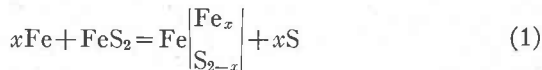
THE PYRITE-MARCASITE RELATION

All evidence points to the fact that pyrite is pure, or very approximately pure, FeS_2 , while marcasite is $\text{Fe} \begin{vmatrix} \text{Fe}_x \\ \text{S}_{2-x} \end{vmatrix}$, where x is a small fraction in the neighborhood of .004, giving marcasite an empirical composition of $\text{FeS}_{1.985}$ or thereabouts. It is, therefore, incorrect to speak of pyrite and marcasite as polymorphous forms of the same compound, in the usual sense of the word polymorphous. It follows that one cannot speak of marcasite as un-

¹⁴ Reference 12, pp. 366 and 367.

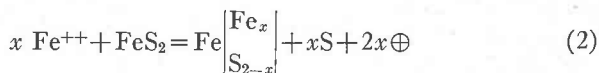
¹⁵ Reference 1, p. 188.

stable with respect to pyrite, any more than one can speak of pyrrhotite as unstable with respect to pyrite. They are chemically distinct. The relation between pyrite and marcasite is, therefore, primarily a chemical one; fundamentally it may be expressed by the equation:



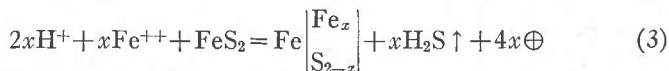
pyrite marcasite

If the iron is added to pyrite in water solution (1) becomes



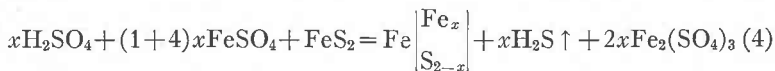
pyrite marcasite

It is known from the work of Allen, Crenshaw, Johnston, and Larsen that in the presence of acid, the right member of this equation tends to be formed in preference to the left member. This fact may be combined with equation (2) to give the following:



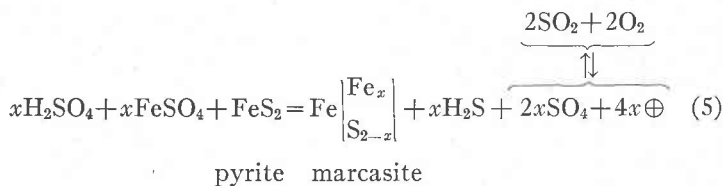
pyrite marcasite

The positive charge appearing on the right may be expected to be absorbed by any substance present at the time of the reaction which is capable of being oxidized. For example, if ferrous iron is used as sulfate to supply the excess iron required by marcasite, as in the experiments by Allen, Crenshaw and Merwin, the following equation may be expected to hold:



pyrite marcasite

where x formula weights of FeSO_4 go to supply the excess iron for marcasite and $4x$ formula weights are used to absorb the positive charge. In part, however, the liberated sulfate is probably also concerned in absorbing the charge, thus:



Possible substantiation for this latter reaction is supplied by Allen, Crenshaw, and Merwin, who mention, “. . . sulfur dioxide, which forms when the temperature and acidity are sufficiently high. . .”¹⁶. These investigators have explained the formation of sulfur dioxide thus (page 396):

“At the higher temperature and the higher acid concentrations a side reaction becomes manifest, viz: the reduction of the sulphuric acid to sulphur by the hydrogen sulphide, followed in turn by the interaction of the sulphur with the sulphuric acid and the appearance of sulphur dioxide.”

Equation (5) may be expected to at least add to the sulfur dioxide formation, if it does not actually account for much of it.

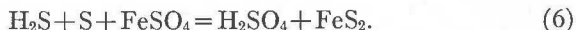
It should be pointed out that acid concentration is not the only variable tending to influence the formation of pyrite or marcasite. Equations (3) and (4) indicate that hydrogen ion concentration and iron concentration tend to push the reaction in the direction of forming marcasite, but that this is opposed by the gas pressure of H_2S , which tends to push the reaction towards the formation of pyrite. Equation (3) also indicates that the concentration of the particular agent utilized for absorbing the positive charge freed from the iron will also tend to push the reaction in the direction of marcasite, while the concentration of the resulting oxidized material, unless solid, will tend to reverse this action and to form pyrite.

Needless to say, other acid radicals could be substituted for the sulfate which appears in equations (4) and (5), with similar results, generally speaking.

One may regard the fact that marcasite forms in acid solution as consistent with the fact that marcasite is lower in sulfur than pyrite. The office of the acid is to remove the sulfur from pyrite crystals already formed, or from normal molecular groups of FeS_2 composition about to precipitate, by the action of H^+ upon S to form the removable gas phase H_2S . In the precipitation of FeS_2 by the action of H_2S on a ferrous salt, the products include not only FeS_2 but acid, according to the equation given by Allen,

¹⁶ Reference 2, p. 395.

Crenshaw and Merwin:¹⁷



If the acid formed on the right of equation (6) is not removed from the sphere of influence of the FeS_2 immediately, these can react, in the presence of FeSO_4 (which must always be present in the system whether FeSO_4 was the original iron sulfate salt used, as in equation (6), or not, because with products H_2SO_4 and FeS_2 , equation (6) must always come to equilibrium and FeSO_4 must be present by its action from right to left) and form marcasite as indicated by equation (4) and perhaps (5). If, however, some material with an alkaline reaction is present to remove the acid formed by equation (6), only the normal FeS_2 or pyrite is formed.

As a consequence, then, of the low sulfur content of marcasite, as compared with the high sulfur content of pyrite, the formation of pyrite in alkaline solutions and the formation of marcasite in acid solutions receives reasonable explanation. In anticipation, it may be said that a like relation holds between sphalerite (the so-called "stable," but actually the high-sulfur, form of ZnS) and wurtzite (the so-called "unstable," but actually the low-sulfur form of ZnS). The evidence¹⁸ for this, together with the structural significance will appear shortly.

¹⁷ Reference 2, p. 396.

¹⁸ M. J. Buerger, The Sphalerite-Wurtzite Relation, to appear shortly.