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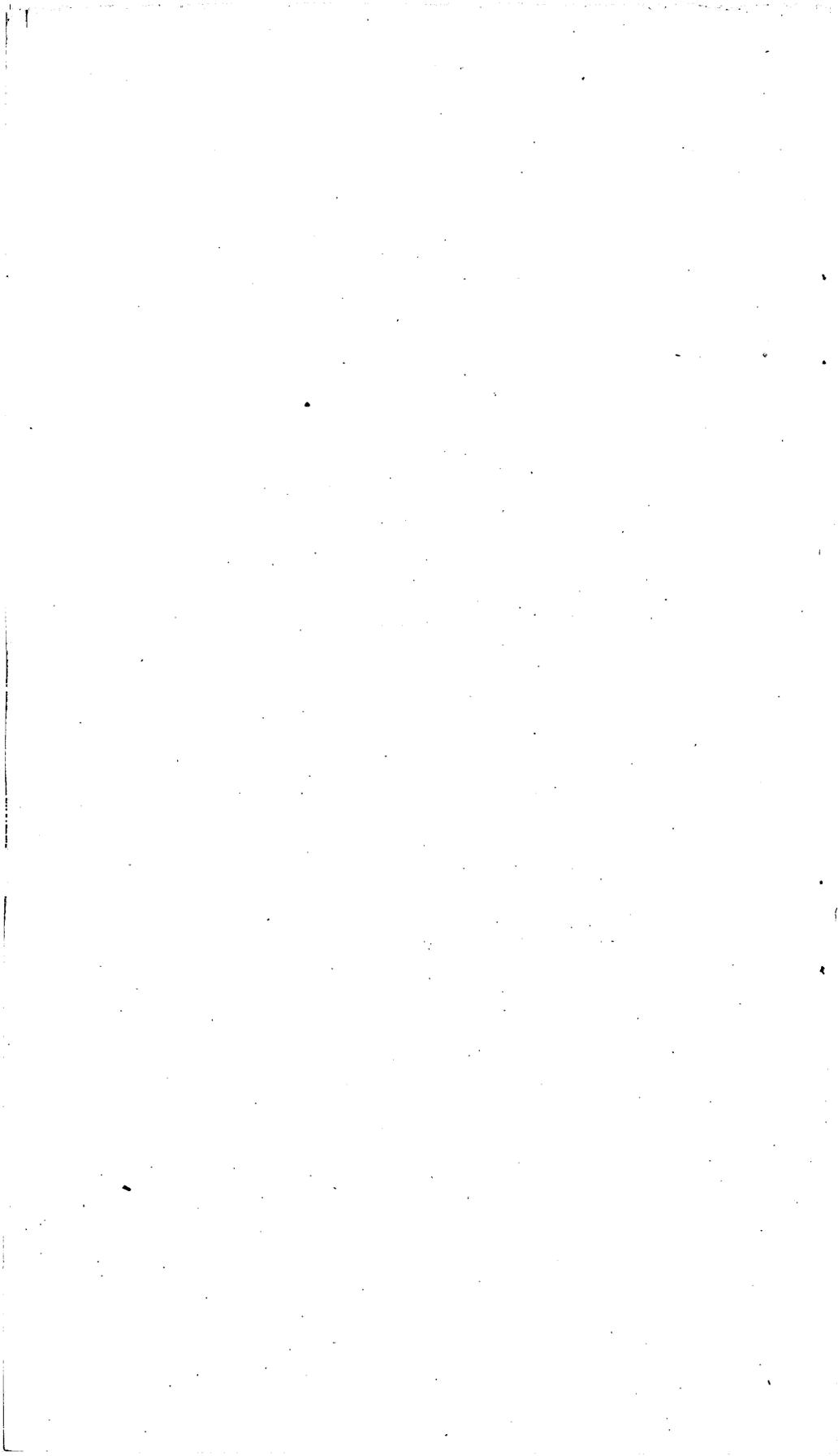
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WASHINGTON

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1901



UNITED STATES GEOLOGICAL SURVEY

CHARLES D. WALCOTT, DIRECTOR

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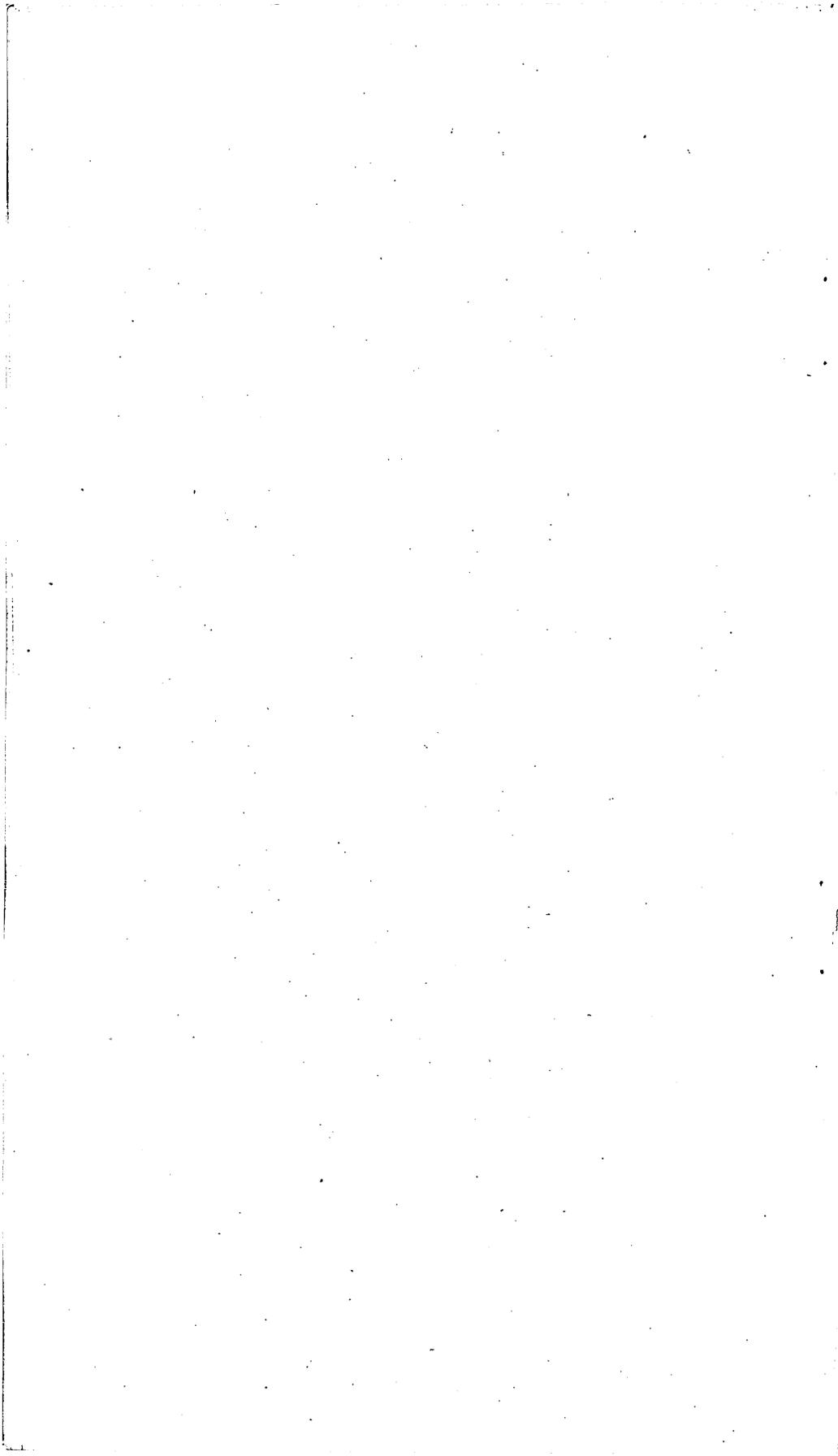
ON

# PYRITE AND MARCASITE

H. N. STOKES



WASHINGTON  
GOVERNMENT PRINTING OFFICE  
1901



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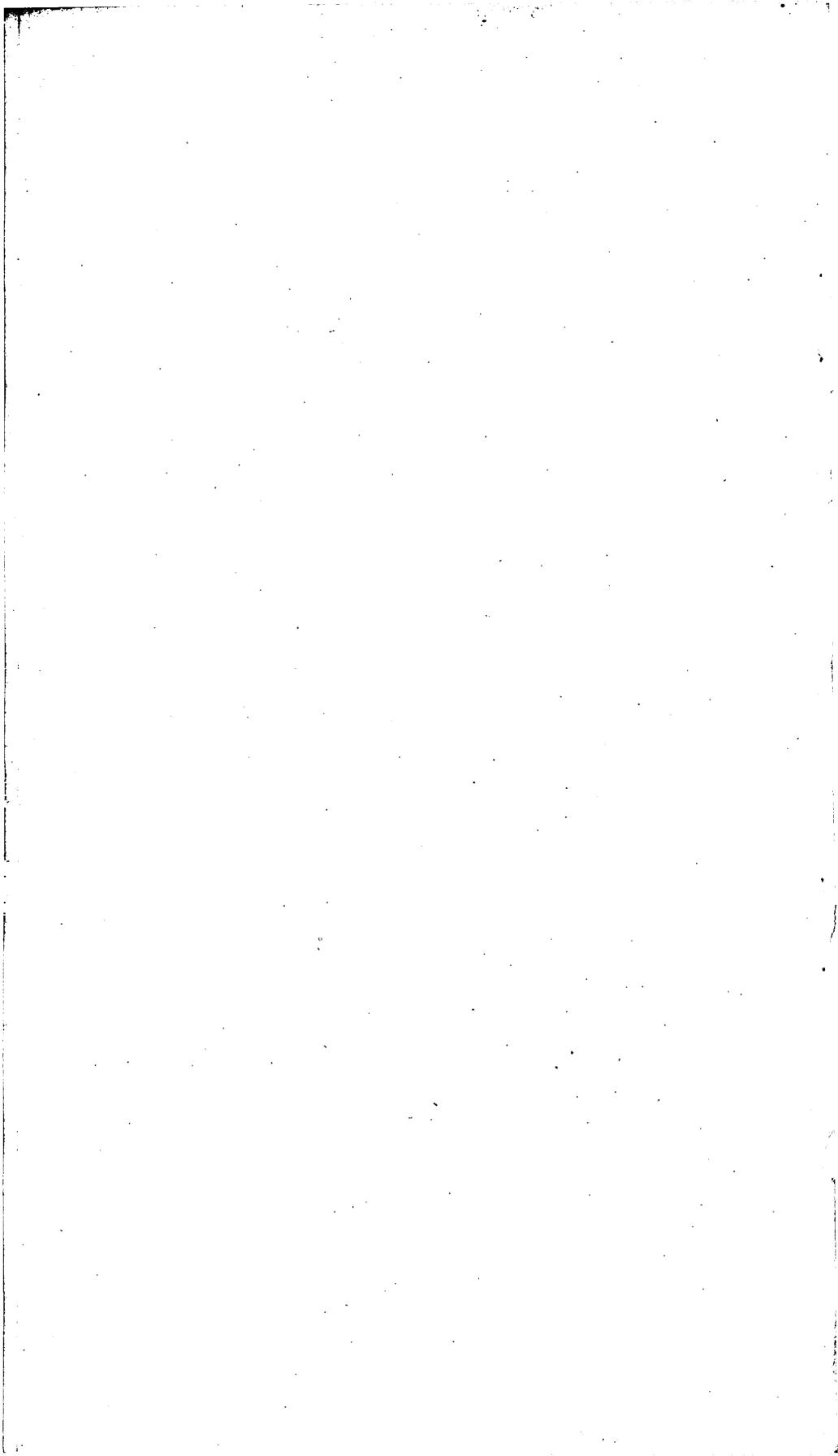
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## LETTER OF TRANSMITTAL.

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DEPARTMENT OF THE INTERIOR,  
UNITED STATES GEOLOGICAL SURVEY,  
DIVISION OF CHEMICAL AND PHYSICAL RESEARCH,  
*Washington, D. C., July 5, 1901.*

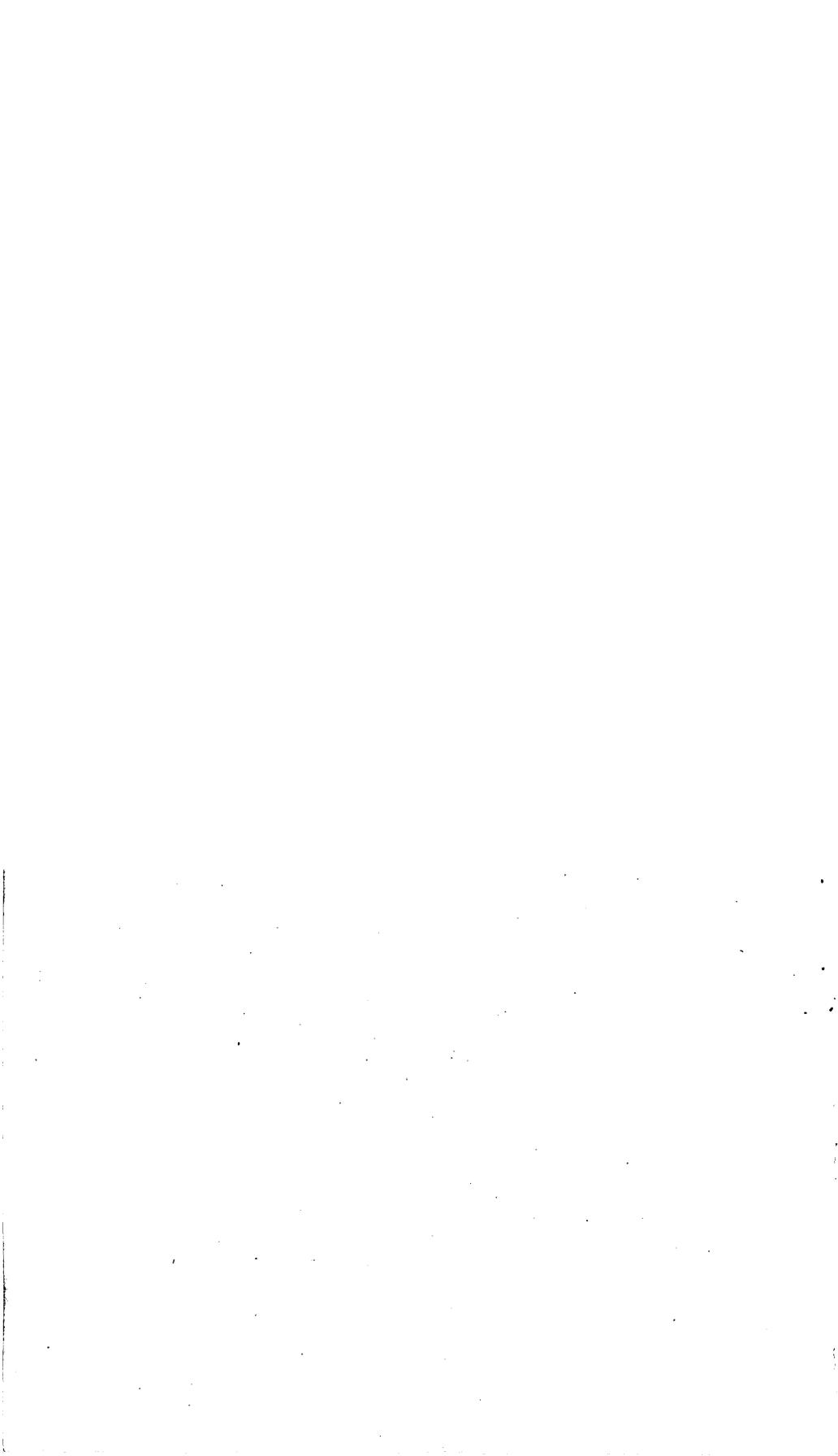
SIR: The subject of the secondary enrichment of ore bodies is one of the most important in chemical geology, and probably also one of the most complex, because nothing like chemical homogeneity is to be anticipated at or beneath the croppings of ore deposits. A long time must elapse before the processes involved are fairly clear.

The memoir by Dr. H. N. Stokes which I transmit herewith, for publication in the Bulletin series, is an important contribution to this subject, describing a method for the quantitative determination of pyrite and marcasite when in mixture, and discussing some of the relations of these most abundant sulphides to those of copper. This memoir represents only a portion of Dr. Stokes's work in this field, and it is to be expected that other papers will follow as soon as practicable.

Very respectfully, your obedient servant,

GEORGE F. BECKER,  
*Geologist in Charge.*

Hon. CHARLES D. WALCOTT,  
*Director of United States Geological Survey.*



# ON PYRITE AND MARCASITE.

By H. N. STOKES.

The object of this paper is to describe a chemical method by which the native forms of iron disulphide may be distinguished with certainty, and by which their relative amounts in mixtures of the two may be quantitatively determined. The method is applied to various supposed pyrites and marcasites, and it is shown that in the absence of well-marked crystallographic features it is extremely easy even for experts to be deceived as to the nature of a given specimen.

## I. UNCERTAINTY OF METHODS OF DISTINGUISHING PYRITE AND MARCASITE.

Pyrite and marcasite are usually distinguished by their differences of crystalline form, color, density, and ease of oxidation.

### CRYSTALLINE FORM.

Pyrite usually crystallizes in cubes, often in pentagondodecahedrons or octahedrons, and frequently in combinations of these and more complicated forms of the isometric system, while marcasite assumes various forms of the orthorhombic system. This criterion is inapplicable when the minerals assume the massive or compact form, or when they occur as concretionary nodules in which the crystalline form can not be made out. Moreover, pseudomorphs are not uncommon, and paramorphs of pyrite after marcasite and of marcasite after pyrite are said to occur, in which events no conclusion can be drawn from this source.

### COLOR.

The color of pyrite is generally said to be pale brass yellow, while that of marcasite is described as tin white, grayish white, greenish, brass yellow, bronze yellow, and in other terms. Dana<sup>1</sup> describes

<sup>1</sup> System of Mineralogy, 6th ed., p. 94. For a list of terms and references see Julien, *Annals New York Acad. Sci.*, Vol. IV, 1887, p. 179.

marcasite as pale bronze yellow. These discrepancies are doubtless due to tarnished specimens having been described. Marcasite frequently assumes a yellowish tarnish, which may vary to copper colored. On fresh surfaces, such as are obtained by breaking or by removing the film by warming with dilute hydrochloric acid, the color is unquestionably tin white or grayish white, closely matching platinum and without a trace of yellow. The white color is not an indication of the presence of arsenic,<sup>1</sup> as it is equally shown by specimens which are free from arsenic. To distinguish pyrite and marcasite by the color, they must be cleaned with hydrochloric acid and immediately examined under a good white light, in comparison with standard specimens also freshly cleaned. The faint yellow of pyrite makes it extraordinarily easy to deceive oneself if the light be yellowish in tint. The differences of the supposed yellow and light-colored pyrites vanish, except in rare cases, when these precautions are observed, and pyrite can usually be distinguished with ease when mixed with marcasite. In the case of fine-grained concretions, or where the surface is too rough to afford a good reflection, it is sometimes quite impossible to draw any conclusion from the color.

#### DENSITY.

*Density according to different authorities.*—The density of both minerals is subject to some variation, as shown by the following figures from different sources:

##### *Density of marcasite and pyrite.*

Authority.	Marcasite.	Pyrite.
Dana <i>a</i> .....	4.85-4.90	4.95-5.10
Rammelsberg <i>b</i> .....	4.90	5.00
Julien <i>c</i> .....	4.80	5.01
Stokes <i>d</i> .....	4.88-4.90	5.02-5.04

*a* System of Mineralogy, 6th ed., pp. 85, 94.

*b* Zeitschr. Deutsch. geol. Gesell., Vol. XVI, 1864, p. 267. Supposed normal density.

*c* Annals New York Acad. Sci. Vol. IV, 1887, pp. 177, 210. Supposed normal density.

*d* See pp. 25, 26.

*Density not a sure criterion of composition.*—My own determinations were made with the pycnometer at 18°-23°, on the purest obtainable material, coarsely powdered. Julien's figure for marcasite is certainly too low. The following list, giving the densities of some specimens of which I have determined the composition (after deduct-

<sup>1</sup> Op. cit., p. 95.

ing impurities), shows how illusive may be conclusions as to the relative amounts of pyrite and marcasite based on density alone:

*Densities of some specimens of pyrite and marcasite.*

No. of specimen.	Density.	Composition, chemically determined.
5	5.041	100 per cent pyrite.
3	5.023	100 per cent pyrite.
33	4.987	83.5 per cent pyrite, 16.5 per cent marcasite.
7	4.891	100 per cent marcasite.
10	4.886	100 per cent marcasite.
12	4.880	100 per cent marcasite.
29	4.856	99.5 per cent pyrite.
30	4.843	99.5 per cent pyrite.
31	4.819	100 per cent pyrite.
17	4.563	100 per cent pyrite.

#### OXIDATION.

While it is unquestionably true that marcasite oxidizes more rapidly than pyrite under the same conditions, a compact, well-crystallized marcasite can be kept almost indefinitely without any change further than a superficial tarnish, whereas finely divided or porous pyrite oxidizes with great rapidity, and this fact has frequently caused pyrite to be mistaken for marcasite.

The amount of oxidation depends upon the time during which the specimen has been exposed; upon the peculiar conditions under which it has occurred, such as exposure to dry or moist air, or to water holding oxygen or other oxidizing agents in solution; upon whether the oxidation products are removed; upon the surface exposed per unit of volume; and upon an oxidation factor characteristic of each mineral, but probably not more than three times greater for marcasite than for pyrite. It is obvious, therefore, that no trustworthy conclusion can be drawn in any case from vitriolization in the absence of definite knowledge of these factors; and even when the conditions of time and exposure are identical, as when the specimens are kept side by side in the cabinet, it is necessary to know the  $\frac{\text{surface}}{\text{mass}}$  factor before rapid vitriolization justifies one in pronouncing a specimen to be marcasite. One of the most extreme cases of rapid vitriolization that I have seen is No. 21 (pp. 36-37), which consists of nodules of practically pure pyrite. Many of the rapidly vitriolizing specimens consist of mixtures of pyrite and marcasite, and apart from the porosity existing in such cases it is possible that an electrochemical action between the two

may assist the oxidation. It is hardly necessary to add that the old idea that marcasite tends to produce ferrous sulphate, and pyrite to give limonite, is untenable.

#### PENFIELD'S METHOD.

Penfield<sup>1</sup> has described a method of distinguishing the two minerals, based on treating the finely powdered substance with strong nitric acid under identical conditions; pyrite dissolves completely, while marcasite leaves a residue of sulphur. While this procedure serves well to distinguish the pure minerals, it is obviously incompetent to detect pyrite in the presence of marcasite.

#### ACTION OF COPPER SULPHATE ON PYRITE AND MARCASITE.

A. P. Brown<sup>2</sup> asserts that when marcasite is heated for six hours at 200° with 10 per cent copper sulphate solution its iron is completely dissolved as ferrous sulphate, while under the same conditions pyrite yields a mixture of 2 mols. ferric and 1 mol. ferrous sulphate; and on this he bases the conclusion that in marcasite the iron is wholly in the ferrous condition,  $Fe''S_2$ , while in pyrite it is four-fifths ferric,  $Fe''S_2(Fe'''S_2)_4$ . As Brown's work might seem to afford a means of distinguishing the two minerals, and as the different constitution, if existing, would have an important bearing on the question of their formation in nature, I have repeated these experiments, but with totally different results. The details of my experiments are given below (p. 42), and I here state merely my conclusion that the only recognizable difference is the greater ease with which marcasite is attacked by the cupric solution, and that no evidence can be obtained in this way as to any difference of chemical constitution.

#### II. BEHAVIOR OF PYRITE AND MARCASITE TOWARD FERRIC SOLUTIONS.

In the course of an investigation on the action of ferric salts on natural sulphides, differences observed in the behavior of pyrite and of marcasite were so marked as to make it seem probable that on these differences there might be based a method of distinguishing these minerals and of determining them quantitatively in mixtures, thus establishing a sure means of ascertaining the composition of concretions and other doubtful specimens and of testing the validity of the conclusion of Julien, quoted below (p. 27), that many supposedly pure pyrites and marcasites are mixtures of the two. While approximate results were soon reached, many fruitless experiments had to be made before all important sources of error were eliminated and before the process could be brought to a reasonably satisfactory quantitative

<sup>1</sup>Brush and Penfield, *Determinative Mineralogy*, 15th ed., p. 252.

<sup>2</sup>Proc. Am. Philos. Soc., Vol. XXXIII, 1894, p. 225. *Chemical News*, Vol. LXXI, 1895, p. 179.

basis. Only the results obtained by the perfected method are presented in this paper.

#### ACTION OF FERRIC CHLORIDE.

It has long been known that ferric salts attack pyrite. L. L. de Koninck<sup>1</sup> found that pyrite is oxidized at 170°–200° C. by ferric chloride or ferric ammonium alum, with formation of a ferrous salt and sulphuric acid. J. H. L. Vogt<sup>2</sup> mentions that pyrite is very slowly attacked in the cold by 30 per cent ferric chloride solution, giving a trace of sulphuric acid. He regards the formation of sulphuric acid as subordinate, and does not ascribe an important rôle to ferric salts in the decomposition of pyrite. Julien<sup>3</sup> observed a reduction of ferric chloride by marcasite. No quantitative study of these reactions has been made, so far as I can ascertain.

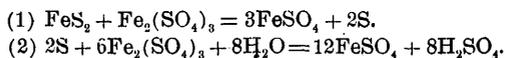
#### PERCENTAGE OF SULPHUR OXIDIZED.

Preliminary experiments showed that very dilute solutions of ferric salts attack pyrite rapidly at the boiling temperature, and much more slowly, but quite appreciably, in the cold. It is upon the determination of the percentage of sulphur oxidized in the total mineral decomposed that the new method is based. If ferric chloride be used, the amount of mineral decomposed can be found from the increment of iron in the solution and the SO<sub>4</sub> determined as barium sulphate. An experiment with a ferric chloride solution containing 1.14 grams Fe<sup>+++</sup> per liter, with a little hydrochloric acid, which was boiled to complete reduction with an excess of powdered pyrite free from sulphate, in a current of carbon dioxide, showed that 65 per cent of the sulphur was oxidized, a result agreeing well with the results presented below.

#### FERRIC SULPHATE OXIDATION METHOD.

Owing to the tediousness of the gravimetric methods and of the SO<sub>4</sub> determination in the presence of iron, I have adopted a much more expeditious indirect method, which involves the use of ferric ammonium alum and titration with potassium permanganate.

*Principle of the method.*—The oxidation of FeS<sub>2</sub> by Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> may be regarded as taking place by two independent reactions:



If the reaction be carried out in the presence of an excess of FeS<sub>2</sub> to complete reduction of the ferric salt, it is easily seen that equation (1) holds even if the theory of Brown be true, that the iron in pyrite is partly ferric, for in this case the ferric salt formed will in turn be

<sup>1</sup> Annales Soc. geol. Belgique, Vol. X, 1883, p. 101. Zeitschr. anorg. Chemie. Vol. XXVI, 1901, p. 123.

<sup>2</sup> Trans. Am. Inst. Min. Eng., Richmond meeting, February, 1901.

<sup>3</sup> Annals New York Acad. Sci., Vol. IV., 1887, pp. 138–139.

reduced by the excess of pyrite. Upon the extent to which the second reaction takes place, as compared with the first, depends the percentage of sulphur oxidized in that portion of the mineral which is decomposed.

If a ferric solution containing a known amount of iron be boiled with an indefinite excess of  $\text{FeS}_2$  under appropriate precautions, and if the increment of iron in the solution be then determined, as well as the ferrous salt formed, this increment gives the amount of sulphide decomposed; three times this increment gives the quantity of ferrous salt formed in equation (1); while any excess of ferrous salt is that formed by oxidizing sulphur to sulphuric acid as in equation (2). From these data the percentage of sulphur oxidized may be computed.

#### DEDUCTION OF AN EXPRESSION FOR OXIDIZED SULPHUR.

It is unnecessary to know the absolute quantities of iron and sulphur involved in these reactions, or the strength of the permanganate solution. It suffices, in deducing an expression for the oxidized sulphur, to employ symbols expressing the permanganate equivalent of the iron, and the symbols used represent simply the volumes of permanganate consumed by a given volume of the solution.

For a given volume let

$a$  = iron in the original solution,

$b$  = resulting ferrous iron,

$c$  = resulting total iron.

Then

$$c - a = \text{increment of iron resulting from decomposition of } \text{FeS}_2,$$

and

$$2 \left( \frac{31.83}{55.60} \right) (c - a) = \text{total sulphur in decomposed sulphide. (A)}$$

Also,

$$3(c - a) = \text{ferrous iron produced according to equation (1)}$$

and

$$b - 3(c - a) = \text{ferrous iron produced by oxidation of sulphur.}$$

According to equation (2), 1 atom of sulphur requires for oxidation 6 atoms of ferric iron, producing 6 atoms of ferrous iron; hence,

$$\frac{1}{6} \cdot \frac{31.83}{55.60} (b - 3(c - a)) = \text{sulphur oxidized. (B)}$$

Calling the percentage of sulphur oxidized  $p$ , we obtain from (A) and (B)

$$p = \frac{\frac{100}{6} \cdot \frac{31.83}{55.60} (b - 3(c - a))}{2 \left( \frac{31.83}{55.60} \right) (c - a)} = \frac{8.333b}{c - a} - 25.$$

It thus appears that three titrations suffice to determine the percentage of sulphur oxidized, and that neither the amount of  $\text{FeS}_2$ , the

volume of the ferric solution used, nor the absolute titer of the latter or of the permanganate need be known. As, however, the proportion of sulphur oxidized varies with the strength of the ferric solution, the extent of reduction, and the temperature, it is necessary, in order to obtain comparable results, to use a solution of standard composition and a standard temperature, and to continue the action to complete reduction.

#### STANDARD SOLUTION AND TEMPERATURE.

The standard solution contains 1 gram ferric iron per liter, and is prepared by dissolving in water 8.61 grams clear crystals of pure ferric ammonium alum, adding 16 cm.<sup>3</sup> 25 per cent sulphuric acid and diluting to 1 liter. One hundred cm.<sup>3</sup> of this solution must show a decided change of color with one drop of the permanganate solution, containing about 1.5 grams per liter, and must be free<sup>1</sup> from nitrate. The sulphuric acid is added to prevent precipitation of basic salt. The experiment is conducted at the boiling temperature. The strength of the ferric solution may vary 1 per cent without appreciable influence, and at least 99.5 per cent must be reduced.

#### OXIDATION COEFFICIENT.

The percentage of sulphur oxidized under these conditions and with the precautions explained in detail below (p. 20) may be called briefly *the oxidation coefficient* of the pyrite or marcasite. The oxidation coefficient of pyrite varies between 60 and 61, and that of marcasite between 16.5 and 18. The oxidation coefficients of mixtures of the two indicate the relative amount of each present, by reference to an empirical curve obtained with artificial mixtures of known composition. A theoretical deduction of the relative proportions from the oxidation coefficient is impossible in the absence of the necessary physical data.

#### THEORY OF THE REACTION.

The mass law states that the active mass of a solid phase is constant; hence, the final composition of the resulting solution must be the same, irrespective of the relative amount of reagent and sulphide used, provided only that the latter, the solid phase, be always in excess. With more, or more finely powdered, material<sup>1</sup>—that is, with a relatively greater exposure of surface, equilibrium is sooner reached, but the composition of the resulting solution, and therefore the percentage of sulphur oxidized, is the same. It is unnecessary

<sup>1</sup> Ostwald (Zeitschr. physik. Chemie, Vol. XXXIV, 1900, p. 495) has shown for certain cases that an extremely finely powdered substance is more soluble than the same in coarser particles, and that the composition of the resulting solution is therefore subject to slight variations. Such effects were looked for in the present instance by using coarse and very fine material obtained by sedimentation, but if they exist they are smaller than the errors of the method.

either to weigh the material or to measure the liquid accurately, but in order to make unavoidable experimental errors as nearly as possible constant, it is desirable always to employ approximately equal quantities, and to boil for nearly equal times.

#### INFLUENCE OF CONCENTRATION.

Since the equation expressing the oxidation of the sulphur is of a higher order than that denoting the oxidation of the iron, it follows that the rate of oxidation of the sulphur must fall off more rapidly than that of the iron, with decreasing concentration of the ferric salt; hence the value of  $p$  must constantly decrease as reduction proceeds, and comparable results can be obtained only by carrying the reduction to completion. This is shown in the following cases, where the experiment was stopped after partial reduction:

*Results of experiments showing constantly decreasing value of  $p$  as reduction proceeds.*

Pyrite.		Marcasite.	
Fe reduced.	$p$	Fe reduced.	$p$
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
67.8	71.4	69.2	23.3
88.7	65.2	78.5	22.5
90.5	64.9	100.0	16.2
95.2	63.2		
99.5	61.5		
100.0	60.4		

#### INFLUENCE OF TEMPERATURE.

The influence of temperature on  $p$  is shown by the following experiments at 20° and at boiling temperature, the reduction being complete in each case:

*Results of experiments showing influence of temperature on  $p$ .*

	Temperature.	$p$
		<i>Per cent.</i>
Pyrite.....	20	80.8
	100	60.4
Marcasite.....	20	30.6
	100	17.4

From the variation in the relative oxidation of the sulphur with concentration and temperature it appears certain that no single equation expresses the oxidation of pyrite and marcasite by ferric salts to ferrous sulphate, sulphur, and sulphuric acid, but that it is the result of two, or possibly three, independent reactions of different orders, which produce results varying according to circumstances. It is therefore extremely probable that other oxidizing agents, as atmospheric or dissolved oxygen, behave in a similar manner. The oxidation with separation of free sulphur presents no difficulties; as is well known, finely powdered pyrite and marcasite on exposure to the air for a short time give free sulphur, which can be detected by extraction with ether, and the formation of sulphur dioxide has been noted by various observers; finely divided moist marcasite evolves it strongly when heated on the water bath. The difficulty is rather to account for the complete oxidation of the sulphur usually occurring in nature. Whether with stronger solutions and continued reoxidation by air, or the presence of retarding agents, 100 per cent can be reached can not be stated at present, and experiments bearing on this point are desirable.

#### REASON FOR THE DIFFERENT BEHAVIOR OF PYRITE AND MARCASITE.

The different proportion of sulphur oxidized under identical conditions in the two cases is doubtless due to the different solubilities of pyrite and marcasite, or at least the different rates at which they are attacked. That the sulphur is not completely oxidized is due to its smaller oxidation rate under the given conditions. The iron is attacked so fast that the oxidation of the sulphur falls behind and a portion is liberated as free sulphur, which, as my experiments show, is scarcely oxidized by the boiling ferric solution when collected to aggregates of sensible size. This phenomenon is a familiar one when precipitated sulphides are treated with nitric acid; a portion of the sulphur is oxidized and the remainder is liberated. When a ferric salt is reduced by hydrogen sulphide the sulphur of the latter is partly liberated, but a very considerable part is oxidized to sulphuric acid.<sup>1</sup> Whatever retards the solution of the sulphide without affecting the concentration of the oxidizer gives more time for the complete oxidation of the sulphur. This may be brought about by certain salts in solution or by a difference of physical structure in the crystals. Pyrite dissolves more slowly than marcasite, hence its sulphur is more completely oxidized. Under conditions where the solution is very slow, it may perhaps approximate completeness in both cases, a subject well worthy of investigation from its bearing on the oxidation of pyrites in nature.

<sup>1</sup> Gmelin *Kraut*, Vol. I, pt. 2, p. 219. I have found that when a 1 per cent boiling solution of ferric chloride is reduced by hydrogen sulphide very nearly one-third of the reduction is effected by the sulphur.

## FURTHER APPLICATIONS OF THE METHOD.

In general, when a mineral is composed of two or more elements, each capable of oxidation, but at different rates, there will be certain conditions under which one will be oxidized to a greater extent than the other, and the amount of this difference may often be determined by analysis of the solution. If the compound is dimorphous, one form will be more soluble than the other, and this will show a greater difference in the degree of oxidation of the two constituents than the less soluble form. The above method therefore makes it possible to distinguish not only between dimorphous sulphides but other dimorphous compounds, such as arsenides, and to determine their relative amounts in mixtures. It should also be possible to determine whether certain complex minerals are mixtures of two distinct kinds of molecules or whether all the components are combined in one molecule.  $\text{FeAsS}$ , for example, should show a behavior different from that of a mixture  $\text{FeS}_2$  and  $\text{FeAs}_2$  in equimolecular proportions. When the metal is more slowly oxidized than the nonmetallic constituent a separation of a portion of the former may be expected. Gold sulphide, for example, might give sulphuric acid and free gold. As pointed out below, it is possible to ascertain in certain cases the form of combination of constituents which exist only as impurities; in a 3 per cent cupriferous pyrite, chalcopyrite can be distinguished from chalcocite and bornite, a determination which could not be made by analysis.

## III. DETAILS OF THE METHOD.

## NECESSARY PRECAUTIONS.

In the following the precautions necessary to obtain strictly concordant results are given in detail, as well as a statement of the abbreviations which are permissible when only approximate results are desired.

To obtain accurate results it is necessary—

1. To employ sulphide absolutely free from oxidation products.
2. To avoid all access of free oxygen during the experiment.
3. To prevent the precipitation of basic ferric sulphate.
4. To prevent change of concentration due to loss by evaporation.
5. To make the titration with the greatest possible accuracy.

## PREPARATION OF THE MATERIAL.

The mineral is somewhat finely ground, an operation which is greatly facilitated by adding water. After drying, it should be kept in a vacuum or in carbon dioxide until used. As both pyrite and marcasite oxidize rapidly when powdered, the oxidation products must be completely removed immediately before the experiment. About one gram of the dry powder is washed by decantation two or three times

with ether, two or three times with 20 per cent hydrochloric acid (1 part concentrated and 1 part water), and heated with the latter for a quarter of an hour or more, to remove basic salts, oxides of iron, and any contaminating sulphides or soluble silicates which may thus be extracted. It should be remarked that under these conditions pure pyrite evolves no perceptible hydrogen sulphide<sup>1</sup> if tested a few moments with lead paper, while marcasite continues to give off minute amounts however long it may be heated with the acid. The evolution of hydrogen sulphide from pyrite indicates the presence of other sulphides. The material is then collected on a Gooch crucible fitted with a disk of Schleicher & Schüll hardened filter paper and washed with dilute hydrochloric acid, and then with water which has been boiled and cooled in carbon dioxide. The washing is conducted in an atmosphere of carbon dioxide, and for this purpose I use the apparatus shown in fig. 1, in which the wash water is delivered from the dropping funnel, and the carbon dioxide, supplied from an ordinary automatic generator,<sup>2</sup> itself affords the pressure necessary to drive the liquid through the filter. The crucible is then sucked out by attaching a pump to the outlet tube, placed for a moment on

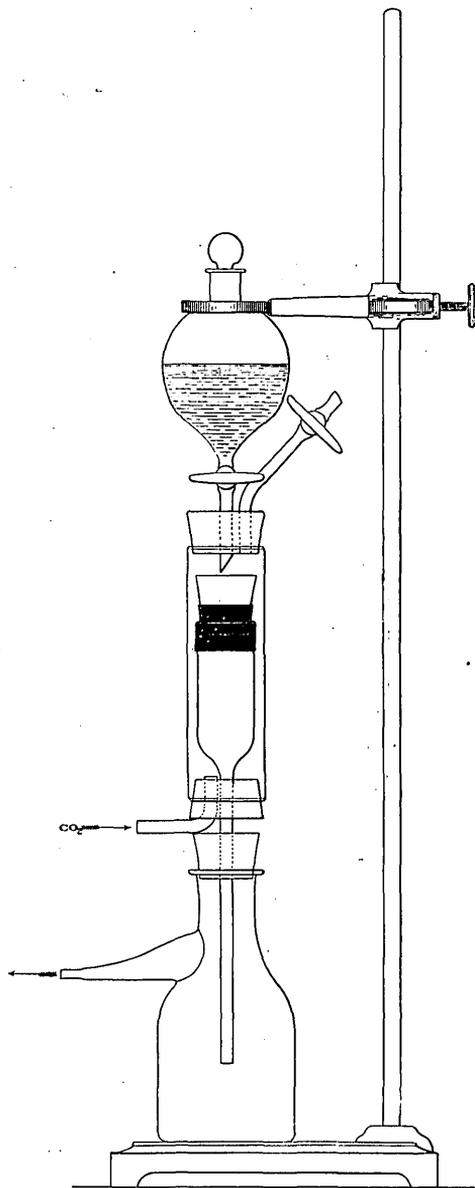


Fig. 1.—Apparatus for washing sulphides in an atmosphere of carbon dioxide.

<sup>1</sup> One-half gram pure powdered pyrite, boiled in the decomposing apparatus for one hour with 7 per cent sulphuric acid, in a slow current of carbon dioxide, caused a slight blackening of lead paper placed in the top of the condenser.

<sup>2</sup> Liquefied carbon dioxide contains air and should not be employed.

a blotter to remove most of the water and transferred to a vacuum desiccator containing sulphuric acid and filled with carbon dioxide, which is then exhausted. The use of carbon dioxide in this connection is essential, as even the best vacuum attainable by ordinary means contains enough oxygen to produce sensible oxidation. The drying is complete in half an hour.

#### OXIDATION APPARATUS.

The decomposition apparatus is represented in fig. 2. A flask holding about 400 cm.<sup>3</sup> is provided with a doubly perforated rubber stopper which has been well boiled out in caustic soda; through this pass the inlet tube for carbon dioxide and the condenser. The latter consists of an elongated calcium chloride tube, into which fits loosely a test tube through which cold water passes. The condenser has a hole at *a* to allow the passage of the steam, so that the return water drops quietly from the end of the tube. It is absolutely essential to prevent the return water from striking the sides of the flask or inlet tube, as at such points a film of basic sulphate invariably forms.

The flask is placed up to the stopper in a cylinder of asbestos board provided with windows of mica or glass on opposite sides, to admit of watching the operation. This rests on a plate<sup>1</sup> of asbestos containing a circular hole covered with gauze, and is

closed at the top by a similar plate. The object of this arrangement is to prevent as far as possible the condensation of water on the sides

<sup>1</sup> In the figure the flask is represented as elevated above the plate. During the boiling it must rest on it.

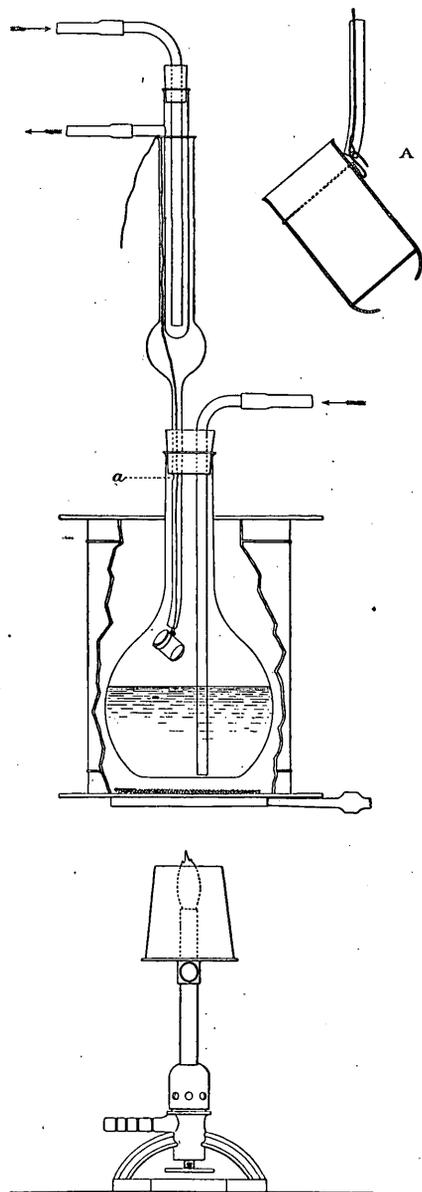


Fig. 2.—Apparatus for oxidizing sulphides with ferric solution.

of the flask; when this occurs, a ring of basic sulphate tends to form at the surface of the liquid. About 250 cm.<sup>3</sup> of the standard solution are used. The small loss by wetting of the condenser is compensated by having it wet at the outset.

Blank experiments of this apparatus lasting two hours show no deposition of basic salt, no loss by volatilization (if the ingoing gas is saturated with moisture), and no reduction of the ferric salt.

#### DETAILS OF THE OPERATION.

As the solution contains enough air seriously to affect the results, and as the percentage of sulphur oxidized varies with the temperature, it is necessary to introduce the substance into the boiling liquid, and not until all the air has been boiled out. For this purpose it is rapidly placed in the small bucket, shown on a large scale in fig. 2, A, which consists of a small test tube cut off and constricted at the bottom and provided with a loosely fitting platinum disk, made tight by pouring in a little iron-free asbestos emulsion, such as is used in Gooch crucibles. The bucket is suspended by a platinum wire, and is dropped into the liquid after this has boiled ten minutes. It is necessary that the powder shall disseminate through the liquid and not settle out on the bottom for any considerable time. If this be not the case, abnormal results are obtained, for reasons which are not clear. The powder, as well as the apparatus, must therefore be strictly free from grease, and, to aid the dissemination, the apparatus must be so mounted on a stand as to admit of agitating the liquid until the powder remains suspended. Pyrite disseminates readily, but marcasite shows a strong tendency to flocculate at first, and the two may generally be distinguished by this means.

During the whole operation a very slow current of carbon dioxide is passed through. This must, of course, be absolutely free from oxygen, and as some air is present even in the most carefully prepared carbon dioxide, I always pass it over red-hot copper.<sup>1</sup> It must also be free from hydrogen sulphide, which is not always the case, and it can easily be freed from this by passing it through a tube filled with beads and containing saturated copper sulphate solution.

The greater part of the ferric sulphate is reduced after a few minutes' boiling, but in order to effect complete reduction the boiling should be continued two hours. The liquid is then cooled and filtered through dry filters into two accurate 100 cm.<sup>3</sup> flasks, which are filled with carbon dioxide and placed in cylinders of the same. In order entirely to avoid contact with the air, it is driven over through the inlet tube by means of carbon dioxide introduced through the condenser. The flasks are then brought to the temperature of the permanganate to be used, and the contents are transferred to flasks

<sup>1</sup> When many determinations are to be made, it is convenient to place the copper in an iron gas pipe, water jacketed at both ends if necessary.

containing sulphuric acid and filled with carbon dioxide and titrated. After reducing by hydrogen sulphide, filtering off the sulphur, and expelling the hydrogen sulphide by boiling in a carbon dioxide current, the total iron is titrated. A portion of the remaining solution should always be tested with sulphocyanate to ascertain the extent of the reduction. This generally gives a faint reaction for ferric iron. If it is decidedly red, either the reduction is incomplete or the mineral contains notable amounts of copper.<sup>1</sup>

As small errors in titration produce considerable deviation, an accurately calibrated burette should be used, so narrow that the bottom of the meniscus can be distinctly seen against a light. Those burettes which have the graduation carried halfway around the tube are particularly good for accurate reading. The permanganate should have a strength of about 1.5 grams per liter, and should be run in only to the very faintest change of color, as compared with a ferric alum solution of approximately the same strength and acidity.

When less accurate results are required the mineral, after extraction with acid, may be simply collected on a hardened filter, washed with acid and water, and dried in the vacuum; special purification of the carbon dioxide, filtering in a carbon dioxide atmosphere, filtration of the reduced solution from sulphur, and other exceptional precautions may be omitted. Results made in duplicate in this way may differ 3 or 4 per cent.

#### ACCURACY OF THE METHOD.

If 100 cm.<sup>3</sup> solution and a permanganate of 1.5 grams per liter be used in titrating, an excess of 0.1 cm.<sup>3</sup> permanganate, or an oxidation of 0.0003 gram of the material, gives the following errors in the value of *p*:

	a.	b.	c.	Oxidation of 0.0003 gram sulphide.
Pyrite .....	+1.00	+0.12	-1.00	-1.00
Marcasite .....	+0.20	+0.05	-0.20	-0.15

Special care is therefore necessary in standardizing the original solution and in the final titration. Practically, duplicate determinations with pyrite tend to agree more closely than those with marcasite, as seen in the table below. This is perhaps due to the greater tendency of marcasite to flocculate, as indicated above (p. 23), and to its greater tendency to oxidize, although the influence of the latter is less than in the case of pyrite. The influence of various impurities is considered below (p. 31).

<sup>1</sup> For the explanation of this see p. 45.

## IV. DATA FOR PYRITE.

The following table gives duplicate determinations of  $p$ , made upon well-crystallized samples of pyrite free from visible impurities, but otherwise selected at random.

*Determinations of  $p$  made upon samples of pyrite.*

No.	Locality.	Density.	$p$ .	Mean value of $p$ .
1	Unknown.....		{ 60.1 59.9 }	60.0
2	Custer County, Colo.....	5.018	{ 60.4 59.7 }	60.0
3	Roxbury, Conn.....	5.023	{ 61.2 60.9 }	61.0
4	Leadville, Colo.....		{ 60.2 60.4 }	60.3
5	Old Jordan mine, Utah.....	5.041	{ 60.5 61.1 }	60.8

Mean value of  $p$ , 60.4.

No. 1. A large cube, with slight tarnish and splendent conchoidal fracture. Traces of silica, copper, and arsenic.

No. 2. Octahedron, with fracture on peripheral part conchoidal, on the interior somewhat uneven or granular. Slight trace of copper.

No. 3. Combination of cube and octahedron, with conchoidal fracture. Traces of copper and arsenic.

No. 4. Cubes. Traces of silica and copper.

No. 5. Cubes, splendent conchoidal fracture. Trace of copper.

## OXIDATION COEFFICIENT OF PYRITE.

From the above figures it appears that the oxidation coefficient of pyrite is not likely to vary more than 0.6 per cent on duplicate determinations, and that it may vary about 1 per cent in typical specimens, which do not contain more than traces of impurities that can influence the result. Whether this difference is due to the chemical action of the impurity on the solvent, to its electrochemical action on the pyrite, or to slight physical differences in the pyrite itself, can not be decided at present. The oxidation coefficient of pure pyrite may be assumed to be 60.4. Figures higher than 61 or lower than 60 may be taken to indicate greater contaminations, which can usually be detected by analysis, and the influence of some of which is pointed out below.

## V. DATA FOR MARCASITE.

The following table gives the values of  $p$  (mostly in duplicate) for various samples of marcasite, which were selected as being free from

visible impurity and showing characteristic crystallization. Other specimens, which were found to contain pyrite, are described in a later section.

*Values of  $p$  for various samples of marcasite.*

No.	Locality.	Density.	$p$ .	Mean value of $p$ .
6	Dover Cliffs, England .....	4.881	16.3	16.3
7	Galena, Ill .....	4.891	{ 16.9 16.1 }	16.5
8	Galena, Ill .....		{ 16.5 26.7 }	16.6
9	Linden mine, Wis .....	4.901	{ 16.3 16.9 }	16.6
10	Galena, Ill .....	4.886	{ 17.4 17.3 }	17.4
11	Hazel Green, Wis .....	4.896	{ 18.1 17.5 }	17.8
12	Weardale, England.....	4.880	{ 18.0 18.0 }	18.0
13	Cornwall, England .....	4.878	{ 18.7 18.3 }	18.5
14	Webb City, Mo.....	4.887	{ 18.6 18.8 }	18.7

No. 6. This is the specimen described by Julien<sup>1</sup> as follows: "No. 14. Marcasite, Dover Cliffs, England. A brilliant cluster of spearheaded crystals—broad, striated, twinned plates—embedded in light gray chalk, grayish white and brilliant on fracture." Some of the crystals carry small pyrite crystals along the plane of twinning, which are visible only after cleaning with acid. Only those free from visible pyrite were used for the determination.

No. 7. A hollow stalactite from Galena, Ill. The inner portion is fibrous, the outer columnar, with pyramidal terminations. Tarnish, copper colored. Color of fresh fracture or clean surface, tin white. It contains a trace of copper and is free from arsenic. Only the outer columnar portion was used.

No. 8. A similar stalactite from Galena, Ill., with greenish gray tarnish on fracture and bronze colored on surface and with decided vitriolization.

No. 9. Curved wedge-shaped crystals of the Joplin type, from Linden mine, Wisconsin. Iridescent blue and yellow tarnish. Fracture, tin-white. The specimen carried a little galena and calcite, from which it was carefully freed by acid and by picking out. Analysis showed a trace of copper and a little lead.

No. 10. Galena, Ill. A compact mass of large acute pyramidal crystals branching out from a common axis. Tarnish, greenish yellow. Color on fresh fracture and on green surface, tin-white. A few crystals of chalcopyrite. Material carefully selected for determination gave traces of silica and copper and no arsenic.

No. 11. Hazel Green, Wis. A thick crust on calcite, with distinct rhombic crystallization. Color, tin-white. Contains traces of lead and copper and is free from arsenic.

<sup>1</sup> Annals New York Acad. Sci., Vol. IV, 1887, p. 172.

No. 12. Weardale, England. Flat, deeply striated crystals, with slight bluish tarnish. Color of clean surface, tin white. No visible impurity was observed, and analysis showed the presence of a faint trace of copper and a little silica and the absence of arsenic.

No. 13. Cornwall, England. Flat crystals, with slight bluish tarnish. Color of cleaned surface, tin-white. A few of the crystals carry minute cubes of pyrite, and such were rejected. Analysis showed no arsenic and a trace of copper and antimony. The high oxidation coefficient makes it possible that it incloses considerably pyrite, but material was wanting for a special determination of this.

No. 14. Webb City, Mo. Curved wedged-shaped crystals of the Joplin type, on sphalerite and calcite and with a little inclosed chalcopyrite. Analysis of a sample used for the determination showed some lead and copper, which probably account for the high figure obtained.

#### OXIDATION COEFFICIENT OF MARCASITE.

From the above figures it appears that specimens of apparently pure marcasite differ somewhat more with regard to the oxidation coefficient than does pyrite. It will appear below that an admixture of small quantities of pyrite lowers the value of  $p$ , notwithstanding the fact that pyrite has a higher oxidation coefficient. It is probable that other sulphides in minute amount exert a similar effect to even a greater extent, possibly in part because of the electrochemical action which they produce. The marcasite with the lowest oxidation number is therefore not the purest. The specimen No. 12 from Weardale was the purest examined, and I incline therefore to adopt the figure 18 as being nearest to the oxidation coefficient of pure marcasite. Figures higher than this, as well as lower than 16.5, must be regarded as indicating contamination, either with pyrite or with another oxidizable mineral. It also appears from the examination of certain samples (Nos. 22 and 23) that marcasite may carry considerable amounts of pyrite so intimately intergrown as not to be visible upon examination of small fragments under a lens after cleaning with acid.

#### VI. MIXTURES OF PYRITE AND MARCASITE.

It is desirable to construct a curve which shall give the oxidation coefficients of mixtures of pyrite and marcasite. Such a curve would enable us to ascertain, in the absence of other indications, whether a given specimen contains one or the other or both of these minerals, and in the latter case to determine their relative amounts. It would enable us to test the hypothesis of Julien,<sup>1</sup> whose statement I quote:

The forms of iron pyrites occurring in nature are intimate mixtures of these three minerals; rarely of pyrrhotite, however, on account of its ready metasomatic alteration into one or the other of the triad. These common mixtures of marcasite and pyrite may originate by inclosure during crystallization, by alteration, and by displacement, and pass progressively into complete paramorphs, well crystallized after the form of one or the other mineral.

The latent constitution of these composite minerals is indicated by variation in

<sup>1</sup>Annals New York Acad. Sci., Vol. IV, 1887, p. 213.

density, exactly proportionate in most cases to the amount of each constituent,<sup>1</sup> and by a similar variation in other physical properties; e. g., hardness, fracture, resistance to decomposition, and even in color, in the case of the paramorphs of marcasitic pyrite.

As a paramorph consists simply of minute crystals of the one substance massed together in a form which characterizes the other, it is obvious that the oxidation coefficient must correspond to that substance of which the specimen really consists, not to that which it imitates, and such a curve would indicate the proportions in the case of a mixed crystal. It would further enable us to follow the possible artificial transformation of one into the other, and would serve as an aid in synthetic work. In such work it is frequently difficult to obtain products sufficiently well characterized to admit of positive identification in the absence of optical properties and well-developed crystallization. Such a curve would render us independent of these.

It is not possible to calculate the curve for mixtures of pyrite and marcasite from the oxidation coefficients of the two minerals. The oxidation coefficient is influenced by the concentration of the ferric and ferrous salts and the sulphuric acid. With the pure mineral these vary in a perfectly constant manner in the case of each sulphide, but when each mineral is decomposing in the presence of the products formed by the other, nothing short of an elaborate investigation could give us the data for calculating the effect in any case. It is therefore necessary to construct the curve empirically, from data obtained from a sufficient number of artificial mixtures.

#### CONDITIONS UNDER WHICH THE OXIDATION COEFFICIENTS OF MIXTURES MAY BE DETERMINED.

We have seen that the oxidation coefficients of pyrite and marcasite are independent of the relative amounts of solvent and solute, and of the degree of comminution, and are constant for a given temperature and concentration provided the reduction be complete. The case of a mixture of the two is more complicated. Here each component deprives the other of a portion of the ferric salt, this effect being greater the greater the surface, or, what is the same, the finer the powder. An artificial mixture of given composition will therefore show a varying oxidation coefficient depending on the relative degree of fineness of the two components. Moreover, since a given volume of the standard ferric solution decomposes about 2.26 times as much marcasite as pyrite, the ratio between the surfaces is constantly changing and it is no longer a matter of indifference whether a large or a small amount of material be acted on by a given volume of solution.

If, however, the minerals be ground together and if the grinding be tolerably thorough, then, considering their approximately equal hardness, it may be assumed that the ratio of the surfaces for a given

<sup>1</sup> Compare table on p. 13.

mixture will remain practically constant, and if the value of  $p$  be obtained by using such an excess of the mixture that this ratio is not appreciably altered during the experiment, or if the same amount of mixture and of solution be used in every case, it becomes possible to obtain concordant values of  $p$  and to construct the desired curve. The assumption that the ratio of surfaces remains constant during grinding is not absolutely true, but practically it is, as the duplicate results presented below were each obtained from different samples, so that the slightly varying hardness of different specimens and the different degree of fineness to which they are ground introduce no greater errors than those which are inherent in the method itself. In each case the materials were broken up so as to pass a 20-mesh but to be retained by a 60-mesh sieve, were carefully weighed, mixed, and ground so as to avoid all loss, and 1 to 1.02 grams of the mixture and 250 cm.<sup>3</sup> of the solution were used in each experiment.

#### VII. DATA FOR ARTIFICIAL MIXTURES.

The following table gives the result for different mixtures, the numbers in the second column referring to the above-mentioned specimens of pyrite and marcasite, respectively:

*Values of  $p$  for mixtures of pyrite and marcasite.*

Per cent pyrite.	Specimens used.	$p$ .	Mean value of $p$ .
0	m. 7	16.5	17.3(18.0)
	m. 10	17.4	
	m. 12	18.0	
5	p. 5; m. 7	15.7	16.0
	p. 5; m. 10	16.5	
	p. 5; m. 12	15.9	
10	p. 5; m. 7	15.2	15.2
	p. 5; m. 10	15.2	
20	p. 5; m. 7	17.3	17.1
	p. 5; m. 10	16.9	
40	p. 5; m. 7	22.3	22.3
	p. 5; m. 10	22.2	
60	p. 5; m. 10	29.0	29.0
	p. 4; m. 10	29.1	
80	p. 5; m. 7	40.5	40.3
	p. 5; m. 10	40.2	
90	p. 5; m. 10	48.9	48.9
	p. 4; m. 10	48.9	
9	p. 5; m. 10	52.9	52.9
	p. 4; m. 10	53.0	
100	p. 4	60.3	60.5
	p. 5	60.8	

## DISCUSSION OF THE CURVE.

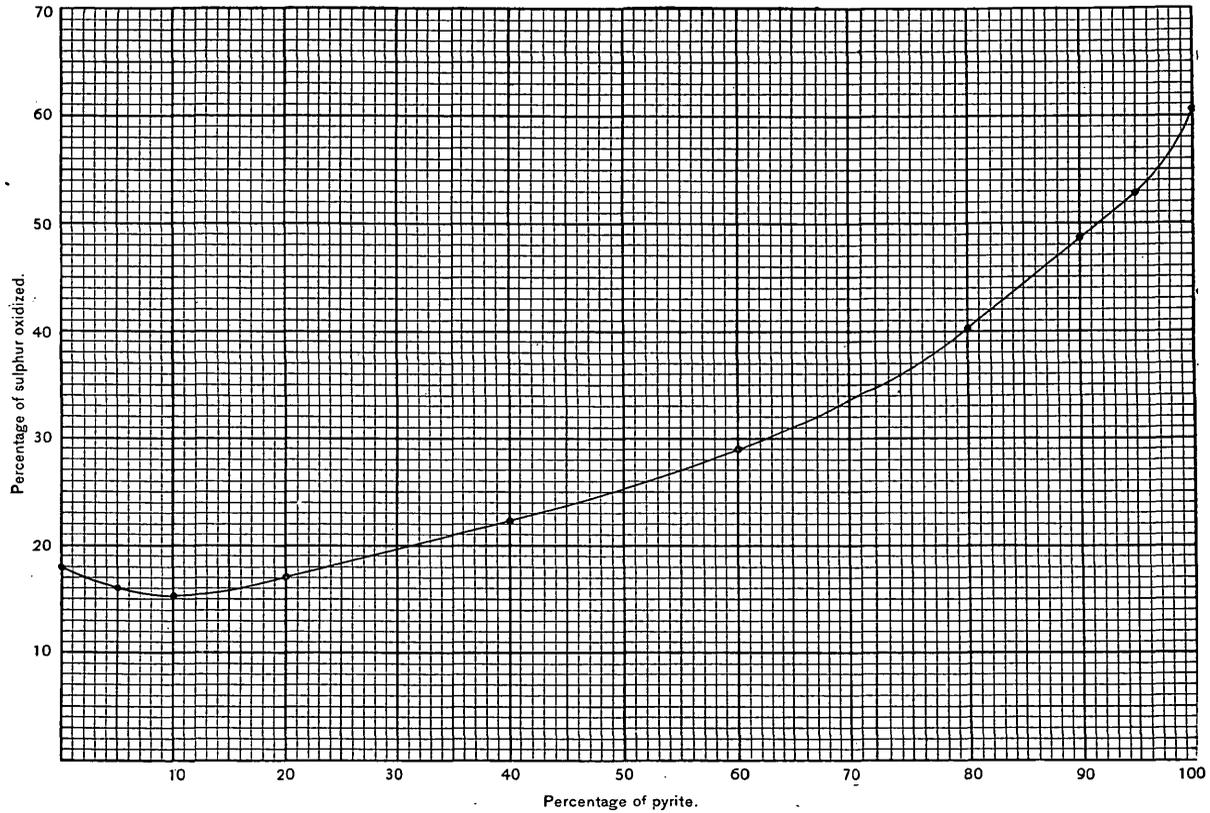
The curve in Pl. I is based on the mean values of  $p$  thus obtained, with the exception of pure marcasite, where the more probable value 18 is used (p. 27).

*Influence of the minimum: indirect determination of small amounts of pyrite in marcasite.*—The most obvious features of this curve are the presence of a minimum point when the amount of pyrite reaches about 10 per cent and the increasing steepness as 100 per cent is approached. The minimum implies that a mixture of marcasite with a little pyrite has a less percentage of sulphur oxidized than has pure marcasite. This unexpected result, which is abundantly confirmed by numerous other preliminary data not published, may be partly due to the fact that pyrite uses up more ferric salt than does the equivalent amount of marcasite; the latter is therefore acted on by a solution weaker in  $\text{Fe}^{+++}$  than if it alone were present, the effect of which is to lower the oxidation coefficient. Possibly there may also be an electrochemical action between the two. A minimum also occurs in the curve for pyrite-galena, while pyrite-chalcopyrite shows a maximum. The existence of these points shows that it is impossible to predict, from a knowledge of the values of  $p$  for any two sulphides, whether the result of the contamination of one with a small quantity of the other will be to raise or to lower the oxidation coefficient. The variation of  $p$  from 16.3 to 18 for nearly pure marcasites is presumably due to small amounts of impurities other than pyrite. Practically these have but little effect on the determination of pyrite and marcasite, for, as seen in the table, the three samples of marcasite, though varying from 16.5 to 18, give essentially the same figures when mixed with even as little as 5 per cent of pyrite.

As a result of the minimum, any specimen in which  $p$  is about 18 or less may have one of two possible compositions. Which of these is actually present may be tested by adding one-ninth its weight of pyrite and determining the value of  $p$  for the new mixture. If depression is produced, the true percentage of pyrite lies to the left of the minimum; if elevation, to the right. In fact, the freedom of a marcasite from pyrite can be regarded as absolutely proved only when this precaution is taken. The determination of  $p$  in the original specimen is not necessary; the marcasite in question may at once be mixed with a known amount of pyrite and the original contents of pyrite thus determined. If  $x$  represent the percentage of pyrite in the original sample, then a mixture of 90 parts of this with 10 parts pyrite will give

$$0.9x + 10 = \text{per cent pyrite in mixture.}$$

The latter is found by one determination and the composition of the original sample deduced. An application of this method may be seen below (pp. 36–38) in the case of the marcasites from Garfield tunnel



CURVE SHOWING OXIDATION COEFFICIENTS OF MIXTURES OF PYRITE AND MARCASITE.

(No. 20), Littnitz (No. 22), and Crow Branch mine (No. 23). In the latter two cases the selected material showed no pyrite under a lens, although the specimen as a whole contained it in visible amount.

It further appears from the curve that small amounts of marcasite in pyrite can be determined with greater accuracy than small quantities of pyrite in marcasite. In the former case the determination can probably be made to 1 per cent with duplicate experiments and in the absence of notable amounts of other sulphides; in the latter it can hardly be more accurate than 2 or 3 per cent. It must be remembered, however, that there is a slight uncertainty close to both ends of the curve, due to the unknown influence of minute contaminations. In other cases, however, greater accuracy than is obtainable could hardly be desired.

#### VIII. INFLUENCE OF IMPURITIES.

When pyrite or marcasite is inclosed in rock, the extraneous material may be removed by digesting with hydrofluoric and hydrochloric acids; but small amounts of insoluble siliceous material can usually be neglected.

##### MISCELLANEOUS IMPURITIES.

The necessity of extreme care in preparing the material is emphasized above. Since  $b > (c-a)$ , an inspection of the equation

$$p = \frac{8.333 b}{c-a} - 25$$

shows that the presence of iron salts or oxides, or access of air during the decomposition, affects the ratio  $\frac{b}{c-a}$  in such a manner as to lower

the value of  $p$ , this effect being greater with pyrite than with marcasite. Free sulphur exerts very little influence, and is moreover removed by the preliminary extraction with ether. Without influence are also sulphates, carbonates, or soluble silicates free from iron, insoluble silicates, quartz, and in general any substance neither contributing iron nor effecting reduction of the ferric solution. Pyrrhotite and limonite are easily eliminated. Zinc blende, galena, magnetite, and hematite, if present in but small amounts and not inclosed in the fine particles of  $\text{FeS}_2$ , are more slowly removed by prolonged digestion with hydrochloric acid. All sulphides are more or less readily attacked, and those free from iron, since they do not contribute to  $c-a$ , should, it might be expected, raise the value of  $p$ . If present in traces, they do not appreciably affect the result; but if existing in large amounts, they introduce considerable errors, and abnormal results are to be explained by a qualitative analysis. In reality their influence can not be always predicted, as pointed out above (p. 30), and some experiments bearing on this point are given below.

The equation

$$p = \frac{8.333 b}{c-a} - 25$$

applies, in its original sense of giving the per cent of sulphur oxidized, only to  $\text{FeS}_2$ . We may, however, use it in a broader way as simply indicating a certain relation between the permanganate values of the ferrous, ferric, and total iron, and in this sense it may be applied to any sulphide or other compound capable of reducing ferric salts, and is useful in instituting comparisons between these and  $\text{FeS}_2$  either alone or in a mixture.

#### HEMATITE AND MAGNETITE.

The presence of these is indicated during the extraction of the powder with 20 per cent hydrochloric acid if repeated portions of acid continue to be colored yellow after heating. Difficultly soluble ferric silicates, of course, show the same result. As these iron oxides are scarcely soluble in the weakly acid ferric solution, their presence in small amounts is without appreciable effect.

#### GALENA.

Galena is rather slowly attacked by the ferric solution, and the value of  $p$  is infinity. A mixture of galena and pyrite ( $p=60.8$ ) containing 3 per cent lead gave

$$p=59.5.$$

From this it appears that small amounts of galena exert a slight depressing influence and that the curve for galena-pyrite varies from 60.4 to infinity, with a minimum near the pyrite end.

#### NICKEL AND COBALT.

These show a very strongly elevating influence on the oxidation coefficient, as shown by specimens Nos. 27 and 32.

#### ARSENOPYRITE.

The action of the ferric solution on arsenopyrite, or on pyrites or marcasites containing arsenic in notable amounts, is very characteristic, in that the value of  $b$  is always greater than that of  $c$ . This is due to the fact that a portion of the permanganate represented by  $b$  is consumed in oxidizing arsenious to arsenic acid. It may be further observed that in such cases a permanent end-reaction for  $b$  can not be obtained, as the last portions of arsenious acid are oxidized but very slowly in the cold by permanganate. In this event the titration must be stopped at the first change of color, and since arsenic acid is precipitated very slowly by hydrogen sulphide, it is necessary to conduct the gas through for several hours at a temperature of about  $80^\circ$

in order to render the precipitation complete and to obtain a correct value for *c*.

An experiment made with the usual precautions, with carefully selected arsenopyrite, gave—

*a*, 39.50  
*b*, 56.90  
*c*, 45.84

On substituting these permanganate values we get

$$p = 49.8$$

The actual sulphur oxidized, as calculated from these figures, assuming that all the arsenic is oxidized to  $\text{As}_2\text{O}_3$ , is 10.3 per cent, and in fact a notable sublimation of sulphur was observed. The data do not indicate whether any arsenic is liberated, or whether orpiment or realgar is formed, but no evidence of these could be obtained. More elaborate experiments would be required to decide whether under certain conditions they can be formed by the action of ferric salts on arsenopyrite.

A carefully prepared mixture of pyrite and arsenopyrite (2.17 per cent), containing 1 per cent arsenic, was oxidized with the following result:

*a*, 38.33  
*b*, 43.17  
*c*, 42.73

The value thus deduced for *p*, namely, 56.7, corresponds to that of a pyrite containing 2 per cent marcasite. As few pyrites contain as much as 1 per cent arsenic, it appears that in general the presence of arsenic will not interfere greatly with the marcasite determination.

#### CHALCOCITE AND BORNITE.

Chalcocite by itself gives an infinite value for *p*. The influence of these minerals on pyrite is stated below. Both are very easily attacked by cold ferric solution.

#### CHALCOPYRITE.

As pointed out in the introduction, it is well known that chalcopyrite is more easily attacked by ferric solutions than is pyrite. An experiment with crystallized chalcopyrite made with the usual precautions gave

*a*, 37.44  
*b*, 44.01  
*c*, 44.11

whence

$$p = 30.0$$

From these figures and the determination of the dissolved copper it appears that not more than 2 per cent of the sulphur is oxidized, and that more copper than iron is dissolved (0.7 atom Fe to 1 atom

Cu), from which it may be concluded that pyrite or marcasite is possibly an intermediate product of the oxidation of chalcopyrite by ferric solutions.

#### IX. FORM OF OCCURRENCE OF COPPER IN COPPER-BEARING PYRITES.

The problem of determining whether a given specimen of cupriferous pyrite contains its copper in the form of chalcopyrite or chalcocite was suggested by a geologist, and the following shows that such determination is possible when marcasite or other sulphides are not present in considerable quantities.

#### OXIDATION EXPERIMENTS.

Mixtures of pyrite with chalcopyrite, chalcocite, and bornite were prepared, each containing 3 per cent copper. For chalcopyrite and chalcocite these mixtures have the following composition:

Pyrite .....	91.33}	or	Cu.....	3.00
Chalcopyrite .....	8.67}		Fe.....	45.20
			S.....	51.80
Pyrite .....	96.24}	or	Cu.....	3.00
Chalcocite .....	3.76}		Fe.....	44.85
			S.....	52.15

The bornite mixture has an intermediate composition. It would be scarcely possible to distinguish these by ordinary analytical methods, especially in the presence of small amounts of impurity. The values of  $p$  were found to be:

Pyrite-chalcopyrite .....	62.7
Pyrite-chalcocite .....	75.9
Pyrite-bornite .....	76.4

It appears that the oxidation method does not admit of distinguishing chalcocite and bornite with certainty in a pyrite with 3 per cent copper, but that these may be readily distinguished from chalcopyrite even when the copper is considerably less than 3 per cent. It can also be determined with some probability whether a mixture of chalcopyrite with the other sulphides of copper is present. In the present case the figures given by chalcocite or bornite and chalcopyrite differ by more than thirteen times the probable error of a determination.

This method will probably be of value in synthetic studies of copper ores. It is thus made possible, for example, to ascertain whether the first action of a cupric salt on pyrite is to produce chalcopyrite alone or a mixture of this with the other sulphides, without having to wait for the slow process of crystallization to produce the minerals in a form in which they can be recognized under the microscope. By

employing fine powders the rapidity of the change will be vastly increased, while the net results, according to the mass law, will be the same.

#### DETECTION OF CHALCOPYRITE IN PYRITE OR MARCASITE AND IN ROCKS.

Chalcopyrite mixed with pyrite or marcasite may be readily detected, if not in too small amount or too finely divided, by exposing the sample to bromine vapor for half a minute, and then to hydrogen sulphide gas; the chalcopyrite is blackened, while the iron sulphides remain bright. Particles of chalcopyrite which would otherwise be overlooked are thus easily detected and their outlines sharply defined. I have used the same procedure to detect and establish the nature of minute grains of chalcopyrite inclosed in rocks.

#### X. MISCELLANEOUS SPECIMENS AND SPECIMENS OF DOUBTFUL NATURE.

With the aid of the pyrite-marcasite curve we are now in a position to determine the quantitative composition of specimens of pyrite and marcasite in regard to which there is some uncertainty. The supposed nature of the specimens, according to the geologist, mineralogist, or dealer from whom they were obtained, is stated, as well as the composition established by my method. It is to be understood that the figures express the relative amount of pyrite and marcasite on a scale of 100, impurities being excluded. In this connection I wish to acknowledge the generosity of Dr. A. A. Julien, who has placed at my disposal a number of the identical specimens described by him in his valuable paper repeatedly referred to above. As the study of these specimens is especially important in confirming or refuting his hypothesis (p. 27), I have grouped them together at the end of this section, and have in each case quoted his original description and specific gravity determination, comparing in parallel columns the results obtained by the specific gravity and the oxidation methods.

*Quantitative composition of specimens of doubtful nature.*

[Figures in parenthesis were determined by the indirect method.]

No.	Original designation, etc.	Locality.	p.	Pyrite.	Marcasite.
				<i>Per cent.</i>	<i>Per cent.</i>
15	Concretion from coal.	Unknown .....	30.1	63.0	37.0
16	Pyritized ammonite.	Folkestone, England	46.9	88.0	12.0
17	Fibrous marcasite.	Red Cloud mine, Colorado.	65.7	100.0	.....
18	Pyrite with marcasite.	Quartzburg district, Oregon.	38.6	78.0	22.0
19	Marcasite .....	Chautauqua tunnel, Idaho.	51.3	93.5	6.5
20	do .....	Garfield tunnel, Idaho.	19.8	30.5 (34.4)	69.5 (65.6)
21	Marcasite nodules.	South Dakota .....	60.3	100.0	.....
22	Marcasite (selected).	Littmitz, Bohemia ...	19.5	29.5 (27.8)	70.5 (72.2)
23	do .....	Crow Branch mine, Wisconsin.	18.6	26.0 (31.0)	74.0 (79.0)
24	Fibrous marcasite.	Sunshine, Colo .....	52.2	a 94.0	b 6.0
25	Marcasite after pyrite.	Folkestone, England	55.4	97.0	3.0
26	Pyrite ore .....	Rio Tinto, Spain .....	65.7	100.0	.....
27	Pyrite octahedra	Unknown .....	80.4	100.0	(c)

a Or more.

b Or less.

c Much cobalt.

No. 15. Nearly spherical concretion from coal; locality unknown. Weight, 9.2 grams. Very hard. The structure is coarsely fibrous and radial, with concentric shells of pyrite and marcasite, easy distinguishable by their color.

No. 16. Pyritized ammonite from Folkestone, England. The walls of the cavities are incrustated with pyrite crystals, but the nature of the mass can not be determined from the color.

No. 17. Concretion from Red Cloud mine, San Juan County, Colo., supposed to be marcasite. It consists of a finely fibrous incrustation on rhyolite, varying in thickness from 1 to 10 millimeters, with mammillary surface, and with a banded structure and cleavage perpendicular to the fibers. The banded structure is due to the inclosure of quartz and a black substance which, judging from the presence of a little copper, lead, and arsenic, may be galena, arsenopyrite, and chalcocite. The latter would account for the high oxidation coefficient, which could not be caused by the first two (pp. 32-33). Carefully selected material gave a specific gravity of 4.563.

No. 18. The occurrence of this material is thus described by Mr. Lindgren, by whom it was submitted for a determination of the yellowish-gray material:

"This specimen is derived from the Present Need mine, Quartzburg district, Grant County, Oreg. The vein, carrying chiefly gold, partly in free form, partly associated with sulphides, is contained in diabase and diabase-porphry. The ore minerals are normal yellow pyrite, a soft, yellowish-gray material supposed to be marcasite, zinc blende, and chalcopyrite." The iron sulphides are easily separated from the rock and other sulphides by hydrofluoric acid. The yellowish-gray material, which is closely veined with pyrite, could not be separated from the latter, but the oxidation coefficient of the mixture indicates that it is marcasite. The portion examined contains a trace of copper and lead and no zinc.

No. 19. This is thus described by Mr. Lindgren: "This specimen is taken from the dump of the Chautauqua tunnel, at De Lamar, Owyhee County, Idaho. The specimen consists of quartz, upon which there is a crust of pyrite. The quartz itself contains arborescent forms of a mineral supposed to be marcasite and described as such in Twentieth Annual Report U. S. Geological Survey, Part III, page 130." The mineral in question was easily separated from the quartz and the mass of the pyrite by digestion with hydrofluoric acid. It formed dark-colored tabular masses, presenting no definite crystalline form, and containing traces of copper and lead with a notable amount of arsenic. The oxidation coefficient (51.3) shows that it consists of at least 93.5 per cent of pyrite, but the proportion thus determined is somewhat too low, owing to the influence of the arsenic.

No. 20. Thus described by Mr. Lindgren: "This specimen is taken from the Garfield tunnel, 250 feet from the portal, near De Lamar, Owyhee County, Idaho, and is described on pages 131 and 171, Twentieth Annual Report U. S. Geological Survey, Part III. The specimen consists of a soft white material, which, according to analysis, is probably kaolinite mixed with sericite. It contains arborescent forms of marcasite." The supposed marcasite was isolated by hydrofluoric acid. It could not be definitely described as such from the color and crystalline form. As the oxidation coefficient (19.8) was too high for pure marcasite, a portion was mixed with one-ninth its weight of pyrite, and then gave—

$$p=22.6=41 \text{ per cent pyrite.}$$

We have, then—

$$0.9x+10=41, \text{ or } x=34.4.$$

This corresponds to  $p=20.6$ , a number agreeing within permissible limits with the original determination. We have, therefore—

	Per cent.
Pyrite directly determined.....	30.5.
Pyrite indirectly determined.....	34.4

and the original conclusion of Mr. Lindgren is only in part confirmed. A little arsenic is also present.

No. 21. Material supposed to be marcasite, from South Dakota. Submitted by Dr. G. P. Merrill. The sample consists of spherules not over one-half millimeter in diameter and so brittle as easily to be crushed by the finger. They had undergone vitriolization to such an extent that the original substance was entirely concealed in the mass of sulphate. The oxidation coefficient shows that the material is pyrite, and the analysis that some copper is present. The normal value of  $p$  indicates that the copper is probably in the form of chalcopyrite.

No. 22. Marcasite from Littmitz,<sup>1</sup> Bohemia, consisting of flat, deeply striated twins of marcasite on a nucleus which on fracture shows both marcasite and

<sup>1</sup> Regarding the Littmitz marcasite, see Sadebeck, Monatsber. K. preuss. Akad. Wiss. Berlin, Vol. XX, 1878, p. 19, and Hintze, Handbuch der Mineralogie, Vol. I, pp. 732, 825.

pyrite. Only the portions free from visible admixture of pyrite were taken for examination, and gave  $p=19.5$ . Admixture with one-ninth pyrite gave  $p=21.0=35$  per cent pyrite. We have, then—

	Per cent.
Pyrite directly determined .....	27.5
Pyrite indirectly determined .....	27.8

No. 23. A specimen from Crow Branch mine, Wisconsin, consisting of a compact nucleus of tin-white marcasite covered with crystals which are completely inclosed in elongated cubes of pyrite, the line of demarcation being clearly discernible on the fracture by the difference of color. Selected portions free from visible admixture of pyrite were used, giving a specific gravity of 4.891. To determine the contents of pyrite the indirect method was used.

	Per cent.
Pyrite directly determined .....	26.0
Pyrite indirectly determined .....	31.0

As only the powdered material was available for the indirect determination, the difference is not surprising (p. 28).

No. 24. Material from Sunshine, Colo. Finely fibrous radial concretions in quartz, which on the freshly cleaned fracture show a faint banded structure. Supposed to be marcasite. A little lead and copper and much arsenic and antimony are present. As arsenic, and probably antimony, would lower the oxidation coefficient, the figure given for pyrite is too low, and the presence of marcasite is doubtful.

No. 25. A large flattened concretion from Folkestone, England, described as "marcasite after pyrite." The fracture is columnar and the surface is covered with rounded projections, apparently tetragonal pyramids, possibly of the type described by Penfield.<sup>1</sup> The color on the freshly broken surface exactly matches pyrite. I have received several other supposed marcasite concretions from Folkestone, all of which are clearly pyrite.

No. 26. Pyrite ore from Rio Tinto, Spain. The fragments are grayish, evolve some hydrogen sulphide with acids, and with the bromine hydrogen sulphide test (p. 35) show very finely disseminated copper sulphide.

No. 27. Brilliant untarnished octahedra in calcite, containing a large amount of cobalt and a little copper, which explain the abnormal oxidation coefficient.

#### CONCLUSIONS.

Of the above thirteen specimens five have been described as marcasite, though consisting nearly or entirely of pyrite, while three other marcasites are shown to contain a large amount of pyrite, which could not be detected without the aid of the oxidation method. As these samples were selected and examined without preconception as to their nature, it seems probable that a very considerable proportion of the concretions which exist in collections or are sold as marcasite are in reality pyrite, while not a few others, even when fairly well characterized by rhombic crystallization, may contain inclosures of pyrite.

<sup>1</sup>Am Jour. Sci., 3d series, Vol. XXXVII, 1889, p. 209.

## DR. JULIEN'S SPECIMENS.

*Quantitative composition of Julien's specimens.*

[The numbers in parentheses are those given in Julien's paper.]

Number.	Locality.	Density.	$\rho$ .	Composition deduced from $\rho$ .	Composition according to Julien, deduced from density.
28 (pyrite 1) .....	Galena, Ill .....	5.015	60.3	Pyrite ..... 100.0	Much marcasite. { Pyrite ..... 27.51 Marcasite ..... 72.49
29 (pyrite 96) .....	Franklin, N. J .....	4.856	59.0	Pyrite ..... 99.5	{ Pyrite ..... 21.18 Marcasite ..... 78.82
30 (pyrite 98) .....	Somerville, Mass .....	4.843	59.6	Pyrite ..... 99.5	{ Pyrite ..... 9.38 Marcasite ..... 90.62
31 (pyrite 101) .....	Monroe, Conn .....	4.819	60.7	Pyrite ..... 100.0	{ Pyrite ..... 1.00 Marcasite ..... 99.00
32 (pyrite 106) .....	Bastrop, Tex. ....	4.791	67.7	Pyrite ..... $a$ 100.0	{ Pyrite ..... 89.45 Marcasite ..... 10.55
33 (marcasite 1) .....	{ Cumberland, Eng- land. ....	4.987	42.9	{ Pyrite ..... 83.0 Marcasite ..... 17.0	Pyrite ..... 89.45 Marcasite ..... 10.55

*a* Contains nickel.

The following descriptions are in part quoted from Julien's paper:

No. 28. "Concretionary nodule. Marsden's diggings, Galena, Ill. No. 1 (fibrous core). Marcasitic pyrite. Very finely fibrous, pale brass-yellow and splendent." Analysis (Julien),  $\text{SiO}_2$ , 0.110; Pb, 0.188; As, 0.056. The fracture varies from fibrous to prismatic, the prisms being evidently elongated cubes, with terminations consisting of cube modified by pyritohedron and octahedron.

No. 29. "No. 96. Marcasitic pyrite. Franklin, N. J. Sharp, brilliant, brass-yellow, striated pyritohedra, yellowish white and splendent on fracture." No admixture of marcasite crystals. The value of  $\rho$  shows that they are practically pure pyrite, the low density being probably due to inclusions.

No. 30. "No. 98. Marcasitic pyrite. Somerville, Mass. Very sharply defined, glittering yellowish cubes, sometimes distorted or rectangular, rarely striated, occasionally with octahedral planes upon their solid angles, yellowish white and brilliant on fracture; scattered through a gray argillaceous slate."

No. 31. "No. 101. Pyrite. Monroe, Conn. Deeply striated, distorted, brilliant cubes of very pale brass-yellow color, with modifications by the pyritohedron: yellowish white, finely granular, and splendent on fracture, and sometimes inclosing grains of white quartz."

No. 32. "No. 106. Marcasitic pyrite. Bastrop, Bastrop County, Tex. Dull and pale brass-yellow octahedra, rarely bright, very pale yellowish white and brilliant on fracture; upon black granular crystalline hematite." The specimen contains a trace of arsenic, a strong trace of copper, and some nickel. It is the latter, possibly in conjunction with the copper, which causes the high oxidation coefficient.

No. 33. "No. 1. Marcasite. Cumberland, England. Hollow incrustation pseudomorphs after barite, implanted on a group of barite crystals. The crusts are grayish white to tin-white and splendent on fracture, with surfaces drusy with pseudo-octahedrons or rhombic pyramids, whose smooth, rectangular terminal faces (the basal pinacoid OP) project but slightly; a few minute rhombic prisms also occur, and some hexagonal though apparently triangular twins." The supposed rhombic pyramids with basis are evidently combinations of cube and octahedron belonging to the 83 per cent of pyrite which it contains.

## DISCUSSION OF JULIEN'S HYPOTHESIS.

The above list includes some of the most pronounced cases of "marcasitic pyrite" described by Julien—that is, material with the crystalline

form of pyrite but supposed to consist very largely of marcasite. The four specimens, Nos. 29, 30, 31, and 32, consist of characteristic pyrite crystals, and if the oxidation method be admissible they are in fact free from marcasite, yet they all show abnormally low densities. The only conclusion which can be drawn from this is that the density alone does not afford a reliable means of detecting the presence of marcasite in pyrite unless the absence of all other contaminating substances be first conclusively proved, and that isometric crystallization in itself affords a proof, almost amounting to certainty, that the sulphide is actually pyrite. It is undoubtedly true that perfect pyrite crystals may inclose marcasite, a good case of which is the Crow Branch specimen, No. 23, but such cases are comparatively rare, and the inclosure can usually be detected by breaking the specimen and carefully examining the color. In case of doubt a determination of the density is practically of no value, and resort must be had to the oxidation method. I have examined some of the marcasite specimens from the same collection, as well as others which are supposed to contain pyrite, and in general the latter can be detected by its color after careful cleaning with acid. I have shown that certain specimens of marcasite do contain pyrite inclosed in such small masses as not to be capable of detection in this way (Nos. 22 and 23). Small, warty excrescences on marcasite crystals are frequently pyrite, and when the conditions controlling the formation of the two sulphides are practically in equilibrium these are likely not only to form but to be completely overgrown and inclosed in the crystal of marcasite. A marcasite which occurs mixed with visible masses of pyrite is therefore likely also to contain such inclosures which can not be seen and whose presence can be detected only by the indirect oxidation method. That both pyrite and marcasite with abnormal density are essentially prone to decomposition is doubtless true, and while in certain cases this may be traced to an admixture of the two, in others it is due to inclosures of another nature. The lack of homogeneity not only permits the existence of fissures admitting air and moisture, but the formation of these is in such cases promoted by unequal expansion and contraction.

Fibrous marcasite is so often referred to that it may well exist, but so far as my somewhat limited range of examinations goes, a fibrous structure affords absolutely no presumption in favor of a specimen being marcasite; on the contrary, fibrous pyrite appears to be much more common than fibrous marcasite, the latter in concretions tending rather to assume the coarsely columnar structure.

#### XI. PARAMORPHISM.

The literature of the paramorphism of pyrite and marcasite is exceedingly scanty, and such as there is lends no support to the view that true transformation paramorphs exist. Those described are apparently either replacement or incrustation pseudomorphs, the

true nature of which is shown by careful inspection. Wöhler<sup>1</sup> attempted, without success, to convert marcasite into pyrite and pyrite into marcasite by heating for four hours at about 400°—experiments which are well worth repeating, with an extension of the time and with the aid of the oxidation method. Julien's assumption of extensive paramorphism is scarcely longer tenable in view of the results described above, although the inclosure of considerable portions of pyrite in some specimens of marcasite lends some support to it. While theoretically possible, the attractive hypothesis that marcasite gradually changes to pyrite without re-solution, and that the porosity of certain pyrites can be thus explained, is thus far without a sound basis, either of experiment or of observation. It is intended to carry out experiments on this point in the immediate future.

## XII. CONSTITUTION OF PYRITE AND MARCASITE; ACTION OF CUPRIC SALTS.

The importance to chemical geology of an experimental study of the action of copper salts on pyrite and marcasite is self-evident. The following experiments were made, however, with the object of ascertaining whether the method of A. P. Brown<sup>2</sup>—namely, heating with neutral copper sulphate solution at 200°—could be used to distinguish these minerals, and incidentally, of testing his hypothesis that the iron in marcasite is wholly ferrous, while that of pyrite is four-fifths ferric. I have therefore confined myself to the conditions of temperature and concentration observed by him.

Brown, in his published experiments, has limited himself to titrating the ferrous iron in the resulting solution, while no determination was made of any ferric iron which might be present either in the solution or in the precipitate. As neutral ferric sulphate is practically completely precipitated as basic salt on heating its solution, and as any ferric salt remaining in solution would inevitably be reduced by the sulphides present, it seems reasonably clear that a single experiment with pyrite, in which only the ferrous salt is determined, in which no account is taken of the ferric salt supposed to be formed, and in which no clear evidence of complete decomposition of the mineral is given, can not have great weight in establishing an important hypothesis. While not questioning the correctness of Brown's single observation so far as it goes, I have been wholly unable to obtain the same results.

In each experiment cited below the material was finely ground, carefully freed from oxidation products in the manner employed in my oxidation experiments (p. 20), and about 0.2 gram heated with 50 cm.<sup>3</sup> of 10 per cent iron-free  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution which had been

<sup>1</sup> Liebig's Annalen, Vol. XC, 256.

<sup>2</sup> Proc. Am. Philos. Soc., Vol. XXXIII, 1894, p. 225. Chemical News, Vol. LXXI, 1895, p. 179.

freed from air by boiling out and cooling in carbon dioxide. The tubes were filled with carbon dioxide, carefully sealed in a current of the same gas, and heated for varying times at 200° C. The filtration and titration with permanganate of the resulting solution were also made in an atmosphere of carbon dioxide, and the end-reaction, which is not very sharp, was determined by comparison with a copper sulphate solution of about the same strength.

EXPERIMENTS WITH CUPRIC SULPHATE AND PYRITE.

*Experiment 1.*—Pyrite No. 4. Oxidation coefficient, 60.3. Time of heating, ten hours.

Pyrite taken.....	0.2024
Ferrous iron in solution.....	.0305
Total iron in solution.....	.0314
Total iron in pyrite used.....	.0944

The solution therefore contains 33.3 per cent of the iron, practically all in the ferrous condition, against 20 per cent as required by Brown's hypothesis. The precipitate was red-brown. In a separate experiment the red substance was found to be left behind on oxidizing the sulphide with dilute nitric acid, and proved to be ferric oxide or a very basic sulphate. It is easily soluble in hot dilute hydrochloric acid, and can thus be separated from the sulphide and determined.

*Experiment 2.*—Pyrite No. 5. Oxidation coefficient, 60.8. Time of heating, eleven hours.

Pyrite taken.....	.2028
Ferrous iron in solution.....	.0510
Total iron in solution.....	Same.
Total iron in pyrite used.....	.0946

The solution contains 53.9 per cent of the iron, all in the ferrous state. The ferric oxide in the red-brown precipitate was extracted by boiling ten minutes with dilute hydrochloric acid in a current of carbon dioxide, whereby some copper also dissolved. The ferric iron thus determined was 0.0272 gram. The final residue, oxidized with aqua regia, gave much iron, which must have come from undecomposed (or imperfectly decomposed) pyrite. From the sum of the two irons above determined it appears that 82.7 per cent of the pyrite was decomposed, and that this portion gave—

62.5 per cent ferrous iron.  
34.8 per cent ferric iron.

Required by Brown's hypothesis, 20 per cent ferrous iron.

*Experiment 3.*—Pyrite No. 5. Time of heating, seven hours.

Pyrite used.....	0.2027
Ferrous iron in solution.....	.0527
Total iron in solution.....	.0523
Total iron in pyrite used.....	.0945

The solution therefore contains 55.3 per cent of the iron entirely as ferrous salt. The ferric oxide, extracted as above from the red-brown precipitate, was equivalent to 0.0225 gram iron. The final residue contained much iron. From these data it follows that 79.1 per cent of the pyrite was decomposed, the dissolved portion giving—

69.9 per cent ferrous iron.  
30.1 per cent ferric iron.

Required by Brown's hypothesis, 20 per cent ferrous iron.

#### EXPERIMENTS WITH CUPRIC SULPHATE AND MARCASITE.

*Experiment 4.*—Marcasite No. 10. Oxidation coefficient, 17.4. Time of heating, seven hours.

Marcasite used .....	0.2062
Ferrous iron in solution .....	.0559
Total iron in solution .....	.0562
Total iron in marcasite used .....	.0961

After extracting the red-brown precipitate, as above, the residual sulphide was found to be free from iron, indicating complete decomposition of the marcasite. From these data it follows that the marcasite yielded—

58.2 per cent ferrous iron.  
41.8 per cent ferric iron.

Required by Brown's hypothesis, 100 per cent ferrous iron.

*Experiment 5.*—Marcasite No. 10. Time of heating, fourteen hours.

Marcasite used .....	0.2096
Ferrous iron in solution .....	.0651
Total iron in solution .....	Same.
Ferric iron from precipitate .....	.0318
Total iron in marcasite used .....	.0977

The precipitate further yielded to hydrochloric acid 0.0626 gram copper, which was present either as cuprous oxide or as metallic copper, while the final residue was free from iron, showing that complete decomposition had been effected. The above data give for this experiment—

66.6 per cent ferrous iron.  
33.4 per cent ferric iron.

Required by Brown's hypothesis, 100 per cent ferrous iron. The copper sulphide remaining after extraction with hydrochloric acid contained 0.2309 gram copper, from which it follows that two atoms of copper are precipitated as sulphide for each atom of iron dissolved. This necessarily implies a reduction of the copper to the cuprous condition, and a corresponding oxidation of a portion of the ferrous salt or of the sulphur, or both. That cupric salts can accomplish both of these results is shown in the two following experiments.

## EXPERIMENT WITH CUPRIC CHLORIDE AND PYRITE.

*Experiment 6.*—0.2545 gram pyrite was heated with 50 cm.<sup>3</sup> of a pure cupric chloride solution containing as much copper as the sulphate used in the foregoing experiments, the tube being filled with the usual precautions to prevent oxidation. The tube was heated five hours at 200° and on cooling was found to contain undecomposed mineral and an abundant crystallization of cuprous chloride. The filtered solution gave—

0.0667 gram iron=0.1429 gram pyrite.

0.5540 gram BaSO<sub>4</sub>=0.1427 gram pyrite.

It appears, therefore, that as far as it was decomposed the pyrite was completely oxidized to ferrous salt and sulphuric acid, with a corresponding reduction of the copper from the cupric to the cuprous state, according to the equation

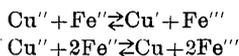


I have further obtained an abundance of sulphuric acid by oxidizing precipitated copper sulphide with cupric chloride solution at 100°, air being rigorously excluded. Doubtless in the above experiments with pyrite and marcasite and copper sulphate an analogous oxidation occurs, being obscured by other reactions. Chalcocite, however, is not perceptibly attacked by 10 per cent copper sulphate solution after fourteen hours' heating at 200°.

## EXPERIMENT WITH FERROUS AND CUPRIC SULPHATES.

*Experiment 7.*—A mixture of equal volumes of 10 per cent solutions of crystallized copper sulphate and crystallized ferrous sulphate (carefully freed from ferric salt by reduction with hydrogen sulphide) was heated, under absolute exclusion of air, for three hours at 200°. A considerable red precipitate was obtained, which consisted of a mixture of ferric oxide or basic sulphate with cuprous oxide and apparently metallic copper. The reduction of cupric by ferrous salts in neutral or acid solution is frequently referred to in the literature, but, so far as I can ascertain, without experimental basis.

*Theory of the reaction.*—The explanation of the result is probably the following: In the mixture we have equilibrium between the cupric, cuprous, ferrous, and ferric ions and copper, as represented by the equations



in which but traces of Cu, Cu', and Fe''' exist.<sup>1</sup> On heating the trace of ferric salt is precipitated in the basic form, the equilibrium is dis-

<sup>1</sup>The slight solubility of cuprous compounds shows that not more than traces can be present.

turbed, and the reaction continues to proceed from left to right, accompanied by formation of  $\text{Cu}'$  and  $\text{Fe}'''$  (and possibly  $\text{Cu}$ ) and their precipitation as insoluble products, until the accumulated acid is in equilibrium with both of these and further precipitation can not occur. The process is further complicated by a partial precipitation of copper as basic salt when the sulphate is used. A mixture of cupric and ferrous salts gives a strong reaction for ferric iron with sulphocyanate. This does not imply an appreciable oxidation of the ferrous iron in the mixture itself, but a shifting of the equilibrium to the right in the above equation through the formation of the slightly dissociated ferric sulphocyanate. It is doubtless to the reduction of the cupric sulphate by sulphur and by ferrous sulphate that the formation of chalcocite from pyrite is to be ascribed.

#### GENERAL CONCLUSIONS FROM THE EXPERIMENTS.

The conclusions which may be drawn from the above experimental data are:

1. At  $200^\circ$  copper sulphate decomposes marcasite more rapidly than pyrite.

2. Both ferrous and ferric salts are formed in both cases, the former being found wholly in the solution, the latter wholly in the precipitate. There is no marked difference in the relative amounts of these in either case. The precipitate also contains, besides cuprous sulphide, cuprous oxide and perhaps metallic copper.

3. The formation of ferric salt is to be ascribed, in part at least, to the reaction of the ferrous salt upon the cupric salt (Experiment 7), while some oxidation of sulphur to sulphuric acid occurs (Experiment 6). Any ferric salt which may fail to be precipitated will be reduced by the sulphides.

4. The relative amounts of ferrous and ferric salts depend simply upon the establishment of equilibrium between the solution and the products of decomposition of the pyrite or marcasite, and not upon any fundamental chemical difference in the two minerals, and consequently the hypothesis of Brown is devoid of valid experimental basis.

It would seem that no method can be depended upon to give us an insight into the state of combination or valency of either iron or copper in their sulphides which does not take due account of the conditions of equilibrium between the reagents and the decomposition products. This applies not only to other experiments of Brown quoted in his paper, but to the attempt of Starke, Shock, and Smith<sup>1</sup> to prove the divalent condition of iron in arsenopyrite and of Morgan and Smith<sup>2</sup> to establish the same for chalcopyrite. That the product of heating chalcopyrite in dry hydrochloric gas consists of a mixture of cupric chloride and ferrous chloride is inconclusive on the question as

<sup>1</sup> Jour. Am. Chem. Soc., Vol. XIX, 1897, p. 948.

<sup>2</sup> Ibid., Vol. XXIII, 1901, p. 107.

to whether chalcopyrite has a constitution represented by  $(\text{Cu}''\text{Fe}'')\text{S}_2$  or  $(\text{Cu}'\text{Fe}''')\text{S}_2$  until the condition of the system  $\text{CuCl} + \text{FeCl}_3 \rightleftharpoons \text{CuCl}_2 + \text{FeCl}_2$  in equilibrium is known, in the absence of water and presence of hydrochloric acid gas. That nearly all the iron was obtained in the ferrous state in some of the experiments with copper sulphate made by Brown and others I can explain only on the assumption that enough acid was originally present or eventually formed to enable any basic ferric salt to act on and be reduced by the residual sulphides and cuprous oxide. In fact, hot dilute sulphuric acid slowly dissolves the mixture of cuprous oxide and basic ferric salt obtained in my experiments, giving a strongly reducing solution.

### XIII. OXIDATION OF PYRITE AND MARCASITE BY POTASSIUM PERMANGANATE.<sup>1</sup>

A few experiments were made to determine the percentage of sulphur oxidized in pyrite and marcasite at ordinary temperature by acidified permanganate, the mineral being always in excess.

An excess of the powdered mineral, freed from oxidation products, was shaken in a stoppered cylinder with a constant amount of dilute sulphuric acid and 100 cm.<sup>3</sup>  $\text{KMnO}_4$ , added in quantities of 5 cm.<sup>3</sup> at a time, the shaking being continued after each addition until the color had disappeared, which required but a few minutes. The filtered solution was then reduced and the iron titrated by the same permanganate solution.

The proportions required are—

For complete oxidation to $\text{Fe}_2(\text{SO}_4)_3$ and sulphuric acid	..... 5 $\text{FeS}_2 + 15 \text{KMnO}_4$
For oxidation of the iron alone to $\text{Fe}_2(\text{SO}_4)_3$	..... 5 $\text{FeS}_2 + 3 \text{KMnO}_4$

For oxidation of the sulphur	..... 12 $\text{KMnO}_4$
------------------------------	--------------------------

Let

$a$  = volume of permanganate used in oxidation of  $\text{FeS}_2$ ,

and

$b$  = volume of permanganate required to reoxidize  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ;

then

$3b$  = volume of permanganate used in oxidizing  $\text{Fe}$  in  $\text{FeS}_2$  to  $\text{Fe}_2\text{O}_3$ ,

and

$a - 3b$  = volume of permanganate used in oxidizing  $\text{S}$  in  $\text{FeS}_2$  to  $\text{SO}_3$ ;

also

$12b$  = volume of permanganate required to oxidize all the sulphur in the mineral decomposed;

whence

$$\text{Percentage of sulphur oxidized} = p = \frac{100(a-3b)}{12b} = \frac{8.333a}{b} - 25.$$

Where 190 cm.<sup>3</sup> permanganate are used,

$$p = \frac{833.3}{b} - 25.$$

<sup>1</sup> For previous experiments on the action of permanganate on pyrite and marcasite, see A. P. Brown, Proc. Am. Philos. Soc., Vol. XXXIII, 1894, and Chemical News, Vol. LXXI, 1895, pp. 131, 155, 171. The experiments of Brown show that with an excess of permanganate the total sulphur oxidized in a given time is greater in the case of marcasite than of pyrite, but they do not establish any relation between the amount of sulphur oxidized and the quantity of mineral decomposed.

The values of  $p$  obtained were:

	1.	2.
Pyrite .....	94.0	90.7
Marcasite .....	84.6	86.7

The duplicate results are therefore not sufficiently concordant, nor is the difference between pyrite and marcasite great enough, to give the method more than a confirmatory value. The difference here, as in the case of oxidation by the ferric-sulphate method, is due to the greater ease with which marcasite is attacked, but the relative oxidation rate of the sulphur is clearly much greater. The difference might possibly be greater at 100°, but here the experiments failed because of the strong tendency of the permanganate to deposit peroxide, even in the presence of much sulphuric acid.

#### XIV. SUMMARY OF RESULTS.

The chief results of this investigation may be thus summarized:

1. When pyrite or marcasite is boiled with an excess of a solution of ferric salt to complete reduction of the latter the ratio of sulphur oxidized to mineral decomposed is perfectly definite and characteristic of each mineral, provided certain standard and easily controllable conditions are observed. Under these conditions the percentage of sulphur oxidized in pyrite is about 60.4 per cent and in marcasite about 18 per cent of the total sulphur. These figures are the characteristic *oxidation coefficients*.

2. The oxidation of pyrite or marcasite to ferrous salt, sulphuric acid, and free sulphur can not be expressed by any single equation, but takes place according to two or more; the relation between which varies with the special conditions.

3. An empirical curve for the oxidation coefficients of mixtures of pyrite and marcasite is constructed by aid of which the composition of naturally occurring mixtures may be quantitatively determined.

4. The influence of various impurities on the results is described.

5. Various concretions and other specimens are examined, and it is shown that in many cases much uncertainty exists in distinguishing pyrite and marcasite by the usual methods.

6. There is no well-established evidence of the existence of true paramorphs of pyrite after marcasite or of marcasite after pyrite.

7. The hypothesis that most natural specimens, even when well crystallized, are intimate mixtures of the two is without foundation.

8. Specimens crystallizing in the regular system are true pyrite, while those forming rhombic crystals are true marcasite. When the two are mingled or intergrown it is generally possible to distinguish each by the color after cleaning with acid, a rule to which there are a few exceptions.

9. The density does not afford a trustworthy means of determining one mineral in the presence of the other.

10. Chalcopyrite may be sharply distinguished from chalcocite or bornite in pyrite carrying 3 per cent copper or less. A method is given for detecting small amounts of chalcopyrite in pyrite and marcasite, or the reverse, or in rocks.

11. There is no evidence as to the state of combination or valency of iron in pyrite and marcasite, or that these differ in the two minerals. Experiments which have been regarded as proving the existence of such differences are inconclusive.

12. The principle of the oxidation method, with appropriate modifications, is probably capable of wider application in distinguishing dimorphous minerals, in determining whether a given complex mineral is a mixture or compound of its simpler constituents, and in determining the nature of small amounts of impurities.

13. The action of acid permanganate on pyrite and marcasite is analogous to that of ferric salts, the percentage of sulphur oxidized in pyrite being higher than in marcasite.

My thanks are due to Dr. A. A. Julien, whose valuable assistance has been noted above, and to Professors Van Hise, Emerson, Merrill, and Penfield, and Messrs. Tassin, Emmons, Ransome, Weed, and Lindgren, who have generously supplied most of the material upon which the foregoing investigation is based.

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