Determination of Oxygen in Some Minerals Using Pyrite

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(Received February 26, 1960)

A few years ago some experiments on the reactions among various kinds of sulfides, sulfates and oxides which occur in volcanic and hot spring districts were carried out by the present authors to ascertain the relations of their formation and occurrence(1). The results of the experiments indicated that the amount of oxygen in some minerals can be easily determined with pyrite.

It has been pointed out that pyrite is easily oxidized during the process of grinding in the air and that a remarkable error may be introduced into the result of chemical analysis of pyrite from this oxidation(2). While no method has yet been found to determine the minute amount of oxygen in pyrite, some reports described oxidation products of pyrite. From those reports, it would be concluded that iron sulfates may be formed by the oxidation(3,4). In addition to these products, fine powder of pyrite may absorb moisture and oxygen from the air, and it should also be considered that the sample of pyrite may be contaminated with the small amount of oxides or sulfates contained originally in the raw minerals. Thus iron oxides, absorbed oxygen and absorbed water could be the sources of oxygen in pyrite samples, even if the samples, were almost pure under microscopic observation. And it should be pointed out that the oxygen in the samples reacts with the pyrite and is liberated as sulfur dioxide on heating the samples at a high temperature in vacuo. If the liberation of sulfur dioxide is quantitative, the amount of oxygen in the samples can be estimated from that of the sulfur dioxide evolved.

When moisture exists, hydrogen sulfide may also be formed, and the situation may be somewhat complicated because of the equilibrium among hydrogen sulfide, sulfur dioxide and water vapour. The nature of these reactions should be carefully investigated to establish an accurate method for the determination of oxygen in pyrite and other minerals. There are some reports on the reactions between pyrites and iron oxides(5), iron sulfates(6,7) and water(8), but the results are insufficient for the present purpose. In the present paper, the results obtained on these reactions and the method for the determination of a minute amount of oxygen in pyrite and the amount of oxygen in other minerals by using pyrite are given.

Experimental

Materials.—Natural pyrites used in the present study had a chemical composition* nearly equal to the ideal chemical formula, FeS_2, and the values obtained for the lattice constant of crystals agreed well with the data described by Parker and Whitehouse(9), and also by Hiemstra(10) (5.416~5.417 Å). Iron monosulfide was obtained by thermal decomposition of the pyrites at about 900°C in vacuo. The chemical composition of the artifical

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1) I. Iwasaki, T. Katsura and M. Yoshida, read before the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, 1957.

2) E. A. Hontoir, *Bull. Inst. Mining. Met.*, No. 553, 95 (1952).

3) A. Wurm, *Z. prakt. Geol.*, 35, 130 (1927).

4) G. E. Mapstone, *Chemistry & Industry*, 1954, 577.

5) F. Martin and O. Fuchs, *Z. anorg. Chem.*, 125, 307 (1922).

6) Kothny, *Met.*, 8, 392 (1911) (cited by Gmelin's Handbook).

7) Gorgew, *Compt. rend.*, 104, 1174 (1887) (cited by Gmelin's Handbook).

8) E. Grünnert, *J. prakt. Chem.*, [2], 122, 91 (1929).

* The accurate chemical composition of these pyrites will be reported in another paper.

9) H. M. Parker and W. J. Whitehouse, *Phil. Mag.*, 14, 939 (1932).

10) S. A. Hiemstra, *Am. Mineralogist*, 41, 519 (1956).

iron monosulfide was somewhat richer in sulfur, and its chemical formula was $FeS_{1.03}$. It was not ferromagnetic and its properties agreed well with those of troilite under microscopic observation. Magnetite was obtained by thermal decomposition of reagent grade α-ferric oxide in a quartz tube at about 1200°C and below 1×10^{-4} mmHg of oxygen pressure achieved by pumping it out. The magnetite obtained as above had almost the ideal chemical composition, 49.9% FeO and 50.1% Fe_2O_3 in molar ratio. Other chemicals, such as α-ferric oxide, ferrous sulfate $FeSO_4\cdot7H_2O$, and ferric sulfate $Fe_2(SO_4)_3\cdot nH_2O$ [78% $Fe_2(SO_4)_3$] employed were all of reagent grade. The reagents were used after removing the water by heating in vacuo.

Apparatus and Procedure. — The apparatus employed is shown in Fig. 1. The maximum temperature attained is about 1000°C.

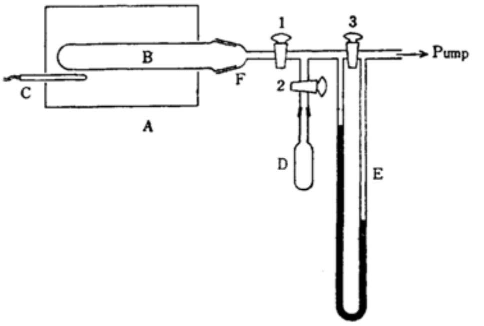

Fig. 1. Apparatus
A. Electric furnace
B. Quartz tube
C. Thermocouple
D. Absorption tube
E. Manometer
1,2,3 Cock

The finely powdered mixture of the sample with the pyrite was packed in a small quartz tube, and then placed at the bottom of a quartz combustion tube B (Fig. 1). Then all of the apparatus was evacuated to a pressure of $10^{-2}\sim10^{-3}$ mmHg. To analyse the gas evolved from the sample, potassium hydroxide was placed in tube D. After evacuation, cocks 2 and 3 were closed, then the temperature was raised at a rate of about 200°C per hr. The pressure of the evolved gas was continuously measured. The correction of the pressure for the temperature change was experimentally determined, and the volume of the evolved gas was calculated in N. T. P. When the reaction came to the end, cock 2 was opened, and the pressure of the unabsorbed gas was determined. This was usually very low in all of the present experiments. Potassium hydroxide which absorbed the acid gas was then dissolved in water and was poured into a suspension of freshly precipitated basic cadmium carbonate. By this procedure hydrogen sulfide is fixed in the precipitate as cadmium sulfide and sulfur dioxide remains in the filtrate as sulfite ions. The amount of hydrogen sulfide from the precipitate and the amount of sulfur dioxide from the filtrate were determined by iodometric titration. As the gas evolved from the reactions of the oxide and the sulfate with the pyrite contained only a negligible amount of hydrogen sulfide, the amount of sulfur dioxide could be determined directly by the manometric method. The nature of the solid products was also examined by chemical, X-ray and microscopic methods.

Results and Discussion

When the powdered pyrite alone was heated in the apparatus, a dissociated sulfur was deposited inside F the silica tube, and in some cases the evolution of a small amount of a gas which was stable at room temperature was observed. The analysis of the gas showed that it consists mainly of sulfur dioxide, hydrogen sulfide and water vapor, and that its amount is influenced to some extent by the degree of pulverization or other conditions. Therefore, a correction must be made for each kind of pyrite, when the volume of the sulfur dioxide evolved by the reaction between pyrites and iron oxides or iron sulfates is measured. From the repeated blank experiments, the blank values for the pyrite used in the present experiments were obtained as shown in Table I:

TABLE I

Temp. range	Correction ml. per 1 g. pyrite
Below 450°C	Almost negligible
450∼550°C	2.5
550∼650°C	3.0

(1) The Reaction between Pyrite and Ferric Oxide.—As will be seen in Fig. 2, the reaction between pyrite and ferric oxide begins at about 500°C and comes to the end at about 600°C. When an excess of pyrite exists, the solid product of the reaction is only troilite, and the reaction may be regarded as follows:

$$7FeS_2+2Fe_2O_3=11FeS+3SO_2 \qquad (1)$$

The amount of sulfur dioxide evolved from

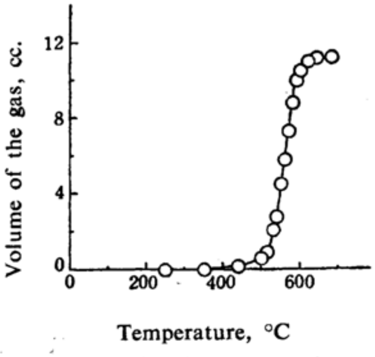

Fig. 2. Reaction between pyrite and α-ferric oxide (I).

Pyrite	200 mg.
Fe_2O_3	50 mg.

the mixture of 200 mg. of pyrite and 50 mg. of ferric oxide was 10 ml. (0°C, 1 atm.) in the range 500∼600°C, and the value calculated from Eq. 1 is 10.5 ml.

When the amount of pyrite was insufficient to reduce all ferric oxide to troilite, the reaction was likely to proceed through two stages as shown in Fig. 3. The first stage of the reaction would correspond to Eq. 1, and the second to Eq. 2, which shows the reaction between the troilite and the remainder of the ferric oxide.

$$FeS + 10Fe_2O_3 = SO_2 + 7Fe_3O_4 \qquad (2)$$

All the results such as the amount of gas evolved through each stage, the range of the reaction temperature, and the properties of the solid products observed by X-ray and microscopic method support the assumption described above. Martin and Fuchs[5] studied the reaction of similar mixtures of pyrite and ferric oxide (weight ratio 1 : 2.25 or 1 : 3) and obtained a mixture of troilite and magnetite as solid products. The co-existence of these solid phases can be interpreted by the results obtained by our experiments, but according to theirs, the reaction began at 570°C, came to the end at 870°C, and the range of the reaction temperature was higher than that obtained by the present authors.

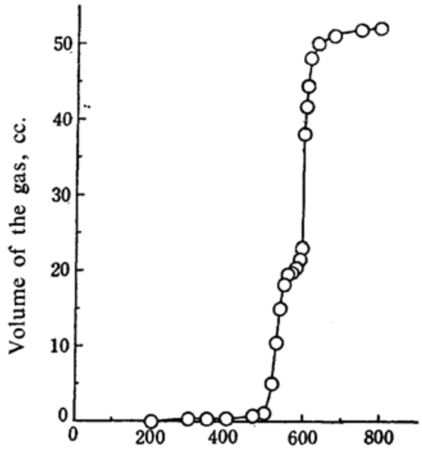

Fig. 3. Reaction between pyrite and α-ferric oxide (II).

Pyrite	250 mg.
Fe_2O_3	2.0 g.

As the ferric oxide reacts completely with the pyrite to liberate sulfur dioxide at about 600°C as shown in Fig. 2, the amount of the ferric oxide in the iron sulfides can be determined by measuring the amount of sulfur dioxide evolved from the samples with a sufficient amount of pyrite.

(2) The Reaction between Pyrite and Magnetite. — Magnetite (Fe_3O_4) also reacts with pyrite to form troilite and sulfur dioxide at a high temperature as shown in Eq. 3.

$$5FeS_2 + Fe_3O_4 = 8FeS + 2SO_2 \qquad (3)$$

The amount of the gas evolved was in good agreement with Eq. 3. The reaction began at about 550°C, and came to the end at about 650°C as shown in Fig. 4. The temperature range of the reaction overlapped with that of the reaction between pyrite and ferric oxide. Magnetite did not react practically with troilite below 1000°C.

As magnetite reacts completely with the pyrite to liberate sulfur dioxide at about 650°C as shown in Fig. 4, the amount of the magnetite in the iron sulfides can be determined by measuring the amount of sulfur dioxide evolved from the samples with a sufficient amount of pyrite.

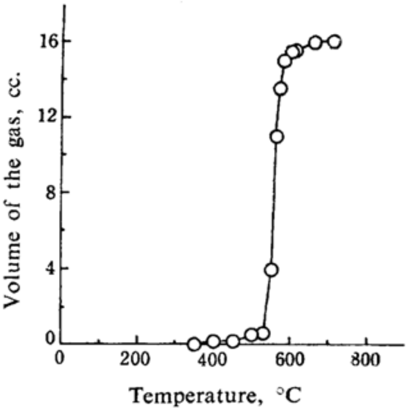

Fig. 4. Reaction between pyrite and magnetite.

Pyrite	200 mg.
Fe_3O_4	100 mg.

(3) The Reaction between Pyrite and Ferric Sulfate.—When sufficient amount of pyrite is present, the reaction between pyrite and ferric sulfate began at about 300°C and came to an end at about 650°C proceeding through three stages as shown in Fig. 5. The final product was only troilite, and the equation of the reaction in each stage can be considered as follows :

The first stage (about 300∼420°C)

$$FeS_2 + 3Fe_2(SO_4)_3 = 7FeSO_4 + 4SO_2 \qquad (4)$$

the second stage (about 450∼520°C)

$$FeS_2 + 8FeSO_4 = 3Fe_3O_4 + 10SO_2 \qquad (5)$$

the third stage (about 550∼650°C)

$$5FeS_2 + Fe_3O_4 = 8FeS + 2SO_2 \qquad (3)$$

The volumes of sulfur dioxide calculated from

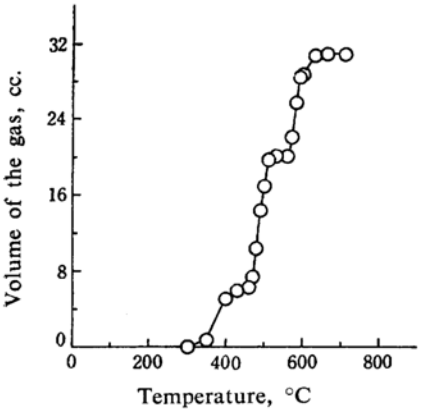

Fig. 5. Reaction between pyrite and ferric sulfate.

Pyrite	200 mg.
$Fe_2(SO_4)_3 \cdot nH_2O$	100 mg.

TABLE II

Example 1 $Fe_2(SO_4)_3 \cdot nH_2O$ 0.1 g., FeS_2 0.2 g.

	SO_2 found, ml.	SO_2 calcd., ml.
First stage	6.0	5.8
Second stage	13	12.7
Third stage	10	9.7

Example 2 $Fe_2(SO_4)_3 \cdot nH_2O$ 0.2 g., FeS_2 0.4 g.

	SO_2 found, ml.	SO_2 calcd., ml.
First stage	12	11.6
Second stage	26	25.4
Third stage	20	19.4

the Eqs. 4, 5 and 3 agreed fairly well with the experimental data for each stage as is seen in Table II. The range of the reaction temperature of the third stage agrees with that of the reaction described in section 2. To ascertain these equations, the reactions were cut off at the end of each stage by a rapid cooling and the solid products were examined. The product of the first stage was extracted by water, and the ferrous ion in the aqueous solution was titrated by a standard potassium permanganate solution. The value for ferrous sulfate in the solution was 56 mg. which agrees well with the value 54 mg. calculated by Eq. 4. The product of the second stage was strongly ferromagnetic with black color, and its X-ray diagram showed the diffraction lines of magnetite. These results showed that the reaction could be adequately expressed by Eqs. 4, 5 and 3. When the amount of pyrite was reduced, the product was changed as was expected from the Eqs. 3—5.

As ferric sulfate also reacts completely with pyrite to liberate sulfur dioxide around 650°C as shown in Fig. 5, the amount of ferric sulfate in the iron sulfides can be determined by measuring the amount of the sulfur dioxide liberated with a sufficient amount of pyrite.

(4) The Reaction between Pyrite and Ferrous Sulfate.—Remembering the three stages of the reaction between pyrite and ferric sulfate described above, the reaction between pyrite and ferrous sulfate would be considered to proceed similarly to the second and the third stage. As will be seen in Fig. 6, the reaction proceeds actually as was expected. Thus, the determination of ferrous sulfate in the mixture of ferrous sulfate and iron sulfides is possible from the amount of sulfur dioxide liberated when they are heated with a sufficient amount of pyrite at about 650°C in vacuo.

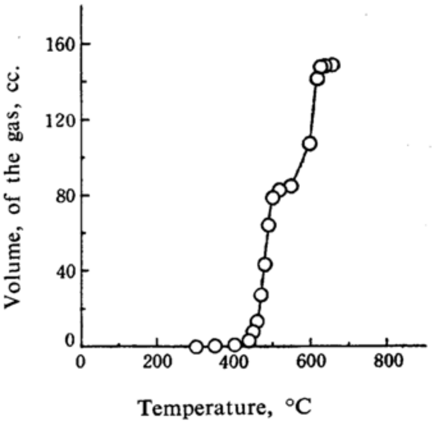

Fig. 6. Reaction between pyrite and ferrous sulfate.

Pyrite	1.0 g.
$FeSO_4 \cdot 7H_2O$	450 mg.

When the amount of pyrite was insufficient, hematite was formed as a final product.

$$FeS_2+11FeSO_4=6Fe_2O_3+13SO_2 \qquad (6)$$

When the amount of pyrite was less than that of the stoichiometric ratio of Eq. 6, sulfur trioxide and oxygen were also liberated by the decomposition of the remainder of the ferrous sulfate.

(5) The Determination of Ferric Sulfate, Ferrous Sulfate and Magnetite in their Mixture.—When a sufficient amount of pyrite is present, the reaction between ferric sulfate and pyrite proceeds through three stages as stated above. The second stage of the reaction corresponds to the reaction between pyrite and ferrous sulfate, and the third stage to the reaction between pyrite and magnetite. Consequently when a mixture of ferric sulfate, ferrous sulfate and magnetite is heated with a sufficient amount of pyrite, all the gas liberated at the first stage may be attributed to ferric sulfate, and that at the end of the second stage to ferric sulfate and ferrous sulfate, and that at the end of the third stage to ferric sulfate, ferrous sulfate and magnetite. Therefore, the amount of each substance in the mixture can be determined from the amount of sulfur dioxide liberated at each stage of the reaction. Some results of these determinations of the amount of each substance by this procedure are shown in Table III. As will be seen in Table III, the accuracy of this procedure is sufficient for the present study.

TABLE III

	Example 1		Example 2	
	Added mg.	Found mg.	Added mg.	Found mg.
$Fe_2(SO_4)_3 \cdot nH_2O$	70	70	50	55
$FeSO_4 \cdot 7H_2O$	50	54	50	48
Fe_3O_4	30	33	50	54

(6) The Determination of a Very Small Amount of Oxygen in Pyrite. — The results of the experiments on the reactions between pyrite and iron oxides or sulfates show that the oxygen contained in iron oxides or sulfates are completely liberated as sulfur dioxide, when the samples are heated at 650°C in vacuo with a sufficient amount of pyrite. Therefore, when the powdered pyrite contains a small amount of oxygen-iron compounds such as Fe_2O_3 and $FeSO_4$, the total amount of oxygen in the pyrite sample can be determined by the present method. But, as already mentioned above, absorbed oxygen and absorbed water which can not be removed by pumping at a low temperature may be conceivable as another source of oxygen.

The absorbed oxygen will be evolved as sulfur dioxide at 650°C, because the vapor pressure of sulfur in equilibrium with pyrite is fairly high in this condition[11-13] and oxygen is readily converted into sulfur dioxide. Minden[14] reported that the evaporated film of lead sulfide chemisorbs oxygen and evolves it as sulfur dioxide above 200°C. His results may support the view that oxygen absorbed on the surface of pyrite is evolved as sulfur dioxide on heating.

On the reaction between pyrite and water at a high temperature, Grünnert[8] concluded that the reaction proceeds as follows:

$$\text{(I)} \quad 2FeS_2 = 2FeS + S_2$$

$$\text{(II)} \quad 3S_2 + 4H_2O = 4H_2S + 2SO_2$$

$$\text{(III)} \quad FeS + H_2O = FeO + H_2S$$

$$\text{(IV)} \quad 3FeO + H_2O = Fe_3O_4 + H_2$$

These equations may explain the results of his experiments using a large amount of water. However, the amount of water absorbed on the surface of pyrite may be too small to follow the reactions III and IV. Therefore, in our case the reaction between pyrite and water may proceed as the following Eq. 7.

$$3FeS_2 + 2H_2O = 3FeS + 2H_2S + SO_2 \qquad (7)$$

in which water vapor, sulfur dioxide and hydrogen sulfide are equilibrated with pyrite and troilite. From these facts, the amount of oxygen in pyrite can readily be determined by that of sulfur dioxide, hydrogen sulfide and water vapor.

When a small crystal of pyrite was heated without being pulverized, a small amount of gas was liberated and the pyrite was completely decomposed to troilite and sulfur. But, when the same sample was pulverized and heated, a larger amount of gas was liberated as will be seen in Fig. 7. From this fact, it is obvious that as a result of pulverization of pyrite, oxidation occurs or absorption of oxygen or water. The evolved gas was completely absorbed by potassium hydroxide, and about two thirds of the absorbed gas was sulfur dioxide and hydrogen sulfide, and the remainder seems to be water vapor as will be shown in the following experiments. Phosphorus pentoxide was placed in tube D in Fig. 1 and cock 2 was

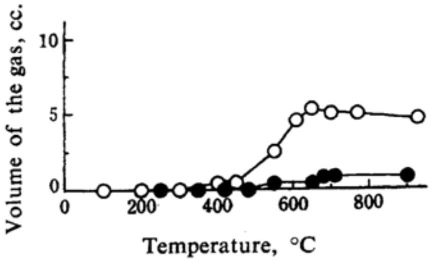

Fig. 7. Evolution of the gas from pyrite (1 g.)

● crystal ○ powder

TABLE IV

	Experiment 1	Experiment 2
Sample weight	3.0 g.	2.0 g.
Total volume of the gas evolved	3.0 ml.	1.7 ml.
SO_2	0.85 ml. (2.9 mg.)	0.70 ml. (2.0 mg.)
H_2S	0.98 ml. (1.5 mg.)	0.52 ml. (0.79 mg.)
H_2O	1.17 ml. (0.94 mg.)	0.48 ml. (0.39 mg.)
O attributed to SO_2	1.4 mg.	1.0 mg.
O attributed to H_2O	0.8 mg.	0.34 mg.
Total amount of O	2.2 mg.	1.34 mg.
O content	0.073%	0.067%

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[12] L. D'or, *J. Chim. Phys.*, **28**, 377 (1931).

[13] G. M. Schwab and J. Philinis, *J. Am. Chem. Soc.*, **69**, 2588 (1947).

[14] H. T. Minden, *J. Chem. Phys.*, **23**, 1948 (1955).

kept open through the experiment. The amount of gas evolved was fairly small and it consists of only sulfur dioxide.

The results of the experiments for the determination of oxygen content of powder pyrite are shown in Table IV. As will be seen in the analytical results, the precision is sufficient for the present study.

Summary

In the present paper a method for the determination of a very small amount of oxygen in an almost pure pyrite was proposed. From the results of the fundamental experiments on the reactions between the pyrite and the other minerals containing oxygen, it was ascertained that oxygen is completely liberated as sulfur dioxide and water vapor by heating in vacuo. The reproducibility of this method is fairly satisfactory, but there are no standard samples to examine the accuracy of this method. The results of the experiments indicate that this method could be used as a method for estimating the degree of oxidation of almost pure pyrites, for determining the amount of oxygen in some minerals, and in some cases for calculating the ratio of the oxygen containing compounds in their mixtures. Moreover, it seems possible to use this method for the determination of oxygen in a mixture of sulfides and oxides or sulfates of other metals than iron, and also oxygen in the metals. After the work reported herein had been almost completed, the authors were informed of the work, "The Sulfur Method of Oxygen Determination in Metals", of Babko et al.[15,16] who reported a somewhat similar study on the determination of oxygen in metals by using elementary sulfur instead of pyrite.

The authors are much indebted to Professor T. Watanabe and Mr. A. Sasaki, Department of Geology, The University of Tokyo for kindly supplying the samples of pyrite and for the microscopic study. We also express our hearty thanks to Dr. S. Akimoto, Geophysical Institute, the University of Tokyo, for his great help and valuable advice in X-ray study.

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